THE TENSILE DEFORMATION PROCESS
OF POLYPROPYLENE AT HIGH PRESSURE

by

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A thesis submitted in conformity with the requirements
for the degree of
Doctor of Applied Science
Graduate Department of Metallurgy and Material Science
University of Toronto

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ABSTRACT

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With the application of high pressure there were two transitions in the tensile response of polypropylene, one associated with the crystalline component and the other with the amorphous component. The first was the development of a distinct bend to lesser slope in the stress-strain curve prior to the stress maximum. This is the yield transition which is associated with the onset of crystalline flow. The second transition is a jump in the tensile response at a particular pressure. This was determined to be due to a pressure-induced rubber-to-glass transition of the amorphous component. Comparing the tensile response across these two transitions results in a more complete understanding of the interaction between the amorphous and crystalline components at various stages of tensile deformation prior to the stress maximum.

Specifically, the onset of yield is attributed to the creation of a void volume of sufficient size to allow nucleation of dislocations. Based on the sensitivity of the yield stress to the glass transition pressure, it is suggested that the nucleation site is at the crystalline-amorphous interface. This geometry defines a constrained ductile interlayer which will generate the triaxial tensile state of stress necessary to form a void. The triaxial tensile state of stress required for void formation must overcome the triaxial compressive state of stress due to the hydrostatic pressure and accounts for the linearity observed between the yield stress and pressure in polymers.

Deformation prior to crystalline yield is largely elastic, and is due to chain extension of the tie molecules within the amorphous component. Prior to crystalline flow the tie molecules are effectively pinned at their entry points into the lamellae, and respond in a manner similar to an elastomeric polymer in the final state of extension. In this case the limiting strain is defined not by specimen fracture but by formation of a void large enough to allow dislocation nucleation. The pressure dependence of the tensile modulus at finite strains is a direct consequence of the critical tensile stress required for void formation for crystalline yield coupled with the deformation response of the tie molecules which are in the final stage of elastomeric extension.
Acknowledgements

The design and fabrication of the high pressure tensile machine was a formidable task, and there were several helpful discussions on various aspects of machine tolerances, fabrication strategies and high pressure design with the following: Dave Abdulla, Dave Laing and Bill Ferris of the Department of Metallurgy, University of Toronto, Gord Agar of the Civil Engineering Department, University of Toronto, and Prof. Roy Pick, Mechanical Engineering Department, University of Waterloo. As well, the author acknowledges a discussion with Prof. A.S. Argon of M.I.T. on the scientific aspects of the thesis.

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Finally, the author wishes to thank Earl Burke, who stayed the course.
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<tr>
<td>( \alpha_f )</td>
<td>thermal expansion coefficient of the free volume</td>
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<td>( \alpha_{\exp} )</td>
<td>thermal expansivity</td>
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<td>( \alpha_o )</td>
<td>thermal expansivity at atmospheric pressure</td>
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<td>( \beta )</td>
<td>compressibility</td>
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<td>( \eta_g )</td>
<td>viscosity at the glass transition temperature</td>
</tr>
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<td>( \mu )</td>
<td>shear modulus</td>
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<td>( \nu_{\text{aim}} )</td>
<td>Poisson ratio at atmospheric pressure</td>
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<tr>
<td>( \nu_a )</td>
<td>frequency factor of the order of the atomic frequency, from Argon model</td>
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<td>( \nu_{\text{mol}} )</td>
<td>frequency of molecular jumps</td>
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<tr>
<td>( \nu_f )</td>
<td>frequency in direction of applied stress</td>
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<tr>
<td>( \nu_r )</td>
<td>frequency in direction opposite to applied stress</td>
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<td>( \tau_{\text{atm}} )</td>
<td>atmospheric shear stress</td>
</tr>
<tr>
<td>( \tau_c )</td>
<td>&quot;cohesion&quot; strength of a material</td>
</tr>
<tr>
<td>( \phi )</td>
<td>pressure coefficient in Coulomb equation</td>
</tr>
<tr>
<td>( \psi )</td>
<td>wall ratio for pressure vessel: equal to ( \text{OD}/\text{ID} )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>bend angle of a molecular kink (see Argon yield model for glassy polymers) equal to strength of a wedge disclination</td>
</tr>
</tbody>
</table>
a  molecular radius of a polymer chain (see Argon model for yield of glassy polymers)
a_t  shift factor from WLF relationship
c  number of volume dependent degrees of freedom of the s-mer molecule
d  displacement
e  engineering strain
f_v  fractional free volume (f_v = V/V)
k  Boltzmann constant
l  lamellar thickness
m  mass per molecule
u  radial displacement
v_\phi  free volume per molecule
y  fraction of occupied sites
z_{eq}  equilibrium distance between a pair of molecular kinks

a, b, c  Unit Cell Parameters

A  area
C  total volume density of rotatable segments (see Argon model for yield of glassy polymers)
E  tensile modulus
E_{aim}  tensile modulus at atmospheric pressure
E_{tangent}  tangent tensile modulus
E_p  tensile modulus at pressure P
F  force
P  pressure
P_g  glass transition pressure
P^*  characteristic pressure scaling parameter
T  temperature
T_g  glass transition temperature
T_m  melt temperature
T_{ml}  melt temperature for lamellae of thickness l
T_{m\infty}  melt temperature for lamellae of infinite thickness
T_2  equal to (T_g - 51.6°C)
T^*  characteristic temperature scaling parameter
V  activation volume (also the shear activation volume)
V^*  pressure activation volume
V_{free}  free volume
\( V_f \) volume of voids
\( V_o \) volume of occupied sites
\( V \) characteristic volume scaling parameter
\( W \) wall ratio for pressure vessel: equal to OD/ID
\( Y_o \) isotropic yield strength
\( Z \) partition function for a set of s-mer molecules

\( \Delta \alpha \) difference in coefficient of thermal expansion
\( \Delta \beta \) difference in coefficient of compression
\( \Delta \theta \) bond opening angle
\( \Delta \phi \) bond twist angle

\( \Delta C_p \) difference in heat capacity above and below \( T_g \)
\( \Delta G \) Gibb's free energy
\( \Delta H \) enthalpy
\( \Delta H_u \) enthalpy of fusion per unit volume of crystalline material
\( \Delta R \) bond extension
\( \Delta S \) entropy
\( \Delta S_u \) entropy of volume change on melting
\( \Delta V_u \) volume change on melting per mole of crystalline repeat unit
1. Introduction

Semi-crystalline polymers exhibit a wide range of mechanical properties depending upon conditions of temperature, pressure, and strain rate. The response is dual in nature, at times being predominantly elastic, at other times predominantly viscous, and most times a mix of both elastic and viscous behaviour. This is due to the fact that two different types of atomic bonding play significant roles in the deformation of polymers (covalent main-chain bonding, and inter-chain bonding due to van-der-Waals bonding, among others) which contrasts with the single bond type for metals.

Attempts to relate concepts and models of deformation from those developed for simpler materials, such as metals, have proved difficult, even though type deformation response is quite similar at times. For example, the tensile stress-strain curves of ductile metals and semi-crystalline polymers can be similar in form, having an initial steep slope rising to a load maximum, followed by a drop to a constant stress value corresponding to formation, stabilization and propagation of a neck. However, the deformation processes involved are distinctly different. The initial modulus response in metals is due to interatomic displacements between the metal atoms, involving only the one bond type. In contrast, the initial modulus in polymers is a much more complex deformation sequence, involving both the stronger main chain bonds and the relatively weak interchain bonds.

Another significant difference between metals and polymers is the ratio of yield stress to modulus. In polymeric materials, this is about an order of magnitude greater than that of metals. This difference is made manifest in the yield response of polymers to relatively low pressures, where it is easily evident that the yield stress is linearly defendant upon the applied pressure. This response is described by the modified-Coulomb yield criterion. Because of their relatively low moduli (with respect to the yield strength) of polymeric materials, this effect is noted at pressures where other materials, such as metals and ceramics, show no discernable pressure response. However, metals and ceramics will also show a pressure response at pressure which are a significant fraction of their modulus as well.

This pressure response has been reported in the literature on a number of polymeric systems. Very little experimental work, if any, has been carried out at temperatures other than ambient. As well, little has been done on the effect of pressure on deformation rate processes.
In this regard, the purpose of the work was twofold:

1. To determine the effect of temperature on the modified-Coulomb yield criterion for polypropylene.
2. To determine the effect of pressure on the stress actuation volume for polypropylene at various temperatures.

There was also noted from the data two unexpected transitions in the tensile response at certain high pressures:
1. A transitional jump in value of the tangent modulus with increasing pressure.
2. A distinct bend in the pre-peak stress of the stress-strain curve.

The first transition was associated with a pressure-induced glass transition. The second transition was proposed to be associated with the sudden onset of crystalline flow. Consideration of these two observations led to a speculative model of the deformation of polypropylene at high pressure.


2. Background

The structure of semi-crystalline polymers is complex and many important aspects, such as the proportion and arrangement of interlamellar tie molecules, still remain unclear. However, an assessment of the structure is essential to understanding the deformation process of semi-crystalline polymers. These two topics, structure and deformation will be addressed first. Next, the effect of pressure on the compressibility, glass transition temperature, melting temperature, viscosity and yield stress for various polymers will be discussed. Finally, yield criterion for polymers under hydrostatic conditions will be reviewed.

2.1 Molecular Structure and Elastic Constants

Polypropylene can be described by its structure and morphology in a hierarchy of scales, from the molecular chain, to the crystal structure, to the lamellar morphology, to the spherulitic morphology to the macrostructure (e.g. skin-core macrostructure).

At the molecular chain level, polypropylene is a vinyl polymer with a methyl group attached to alternate carbon atoms along the main chain. The methyl group restricts the rotation of the C-C main chain bond so that only certain configurations can be assumed. This leads to products of different tacticity (Figure 2.1). Isotactic polypropylene (i-PP) chains are constructed from the head-to-tail addition of propylene monomers such that the methyl groups have the same configuration with respect to the polymer chain (i.e. are on the same side of the polymer chain). Syndiotactic polypropylene chains are head-to-tail additions of propylene monomers such that the methyl groups have alternating configuration with respect to the polymer chain. Atactic polypropylene chains have methyl groups which are not regularly configured, and as a result, atactic polypropylene cannot crystallize. Isotactic polypropylene can crystallize and is the form studied here.

In reality, the consistency of the tacticity is rarely 100%, so that occasional disruptions along the polymer chain in tacticity do occur. For crystallization to occur, relatively high levels of tacticity are required.

At the crystal structural level, i-PP can crystallize in several different forms (α, β, γ for example). The α-form is dominant and is the form examined in the following discussion.
Figure 2.1: Chain conformation and crystal structure of polypropylene.
Top: Various tactile forms of polypropylene.
Middle left: Isotactic chain making one complete turn for every three monomer units.
Bottom: Mode of packing polypropylene chains in a crystal-view of basal plane.
The methyl groups prevent the isotactic polypropylene from assuming the planar zig-zag conformation (steric hindrance). Instead, the isotactic polypropylene conforms in a 3, helix (three monomer units per one turn of the helix, shown in Figure 2.1). Both right-hand and left-hand twists occur (usually not on the same molecule), and both can fit in the same crystal structure. Another consequence of the methyl group stiffening the chain is an increased melt temperature as compared with polyethylene (practically about 175°C instead of 135°C). The glass transition temperature ranges from -24°C [1][2] to 0°C [3], depending upon the technique used.

The crystal structure at ambient pressure of the α-form is monoclinic, with β = 98°12', and has a theoretical crystallographic density of 0.937 g/cm³ (Table 2.1). Amorphous polypropylene has a density of 0.85 g/cm³.

| TABLE 2.1: Crystallographic Parameters of Polypropylene [4] |
|-----|-----|-----|-----|-----|
| Conformation | Crystalline System | Unit Cell Parameters (Å and Degrees) | Number of Monomers per Unit Cell | Crystallographic Density (g/cm³) |
| Helix, 3/1 | Monoclinic | a | b | c | Other | 12 | 0.937 |

2.1.1 Bond Strengths and Modulus

Small strains in a material, due to temperature, pressure or an externally applied force, can be related to the bond strengths of that material. In other words, materials' properties of thermal expansion, compressibility and modulus are related by their dependence upon the interatomic potentials of the atomic bonds.

In the case of a linear polymer such as polypropylene, it can be characterized by strong covalent carbon-carbon bonds along the main chain backbone and relatively weak van der Waals forces between chains. The strength difference between these two bonds approaches two orders of magnitude. The carbon-carbon covalent bond has an average bond energy of 83 kcal/mol [5], whereas the van der Waals bond energy varies over the range from 1-2 kcal/mol, depending upon the distance between atoms.

The moduli, both experimental and theoretical, show a significant range of values. Experimental values vary due to simplifying assumptions made. For example, determination of moduli using x-ray diffraction assumes the material is strained homogeneously which, in the case of linear polymers, requires perfect alignment of the
chains of infinite length. Simplifying assumptions are also made in the theoretical calculations. For example, Asahina et al. [6], found it necessary to assume that bond stretching did not occur (or was of negligible consequence) in order to calculate a modulus value for polypropylene.

A measure of this difference can be found in the modulus of highly oriented polymers in the chain direction and transverse to the chain direction. Along the main chain direction three types of bond deformation can be described; bond extension (ΔR), bond angle opening, or valence angle (Δθ), and in the case of a helically wound polymer chain, bond twisting or torsional effects (Δφ). The relative strengths of these bonds, ΔR:Δθ:Δφ, is of the order of 100:10:1. This intuitively leads one to predict that the deformation due to each type would be the inverse, 1:10:100. In actual fact, the proportions are not nearly as large as this.

One theoretical estimate of the modulus of polypropylene has been made by Wool and Boyd [7] which shows a rather intriguing modular response of this helical polymer to strain. Their results show that for the helically wound polypropylene chain, the slope of the modulus-strain curve increases with increasing strain (Figure 2.2). In the figure, the left hand axis is the force per chain, and the right hand axis is our calculation of the stress, determined by dividing the force on a chain by the chain cross-sectional area (34.4 x 10^{-16} Å²). The initial modulus of 30 GPa increases to 40 GPa at strains of 5%. The ratio of deformation in ΔR:Δθ:Δφ was determined to be 1:2.4 :9, which is significantly different from 1:10:100 intuitively assumed for helically wound polymers.

2.1.2 Transverse and Amorphous Modulus

The transverse modulus for polyethylene and polypropylene crystals is also shown in Table 2.2. The results for polyethylene and polypropylene are similar, with the polypropylene showing the slightly lower modulus.

The amorphous modulus varies dramatically above and below the glass transition temperature. Typical glass moduli are 3-4 GPa, which fall to .0001-.001 GPa in the rubbery state. In semi-crystalline polymers, the amorphous regions are constrained by the surrounding lamellae, particularly between parallel stacks of lamellae. During crystallization, tie molecules bridging lamellae become pulled taut, decreasing chain mobility and increasing the modulus for the amorphous interlayer. Estimates of the modulus of the amorphous interlayer in semi-crystalline polymers are in the range of 0.5 - 1.0 GPa [8].
Figure 2.2: The force-strain curve for a polypropylene segment. Left-hand axis is the force per chain. The right-hand axis is the stress on the chain. Two models were used for the bond-stretching mode, harmonic and anharmonic. Other deformation modes (bond angle opening and bond twisting) remain the same for both the harmonic and anharmonic cases. [Redrawn from R.P. Wool and R.H. Boyd, J. Appl. Phys., 51 (1980) 5116]
### Table 2.2 Crystal Elastic Moduli along Chain

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chain Structure</th>
<th>Method</th>
<th>Modulus (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Basal plane</td>
<td>X-ray Diffraction</td>
<td>235, 255</td>
<td>B, C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Raman Spectroscopy</td>
<td>340, 358, 290</td>
<td>D, E, F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Neutron Inelastic</td>
<td>329, 329</td>
<td>G, H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Scattering Calculation</td>
<td>182, 340, 257, 316</td>
<td>I, J, K, L</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Planar Zig-Zag</td>
<td>X-ray Diffraction</td>
<td>255</td>
<td>A</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>Planar Zig-Zag</td>
<td>X-ray Diffraction</td>
<td>165</td>
<td>M</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Helix</td>
<td>X-ray Diffraction</td>
<td>41-47, 34</td>
<td>B, M</td>
</tr>
<tr>
<td>(isotactic)</td>
<td>3/1</td>
<td>Raman Spectroscopy</td>
<td>37, 88</td>
<td>N, O</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Helix</td>
<td>X-ray Diffraction</td>
<td>12</td>
<td>B</td>
</tr>
<tr>
<td>(isotactic)</td>
<td>3/1</td>
<td>Calculation</td>
<td>195</td>
<td>I</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Helix</td>
<td>X-ray Diffraction</td>
<td>12</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>3/1</td>
<td>Calculation</td>
<td>195</td>
<td>I</td>
</tr>
</tbody>
</table>

### Crystal Elastic Moduli across Chain

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Method</th>
<th>Modulus (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>X-ray Diffraction</td>
<td>3.2 - 3.9</td>
<td>B</td>
</tr>
<tr>
<td>Polypropylene (isotactic)</td>
<td>X-ray Diffraction</td>
<td>2.8 - 3.1</td>
<td>B</td>
</tr>
</tbody>
</table>

### Elastic Moduli of Amorphous Component

<table>
<thead>
<tr>
<th>State</th>
<th>Modulus (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy, T &lt; T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>3-4</td>
<td></td>
</tr>
<tr>
<td>Rubbery, T &gt; T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>.0001-0.001</td>
<td></td>
</tr>
<tr>
<td>Rubbery Constrained (Amorphous Interlayer)</td>
<td>0.5-1.0 (estimated)</td>
<td>R</td>
</tr>
</tbody>
</table>

### References
I. Treloar, L. R. G. (1960) *Polymer*, 1, 195/279/290
R. Krigbaum, W. R., Roe, R. J. and Smith, K. J. (1964) *Polymer*, 5, 533
Pressure will affect the modulus values, causing them to increase. A rough measure of this sensitivity is the ratio of pressure to modulus. Using this measure it is apparent that the amorphous phase will be most sensitive to the pressure, followed by the transverse modulus of the crystalline phase, and then the modulus of the crystalline phase in the chain direction. This will be discussed in greater detail later.

2.2 **Morphology of Undeformed Polypropylene**

Studies on the morphology of polypropylene at the lamellar and spherulitic level closely parallel those conducted for polyethylene, although they are not as extensive.

Early insight into the crystalline arrangement of semi-crystalline polymers came from single crystals formed by precipitation of the polymer from dilute solution (PE [9], [10], [11], PP [12], [13], [14]). The crystals were thin, nearly flat with straight edges which met at fixed angles. The thickness ranged from 5-25 nm, increasing with increasing temperature. The lateral dimensions varied between 1-50 μm. The chain direction was determined by electron diffraction to be in the thickness direction, normal to the flat surface of the lamella [15][16]. The length of the polymer molecule is many times longer than the lamellar thickness, which necessitates that the chain fold forth and back in the thickness direction. Since the strong main chain bonds are oriented in the thickness direction the lamellar structure is relatively weak.

The structure of lamellae crystallized from the melt was determined to be similar to those crystallized from dilute solution. The orientation of the main chain within the lamellae is 90° to the planar surface of the lamellae [17]. The thickness, or fold length, of the lamella increases with increasing temperature, which is also the case for dilute solution. It was determined that the lamellar thickness could be related to the melt temperature by the following equation [18],

\[
T_{m-} - T_{mi} = 2\frac{\sigma_f}{l \Delta H_u}
\]

(2.1)

where \(T_{m-}\) is the melt temperature of a lamella of infinite thickness, \(T_{mi}\) is the melt temperature of a lamella of thickness \(l\), \(\sigma_f\) is the surface free energy of a surface containing folds, and \(\Delta H_u\) is the enthalpy of fusion per unit volume of crystalline material.
The significance of this relationship is that the melt temperature of the polymer is a function of structure. One implication of this is that if polyethylene is first crystallized at 110°C and then brought to a temperature of 125°C, it will first melt and then recrystallize with a lamellar thickness defined by the new crystallization temperature.

The lamellae grow radially from a central nucleation region into spherulites, approximately 100 \( \mu \)m in diameter. Studies in the morphological development have been carried out for polyethylene [19], [20], and isotactic polypropylene [21] by Bassett et al., and their view of this matter follows. First, a chain folded monolayer single crystal flares out at its ends by non-crystallographic branching, forming a sheaf-like multilayered lamellae structure called an axialite (Figure 2.3). At this point, individual dominant lamella grow radially outward at both ends of the axialite, defining a conical region. A second wave of crystallization then follows in two regions. Between the dominant lamella, intermediate lamellar aggregates form by branching. As well, higher angle lamellae branch out from the ends of the original sheaf like structure. These gradually curl around, filling in the region normal to the axialite axis, and in doing so form a structural feature called "eyes" or Popoff leaves. Except for this central feature, the spherulite is radially symmetric. Crystallization is completed by branching, secondary crystallization and isothermal thickening of the lamellae. A significant portion of the structure may remain non-crystalline.

Several forms of polypropylene exist, the \( \alpha \)-form of isotactic polypropylene, the several polymorphic forms of iPP such as \( \beta \), \( \gamma \) and mesomorphic (smectic), and syndiotactic polypropylene. The dominant form for isotactic polypropylene is \( \alpha \) [22].

The growth direction for the \( \alpha \)-form of isotactic polypropylene is in the \( \alpha^* \) crystallographic direction. As with polyethylene, there is a twisting action of the lamellae during growth. As the spherulitic structure fills in, lamellae adjust their positions relative to each other, through isothermal thickening, forming regions of parallel lamellae called stacks. This morphological unit has been found by Peterlin [23] to act co-operatively during tensile deformation in the process of micronecking.

The \( \alpha \)-form of isotactic polypropylene also exhibits a distinct morphological feature when crystallized at temperatures less than 155°C. Under these conditions a phenomenon known as "cross-hatching" occurs, the term being derived from birefringence studies of
Figure 2.3: Stages of spherulitic growth.
Top: Axialite with some flaring at ends of sheaf-like structure.
Middle: Higher angle flaring into conical sections at ends of sheaves.
Bottom: Full development of the spherulite structure.

Figure 2.4: Schematic of the lamellar and interlamellar structure.
polypropylene. It has been determined [24] that close to orthogonal branching occurs, initiating on the sides of the \( \alpha \) laths on the \( \{010\} \) faces. The \( \alpha \) and \( c \) crystallographic axis of the branches are laid down on the \( c \) and \( \alpha \) axis of the parent lamellae, resulting in a branching angle of \( 80^\circ \). (This is a consequence of the close values for the \( \alpha \) and \( c \) unit cell parameters (See Table 2.1).) As a result parent and daughter are optically opposite, cancelling one another out, which gives rise to the cross-hatched appearance.

Two other important structural features other than the lamellae which have a profound effect upon deformation are tie molecules and the non-crystalline interlayer between lamellae (Figure 2.4). Tie molecules are molecular chain segments bridging two different lamellae. Without these connections the interlamellar boundary would be exceptionally weak, being held together by weak van der Waals forces.

Direct evidence of tie molecules was determined by crystallization of polyethylene mixed with low molecular weight diluent [25] [26]. The growth mode is not affected by the diluent. Upon crystallization of the melt into a two dimensional spherulite, the low molecular weight diluent was dissolved away, and the resultant structure examined by electron microscopy. The interchain links were found to be crystalline bundles oriented in the direction of the interchain link. It was concluded that the intercrystalline link was pulled taut during crystallization, and this straight taut segment acted as a nucleation line for the adjacent chains to crystallize upon.

Estimates of the percentage of molecules which act as interlamellar connections vary widely. Using SANS (small angle neutron scattering) gives estimates of 4%-8% [27] and 12% [28]. Molecular weight analysis of samples treated with fuming nitric acid gave a range of 5%-30% [29].

SANS techniques were also used to compare the radius of gyration of melt crystallized polymer and the polymer melt [30]. Both were found to be similar, from which it was concluded that the entanglements in the molten state must be largely conserved in the solid state [31]. Entanglements are a particularly important structural feature which determine the ultimate extension attainable during deformation. The average length between entanglements is constant for a given polymer, so that molecular chains with a high molecular weight have proportionately more entanglements than a low molecular weight chain. The interlamellar layer is customarily referred to as an amorphous layer.
Certain components of this interlayer are properly labelled as amorphous, such as the cilia (loose chain ends), and loose loops, as well as untaut tie molecules. However, other components, such as chain folds and taut tie molecules, impart properties to the interlayer significantly different than what is typical for an amorphous material. As was mentioned previously, estimates of modulus for the interlayer are two to three orders of magnitude greater than for an ideal amorphous material.

2.3 Deformation of Semi-Crystalline Polymers

The structure of semi-crystalline polymers consists predominantly of radially oriented lamella in an amorphous matrix. The crystalline lamella can be thought of as strong blocks surrounded by an elastic network (the amorphous interlayers).

Generally, deformation proceeds initially with an elastic response, due in large part to the amorphous network, followed by the onset of plastic deformation, due mostly to slip in the crystalline component. During the initial elastic deformation of the amorphous component there is considerable reorientation of the lamella to positions more favourable to slip, as well as an increase in stress as the interlayer reaches the limit of its extension. Plastic deformation proceeds when the critical stress required to initiate slip, which is decreasing due to reorientation, becomes equal to the increased stress due to extension of the amorphous matrix.

2.3.1 Deformation of the Crystalline Lamella

Most of the plastic deformation takes place by crystal slip. A slip system is defined by a plane, referenced to the unit cell of the crystal by the vectors (hkl), which is the unit normal vector to that plane, and a specific direction in that plane, referenced to the unit cell of the crystal by the vector [uvw]. When a critical resolved shear stress (CRSS) for a particular plane and direction in that plane is reached, dislocation motion occurs, resulting in a translation of the crystal on one side of the plane with respect to the other.

Not all of the slip systems are available. The slip plane cannot cut through the polymer main chain due to the high main chain bond strength relative to the interchain bonds. Slip planes are therefore restricted to planes parallel to the chain direction, or c-axis.
Figure 2.5: Models of dislocations in polyethylene:
(a) screw dislocation with Burgers vector normal to the chain,
(b) edge dislocation with Burgers vector normal to the chain,
(c) screw dislocation with Burgers vector parallel to the chain, and
(d) edge dislocation with Burgers vector parallel to the chain.
This is described by the \( \{hk0\} \) family of planes.

As well, the lamellar structure would be expected to hinder slip along planes cutting through chain folds in the surface of the lamella. In other words, slip planes would be expected to coincide with the crystallization fold plane, which is defined as the direction in which the chains fold and crystallize on the edge of the lamella during lamellar growth.

Two types of slip systems are defined: slip with the Burgers vector in the chain direction, known as chain slip, and slip perpendicular to the chain, known as transverse slip. Models of four dislocation systems for the orthorhombic polyethylene crystal are shown in Figure 2.5: (a) transverse slip by screw dislocation; (b) transverse slip by edge dislocation; (c) chain slip by screw dislocation; (d) and chain slip by edge dislocation [32].

For the polyethylene system, Galeski et al [33] determined from WAXS pole figures of single-crystal-textured HDPE that the active slip systems were \((100)[001]\) and \((010)[001]\). They found no evidence of \((110)[001]\) chain slip or \((010)[100]\) or \((110)[1\overline{1}0]\) transverse slip. This contradicts earlier work by Allen and Bevis [34][35] who examined the deformation processes in thin melt-cast films of HDPE mounted on Mylar substrate. The Mylar substrate was given various extensions and selected area electron diffraction done on the equatorial and meridional regions of the two dimensional spherulite as well as regions between. They claimed that the \((110)\) planes are involved in the deformation process in all three regions. Their explanation was that these planes were the close packed planes for orthorhombic polyethylene. They found no evidence for slip deformation modes involving either the \((100)\) or the \((010)\) planes.

In work related to Galeski et al., Bartczak et al.[36] noted that only three major slip systems were determined, \((100)[001]\) and \((010)[001]\) chain slip and \((110)[010]\) transverse slip. Since five independent slip systems are necessary for compatible deformation of polycrystalline assemblies, there is a need for an alternate mechanism. They suggested that the amorphous regions play a critical facilitating role by modifying the orientation of the stacks of lamella which are more favourable for slip. In other words, the lamellar stack rotates until a slip system is activated.
Figure 2.6: Models of deformation in amorphous regions: (a) interlamellar slip, (b) interlamellar separation, (c) stack rotation.

2.3.2 Deformation of the Amorphous Matrix

The initial elastic strain is a largely reversible deformation of the amorphous matrix which reorients the lamellae in directions favourable to crystallographic slip. This involves accommodating the relative motion between adjacent lamellae and larger lamellar domains (stacks). Within the rubbery temperature range, the elastic deformation of the amorphous matrix is relatively easy, largely reversible, but severely limited in the total strain that can be accommodated. The limited strain is due to the tie molecules between lamellae, which soon become taut. The elastic stress is then quickly distributed throughout the spherulite and between spherulites.

Three deformation modes in the amorphous component have been suggested; interlamellar shear, interlamellar separation and lamella-stack rotation (Figure 2.6). Conceptually, this can be misleading. Lamella-stack rotation is the motion of a group of lamella as a solid block, with no relative motion between the lamella of that block. The amorphous deformation in the region surrounding this block is just a combination of the first two deformation modes. As well, the first two modes are limiting cases only, with most of the deformation being a mix of the two. Finally, the deformation mechanisms of the amorphous region are not directly determined but inferred from the relative motions of the crystalline component through WAXS and SAXS, as well as from the elastic component of strain.

The evidence for interlamellar shear comes from SAXS studies[37]. These studies indicate that the lamella oriented close to 45° to the tensile draw direction rotate towards the draw direction. The lamella must slide by one another in order to accommodate this motion. SAXS studies also show that in some orientations the scattering angle increases, indicating that the interlamellar spacings are decreasing. This can be accommodated by chain tilt within the lamellae as well as interlamellar sliding.

The evidence for interlamellar separation comes from SAXS again. Early in the deformation process the meridional scattering becomes faint and at decreased scattering angle before disappearing. This indicates an increase in the interlamellar spacing in the spherulitic regions with lamellae normal to the tensile direction. Possible mechanisms are stretching without cavitation and stretching with cavitation. It has been postulated [38] that stretching without cavitation may be accommodated by bending of the lamellae
between localized tie molecules. Evidence for cavitation comes from studies linking the appearance of stress-whitening with large changes in polymer volume [39].

Direct observation of lamellar stack rotation was made using high-resolution scanning electron micrographs[40]. Lamella stacked three to ten deep rotated as a rigid body without any evidence of motion between each.

### 2.3.3 Spherulitic Deformation

Many of the techniques available for analyzing the molecular mechanisms involved in deformation are restricted to thin samples. Although some of the insights are quite useful, the thin samples do not experience the same constraints as exist in a bulk sample. The development of the deformation structure depends upon the interaction of many levels of structure and morphology simultaneously. SAXS techniques can provide a dynamic assessment of the overall development of deformation.

A group of papers examining the tensile deformation of spherulitic polypropylene using SAXS and WAXS was published by Peterlin and Balta-Calleja [41][42]. The SAXS patterns for polypropylene drawn at 20°C to various draw ratios are shown in Figure 2.7. The initial structure generates a uniform diffraction ring with a long period \( L_0 \). Upon deformation, prior to necking, the SAXS pattern undergoes an abrupt change to a four-point diagram (spots centred at 45° - 53° to the draw direction) superposed on a laterally elongated faint halo. Necking begins between a deformation ratio of 1.1 and 1.3, and is marked by two meridional maxima with a new long period \( L_T \). This new long period depends upon the temperature of deformation, and is independent of the initial long period and the amount of deformation. Necking is complete by a draw ratio of 2.7, the four-point diagram having disappeared.

It will be recalled that the long period is inversely proportional to the SAXS scattering angle. Since scattering depends upon a parallel array of equally spaced structures, then disappearance of a SAXS scattering can be due to either irregular spacing, or a condition which disrupts the parallelism.

The meridional scattering is reflective of lamella whose surfaces are normal to the draw
SAXS of Drawn Polypropylene

![SAXS images of polypropylene at various stages of uniaxial tensile deformation. Molten polypropylene was quenched in ice water and subsequently drawn at room temperature. The draw ratio given is the resulting plastic strain after the sample was removed from the tensile machine. [Redrawn from A. Peterlin and F.J. Baltá-Calleja, *J. Appl. Phys.*, 40 (1969) 4238]]

Figure 2.7: SAXS images of polypropylene at various stages of uniaxial tensile deformation. Molten polypropylene was quenched in ice water and subsequently drawn at room temperature. The draw ratio given is the resulting plastic strain after the sample was removed from the tensile machine. [Redrawn from A. Peterlin and F.J. Baltá-Calleja, *J. Appl. Phys.*, 40 (1969) 4238]
direction (i.e. equatorial regions of the spherulite). The meridional long period increases slightly before quickly disappearing. This has been attributed by Peterlin and Baltacalleja to the development of an irregular increase in the spacing of the lamellae oriented normal to the draw direction. However, Hay and Keller [43] reported that in regions of the spherulite where the radius vector is nearly perpendicular to the draw direction (i.e. in the equatorial zones of the spherulite), deformation is extensional accompanied by some compression in the transverse direction. Electron microscopy by Allen and Bevis [44] show a structure that is slightly crumpled in the transverse direction, consistent with a compressive strain. Thus in the equatorial regions, the slight compressive transverse stress appears to cause some buckling in the transverse direction, which would disrupt the meridional SAXS reflections, causing them to disappear.

The equatorial scattering of the SAXS pattern is reflective of lamella whose surfaces are parallel to the draw direction. The equatorial long period initially decreases, and disappears at a point later than the meridional scattering. The decreased long period has been attributed to a chain tilt of up to 30°. The variation in tilt angle would cause the lamellar spacing to become irregular, and account for the disappearance of the equatorial scattering. The structure of the lamellae whose surfaces are close to parallel to the draw direction is quite unstable, and the severe chain tilt adds to this instability. Fracturing of the lamella marks the beginning of the structural breakup (i.e. micro-necking).

The four-point SAXS image persists until the end of necking and the diagonal long period remains constant. As deformation progresses, the four-point pattern shifts from 45° to 20° from the draw direction (i.e. lamellar normals 45° to 70° to the draw direction). There does not appear to be any chain tilt occurring (no change in the long period) nor is there a gradual shift in the lamellar orientation towards the draw direction. This would indicate that the transformation is sudden and highly localized (i.e. micronecking). The gradual shift in the angle of the four point diagram can be attributed to the relative stability of lamellae oriented on the diagonal closer to the equatorial plane. It will recalled that the equatorial plane does not reflect since it has crimped rather than formed a microneck. The formation of the new meridional maximum is still a point of controversy. The long period is dependent on the temperature of deformation, and is independent of the initial long period. This relationship is identical to the one found
between the long period and the crystallization temperature. It would appear that a localized region had melted and recrystallized. At first it was conjectured that the work done during deformation was sufficient to increase the temperature of the polymer above its "equilibrium" crystallization temperature. Although there is evidence for some self-heating occurring in polymers at some strain-rates, further test at extremely low strain rates where self-heating effects were negligible showed that heating above this "equilibrium" temperature did not occur. Another alternative to consider is that the melt temperature itself is reduced sufficiently to allow either some melting of the structure. A number of arguments can be extended to support this. First, it will be recalled that the fold period has been related to the crystallization temperature by the equation (2.1). Rearranging we obtain

\[ T_{m2} = T_{m0} - \frac{2\sigma_f}{l\Delta H_u} \]

From this we note that as the lamellar thickness, \( l \), decreases (due to chain tilt), the crystallization temperature, \( T_{m2} \), also decreases. Further, as the lamellar structure begins to break up, new surfaces would be created, and an additional factor accounting for width and length of these blocks broken from the lamella would have to be included in the equation. The net effect would be a further decrease in the crystallization temperature. Second, the lamellar structure itself is stressed elastically due to the chain tilt which occurs. Finally, the reduction of area in the neck region is abrupt, and it may be reasonably assumed that there is considerable constraint on the necking region from the adjacent non-necking region. A state of triaxial tension will exist within the necked region. (This triaxial state of stress is sufficient to cause cavitation (stress-whitening) at atmospheric pressure and temperature). As will be seen in the following section, hydrostatic pressure will increase the melting temperature by \( 0.020^\circ C/atm \) - \( 0.040^\circ C/atm \). A triaxial tensile stress will instead decrease the melt temperature, presumably by a similar amount. These three factors would effectively reduce the melt temperature. That actual melting need take place may not be necessary. A partial melt back sufficient to increase the local amorphous content may be all that is required for the remaining blocks of lamella to re-orient and adjust their fold length according to the temperature at which deformation is taking place.

Another explanation was offered by Galeski et al.[45] who suggested that the breakup of the thinned crystalline lamellae is due to a deformation instability related to the
increase of interface stretching resistance of the crystalline and amorphous layers and is initiated by thickness irregularities (i.e. the surface energy of the interface increases due to elastic strain).

The recrystallization/reorientation of these local regions will nucleate on the chain structure extended in the draw direction, and grow laterally in a morphologically similar way as the "shish-kebab" chain extended structure formed from dilute solution [46]. The lamellae surface would be normal to the draw direction and result in the meridional scattering.

2.4 Pressure-Volume-Temperature Properties of Polymers

Pressure-volume-temperature (PVT) studies have led to models describing the void structure in amorphous polymers, and this in turn has led to efforts to relate this structure to viscosity. This relationship between volume and flow properties will be briefly reviewed here.

(The term "void" has been used historically to describe the change in the thermal expansion across the glass transition, among other phenomenon. However, it is doubtful voids are formed at all, and the increase in volume is due to local dilation, or to a local increase in vacancy population. (The inference when the term "void" is used, is that vacancies coalesce to form voids, which the author is uncertain has ever been shown.) It's use is continued here since it reflects the terminology of the literature cited, and the author is at a loss for a better description.)

Initial studies examined the volume as a function of either temperature or pressure. It will be recalled that volume-temperature studies indicated a transition in the volume expansion coefficient at the rubber/glass transition, and this formed the basis for the free-volume theory for amorphous polymers. From these studies, the difference between the extrapolated glass volume and the liquid volume was defined as the void volume, and this was subsequently related to the viscosity through the empirically derived Doolittle equation. This established the relationship between structure and flow properties for polymers.

Volume-pressure studies occurred much later due to the difficulties of working with high
pressure. What was immediately apparent from these studies was that increasing pressure could induce a rubber/glass transition in much the same manner as decreasing temperature. There has been considerable effort to determine a theoretical basis for the pressure-temperature relationship for this rubber/glass transition. A source of confusion is the non-equilibrium nature of the glassy state, which will be addressed later.

Equations of state for the P-V-T liquid surface have been developed for a number of polymers, both empirically as well as theoretically based, and some of these will be examined. What results is a hole-based model which relates void content with pressure and temperature, and gives some basis for understanding the rubber/glass transition.

2.4.1 Compressibility

Matsuoka and Maxwell [47] examined the compressibility of polyethylene and polystyrene at pressures to 200 MPa (30,000 psi). Both polymers showed a time-dependant response to pressure. The compressibility response decreased with increasing pressure. Warfield [48] compared the compressibility for amorphous and crystalline polymers and found in all cases that the compressibility decreased with increasing pressure. This phenomenon was noted previously by Bridgman [49] who considered two contributors to compressibility. At low pressure, there are holes and voids within the material, and compression is largely a function of closing these spaces. At high pressure most of the holes have disappeared and compressibility arises mostly from the shortening of the equilibrium separation between the molecules. This is largely temperature independent. A theoretical model proposed by Bueche [50], based upon compressibility due to both hole and equilibrium molecular separation, gave qualitative support for this. This dual response to pressure is seen in the specific volume-pressure diagram for polystyrene from the work of Warfield (Figure 2.8). Both the low and high temperature compressibility curves converge at a pressure of 1 GPa (10,000 atmospheres). At high temperatures, above the glass transition temperature, the polystyrene has a greater free volume than at room temperature and is more easily compressed as a result. This free volume seems to disappear at 1 GPa, at which point compression is interpreted as being due solely to intermolecular forces. It should be noted that this convergence was not observed with the other polymers examined by Warfield.
Figure 2.8: Compressibility of polystyrene at 22°C and 140 °C. \( V_{25} \) is the volume at 25°C. [R.W. Warfield, *J. Appl. Chem.*, 17 (1967) 263]

Figure 2.9: Compressibility of polystyrene from the rubbery state. The change in slope marks the pressure-induced glass transition. \( V_{75} \) is the volume at 75°F. [S. Matsuoka and B. Maxwell, *J. Poly. Sci.*, 32 (1958) 131]
2.4.2 Glass-Transition Temperature

Increasing the pressure can induce the rubber/glass transition in polymers. The glass transition temperature increases 15-35°C per 100 MPa pressure for a variety of polymers. Compressibility isotherms for polystyrene traversing the glass transition for a series of temperatures are shown in Figure 2.9 from the above cited work of Matsuoka and Maxwell. \( V_{75} \) is the volume of the polystyrene at 24°C (75°F). The polymer is first heated and then the pressure is increased incrementally to ensure the transition is from the rubbery state to the glassy state. The polystyrene undergoes a transition from liquid to glass as pressure increases. For example, the isotherm at 104°C (220°F) shows an increased slope at a pressure of 60 MPa (9000 psi), which marks the transition between the rubbery state and the glassy state. At pressures above this, the polystyrene chains are "squashed" together sufficiently to stop rotational motions of the chains. At higher temperatures, the pressure required to induce the rubber/glass transition must also increase to balance the increased kinetic energy. The compressibility, \( \kappa \), is derived from the slope of the lines. The transition between liquid to glass is gradual. This contrasts with volume-temperature measurements at a given pressure, where the glass transition is more sharply marked.

Determination of the change in the glass-transition temperature with pressure, \( dT_g / dP \), has been both experimentally and theoretically confusing. Experimentally it has been determined that the pressure at which the glass is formed defines the glass structure for that pressure. At this point the glassy structure can be considered in a "pseudo-equilibrium" state. The kinetics of the glassy state are so restricted that changing the pressure at this point does not result in an equilibrium structure. The volume resulting from this variation of temperature and pressure is not uniquely defined. This effect can be seen in Figure 2.10 for a polyurethane elastomer. The change in slope of each of the curves defines the glass-transition temperature. The glassy region of the 1 kb and 2 kb curves is represented by two curves. The upper curve represents the condition where the elastomer is first pressurized at room temperature to form a glass and then heated through the glass/rubber transition. The lower curves represent cooling of the elastomer from the rubbery state (as do the remaining curves). From this one can see that for the 1 and 2 kb curves two glass volumes result from the two paths taken to the same conditions of temperature and pressure. In other words, the glassy structure is not an equilibrium structure since it is not uniquely defined.
Figure 2.10: Specific volume of a polyurethane elastomer as a function of temperature for various pressures.

2.4.3 Free Volume Theory

The change in the slope of the volume-temperature curve, seen in Figure 2.10, has been interpreted as being due to the introduction of voids into the amorphous polymer structure, and is the basis for the free volume theories. Free volume theories envisage the liquid as a mixture of free volume and occupied volume, \( V = V_f + V_o \), where \( V_f \) is the volume of voids, or vacant lattice spacings, and \( V_o \) is the volume of occupied sites. The fractional free volume, \( f_v \), is defined as \( V_f/V \). The change in slope of the V-T diagram is associated with a sudden expansion in the free volume which is related to the onset of increased molecular mobility. Up to \( T_g \), it is assumed that the free volume is unchanged (but not necessarily zero). Above \( T_g \), the free volume is defined as increasing linearly with temperature.

\[
\frac{f_v}{f_g} + \alpha_v(T - T_g)
\]

where \( f_v \) is the fractional free volume, \( f_g \) is the fractional free volume at \( T_g \), and \( \alpha_v \) is the thermal expansion coefficient of the free volume.

Perhaps the most critical part of the theory is the empirical relationship between the volume fraction of voids and the viscosity. It was determined by Doolittle [51] in studies on monomeric liquids that the viscosity is a function of the volume fraction.

\[
\log \eta = A + \frac{B V_o}{V_f}
\]

where \( \eta \) is the viscosity, \( A \) and \( B \) are constants, \( V_o \) is the occupied volume and \( V_f \) is the free volume. The ratio of viscosities at two temperatures \( T_g \) and \( T (> T_g) \) has been found empirically to be related to the shift factor \( a_T \) from the WLF relationship,

\[
a_T = \frac{\eta_T}{\eta_g}
\]

Here \( \eta_T \) is the viscosity at temperature \( T \), and \( \eta_g \) is the viscosity at the glass transition temperature. This ratio eliminates the constant \( A \).
Substituting in the Doolittle equation and the free volume equation, we obtain

\[ \ln \alpha_r = \frac{-b}{F_g} \left( T - T_g \right) \]

\[ \frac{f_g}{\alpha_r} + T - T_g \]

This is the form of the empirically derived Williams, Landel, Ferry (WLF) equation [52] which relates the shift in the frequency-temperature response of amorphous polymers around the glass-transition temperature. The WLF equation was found to hold for most amorphous polymers. Thus the free-volume theory gave a theoretical basis for the previously empirically derived WLF equation.

The ratios \( b/f_g \) and \( f_g/\alpha_r \) can then be related to the empirically derived values from the WLF relation. From this, \( f_g \), the free volume at the glass transition, has a value of 0.025 (2.5%). The fit with the thermal expansion coefficient of the free volume, \( \alpha_r \) is more variable, and has an approximate value of \( 4.8 \times 10^{-4} \text{ K}^{-1} \). The term \( f_g/\alpha_g \) has a value of 51.6 °C, and it has been suggested that this has some thermodynamic significance.

The rough fit between the free volume theory and the WLF equation does not necessarily prove all aspects of the free volume theorem. The interpretation of what the free volume represents is difficult to precisely define. The free volume has been variously defined as the specific volume of the liquid minus either the volume of the molecules computed from the van der Waals radii, or the volume swept out by the molecular segments as they rotate. Other models for the experimentally unverifiable free volume give values at the glass transition which are significantly larger. The approximate equality of the difference in the thermal expansion coefficient of the liquid and glass raises further questions as to how literally these relations should be taken. Nonetheless, the correlation between the theory and experimental results is striking.

Some modifications or reinterpretations of the WLF relationship have been suggested. If the WLF is rewritten as

\[ \ln \eta_r = \ln \eta_g + \frac{-b/f_g (T - T_g)}{51.6 + T - T_g} \]
it can be seen that the viscosity becomes infinite at \( T = T_g + 51.6^\circ C \). This has led to the view that this temperature, referred to as \( T_2 \), is associated with a second order thermodynamic transition [53], [54].

2.4.4 P-V-T Surfaces and Equations of State

There are a number of empirically derived equation of state of which one will be mentioned, the Tait equation [55]

\[
1 - \frac{V}{V_o} = C \ln \left[ 1 + \frac{P}{B(T)} \right]
\]

where \( V \) and \( V_o \) are the specific volumes at pressures \( P \) and \( P=0 \) respectively, \( C \) is a constant, and \( B(T) \) is an exponentially decreasing function of temperature. The equation is widely used because of the ease in manipulating the data.

The compressibility \( \kappa \) and thermal expansivity \( \alpha \) can be derived from the Tait equation as follows.

\[
\kappa = - \left( \frac{\delta \ln V}{\delta P} \right)_T = \frac{V_o C}{V(P + B(T))}
\]

\[
\alpha = \left( \frac{\delta \ln V}{\delta T} \right)_P = \alpha_o + \kappa P \frac{d \ln B(T)}{dT}
\]

where \( \alpha_o \) is the expansivity at atmospheric pressure.

Two theoretical equations of state, based on statistical thermodynamics, have been applied to polymer liquids with success. A more complete description may be found in the accompanying references. In the first, called the cell theory [56], the liquid molecules are placed on a quasicrystalline lattice and the equation of state is obtained from the condition \( P = kT(\delta \log Z/\delta V)_T \), where \( Z \) is the partition function for a set of s-mer molecules. The following equation of state results.

\[
\frac{P\dot{V}}{\dot{V}} = 6 + \left[ 1 - 2^{-1/6} \right]^{-1} + 7.227 \left[ \frac{1.011}{\dot{V}^2} - 2.409 \right]^{-1} + \frac{1}{\dot{V}^2} \left[ \frac{1.011}{\dot{V}^2} - 1.2045 \right]
\]
for which \[ \tilde{P} = \frac{P}{P^\circ}, \quad \tilde{V} = \frac{V}{V^\circ}, \quad \text{and} \quad \tilde{T} = \frac{T}{T^\circ} \]

where \(P^\circ, V^\circ,\) and \(T^\circ\) are the characteristic pressure, volume, and temperature scaling parameters. \(V^\circ\) and \(T^\circ\) are obtained by fitting the experimental data to the theoretical volume-temperature curve at atmospheric pressure (\(P=0\)). The pressure parameter, \(P^\circ\), is then obtained from high pressure data. The scaling parameters are characteristic of the structure of the polymer segments.

The second theoretical equation of state is the hole theory, derived from the cell theory\[57\]. Holes are introduced into the quasilattice, and an additional variable, \(y\), the fraction of occupied sites, must be factored in. The value for \(y\) is obtained by minimizing the free energy of the state with respect to \(y\). The resulting equation for the hole theory is

\[
\frac{\tilde{P} \tilde{V}}{\tilde{T}} = \left[ 1 - \frac{2^{-1/6}y}{(y\tilde{V})^{1/3}} \right] + \frac{2y}{\tilde{T}} \frac{1}{(y\tilde{V})^2} \left[ \frac{1.011}{(y\tilde{V})^2} - 1.2045 \right]
\]

The free energy is then minimized with respect to \(y\), which results in

\[
\left[ \frac{s}{3c} \right] \frac{s-1}{s} \frac{-\ln(1-y)}{y} = \left[ 2^{-1/6}y \right] \left( y\tilde{V} \right)^{1/3} - \frac{1}{3} \left[ \frac{2^{-1/6}y}{(y\tilde{V})^{1/3}} \right] + \frac{y}{6\tilde{T}} \left[ \frac{1}{(y\tilde{V})^2} \right] \left[ 2.409 - \frac{3.033}{(y\tilde{V})^2} \right]
\]

where \(3c\) is the number of volume dependent degrees of freedom of the \(s\)-mer molecule. It is usually assumed that \(s/3c\) is unity and that \(s\) is very much greater than 1, eliminating these quantities from the equation. The quantities \(T^\circ\) and \(V^\circ\) are first evaluated from the experimental results for \(P=0\), in a manner similar to the cell theory, except that the two equations must be solved iteratively. \(P^\circ\) is subsequently determined from the experimental results at an elevated pressure. In spite of the numerical awkwardness, both the cell and the hole theories agree well with experimental data. The lines drawn in Figure 2.10 for the polyurethane elastomer were derived from both of these theories.
2.4.5 The Effect of Pressure Upon The Glass Transition Temperature

The addition of pressure as a variable in the study of the glass-transition necessitates the generation of pressure-volume-temperature (P-V-T) surfaces both above and below the transition. These P-V-T surfaces have been found not to be uniquely defined in the glassy regime. As previously mentioned, the volume change from any point in the liquid regime to any point in the glass regime is dependent upon the P-T path taken. The glassy structure is defined at the pressure at which it is formed, and can be thought of as a "pseudo-equilibrium" structure. Subsequent pressure changes result in a non-equilibrium structure that kinetically cannot change to the new equilibrium structure. This effect was not immediately obvious, and contributed much confusion over relationships between the glass transition temperature and pressure.

The glass transition temperature increases 15-35 °C / 100 MPa for a variety of polymers. Several theoretical explanations have been proffered to account for this effect. The free volume theory has been extended to account for the effect of pressure by the following equation

\[ f = f_g + \alpha_g (T - T_g) - \beta_g (P - 1) \]

Here the free volume contributions due to temperature and pressure are assumed to be independent of one another. Since \( f = f_g \) at the glass transition, then the derivative is \( \frac{dT_g}{dP} = \beta_g / \alpha_g = \Delta \beta / \Delta \alpha \), where \( \Delta \beta \) and \( \Delta \alpha \) are the change in the compressibility and expansivity upon passing from the liquid to the glassy state.

Thermodynamic theory assumes that the glass transition temperature is a true second-order thermodynamic transition. The transition temperature, \( T_2 \), is defined as the temperature where the configurational entropy becomes zero \( (T_2 = T_g - 51.6 \, ^\circ \text{C}) \). Assuming equilibrium exists, then the Ehrenfest equation gives [58]

\[ \frac{dT_2}{dP} = \frac{T_2 \Delta \alpha}{\Delta C_p} = \frac{\Delta \beta}{\Delta \alpha} \]

where \( \Delta \alpha \) is the difference in the coefficients of thermal expansion above and below the transition temperature, and \( \Delta C_p \) and \( \Delta \beta \) are the differences in heat capacity and
coefficient of compressibility above and below the transition temperature.

For a glass formed at atmospheric pressure (i.e. a low temperature glass), the effect of pressure on the glass-transition temperature has been seen to be given by the Ehrenfest equation, $T_g^o / dP = \Delta \beta / \Delta \alpha$ where $T_g^o$ is the glass transition temperature at atmospheric pressure. For glass formed at the glass formation pressure, the Ehrenfest equation is found to be low, with $dT_g/dP < \Delta \beta / \Delta \alpha$ [59]. Several modifications of the Ehrenfest equation have been suggested. Goldstein [60] found that $TV \Delta \alpha / \Delta C_p$ is approximately equal to $dT_g/dP$, rather than $\Delta \beta / \Delta \alpha$. Questad et al [61] modelled the transition using void volume (from the hole theory) as a structural ordering parameter. Experimental pressure-volume-temperature data for a polyurethane elastomer was fitted to the cell[62] and hole[63] equation of state theories. The model has been compared with experimental data on liquid argon, oligomer fluids and polymer fluids [64][65][66]. As applied to this elastomer, $y$ (the fraction of occupied sites) can be determined in the liquid regime to the glass-transition. The hole fraction, $1-y$, is plotted against temperature for a variety of pressures in Figure 2.11. The glass transition temperature for the high pressure glasses (glass formed from the liquid at the elevated pressure) is denoted by the x's at the end of each curve. The dots denote the low pressure glass-transition (glass formed at atmospheric pressure first and then pressurized). The hole fraction, as determined using the hole theory, is seen to be larger than that predicted from the free volume theory. The fraction of holes is seen to decrease with decreasing temperature and increasing pressure, as would be expected. At the glass transition the hole fraction decreases with increasing pressure for the high pressure glasses (Figure 2.12). This reflects the structural change upon formation of the glass. For the glass formed at atmospheric pressure, there is no change in the structure, as determined by hole fraction. Questad et al. suggested the following modification to the Ehrenfest equation which incorporated a structural component, $y$.

$$\frac{dT_g}{dP} = \frac{\Delta \beta}{\Delta \alpha} + \left( \frac{dT_g}{dy} \right) \left( \frac{dy}{dP} \right)$$

where $dT_g$ is the glass-transition temperature of the glass formed at elevated pressure. Good agreement was found with the polyurethane elastomer studied.
Figure 2.11: Hole fraction, $1-y$, as a function of temperature at various pressures, for a polyurethane elastomer.

Figure 2.12: Hole fraction, $1-y$, at the glass transition for glasses formed at atmospheric pressure and glasses formed from the liquid at the elevated pressures studied. Material is a polyurethane elastomer.
2.5 Crystallization Response Under Pressure

The influence of hydrostatic pressure on the crystallization process is quite dramatic in most cases due to the large expansion which occurs upon melting. High pressures inhibit melting, causing an increase in melting temperatures.

The effect of pressure on the melt temperature is described by the Clausius-Clapeyron equation

$$\frac{dT_m}{dP} = \frac{\Delta V_u}{\Delta S_u}$$

where $T_m$ is the melting temperature, $\Delta V_u$ is the volume change on melting per mole of crystalline repeat unit, and $\Delta S_u$ is the entropy of volume change on melting. The effect of configurational entropy on the glass transition can be seen from the values for polyethylene and polypropylene given in the following table.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$dT_m/dP$ ($^\circ$C / atm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>0.02</td>
<td>[67]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.021</td>
<td>[68]</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.040</td>
<td>[69]</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.0395</td>
<td>[70]</td>
</tr>
</tbody>
</table>

Polyethylene has a higher configuration entropy change which is indicative of less order in the melt. Polypropylene retains a greater degree of order in the melt, probably indicating that the solid state helical conformation is retained upon melting.

Crystallization under high pressures often results in different crystal structures, as well as morphologies, and a great deal of study has taken place in this area. At atmospheric pressure, polypropylene crystallizes from the melt into monoclinic $\alpha$-form. Crystallization of polypropylene from the melt at relatively low pressures (32 MPa or 320 atm) results in almost complete crystallization in the triclinic $\gamma$-phase [71]. There was no indication from the literature that this transformation occurs in the solid state at the pressures and temperatures studied in this work.
2.6 The Effect of High Pressure on the Deformation of Polymers

Both the yield and modulus of polymers increase significantly with increasing pressure. At pressures which cause a significant polymer yield response, metals show no discernable effect. The reason for this is the relatively low modulus value of polymers compared with metals. Both materials will show a pressure response of their yields when the pressures become a significant portion of the modulus.

Before progressing further in the discussion, a point which needs clarification is the definition of yield. The stress-strain response for most materials is characterized by an initial steep slope which becomes less steep as the strain is increased. Aside from this general description the form of the curves vary widely. As a result there are many definitions for selecting a value for the yield point. Some definitions follow quite naturally from the form of the stress-strain curve, such as a stress maximum, or an abrupt change in slope of the stress-strain curve. Others are arbitrarily defined, such as the offset method.

Definitions of tensile yield for metals which exhibit a significant elastic response are much different than for polymers which do not, although the shape of the stress-strain curves may be similar. For example, consider a ductile steel which forms a necked region when deformed in tension. It is characterized by a pronounced initial elastic response. In this case the yield is determined using a 0.2% offset method. A straight line is drawn alongside the stress-strain curve, offset to the right by 0.2% strain, with a slope equalling that of the initial slope of the stress-strain curve. The point at which this straight line intercepts the stress-strain curve is defined as the yield point, and the stress at this point is defined as the yield stress. This stress is often much less than the stress maximum. For ductile polymers which exhibit the same necking characteristic when tested in tension, there is no pronounced linear elastic response, and the yield stress is defined instead as the stress maximum.

In compression, the stress-strain curve for polymers shows the stress increasing monotonically with strain, with the change in slope being defined as the yield point. The change in slope is often gradual, and in this case the yield is more precisely defined by the intersection of the slopes of the curves on either side of the transition.
The Young's modulus is a difficult concept to apply to polymers. Only under unusual conditions, such as high pressures or low temperatures, does the initial response of the stress-strain curve approach linearity. Unlike metals, there is some flow associated with the initial portion of the stress-strain curve. An indication of this is the strain rate sensitivity of the modulus of polymers, as well as the pressure sensitivity. As such, the Young's modulus is not a constant, and is not a direct measure of atomic displacement in polymers. From a practical perspective, measurement of the modulus under conditions of high pressure using extensometers is rarely done. The limited space available within the pressure vessel as well as the requirement of having multiple electrical feedthroughs make this technically difficult. As a result the literature often cites a relative effect of the modulus response to the pressure, such as the ratio of the modulus at elevated pressure to the modulus at atmospheric pressure.

In the following section, the typical response to pressure of an amorphous polymer, an elastomer, and a semi-crystalline polymer will be examined first. From this the overall effect of pressure on the modulus and peak stress of polymers will be addressed. Finally, yield criteria appropriate to these materials will be discussed.

In both amorphous and semi-crystalline polymers, the glass transition affects the modulus response significantly. It has been noted that the glass transition is a function of both temperature and pressure. In order to avoid confusion, the polymer state will be referred to as a rubber or a glass, rather than being above or below the glass transition temperature, \( T_g \), or the glass transition pressure, \( P_g \).

### 2.6.1 Amorphous Polymers in the Rubbery State

In the rubbery state, the local interactions between adjacent chains are relatively weak, and upon deformation large scale interactions, due to entanglements in the case of amorphous polymers, or crosslinks in the case of elastomers, soon exert a predominating influence. In both cases the local resistance to flow becomes negligible compared to the 'elastic' restoring force due to the thermal vibrations of the polymer chains. When the chain network approaches full extension the stress begins to rise quite quickly. In the case of elastomers, this stress rises asymptotically at a limiting strain. In the case of uncrosslinked amorphous polymers in the rubbery state, the stress increase may be somewhat relieved by large scale flow involving steady state disentangling. Except for the initial state of deformation an Eyring flow model cannot be appropriately applied,
since the flow resistance is negligible compared with the restoring force of the extended chain network.

2.6.2 Elastomers

Elastomers are utilized in their rubbery state. Under these conditions the attraction between molecular chains is negligible, and the force to be reckoned with is the line tension experienced by the molecular chains due to the thermal vibrations of their constituent atoms. The stress-strain response of elastomers may be divided into three stages: an initial steep increase in stress (stage 1), followed by a linear region of low positive slope (stage 2), and ending with a final steep increase in stress at a limiting strain (stage 3). Figure 2.13 shows the effect of pressure on the tensile response of a polyurethane elastomer (Questad et al. [72]). Increasing pressure increases the stress level of the stress-strain curve. It is also noted that there is a jump in the stress level between 3 and 4 kb (300 and 400 MPa), coinciding with the pressure-induced glass transition.

At pressures below the glass transition, both the modulus and the "yield" stress of the initial portion of the curve increase with increasing pressure. The slope of the second stage of deformation does not appear to change significantly with pressure. There is no evidence of the third and final stage of elastomeric deformation at the strains tested. At the glass transition, the Young's modulus increases dramatically, from 0.002 GPa (2 x 10⁷ dynes/cm²) characteristic of a rubber, to 1 GPa (1 x 10¹⁰ dynes/cm²) characteristic of a glass (Figure 2.14)[73]. The bulk modulus shows very little change through the glass transition. The dramatic increase in Young's modulus was previously noted by Paterson in work on natural rubber[74]. The Young's modulus increased by 30% when pressurized to 400 MPa (4 kb). At the rubber/glass transition at 500 MPa (5 kb), the modulus increased by 1000 %. The occurrence of the rubber/glass transition occurs at pressures specific to the elastomer, rather than at the same pressure for all elastomers.

At pressures above the glass transition (i.e. in the glassy state), the first stage shows a stress maximum, followed by a decrease to a "draw" stress, at which point the second stage begins. It was determined by optical inspection during the test that no neck had formed, and that second stage stretching above the pressure-induced glass transition behaved similarly to that below. However, the elastomer no longer contracts
immediately upon release of the stress, but does so over a period of time (the relaxation varies as the log of time). Thus molecular motions are possible in the glassy state under a state of stress. The initial stress level of the second stage of deformation increases as the pressure is increased, with a considerable jump in this stress level at the glass transition.

At atmospheric pressure, the nature of the elastomeric chains in the rubbery state is characterized by freely jointed chains with negligible interaction due to interchain bonding between chains. The chain generates a line tension due to thermal vibrations. The restoring force due to extension is due to both (conformational) energy minima and entropy maxima considerations which govern the free energy. Application of pressure would hinder chain motion and the resultant stress would be composed of both a flow component as well as an elastomeric restoring force component. Above the glass transition pressure (in the glassy state), the flow component dominates the elastomeric component, resulting in a relatively flat stress response during extension. The effect of the restoring force, causing the structure to contract over time, indicates however that some molecular motions are possible.

Figure 2.14: Young's modulus and bulk modulus for a polyurethane elastomer as a function of pressure. [D.L. Questad, K.D. Pae, B.A. Newman, and J.I. Scheinbeim, *J. Appl. Phys.*, 51 (1980) 5100]
2.6.3 Amorphous Polymers in the Glassy State

Amorphous polymers in the glassy state tend to be brittle at atmospheric pressure. The modulus of amorphous polymers increases with increasing pressure, although not to the same degree as in the rubbery state. Similarly, the yield stress or fracture stress also increases with increasing pressure. What is most interesting is that for many the strain at fracture will increase with increasing pressure. This is observed for polymethyl methacrylate (PMMA) [75], polysulfone (PSF) and polyimide [76]. An exception to this is polycarbonate (PC), which exhibits considerable ductility at atmospheric pressure. Increasing pressure causes the strain to fracture to decrease [77].

The mechanical response of polystyrene to pressure is shown in Figure 2.15 [78]. At atmospheric pressure, the Young's modulus increases as does the fracture stress. At pressures of 3 kb (300 MPa) the polystyrene response changes from brittle to ductile, showing an engineering stress maximum followed by necking. Converting to true stress, and defining the yield stress using the 0.5% offset method, the brittle-ductile transition is seen clearly in Figure 2.16. The pressure is seen to hinder the fracture process at pressures greater than 40 ksi (276 MPa) by inhibiting the formation of cracks or crazes. Studies of other brittle polymers in media that promote crazing support this view. The increase in Young's modulus for the polystyrene is only 20% as the pressure is increased from atmospheric pressure to 40 ksi (276 MPa), and increases very little thereafter. This increase in modulus with pressure is small relative to that of other amorphous polymers, and has been attributed to the lack of a strong secondary relaxation process below the glass transition temperature.

The pressurizing fluid has been noted to cause premature fracture in amorphous polymers. The effect of these fluids is most dramatic in tension tests, but is of a minor consequence in compression tests. The source of the problem is the requirement of a low viscosity fluid to work the high pressure pumps. High viscosity fluids will either freeze at high pressure or become too sluggish to transmit the pressure through the small orifice in the high pressure tubing. Unfortunately, the low viscosity fluids also tend to be good solvents, particularly when the polymer is extended, and this leads to crazing in the often brittle amorphous polymer.

For example, polycarbonate has been tested in tension at high pressure with
kerosene[79], and castor oil[80] as the pressurizing medium. Kerosene is known to be a crazing agent for polycarbonate, and reduced the fracture strain at pressures to 300 MPa. The fracture strain at atmospheric pressure was 120% when tested in castor oil but only 28% when tested in kerosene. Above 300 MPa the difference between the two fluids used was minimal. In another example, heptane is known as a stress cracking agent for polysulfone, whereas kerosene has little effect. The ductility of the polysulfone tested in tension increased dramatically with increasing pressure when the kerosene was used, but failed by brittle fracture when heptane was used [81]. Crazing, which was evident at low pressures when kerosene was used, was not evident at 60 ksi (400 MPa). When heptane was used instead, crazing continued to occur at 80 ksi (530 MPa), the maximum pressure tested. Although the elongation to fracture was quite sensitive to the pressurizing medium, the modulus and the stress maximum were unaffected. When the polysulfone was tested in compression in the heptane, the polysulfone remained ductile at all pressures.

From these results, it can be seen that brittle fracture is dependant upon crack formation. Conditions which pack the polymer molecules closer together, such as testing at high hydrostatic pressures or in compression inhibit crack formation, and the amorphous polymer will tend to deform in a ductile fashion. Conditions which tend to loosen or open up the polymer structure, such as tensile testing, low pressures, or testing in a solvent which promotes crazing, will tend to promote brittle failure.

Figure 2.16: True yield (0.5% offset) and true fracture strength for polystyrene at various pressures. [G. Biglione, E. Baer, and S.V. Radcliffe, Proceedings of the Second International Conference on Fracture, Brighton, Chapman and Hall, London (1969) 503]
2.6.4 Semi-Crystalline Polymers

Tensile deformation for semi-crystalline polymers at atmospheric pressure is ductile, with necking and subsequent cold-drawing occurring in most cases (low density polyethylene (LDPE) [82], polypropylene (PP) [83], polyoxymethylene POM [84], polyethylene terephthalate (PET) [85], and polychlorotrifluoroethylene [86],[87]). An exception to this is polytetrafluoroethylene (PTFE) [88], [89], which does not form a neck but cold draws. The effect of pressure on the tensile properties of HDPE (high density polyethylene) is shown in Figure 2.17 [90]. At all pressures there is a peak stress and a draw stress, reflecting the formation of a stable neck and propagation of that neck along the length of the sample. At the peak stress the elongation of the gauge region ceases to be uniform, with a rapid reduction of cross-sectional area occurring at a point in the gauge region. If the yield stress remains unchanged in the reduced section, the load will decrease as the cross-sectional area decreases, until fracture occurs. However the yield stress actually increases. During the necking process the polymer morphology transforms from a spherulitic structure to a fibrillar structure oriented in the draw direction, and the resulting orientation strengthening counters the load drop due to the reduced cross-sectional area. At some point in the necking process, the two tendencies become balanced. Further deformation then occurs at either end of the now stable reduced section and propagates along the gauge length of the specimen.

In general, semi-crystalline polymers will decrease their strain to fracture with increasing pressure, in contrast to that of amorphous polymers in the glassy state. Both the Young’s modulus and the peak stress increase with increasing pressure as was the case for amorphous polymers. The peak stress increases linearly with pressure to 80,000 psi (530 MPa). This finding is generally true of all of the semi-crystalline polymers.
Figure 2.17: Tensile stress-strain curve for polyethylene at various pressures. [D.R. Mears, K.D. Pae., and J.A. Sauer, J. Appl. Phys., 40 (1969) 4229]
2.6.5 Pressure Dependency of the Elastic Modulus and Peak Stress

The elastic modulus increases with increasing pressure for both amorphous and semi-crystalline polymers in both the rubbery and the glassy state. The modular response with pressure suggests some sort of flow dependency, since the pressure dependency is similar to that of the strain rate. In the case of metals, the modulus reflects the elastic response of the atoms from their equilibrium positions. In the case of polymers, there are an additional two components; first, there is the elastic response of the amorphous component, and second there is a small amount of flow where some of the atoms move from one site to another. This small amount of flow relieves some of the stress, and accounts for the time and pressure dependency of the modulus.

The experimental determination of the modulus under conditions of high pressure is characterized by considerable scatter. None were determined using an extensometer, and many of the sensing gauges could give only coarse readings of stress. In spite of this some general conclusions can be made.

1. The modulus increases as the pressure increases. The relationship is linear, or nearly so, for many polymers.
2. The pressure dependence of the rubbery state is greater than the glassy state.
3. A pressure-induced glass transition causes an abrupt change in the modulus-pressure dependency.

It has been argued that since the pressures are approaching the magnitude of the elastic modulus, the pressure-induced strain will be finite, and therefore elasticity theory based on infinitesimal strain would no longer be applicable. Birch [91] applied the finite deformation theory of elasticity developed by Murnaghan [92] for uniaxial stress. In the case where uniaxial stress produces infinitesimal strains superimposed on a hydrostatic pressure which produces finite strains, the modulus will be a function of the magnitude of the pressure. An approximation gives

\[ E_P = E_{atm} + \chi P \]

where \( E_P \) is the modulus at pressure \( P \), \( E_{atm} \) is the modulus at atmospheric pressure, and \( \chi \) is a material constant. A further approximation for \( \chi \) gives
\[ \chi = 2 \left( 5 - 4 \nu_{\text{atm}} \right) \left( 1 - \nu_{\text{atm}} \right) \]

where \( \nu_{\text{atm}} \) is the Poisson's ratio at atmospheric pressure.

Pae and Bhateja [93] compared this theory with the high pressure work on polymers for which there was sufficient data. The trend of increasing modulus with pressure was noted for amorphous polymers in the glassy state as well as semi-crystalline polymers at high pressures, however the estimates were consistently low. They concluded that some of the increase in polymer modulus with increasing pressure was due to this non-linear elasticity contribution due to the high pressure. Perhaps one of the major sources of uncertainty was the unstated assumption that the Poisson's ratio remained constant as the pressure increased.

The peak stress (often referred to as the yield stress) increases linearly with pressure for both amorphous and semi-crystalline polymers. The pressure dependency of amorphous polymers in the glassy state is less than in the rubbery state, and less than that of semi-crystalline polymers in the rubbery state. For the most part, a pressure-induced glass transition occurring in semi-crystalline polymers has not been noted as having an effect upon the peak stress.
Polymeric yield shows a strong pressure dependence, which is unlike that for metals. Standard yield criteria, such as the Tresca yield criteria \( (\sigma_1 + \sigma_3) = \text{constant} \) and the von Mises yield criteria

\[
( (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 ) = 6K^2
\]

where \( \sigma_1, \sigma_2, \text{ and } \sigma_3 \) are the principal components of stress and \( K \) is a constant, assume that yielding is independent of pressure, and are not directly applicable.

In the simplest case at room temperature and pressure and constant strain rate, the yield stress of polymers is linearly dependent on pressure (the modified-Coulomb yield criteria). When temperature and strain rate are varied, yield is found to be a thermally activated process. In this case the Eyring equation is applied, with the activation enthalpy being linearly dependent on the stress. This relationship is valid over a limited range of temperatures and pressures.

A molecular model for yield in glassy polymers was developed by Argon[94], based on the elastic strain field around a pair of equal and opposite kinks in the molecular chain. The derived relationship is similar in form to the Eyring equation, except that the activation enthalpy term is also a function of the shear modulus. Since the shear modulus of polymers is a function of temperature, the activation enthalpy is also similarly dependent on temperature. The result is a much better fit to yield data for glassy polymers over a wide range of temperature and strain rate. Each of these will be addressed more fully in the discussion which follows.
2.6.6.1 Yield Criteria: The Effect of Pressure

The yield stress in polymers increases linearly with hydrostatic pressure, according to the modified-Coulomb criteria as follows.

\[ \tau = \tau_{atm} + \phi P \]

where \( \tau \) is the shear yield stress at pressure \( P \), \( \tau_{atm} \) is the yield stress at atmospheric pressure, and \( \phi \) is the coefficient of increase of shear yield stress with pressure. This relationship is known as the modified-Coulomb yield criteria since it is similar to the one used by Coulomb for the yielding of soils [95],

\[ \tau = \tau_c - \lambda \sigma_N \]

where \( \tau_c \) is the 'cohesion' of the material, \( \lambda \) is the coefficient of friction, and \( \sigma_N \) is the normal stress on the yield plane.

2.6.6.2 Yield Criteria: The Effect of Time and Temperature

Yielding in polymers is also a thermally activated process. Mechanical properties are therefore dependent on temperature and strain rate. Along this line Eyring developed a model to explain flow in dilute polymeric solution, the flow rate being related to the flow stress by an Arhenius-type relationship. The Eyring model was extended to the non-steady state flow case for yielding in polymers. This equation has been found to be valid over limited ranges of strain rate. Although the Eyring interpretation may be appropriate for certain conditions of deformation of amorphous polymers in the rubbery state, extension of the model to the glassy state, or to yield in semi-crystalline polymers, is not. What is evident, though, is that yield is a thermally rate-activated process.

As mentioned, the molecular model developed by Eyring and his co-workers predicted the viscosity of liquids [96]. This model was later extended to the stress-strain relationship of polymers, and supports the view of the polymer as a viscous liquid [97]. The model predicts the rate at which molecules move from one position to another
under an externally imposed shear stress.

The model considers a molecule in a quasi-lattice, whose mean position is determined by a potential energy well defined by that molecule and its adjacent neighbours. The probability that the molecule will jump from its position to an adjacent position will depend on having sufficient thermal energy to jump out of the potential energy well, as well as the probability of actually crossing over the barrier to the adjacent position. At any temperature, the probability of the molecule jumping to an adjacent position will be a function of the fraction of holes in the polymer, the molecular frequency (the number of tries per unit time), and having sufficient thermal energy to jump over the energy barrier. The fraction of holes is related to the thermal expansion. The molecular frequency can be shown to be equal to $kT/h$, which is the universal frequency whose value is dependant only on the temperature ($k$ is the Boltzmann constant and $h$ is the Plank constant). The probability of having sufficient thermal energy is determined by the Boltzman factor $\exp(-\Delta E/kT)$, where $\Delta E$ is the free energy per molecule. The frequency of molecular jumps, $v_{mol}$ is then given as

$$v_{mol} = \left( \frac{v_\phi^{-1/3} kT}{(2\pi mkT)^{1/2}} \right) e^{-\Delta E/kT}$$

where $v_\phi$ is the free volume per molecule, $m$ is the mass per molecule, and $\Delta E$ is the height of the energy barrier. The pre-exponential factor changes very little as compared with the exponential factor and is assumed to be constant. The height of the energy barrier can be equated to the Gibb's free energy $\Delta G = \Delta H - T\Delta S$ ($\Delta H$ is the enthalpy and $\Delta S$ is the entropy). If one separates the exponential into two terms, the entropy term is seen to be a constant, $(\exp(\Delta S/k))$, and can then be included in the pre-exponential factor.

It is now assumed that an applied stress, $\sigma$, produces a linear shift, $V\sigma$, of the energy barrier. This is visualized on the molecular level as a stress applied on an area $A$ of the molecule normal to the direction of applied stress, causing a displacement $d$. Thus work equal to $Fd = \sigma Ad = \sigma V$ is done in the direction of applied stress. (The quantity $V$ is interpreted as being the volume of the displaced molecular segment.) In effect, the height of the energy barrier in the direction of stress is decreased by the amount $V\sigma$. 
The frequency in the direction of applied stress, \( v_f \), is then given by

\[
v_f = v_o e^{\frac{-(\Delta H - V\sigma)}{RT}}
\]

where \( v_o \) is assumed to be constant, or nearly so. In the opposite direction, the energy barrier is increased by \( V\sigma \), since work must be done to move the molecule in the direction opposing the applied stress. The frequency in the opposite direction of applied stress, \( v_r \), is then given by

\[
v_r = v_o e^{\frac{-(\Delta H + V\sigma)}{RT}}
\]

The net flow in the direction of applied stress is then given by

\[
v_{\text{net}} = v_f - v_r = v_o e^{\frac{-\Delta H}{RT}} \left( e^{\frac{V\sigma}{RT}} - e^{-\frac{V\sigma}{RT}} \right)
\]

Finally, the assumption is made that the net flow in the forward direction is directly related to the rate of change of strain,

\[
\dot{\epsilon} = \dot{\epsilon}_o e^{\frac{-\Delta H}{RT}} \sinh \left( \frac{V\sigma}{RT} \right)
\]

where \( \sinh x = e^x - e^{-x} \). For relatively high stress, \( \sinh x = \frac{1}{2} e^x \), and the following equation is arrived at.

\[
\dot{\epsilon} = \frac{\dot{\epsilon}_o}{2} e^{\frac{-\Delta H - V\sigma}{RT}}
\]

Rearranging this we obtain

\[
\ln \dot{\epsilon} = \left[ \frac{-V}{R} \right] \frac{\sigma}{T} + \left[ \ln \left( \frac{\dot{\epsilon}_o}{2} \right) - \frac{\Delta H}{RT} \right]
\]
By assuming that the second term is constant, or nearly so over a limited range of
temperature, one can obtain a value for the quantity \( V \) by plotting \( \sigma/T \) versus \( \ln \dot{\varepsilon} \), and
determining the slope of the curve \( (-V/R) \). This equation has been found to be linear for
certain amorphous polymers such as polycarbonate [98]. Further, if the same
mechanisms are governing deformation at two separate temperatures, the lines will be
parallel, and the distance between those lines will give a value for the activation energy
\( \Delta H \).

It was shown that the peak stress followed a Coulomb dependency upon the hydrostatic
pressure according to the relationship \( \tau = \tau_{\text{atm}} + \phi P \). This criterion may be combined
with the Eyring equation to generate the following equation

\[
\dot{\varepsilon} = \frac{\dot{\varepsilon}_0}{2} \left( 1 - \frac{\Delta H - \tau_{\text{atm}} V^* PV}{RT} \right)
\]

where \( \phi = V^*/V \). Some researchers have interpreted the quantities \( V \) and \( V^* \), the shear
and pressure activation volumes respectively, as being independent quantities. The term
\( PV^* \) then represents the work done against the hydrostatic pressure to form a hole of size
\( V^* \) [99].

### 2.6.6.3 A Theoretical Model For Yielding In Glassy Polymers

A molecular model for yield of glassy polymers was developed by Argon based upon the
strain field generated by a molecular chain when it is bent. The glassy polymer chain is
modelled as an elastic rod, and the elastic energy required to place bends (or kinks),
equal in magnitude and opposite in direction, in one of the glassy rods is determined.
Using an elastic model developed by Li and Gilman [100], the free energy of the two
kinks is given by

\[
\Delta F = \frac{3\pi\mu\omega^2a^3}{16(1 - \nu)} - \frac{9\pi\mu\omega^2a^3}{8(1 - \nu)} \left( \frac{a}{z} \right)^5
\]

where \( \mu \) is the shear modulus, \( \omega \) is the angle of the bend and is a measure of the strength
of the bend, \( a \) is the radius of the elastic rod, \( z \) is the distance between kinks, and \( \nu \) is
the Poisson's ratio. The first term is the self energy of the two kinks and the second term
is their interaction energy. The shear stress term, \( \tau \), is introduced when the work done is added to the relationship, giving the free enthalpy in the body

\[
\Delta G = \Delta F - \Delta W
\]

\[
\Delta G = \frac{3\pi \mu \omega^2 a^3}{16 (1-\nu)} - \frac{9 \pi \mu \omega^2 a^3}{8 (1-\nu)} \left( \frac{a}{z} \right)^5 - \pi \mu \omega^2 a^3 \left( \frac{\tau}{\mu} \right) \left( \frac{z}{a} \right)
\]

Differentiating with respect to \( z/a \) gives the activation free enthalpy for formation of a pair of molecular kinks with given strength \( \omega \) under an applied shear stress.

Next a pressure term is added by assuming that kink formation creates a separation at the kink between adjacent elastic rods if the bend angle is greater than a critical angle, \( \omega_c \). The final expression for the total activation free enthalpy for the production of a pair of molecular kinks (\( \omega > \omega_c \)) is

\[
\Delta G_f = \frac{3\pi \mu \omega^2 a^3}{16(1-\nu)} \left[ 1 - 8.5(1-\nu)^{5/6} \left( \frac{\tau}{\mu} \right)^{5/6} \right] + 0.15\mu a^3(\omega - \omega_c)^2 \left( \frac{P}{\mu} \right)
\]

Next, the shear strain is derived based upon molecular motions, and then integrated with the energy of formation equation to give the following expression

\[
\dot{\gamma} = \pi C v_s \omega^2 a^3 \left( \frac{z}{a} \right) \exp \left[ -\frac{3 \pi \mu \omega^2 a^3}{16(1-\nu)kT} \left( 1 - 8.5(1-\nu)^{5/6} \left( \frac{\tau}{\mu} \right)^{5/6} \right) - \frac{0.15\mu a^3(\omega - \omega_c)^2}{kT} \left( \frac{P}{\mu} \right) \right]
\]

where \( C \) is the total volume density of potentially rotatable segments, and \( v_s \) is the frequency factor, of the order of the atomic frequency.

It is noted that the Argon equation has the general form

\[
\dot{\gamma} = \dot{\gamma}_o \exp \left[ \left(-A\mu + B\tau^{5/6} - CP\right)/kT \right]
\]
which is quite similar to the Eyring equation. The shear stress is raised to the factor 5/6 instead of one for the Eyring equation, and numerically the two are close in value. As well, the activation energy term, $A\mu$, is due specifically to the elastic energy of the kinks, both self energy and interaction (between kinks) energy.

Comparison was made experimental results on a number of glassy polymers at atmospheric pressure. In this case the pressure term drops out of the equation. The temperature dependency of the ratio $\tau/\mu$ is then given by the expression

$$\frac{\tau}{\mu} = \frac{0.077}{1 - \nu} \left[ 1 - \frac{kT}{A\mu} \ln \left( \frac{\dot{\gamma}}{\dot{\gamma}_0} \right) \right]^{4/5}$$

where $A = \left( \frac{3\pi \omega^2 a^3}{16 (1-\nu)} \right)$ and $\dot{\gamma}_0 = \pi C \nu a^3 (z/a)_{eq}$.

Experimental data carried out by Foot and Ward[101] for polyethylene terephthalate shows a good fit to the Argon model (Figure 2.18). Similar fits were noted in Argon's article for atactic polystyrene, bisphenol-a carbonate, and poly-methyl-methacrylate.

In polymers there is a general trend in which the temperature dependence of the shear modulus is similar to the temperature dependence of the shear yield stress. Since the activation energy term is a function of the shear modulus, it is a function of the temperature (due to the temperature dependence of the shear modulus). This is an important factor in the good correlation between the model and the data for glassy polymers over large ranges of strain rate and temperature. In this respect it gives a better fit to the data than the Eyring equation. However, both the shear stress and the shear modulus have to be determined for the Argon theory, rather than just the shear stress for the Eyring model. The other similarity between the Eyring and the Argon model is that Argon defines the activation volume as $(3\pi \omega^2 a^3 \ 8.5) / (16 (1-\nu)^{1/6})$, or $5.3\omega^2 a^3$. (The interpretation of the activation volume is not clear. One interpretation is that the activation volume represents the volume of the polymer segment which has to move as a whole in order for plastic deformation to occur.) This turns out to be the pre-shear stress factor $B$, which is the quantity defined as the shear activation volume from the Eyring equation.
Figure 2.18: Theoretical and experimental results for the temperature dependence of the plastic resistance of polyethylene-terephthalate. (Redrawn from data of Foot and Ward, as referred to in Mechanical Properties of Solid Polymers by I.M. Ward, John Wiley & Sons, 2nd Edition (1983), p.389, ISBN 0 471 90011 7)
Lastly, for many glassy polymers, the ratio of the shear stress to the shear modulus, extrapolated to 0 K, are of similar constant value. The Argon model predicts that the shear stress at absolute zero Kelvin is a function of just the shear modulus and the Poisson's ratio:

\[
\left( \frac{\tau}{\mu} \right)_{T=0} = \frac{0.077}{(1 - v)}
\]

Both the Eyring and the Argon models predict the strain rate-shear stress relatively well over ranges of strain rate and temperature. However, there are significant differences in interpretation of the mechanisms involved. The Argon theory considers yield as a nucleation controlled process, determined by the elastic stress field surrounding a kink. In contrast, the Eyring approach considers yield a flow problem, where flow can occur at infinitesimal stress.


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3. Equipment

3.1 Introduction

A high pressure tensile testing machine was designed, fabricated and proven for this work. The machine is capable of testing samples in tension at various strain rates, at pressures up to 400 MPa and temperatures up to 200°C. The maximum design load is 4500 N (1000 lb). Tensile samples can be extended up to 16 cm.

Schematics of the apparatus are shown in Figures 3.1 and 3.2, and a study of these figures will give an indication of the workings of the machine. Tensile testing is carried out in the top pressure vessel. The bottom pressure vessel functions to compensate for fluid volume changes in the top vessel due to shaft withdrawal. It is also referred to as the volume compensator to distinguish it from the top pressure vessel. Located centrally is the actuation shaft, which passes from the top pressure vessel, through the crosshead of an Instron machine, and into the volume compensator. The actuation shaft is connected to the load cell and to the bayonet connector, shown in the schematic of the pressure vessel in Figure 3.3. The bayonet connector is designed for a .635 cm rod, positioned horizontally, to be inserted into it and, with a 1/4 turn, engaged. This is the action used to attach the gripping assembly and test sample upon loading. The schematic of the bayonet connector and the gripping assembly illustrated in Figure 3.4 shows this in greater detail. The sample itself is mounted in a set of grips. The top grips are attached to the top closure. The bottom grips include the .635 cm rod mounted sideways (horizontally) which engages the bayonet connector. Tensile testing is initiated by moving the crosshead of the instron machine, which is connected to the actuation shaft, downward.

3.2 Machine Design and Fabrication

3.2.1 Pressure Vessel Design

The stress distribution for cylindrical monobloc pressure vessels is derived in Appendix A. Within the elastic limit of the vessel material, the largest stress component occurs at the bore in the transverse direction, and is tensile in nature. This has
Figure 3.2: Side section of the high pressure tensile testing machine.
Figure 3.3: Pressure vessel and its internal components.
machining and design repercussions. First, the inner bore should have a smooth surface finish to reduce the effect of machining marks acting as stress raisers. Second, any port entering the side of the vessel increases the local stress by a factor of three. Therefore, ports should be located in the end closures, where the stresses are smaller and compressive in nature. And third, but not quite so directly, it emphasizes the importance of ductility and fracture toughness of the vessel material.

The elastic limit for cylindrical monobloc pressure vessels can be related to the pressure and vessel geometry, and is derived in Appendix A as well. The equation relating these is given as

\[ Y_o = \sqrt{3} P \frac{W^2}{W^2 - 1} \]

where \( Y_o \) is the yield strength of the vessel material, 
\( P \) is the maximum test pressure, and 
\( W \) is the wall ratio (OD/ID).

It can be seen from this equation that increasing vessel wall thickness beyond a certain point has little effect on increasing the yield criteria (see the elastic limit curve in Figure A.4, Appendix A). Specifically, given a wall ratio, \( W \), of 3 will require a yield strength 9/8 times greater than that for a cylinder of infinite wall ratio.

Above the elastic limit, the pressure vessel will begin to plastically deform. The burst limit for a vessel composed of elastic-perfectly plastic material is derived in Appendix A, and is given by

\[ P_{\text{burst}} = \frac{2 Y_o}{\sqrt{3}} \ln W \]

Analysis of the stress distribution shows that deformation begins initially at the bore of the vessel and grows radially outward. Given an elastic-perfectly plastic material, failure occurs when the deformation zone reaches the outside diameter. For a vessel with a wall ratio of 3, this pressure is 2.5 times that for the elastic limit. The technique of autofrettage takes advantage of this growing deformation zone to produce pressure vessels with a greater elastic limit. By partially over-pressurizing the vessel, an inner
deformation zone is created. Further deformation will not occur until this over-pressure is surpassed. However, the burst limit remains unchanged.

A vessel design with an ID of 3.8 cm and an OD of 12.7 cm was chosen as a compromise between the internal space requirements for the tensile components and the overall size and weight of the pressure vessel.

### 3.2.2 Pressure Vessel Material

Materials were then examined which could meet the strength requirements. The family of high strength low alloy steels were examined, and two alloys initially selected, 4340 and 300M. A review of the effect of chemistry, ladle processing, and heat treatment on their mechanical properties is given in Appendix B. Both are basically the same composition with the 300M having a Si addition for solid solution strengthening and a vanadium addition for grain refining. These additions have a significant effect on the TME temperature (tempered martensite embrittlement).

The material selected was 4340 VAR steel (0.4C 1.8Ni 0.8Cr 0.25Mo). Vacuum arc remelting (VAR) reduces the incidence of inclusions which become elongated in the longitudinal direction during thermo-mechanical processing. This practice increases the fracture toughness in the transverse direction, which was seen from the stress distribution analysis to be the direction of the largest tensile stresses. The inner bore was machined prior to heat treatment so that quenching would occur from the surfaces of both the inner and outer diameter. Heat treatment consisted of austenitizing at 800 °C, quenching in 50 °C oil, and then tempering at 510 °C. The resulting yield strength was 1250 MPa at room temperature. The yield strength at 230 °C for this material is 1000 MPa (See Figures B.6 and B.7 in Appendix B). This is greater than the yield criteria, and except for local stress raisers, the material is strained elastically only. This gives an elastic design safety factor of 1.31 for the most adverse conditions. The safety factor using the burst limit as the criteria is 3.5 for the same conditions.
3.2.3 Component Design

The design specifications for the various components and assemblies of the machine are given in Appendix D. They include the dimensional drawings, tolerances, surface finishes as well as the design rationale used.

Pressure Vessel Closures

The end closures have a 500,000 N (106,000 lb) load exerted on them at maximum pressure, and must be robust enough to withstand the pressure while maintaining the seal. Sealing between the closure and vessel is by "O"-ring and metal backup ring. Both closures contain hydraulic ports. The bottom closure also contains three additional ports for electrical feedthroughs. The top closure consists of two pieces, the plug and the retaining screw. This allows the plug and the attached loading assembly to be placed into position without a screwing motion. The 0.95 cm diameter actuation shaft passes through the centre of the bottom closure. The seals and metal backup washers sealing between the shaft and bottom closure are also housed in the bottom closure.

Actuation

A decision was taken to use reciprocal rather than rotary motion to actuate the tensile test. Rotary motion had the advantage that there is no motion in or out of the pressure vessel. Therefore, the fluid volume inside the pressure vessel stays the same, and the pressure remains unchanged during the tensile test. The major drawback is that the rotary motion has to be mechanically translated to a reciprocal motion inside the pressure vessel. Reciprocal motion of the actuation shaft had the opposite set of advantages and drawbacks. This motion is direct and requires no additional mechanisms to pull the tensile sample. However there was still the significant problem of maintaining pressure during the test. As the shaft is withdrawn from the pressure vessel, the fluid volume increases by an amount equal to the volume of the shaft that is withdrawn. The pressure inside the vessel would gradually decrease during the tensile test as a result. The solution devised was to make a second vessel and position it so that the two cylindrical axes coincide. The actuation shaft runs along this axis into each vessel. Motion of the shaft will then result in the volume of shaft entering the one vessel being equal to the volume leaving the other. By connecting the two vessels hydraulically, the fluid volume in the system will remain the same and the pressure will therefore
remain constant during the test. An additional advantage of this approach is that the outward thrust from the pressurized vessels on the actuation shaft is balanced. This thrust is sizeable. For an actuation shaft with a diameter of 0.82 cm, the outward thrust is equivalent to a three metric ton load.

Strain rate was controlled using an Instron testing frame. Integrating the vessel with the Instron frame posed a number of problems. First, the height of the Instron crosshead added sufficient extra length to the actuation shaft which bridges the two vessels so that buckling of the shaft would occur. Some means of reinforcement had to be employed. Second, any misalignment between shaft and crosshead motion could cause high lateral forces to be exerted on the shaft at either end of its travel. This meant that a "floating" interface be used between the crosshead and the component clamped onto the actuation shaft. The solution to this is described in the section on Actuation Assembly, in Appendix D.

Another problem of integrating the vessel with the Instron frame was the clearance required for insertion of the sample into the machine. The sample, grips, loading tube and top closure are inserted as a unit. This assembly measures 35 cm in length. Fortunately, there was a 7.5 cm diameter hole located centrally in the top frame of the Instron, and insertion was then done through this hole.

*Internal Components*

The internal components within the pressure vessel include the tensile grips and loading tube, the bayonet connector, and the load cell. This is shown schematically in Figure 3.4. The tensile grips had to be designed and fabricated to fit the restricted internal dimensions of the pressure vessels. The top and bottom grips have two axes of rotation, similar to a universal joint, to compensate for any misalignment of the tensile sample. The gripping action is by sliding wedges. As the sample pulls the grips, the wedge shape forces the grips further into the sample, so that they are self-tightening. The surface of the wedges are serrated in a pyramidal pattern to allow the grips to bite into the sample.

Loading of the sample is done with a bayonet type connection. As previously mentioned, a pin mounted sideways in the bottom grip is inserted into the bayonet connector and given a quarter turn to engage. Twisting is done by a tube which passes
down the outside of the grips. The bottom of the tube has an edge which turns the pin into position. There is 1 cm of travel of the actuation shaft/load cell/bayonet connector before engagement takes place. In this manner there is no sliding or other interference during the tensile test by the loading tube.

All of the components are designed for a maximum load of 4500 N (1000 lb), with suitable safety factors.

3.2.4 Hydraulic System

A schematic of the hydraulic system is shown in Figure 3.5. Hydraulic oil was used as the pressurizing medium (Shell TELLUS hydraulic oil). Pumping is done by a manually operated piston screw pump. The system is pressurized by alternately drawing oil from the reservoir and pushing it into the vessel. The valves on either side of the pump are opened and closed in synchronization with the drawing and pushing actions of the pump. This cycle is repeated until the desired pressure is attained. At the top of the vessel is a valve which allows air to be purged from the system prior to pressurization. A rupture disc, designed to burst at 450 MPa, is attached to the high pressure tubing linking the two pressure vessels. Pressure was measured with an Astral pressure gauge, with a full scale of 550 MPa and an accuracy of 2% F.S..

Maintaining pressure during the withdrawal of the actuation shaft was accomplished with the addition of the volume compensator, as mentioned previously. The other option was to use a large accumulator, in which gas at the top of the accumulator is compressed to the pressure of the system. Since the compressibility of the gas is so large, a small change in volume will not cause a large change in the pressure of the system. In order to operate at pressures of 420 MPa, however, gas must be charged from compressed bottles at 15 - 20 MPa first, prior to pressurization of the system. As well, the size of the accumulator must be significantly larger than the vessel in order to be effective. Considerations of cost forced another option to be considered and the volume compensator concept was developed which eliminated this problem. The chance that was taken was that the alignment of the actuation shaft could not be maintained well enough to maintain the seal or prevent buckling of the shaft. It turned out that the actuation process was more forgiving than was anticipated, and no problems were encountered.

A further simplification was suggested by Roy Pick of the Mechanical Engineering
Department, University of Waterloo. A 0.95 cm high pressure tube could replace the 0.95 cm actuation shaft, thereby eliminating the outside hydraulic connections. Thus, as the shaft moved during actuation, the pressurized fluid could flow directly from the one vessel into the other through the tube. This was not done for the following reason. The actuation shaft is strained compressively by the pressure inside the two vessels, causing its diameter to increase. This compressive strain would also be experienced by the high pressure tube. In addition to this, the high pressure tube will also undergo an additional expansion due to pressurization of the tube. Calculations using the pressure vessel stress and strain analyses given in Appendix A showed that the radial strain of the tube to be twice that of the shaft at any given pressure. In order to minimize the tolerance requirements for the sliding seal, it was decided not to take this chance. It should also be kept in mind that the hardness of the two components are different, the high pressure tube being more ductile, with a lower yield stress.

High pressure systems are distinguished mostly by the connections and seals used. Some notes on these specific to this system are included in Appendix E.
Figure 3.5: Schematic of high pressure hydraulic system.
3.2.5 Load Cell Design

The basis of strain gauge measurement is the relationship between the resistance change and the length change of an alloy conductor. Alloys have been developed in which the relationship is linear not only in the elastic strain range but the plastic strain range as well. Measurement of the resistance changes, which are quite small, is done with a Wheatstone bridge. Resistances are determined by adjusting a potentiometer until the Wheatstone bridge is balanced.

The data acquisition system employed used an analogue to digital (A/D) conversion which measured voltages rather than resistances. When used with a Wheatstone bridge circuit, the bridge is in the unbalanced state and the relationship between strain and voltage change deviates from linearity, the deviation increasing with increasing strain.

There are other secondary effects which must also be compensated for. An increase in temperature will result in expansion of both the strain gauge and the substrate it is mounted upon. The differential expansion between the two will result in an apparent strain due to temperature. By suitable arrangement of the bridge circuit, these effects can be made to cancel one another, so that the net voltage output will reflect only the extension or compression of the substrate due solely to the applied load. Similarly, any pressure effects can be made to cancel by suitable arrangement of the gauge. Strain gauge arrangement within the bridge circuit can also be used to augment the output signal by factors up to four. This is particularly advantages when the signal is small.

Strain gauge theory examining the non-linearity of unbalanced bridges, compensation for temperature and pressure, as well as signal augmentation are discussed more fully in Appendix C.

Tensile loads can be measured from strain gauges mounted either inside or outside the pressure vessel. External measurement must account for the friction between the sliding seal and the actuation shaft. This requires that two tests be done, one with and one without a tensile sample, for each combination of temperature, pressure and strain rate. The difference between the two values would give the actual load due to the tensile sample alone. For sensitive and reproducible results, the no-load signal must be significantly smaller than that of the load signal, with little variability. Given situations involving load measurement of polymers at either elevated temperatures (low tensile loads) or varying
strain rates (subtle changes in load), this approach could not give the required sensitivity.

The internal load cell approach required developing a sensing device to work under conditions of elevated temperatures and pressures. The load cell system designed is composed of three separate elements: the mechanical transducer, the strain gauges, and the electrical feedthrough. The mechanical element had to be both rigid and sensitive. A 1.6 cm diameter cylinder with a 0.3 mm wall thickness, of high strength and moderate stiffness (Ti-6Al-4V) was used (Figure 3.6). The strain gauge circuit had to be stable under various conditions of temperature and pressure. Techniques were available for adjusting to variable temperatures, and these same techniques were extended to compensate for the effects of pressure. This approach proved successful. Finally, the voltage for the strain gauge circuit had to be transmitted through the wall of the pressure vessel under conditions of 200 °C and 400 MPa. This was accomplished by drilling a hole through a high pressure plug and inserting a stainless steel sheathed thermocouple wire. The two pieces were then silver soldered together.

The specifications for the load cell designed and fabricated are given in Appendix F. The load cell circuit used in shown in Figure 3.7. Included with the Wheatstone bridge circuit are two balancing arms which allow for coarse and fine adjustment to zero the output prior to testing. An analysis of the balancing arm circuit is included in Appendix F.

Calibration was done in two stages. First, calibration was done a room temperature and pressure using calibrated weights. This method of testing was not possible at elevated pressures since the calibration weights are much larger than the internal dimensions of the pressure vessel. In this case a helical steel spring was given a 2.5 cm extension at pressures ranging from atmospheric pressure to 385 MPa in 33 MPa intervals. The extensional load was the same at all pressures tested.

Signal output from the bridge was sent to an amplifier, then to an A/D convertor, and finally to an IBM compatible PC. A computer program was written to allow real time graphing of the tensile test. This program is listed in Appendix G, along with specifications for the amplifier and A/D systems used.
Figure 3.6: Front section and view of the load cell and strain gauge pattern.
Figure 3.7: Load cell circuit incorporating two balancing arms with the Wheatstone bridge strain gauge circuit.
3.2.6 Heating

The machine was designed for a maximum testing temperature of 200 °C. This temperature has been shown to be well within the design capacity of the pressure vessel material (Appendix B). This allowed heating to be done from outside the pressure vessel. The temperatures were achieved by resistance heating, using thermocouple wires as the resistance element (Type K, AWG 24), wound round the outside diameter of the vessel. The cylindrical vessel is mounted on a 2.5 cm thick plate. The plate added sufficient thermal mass that two sets of windings were required, one for the bottom 12 cm and another for the top 48 cm. A schematic of the heating system is shown in Figure 3.8. The overall heat input is determined by the resistance of the wire and the voltage setting of a variable transformer. The temperature of the pressure vessel was monitored throughout the tensile test. Thermocouples were attached at 6 cm intervals from top to bottom of the outer diameter of the vessel and sent to the data acquisition system. Control of the temperature was done by adjusting the variable transformers, one for each set of windings. As a safety feature, all power to the variable transformers runs first through an oven temperature controller. It functions not to set the temperature, but to shut off the power to the variable transformers should the set temperature be surpassed. The pressure vessel was insulated with fibreglass bats, to a thickness of 13 cm, which are contained in a cylindrical housing of sheet steel.

The central 48 cm of the vessel's 60 cm length was maintained within +/-0.5 °C of the set temperature for each of the tensile tests conducted.
Figure 3.5: Schematic of the heating circuit for the lenslet imaging apparatus.

AWG 24 = 0.51 cm
Braided Abrenglass 500 °C
Type K Thermocouple (Yellow & Red)

Heating Element
3.3 Sample Dimensions and Fabrication

The polypropylene tested had a number average and weight average molecular weight of 71,000 and 377,000 respectively. The polypropylene was obtained in sheet form, 3.2 mm thick, stress relief annealed. Sample dimensions were determined at the same time the grips were designed to match the constraints of the small internal space and the maximum anticipated load. The shape is the standard dog-bone shape used in the ASTM tensile testing specifications. Sample dimensions are shown in Figure 3.9. The sample is machined to dimensions using a table mounted router and a template. Variation in the width dimension was less than .03 mm. Any sample exceeding this was discarded.

Tests were made to determine if the hydraulic oil would affect the tensile results. These results are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Strain Rate (1/min)</th>
<th>Coating</th>
<th>Yield Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Air</td>
</tr>
<tr>
<td>atmospheric</td>
<td>.2</td>
<td>none</td>
<td>28.79</td>
</tr>
<tr>
<td>atmospheric</td>
<td>.02</td>
<td>none</td>
<td>24.66</td>
</tr>
<tr>
<td>atmospheric</td>
<td>.008</td>
<td>none</td>
<td>22.82</td>
</tr>
<tr>
<td>atmospheric</td>
<td>.002</td>
<td>none</td>
<td>21.17</td>
</tr>
<tr>
<td>atmospheric</td>
<td>.002</td>
<td>none</td>
<td>21.18</td>
</tr>
<tr>
<td>atmospheric</td>
<td>.002</td>
<td>none</td>
<td>21.36</td>
</tr>
<tr>
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<td>.002</td>
<td>gold</td>
<td>21.25</td>
</tr>
<tr>
<td>100 MPa</td>
<td>.002</td>
<td>gold</td>
<td>37.14</td>
</tr>
<tr>
<td>100 MPa</td>
<td>.002</td>
<td>none</td>
<td>37.15</td>
</tr>
</tbody>
</table>

At atmospheric pressure and 25°C, there is no difference in the yield stress between the samples tested in oil and air. The effect of coating the sample with a thin layer of gold (60 - 120 micron thickness) at 25°C has no effect on the yield stress when tested at atmospheric pressure or at 100 MPa. Even though there was no evidence of the oil having an effect on the yield stress, the polypropylene samples were gold coated as a precaution.
All dimensions in centimeters

Figure 3.9: Sample dimensions. Scale 1:1.
3.4 Procedure

Polypropylene sheet, 3.2 mm thick, was routed to the sample dimensions given in Figure 3.9. The samples were gold coated using a sputtering method to a thickness of 60 - 120 microns.

Testing was done in a matrix fashion, at four pressures, three temperatures and three strain rates. The pressures tested were 0, 100, 200 and 300 MPa, the temperatures were 25, 50 and 75 °C, and the strain rates were 0.2, 0.02 and 0.002 min⁻¹. Testing at strain rates faster than 0.2 min⁻¹ have been reported to result in self-heating of the sample, and so faster strain rates were not tested. Testing at 0.002 min⁻¹ takes 500 minutes for the test alone to achieve 100% extension, not including loading, pressurization, conditioning, and unloading. Strain rates slower than this were therefore not examined.

All samples were loaded and pressurized at temperature for 45 minutes prior to testing. This conditioning step was found to be necessary to stabilize the system. There are a number of time dependant adjustments the system must make due to these pressures. The polymer compresses in a viscoelastic manner, as does the laminate backing on the strain gauges. Any residual air within the vessel dissolves into the oil, causing the pressure to decrease. Each of these effects has been monitored at various times during the course of experimentation. The viscoelastic effects are stable after 10 minutes. The pressure stabilizes within 10 minutes as well. The conditioning period of 45 minutes was chosen so as to be on the conservative side.

Two tests were done for each combination of pressure, temperature, and strain rate. Tests carried out at strain rates of 0.2 and 0.02 min⁻¹ were continued to 100% extension, or failure, whichever came first. At strain rates of 0.002 min⁻¹, only one test was continued to 100% strain. The second test was terminated once the load maximum had been achieved.

Force-time data was collected and later converted to both stress-strain and tangent modulus-strain data.
4. Results

The results will be presented in two sections. The first section will examine the effect of pressure and strain rate on the uniaxial tensile stress-strain curves, first at a temperature of 25°C, followed by 50°C, and then 75°C. The second section will then examine the effect of the same set of variables, pressure and strain rate, on the derived tangent modulus-strain curves, first at 25°C, followed by 50°C and then 75°C.

The stress definition used was the engineering stress, \( s = F/A_0 \), where \( A_0 \) is the initial cross-sectional area at room temperature and pressure, and \( F \) is the force. The strain was determined from crosshead displacement and the initial gauge length at room temperature and pressure. No adjustment was made for dimensional changes in gauge length due to temperature or pressure.

Further data manipulation was carried out on the stress-strain data. This was possible because of the sensitivity of the internal load cell as well as the frequency of data sampling. The tangent modulus (defined as the slope of the tangent to the stress-strain curve) was plotted against strain.

The tensile test results were gathered in two groups. In the first group, tensile tests were run at 69 MPa pressure intervals, at room temperature, with single tests at five different strain rates, from 0.002 to 0.2 min\(^{-1}\). These results were reviewed, and the peak stress was plotted against the pressure for each of the strain rates. The relationship was close to linear in each case, with some variability.

The testing protocol was adjusted for the second group of tests. Each test was duplicated to determine the variability of each test condition. Two tests were carried out at each of the three strain rates tested, 0.002, 0.02 and 0.2 min\(^{-1}\) (the same strain rate range as the first set). The pressure increment was increased to 100 MPa and tests at room temperature repeated before conducting the 50 °C and 75°C tests. As well, a conditioning period of 45 minutes was introduced to allow the pressure to stabilize within the vessel, as well as time for the polypropylene sample to adjust to the pressure and temperature conditions. The reproducibility of the second group of stress-strain curves was extremely good.


4.1 The Stress-Strain Curve

4.1.1 EFFECT OF PRESSURE

4.1.1.1 Temperature: 25°C

Figure 4.01 shows the effect of pressure on the stress-strain curve at 25°C in 69 MPa intervals for a strain rate of 0.200 min⁻¹. At atmospheric pressure there is an initial steep increase in the stress, reaching a stress maximum (peak stress), followed by a decrease in the engineering stress, related to the formation of a localized reduced section, or neck. During neck formation, the microstructure transforms from a spherulitic structure to a fibrillar structure in which the polymer chains become aligned in the tensile direction. The result is orientation strengthening in the necked region, which stabilizes the neck. Further deformation then occurs in a highly localized region at the necked/non-necked interface. This localized neck formation region propagates towards either, or both, ends of the specimen. During neck propagation, also known as cold drawing, the stress remains constant until the neck formation region reaches both ends of the specimen, which in this case is at strains much greater than the 100% strain displayed here.

The most immediate and obvious effect of applying pressure is the increase in the overall level of the stress-strain curve. There are specific features of this effect that are noteworthy. First, the modulus also increases with increasing pressure. This remarkable effect is characteristic of the response of polymers to a superimposed hydrostatic pressure and differentiates them from the pressure response of metals, where the same pressures have a negligible effect upon the modulus.

At the higher pressures, the modulus increases in value over the strain range 3-10%. The effect is most pronounced at 207, 276 and 345 MPa pressure, but is also slightly discernable at 138 MPa. As well, there is a distinct bend in the curve to lesser slope at pressures of 207, 276 and 345 MPa, occurring at 10% strain and at values of 50-80% of the peak stress.

The strain at the peak stress occurs at approximately 20% extension for various pressures, which implies that the ratio of modulus to peak stress is approximately constant. In other words, the modulus response to pressure is similar to that of the peak stress.

The most direct measure of the increase in the stress response to increasing pressure is
the stress maxima, or peak stress. The amount of increase in the stress maximum for each pressure interval is approximately constant, suggesting a linear relationship between peak stress and pressure. (As will be shown in the Discussion section, this is not exactly true. There is a small but distinct discontinuity in the linear relationship at pressures corresponding to the pressure-induced glass transition.)

Stress-whitening, which occurs during neck formation at atmospheric pressure, is due to the formation of microvoids (which scatter light). In fact, as close inspection of the photographs of the deformed polypropylene samples, displayed in Figure 4.02, shows, there is mild stress-whitening observed in the non-necked gauge region, indicating that some microvoid formation occurs prior to the onset of necking.

Neck development occurs in the region between the peak stress and the draw stress. It begins progressively earlier and faster as pressure is increased. At 0.1 MPa pressure, neck development is gradual, reaching a stable draw stress at 80% strain. This point is reached at 70% strain at pressures of 69 MPa. At 138 MPa pressure, the transition is not as gradual, with a "collapse" in stress values to the draw stress occurring between 40-50% strain. This "collapse" occurs sooner and at a faster rate as the pressure increases, occurring between 33% and 41% strain at 207 MPa pressure, and 27% and 35% at 276 MPa pressure. At 345 MPa pressure, failure occurs before the neck is fully developed.

Stress-whitening is not observed at pressures of 35 MPa and above, indicating that microvoid formation (of a size greater than 1/20 of the wavelength of light) is prevented from occurring by the hydrostatic pressure (Figure 4.02). It has been speculated that microvoid formation is a necessary step in neck formation and cold drawing. It is obvious from these results that this is not necessarily so.

The draw stress also increases with increasing stress, with the incremental increase being the same for each pressure increment. The fracture strain above 207 MPa is less than 100%, and decreases with increasing pressure. At 345 MPa, fracture occurs before cold drawing can fully develop. Where fracture does occur, the fracture is located in the necked region, with the fracture surface transverse to the tensile direction. The fracture surfaces show a considerable amount of mismatch, indicative of a considerable elastic component to the strain in the necked region. The same transverse fracture for polypropylene tested at high pressure was reported by Mears and Pae [1] with cylindrical specimens.
4.1.1.2 Temperature: 50°C

The effect of pressure on the stress-strain curves at a temperature of 50°C is shown in Figure 4.03. The general response to pressure noted at 25 °C is evident at 50 °C.

The modulus increases in discrete steps with pressure. At 200 and 300 MPa pressure, the curves sweep upward to 8% strain (i.e. the modulus increases) at which point there is a bend in the curves to lesser slope. The same bend was observed at 25°C at a slightly greater strain, with the bend occurring at 10% at the higher pressures.

The peak stress increases with pressure, with the amount of increase for each pressure interval being approximately equal. In actual fact, the interval between 200 and 300 MPa pressure is slightly greater, and this will be shown to correspond with the pressure-induced glass transition at this temperature. The peak strain (the strain at which the peak stress occurs) decreases from 23% at 0.1 MPa pressure, to 21.5% at 200 MPa pressure and then down to 19% at 300 MPa pressure.

Neck formation is quite gradual at atmospheric pressure, with the draw stress value stabilizing at 100% strain. As the pressure increases, the strain at which the draw stress stabilizes decreases. The appearance of a more rapid transition to the draw stress appears in one of the curves at 100 MPa pressure, starting at 45% strain and stabilizing between 55% and 70% strain. At 200 MPa pressure the stabilization of the draw stress occurs at earlier strains (50% strain), and at 300 MPa pressure occurs at 40% strain.

Failure was not evident in these curves at any of the pressures. Finally, the draw stress increases in similar increments for each pressure increment.
4.1.1.3 **Temperature: 75°C**

The effect of pressure on the stress-strain curve at 75°C is shown in Figure 4.04 for a strain rate of 0.200 min⁻¹. In general, the curves are remarkable for what is not evident as compared with the curves at 25°C and 50°C, due to the fact that there is no pressure-induced glass transition at the pressures tested.

The step-wise increase in modulus with pressure increment is noted. The pressure also has a marked effect upon the strain at which the peak stress occurs. The strain at which the peak stress occurs has a maximum value not at 0.1 MPa pressure, but at 100 MPa pressure. These strains are 20, 24, 23 and 22 % for pressures of 0.1, 100, 200 and 300 MPa respectively. The peak stress increases in step-wise fashion, with the stress interval between pressure intervals being constant. There is no interval which is slightly larger which would be characteristic of the pressure transition.

Neck formation also shows the 100 MPa pressure to be the latest to reach a stable neck at 100% strain. This is greater than that seen at atmospheric pressure (55% strain). At pressures greater than 100 MPa, the strain at which a stable neck is formed decreases with increasing pressure. Also, at 200 and 300 MPa pressure, one of the two curves shows a rapid transition to the draw stress, reaching it at strains 15% sooner than its twin. It has been previously noted that the neck formation process is unstable. Further, invariably the curve showing the more rapid transition always has the slightly greater draw stress value. The draw stress increases with pressure, with the stress interval being approximately constant.
Figure 4.01: Tensile engineering stress-engineering strain curves for polypropylene. 
\( T=25^\circ C \) and \( \dot{\varepsilon} = 0.020 \text{ min}^{-1} \) for various pressures.
Figure 4.02: Photographs of polypropylene samples strained to 100%, or fracture, whichever came first, at varying pressures. Temperature = 25°C. Strain rate = 0.2 min⁻¹. Magnification = 0.75.
Figure 4.03: Tensile engineering stress-engineering strain curves for polypropylene. $T=50^\circ C$ and $\dot{\varepsilon} = 0.200\text{ min}^{-1}$ for various pressures.
Figure 4.04: Tensile engineering stress-engineering strain curves for polypropylene. T = 75°C and $\dot{\varepsilon} = 0.200 \text{ min}^{-1}$ for various pressures.
4.1.2 EFFECT OF STRAIN RATE

4.1.2.1 Temperature: 25°C

As was mentioned, the testing protocol was adjusted for Group II. A 45 minute conditioning period was added to allow both the vessel and the viscoelastic polypropylene to equilibrate to the test conditions. (The pressure vessel took about 10 minutes for pressure to stabilize. It is speculated that small pockets of air remaining in the vessel would slowly dissolve into the pressurized oil. As this occurred the volume available for the oil would increase, decreasing the pressure in the vessel. The pressure was increased slightly over this 10 minute period to compensate.)

The effect of strain rate on the stress-strain curves at 25°C for pressures of 0.1, 100, 200, and 300 MPa are shown in Figures 4.05 - 4.08. Two sets of tests were done at each of the three strain rates. The overlap of the two curves, from the initial modulus to strains past the peak stress shows extremely good reproducibility. The reproducibility of these curves is indicative of the repeatability of both the experimental conditions and the signal measurement system as well as the low variability of the polypropylene response to tensile deformation under those experimental conditions.

The modulus at 0.1 MPa pressure is seen to be affected by the strain rate, increasing with increasing strain rate (Figure 4.05). Soon after the start of the deformation, the curves of varying strain rate differentiate, indicating that the deformation has two components, plastic and elastic, from that point on. As the pressure increases, the modulus is less sensitive to the strain rate. At pressures of 200 MPa (Figure 4.07), there is little difference in modulus due to strain rate to 30 MPa stress. At 300 MPa, there is no difference in modulus due to strain rate until a stress of 55 MPa is reached, at which point the various strain rate curves begin to part (Figure 4.08).

There is a distinct bend in the upper portion of this section of the stress-strain curve at high pressures. At 200 MPa and a strain rate of 0.2 min⁻¹ (Figure 4.07), the bend occurs at approximately 62 MPa at a strain of 9%. The bend is not as distinct at the lower strain rates, occurring at 50 and 45 MPa for the 0.02 and 0.002 min⁻¹ strain rates respectively. The bend is even more pronounced at 300 MPa, occurring at 81 MPa for a strain rate of 0.2 min⁻¹, 73 MPa for a strain rate of 0.02 min⁻¹, and about 66 MPa for a strain rate of 0.002 min⁻¹. Again, the bend is less distinct as the strain rate decreases, and occurs slightly
earlier (in terms of strain, not time) at the slower strain rates. Specifically, the bend occurs at 10% strain for a strain rate of 0.2 min\(^{-1}\), and about 9% for strain rates of 0.02 and 0.002 min\(^{-1}\).

The peak stress values show little deviation in value and are clearly sensitive to strain rate. The interval in the peak stress between the 0.002 min\(^{-1}\) and the 0.020 min\(^{-1}\) strain rates is seen to be the same as the interval between the 0.020 min\(^{-1}\) and the 0.200 min\(^{-1}\) strain rates, which is indicative of a rate-activated process. The peak strains (the strains at which the peak stress occurs) are also affected by the pressure, occurring earlier as the pressure increases. At 0.1 MPa pressure, the peak strain occurs at 20%, 19% at 100 MPa, 18% at 200 MPa and 17% and 300 MPa pressure.

Neck formation (the section of the curve between the peak stress and the draw stress) shows some variability in response. In some cases the transition is gradual, but in others there is a point of sudden decrease marked by an abrupt change in slope down to the draw stress. At pressures of 200 MPa and greater, the process of neck development occurs at a more rapid rate, as determined by the strain at which the draw stress becomes constant.

The draw stress is also affected by the strain rate, increasing as the strain rate increases. The variability of the draw stress is greater than for the peak stress. If the neck formation process in the two samples is similar, then the draw stress values will be quite close. However, if the one sample abruptly decreases in value during neck formation and the other does not (e.g. 0.2 min\(^{-1}\) strain rate in Figure 4.05), then the sample which undergoes the transition first will invariably end up with the greater draw stress. This observation holds in general for all the samples tested. Hence, the greater variability of the draw stress values is related to the neck formation process. Since different neck formation paths leads to different neck geometries, it may be noted in passing that the geometry of the neck affects the final drawing stress, and that the neck formation process is inherently unstable.

The peak and draw stress values for Set I at 25 °C are shown in Table 4.1, and for Set II at 25 °C in Table 4.2.
The effect of strain rate on the stress-strain curves at 50 °C for pressures of 0.1, 100, 200 and 300 MPa is shown in Figures 4.09-4.12. Aside from the fact that the overall stress level of the curves is less than for the 25 °C curves, the main features remain the same, i.e. the modulus and peak stress are affected by the strain rate.

The modulus at 0.1 MPa shows an initial section, to 8 MPa stress, which is undifferentiated with respect to strain rate (Figure 4.09). As the pressure is increased to 200 MPa, the strain rate insensitive region becomes proportionately larger with respect to the peak stress (Figure 4.11). There is no distinct bend in the curve in the upper portion of this initial section, which was noted at 25°C. At 300 MPa and 50 °C, the bend in the curve is also observed, occurring around 50 MPa stress at a strain rate of 0.200 min⁻¹ (Figure 4.12). The bend occurs at lower stress levels as the strain rate decreases and is less prominent, consistent with the trend noted at 25 °C. One difference is that the bend at 300 MPa occurs at 3.5% strain, which is earlier than the 5% strain noted at 25 °C for the same pressure.

The peak stresses are affected by the strain rate, with the ratio \( \Delta s / \Delta \ln \varepsilon \) being constant, where s is the engineering stress and \( \varepsilon \) is the engineering strain. The strain at which the peak stress occurs also decreases with increasing pressure, decreasing from 21% at 0.1 MPa to 19% at 300 MPa pressure.

Neck development occurs at much earlier strains when the pressure reaches 300 MPa than at lower pressures. At 25 °C, this same transition occurred at lower pressures (200 MPa). Fracture before 100% strain shows the same temperature and pressure dependency as does neck development. At 25 °C, this occurs in the 200 MPa pressure tests, but is delayed at 50 °C, occurring in the 300 MPa pressure tests.

The peak and draw stress results at 50 °C are summarized in Table 4.3.
4.1.2.3 Temperature: 75°C

The effect of strain rate on the stress-strain curves at 75 °C for pressures of 0.1, 100, 200 and 300 MPa are shown in Figures 4.13 - 4.16. The main difference in the 75 °C data, aside from the lower levels of stress, is that the transition in deformation noted between 100 and 200 MPa at 25 °C and between 200 and 300 MPa at 50 °C is not evident in any of the 75 °C curves at the pressures examined.

The modulus at 0.1 MPa is also unusual (Figure 4.13). There is no initial section of the stress-strain curve which is unaffected by strain rate. In other words, there is no purely elastic region, with a flow component to the strain immediately upon deformation. As the pressure is increased to 100 MPa and greater, the initial elastic section of the curve returns (Figures 4.14 - 4.16).

Peak stresses are again affected by strain rate in a manner consistent with a rate-activated process. In general, the values of peak stress are quite consistent. The strains associated with the peak stress occur between 20 and 25%.

There is no evidence of a transition in the neck development to significantly earlier strains, noted in the 200 MPa curve at 25 °C, and the 300 MPa curve at 50 °C, nor is the accompanying fracture before 100% strain evident.

The peak and draw stress results for 75 °C are given in Table 4.4.
Figure 4.05: Tensile engineering stress-engineering strain curves for polypropylene. 
$T=25^\circ C$ and 0.1 MPa pressure for various strain rates.
Figure 4.06: Tensile engineering stress-engineering strain curves for polypropylene. T=25°C and 100 MPa pressure for various strain rates.
Figure 4.07: Tensile engineering stress-engineering strain curves for polypropylene. T=25°C and 200 MPa pressure for various strain rates.
Figure 4.08: Tensile engineering stress-engineering strain curves for polypropylene. T=25°C and P = 300 MPa for various strain rates.
Figure 4.09: Tensile engineering stress-engineering strain curves for polypropylene. 
T=50°C and P = 0.1 MPa for various strain rates.
Figure 4.10: Tensile engineering stress-engineering strain curves for polypropylene. T=50°C and P = 100 MPa for various strain rates.
Figure 4.11: Tensile engineering stress-engineering strain curves for polypropylene.
T=50°C and P= 200 MPa for various strain rates.
Figure 4.12: Tensile engineering stress-engineering strain curves for polypropylene. T = 50°C and 300 MPa pressure for various strain rates.
Figure 4.13: Tensile engineering stress-engineering strain curves for polypropylene. T=75°C and P= 0.1 MPa for various strain rates.
Figure 4.14: Tensile engineering stress-engineering strain curves for polypropylene. T=75°C and P= 100 MPa for various strain rates.
Figure 4.15: Tensile engineering stress-engineering strain curves for polypropylene. 
T=75°C and P = 200 MPa for various strain rates.
Figure 4.16: Tensile engineering stress-engineering strain curves for polypropylene. 
T=75°C and P = 300 MPa for various strain rates.
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1. The second test carried out at a strain rate of .002 1/min was terminated after the load maximum was determined.
2. No neck developed before failure.

Table 4.1: Peak Stress and Draw Stress at 25 °C. Set 1.
1. The second test carried out at a strain rate of .002 1/min was terminated after the load maximum was determined.

Table 4.2: Peak Stress and Draw Stress at 25 °C. Set 2.
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1. The second test carried out at a strain rate of .002 1/min was terminated after the load maximum was determined.

Table 4.3: Peak Stress and Draw Stress at 50 °C.
1. The second test carried out at a strain rate of .002 1/min was terminated after the load maximum was determined.

Table 4.4: Peak Stress and Draw Stress at 75 °C.

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4.2 The Tangent Modulus-Strain Curve

An intriguing feature of the high pressure deformation response of polypropylene came from the determination of the tangent modulus-strain curve. The tangent modulus is defined as the slope of the tangent to the stress-strain curve and this was plotted as a function of strain. Construction and analysis of the tangent modulus-strain curve is not done routinely. However, with the advent of A/D (Analogue to Digital) systems using personal computers, the technique is more readily implemented. In this study, data was collected with the use of both a multiplexer board and a data acquisition board (with analogue to digital conversion) linked to a computer. The resulting output could then be averaged and stored to file for subsequent data manipulation, such as conversion of the voltage input to stress and strain, determination of the derivative, data smoothing and finally graphing. This results in a finely discriminating tangent modulus-strain curve which was reproducible and gave an additional insight into the initial stages of tensile deformation that would not necessarily be evident from the stress-strain curve alone.

In the following discussion the effect of pressure on the tangent modulus-strain curves will be examined first at a temperature of 25 °C, followed by 50 °C and finally 75°C. That will be followed by a discussion of the effect of strain rate on the tangent modulus-stain curve at the same temperatures.

4.2.1 THE EFFECT OF PRESSURE

4.2.1.1 Temperature: 25 °C

There were two sets of tests carried out at 25 °C. The first set tested at 69 MPa pressure intervals, between atmospheric and 345 MPa pressure, at strain rates of .200, .080, .020, .008 and .002 min⁻¹. The variability was more than acceptable for certain relationships, such as the peak stress-pressure curve. However, the variability was only marginally acceptable for the peak stress-log strain rate curves for the various pressures. Specifically, the slopes of these curves were not sufficiently parallel from one pressure to another, making interpretation tenuous.

It was determined that the source of variability was the pressure, and that the problem
was twofold in nature. The pressure gauge utilized would not immediately respond to a slight initial decrease in pressure, sticking temporarily in position. This was remedied by periodically tapping the gauge to free the dial indicator. When this was done it was then determined that the vessel would decrease pressure for the first 10 minutes after initial pressurization before stabilizing. (It is speculated that small pockets of air remaining in the pressure vessel would dissolve into the pressurized oil, creating more available volume for the pressurizing oil, and result in the pressure decrease.) This was remedied by incorporating a 45 minute conditioning period at pressure prior to starting the tensile test for the second set of tests. Further changes made for the second set of tests were that the 0.080 min⁻¹ and 0.008 min⁻¹ strain rate tests were dropped, duplicate tests were done at 0.200, 0.020 and 0.002 min⁻¹ strain rates, and the pressure interval tested was increased to 100 MPa from 69 MPa. With repeat tests the variability would be directly evident.

The first result of this new testing protocol was seen in the peak stress-pressure curves, where the overlap in the duplicate tests was such that the second point was often indistinguishable from the first. The second result was that the variability in the slopes of the peak stress-log strain rate curves for various pressures was drastically reduced. The effect of pressure at 25°C for a strain rate of .020 min⁻¹ is shown in Figure 4.17 for Set I. There are several features which develop as the pressure is increased. First, the overall level of the tangent modulus-strain curve increases with increasing pressure. However, the most notable and intriguing feature is the emergence of a second maximum. This maximum is first apparent in the 69 MPa pressure curve at 5% strain. At 138 MPa pressure the maximum increases in value and shifts to 7% strain. Further increases in pressure do not shift the position (in terms of strain) of the maximum appreciably, however the maximum continues to increase.

As the pressure is further increased from 138 MPa to 207 MPa, the second modulus maximum does not shift to higher strains but remains the same (7% strain). There are five other noteworthy changes. First, there is a larger increase in the second modulus maximum between 138 MPa and 207 MPa than there is between 69 and 138 MPa pressure and 207 and 276 MPa pressure. This will be shown to be associated with the pressure-induced glass transition, in which the amorphous phase of the polypropylene is in the glassy state at pressures of 207 MPa and above. Second, there is a much greater drop immediately after the maximum at 207 MPa (a "precipitous" drop) occurring at 10%
strain. Associated with this is a bend in the stress-strain curve at that same strain. The interpretation given (to be made in the Discussion section) is that the precipitous drop marks the initiation of widespread yielding. Deformation to that point is considered predominantly elastic. Third, the value of the tangent modulus after the precipitous drop at pressures above the glass transition is approximately the same (240 - 270 MPa). Fourth, again at pressures in the glassy regime, the section of curve following the precipitous drop (11% - 13%) has a shallower slope from that both before and after. At times this region may be flat (plateau) or even rise slightly. This region is noted in all the curves above the pressure-induced glass transition. And fifth, the curves for 207 and 276 MPa pressure (in the glassy regime) follow relatively closely from the end of the precipitous drop to the peak strain (zero modulus). Consequently the shape of the stress-strain curves is the same from 10 to 20% strain, even though their stress levels differ. This suggests that deformation processes from the yield point onward to the peak stress are similar at these pressures.

4.2.1.2 Temperature: 50 °C

In general, there are similar trends noted at 50°C as at 25°C. The level of the tangent modulus-strain curve increases as the pressure is increased. As well, there is the emergence of a second modulus maximum with increasing pressure, however the development is delayed to greater pressures than at 25°C.

Figure 4.18 shows the tangent modulus-strain curve at a temperature of 50°C and a strain rate of 0.200 min⁻¹ for pressures of 0.1 MPa, 100 MPa, 200 MPa and 300 MPa. At 0.1 MPa pressure, the curve is rather featureless, steadily decreasing in tangent modulus values with increasing strain, to a peak strain of 24%.

At 100 MPa, there is evidence of a slight maximum appearing at 3.5% strain (270 MPa), followed by a gradual decline to a peak strain at 23%.

At 200 MPa, the second modulus maximum is well defined, occurring at 4% strain. This is followed by a three stage decline to the peak strain at 21%. The first stage has a steeper decline (4-8% strain), followed by a region of shallower decline (8-12% strain), and finally a region (12-21% strain) where the curve becomes steeper once again.
At 300 MPa, there is a disproportionately large interval jump in the second modulus maximum values (i.e. larger than the jump noted between 0.1 and 100 MPa, or between 100 and 200 MPa). This marks the pressure-induced glass transition at 50°C, with the amorphous phase being in the rubbery state at 200 MPa, and in the glassy state at 300 MPa. There is a region of precipitous decline between 6.5-8.5% strain. The first stage of the three part decline occurs between 6.5% and 8.5% strain, with the value of the tangent modulus dropping to 250 MPa. This is approximately the same value noted after the first stage decline at 25°C at pressures above the pressure-induced glass transition. The second stage of the decline is marked by a plateau, between 8.5% and 11% strain. The final third stage, between 11% and the peak strain of 18%, has a steeper slope.

Close comparison with the tangent modulus curves at 25°C indicates that the curve at 200 MPa and 50°C is very similar to the curve noted at 100 MPa at 25°C, both in terms of tangent modulus values and the strain at which particular features are evident (i.e. strain intervals for the first, second and third stages of decline after the maximum). However, comparison between the curve at 300 MPa and 50°C and that at 200 MPa and 25°C shows that, although the second maximum values are similar (700 MPa versus 800 MPa), the occurrence of specific events is not. The decline after the maximum is less steep at 50°C, and the final third stage of descent is also less steep.

4.2.1.3 Temperature: 75°C

The results at 75°C are not as spectacular as those noted at 25°C and 50°C, due mainly to the fact that the pressure-induced glass transition was not evident at the pressures tested.

Figure 4.19 shows the tangent modulus-strain curve at a temperature of 75°C and a strain rate of 0.200 min⁻¹ for pressures of 0.1 MPa, 100 MPa, 200 MPa and 300 MPa. Overall, the jump in modulus values between pressure intervals is similar, with no distinctly large jump between intervals indicative of the pressure-induced transition of the amorphous phase from the rubbery to the glassy state. Still, the pre-transition features (i.e. the emergence of a modulus maximum) is evident at 200 MPa pressure at 4.5% strain. This maximum becomes larger and better defined at 300 MPa pressure (4.5% strain and 350 MPa tangent modulus).
As well, the further pre-glass transition development of a three stage decline is slightly developed at 300 MPa. The first stage occurs between 5 and 9% strain, finishing at an tangent modulus value of 200 MPa, a value slightly lower than the values noted for 200 and 300 MPa pressures at 50°C (250 MPa tangent modulus). The second slightly shallower interval occurs between 9 and 12.5% strain, and the third stage occurs between 12.5% strain and the peak strain of 24%. The peak strains actually increase with increasing pressure to 200 MPa pressure (22.5% strain to 25% strain) before beginning to decline at 300 MPa pressure (24% strain).
Figure 4.17: Tangent modulus-engineering strain curves for polypropylene. T=25°C and a strain rate of 0.020 min⁻¹ for various pressures.
Figure 4.18: Tangent modulus-engineering strain curves for polypropylene. 
T=50°C and a strain rate of 0.200 min⁻¹ for various pressures.
Figure 4.19: Tangent modulus-engineering strain curves for polypropylene. T=75°C and a strain rate of 0.200 min⁻¹ for various pressures.
4.2.2 THE EFFECT OF STRAIN RATE

4.2.2.1 Temperature: 25 °C.

Certain sections of the tangent modulus-strain curves show greater sensitivity to the strain rate than others. In general, the initial modulus, as well as the second modulus maximum (where it occurs), show a significant response to the strain rate, with the height increasing with increasing strain rate.

The curves for various strain rates at 0.1 MPa pressure, shown in Figure 4.20, all show an initial spike followed by a gradual decline to the peak strain (20%). The initial spike shows a significant strain rate response, the higher the strain rate the higher the peak. Between 3-4% strain is a plateau, which also shows a strain rate effect. Finally, from the plateau to the peak strain (4-20% strain), the decline shows a slight effect due to strain rate. This portion of the curve approaches the abscissa asymptotically.

The curves at 100 MPa, shown in Figure 4.21, show greater variability over the first 3% strain. There are major differences due to strain rate at the second modulus maximum (3-5% strain) with the larger strain rates having the higher maximum values. There is a steep decline to 8% where the curves flare out to the peak strain at 19%. The differences due to strain rate over this range are negligible.

The effect of strain rate on the tangent modulus-strain curve for 200 MPa pressure at 25°C is shown in Figure 4.22. At this pressure the distinctiveness and reproducibility of the second modulus maximum is noteworthy. The effect of increasing the strain rate is to increase this maximum. In other words, the response is not entirely elastic at these strains and under these testing conditions. There is some plastic flow which reduces the height of the second maximum. There is a 200 MPa difference in the tangent modulus, with the 0.2 min⁻¹ strain rate curve peaking at over 800 MPa, and the 0.002 min⁻¹ strain rate curve peaking at just over 600 MPa. The greater strain rates have a steeper decline following the maximum (8-10% strain), and plateau at 200 MPa (10-12% strain), which is 50 MPa lower than that for the lower strain rates. In other words there is a crossing over of the curves at this point. There is little difference due to strain rate from the plateau to the peak strain.

The curves at 300 MPa (Figure 4.23) are similar in overall shape to the curves at 200 MPa. The differences in the second modulus maximum (5-8% strain) due to strain rate are
significant (200 MPa). Again, the highest strain rate declines the quickest, crossing over the other lower strain rate curves. The curve does not "plateau" after the precipitous decline, noted at 200 MPa, but tilts gently downward (11-14% strain) before increasing its rate of descent down to the peak strain. There appear to be differences due to the strain rate for this portion of the curve (14-18% strain), with their order reversed from what is the norm, that is the curve with the greater strain rate has the lower tangent modulus value.

The second modulus maximum determined from the tangent modulus-strain curves is shown in Table 4.5.

4.2.2.2 Temperature: 50 °C

The curves at 0.1 MPa pressure (Figure 4.24) show a smooth decline to the peak strain (20-25%), approaching the abscissa at a relatively shallow angle. There is a sizeable difference due to strain rate. What is notable is that there are few distinguishing features.

The curves at 100 MPa pressure (Figure 4.25) show a slight maximum (2.5-4.5% strain), and are considerably more sensitive to strain rate. Following this there is a gradual tapering to the peak strain (21%) with the decline also showing considerable strain rate sensitivity.

In the curves at 200 MPa pressure (Figure 4.26) appears the beginnings of the precipitous drop from the maximum. The material is on the verge of the pressure-induced glass transition. The maximum is quite strain rate sensitive. There is a 100 MPa difference in tangent modulus values between the .2 and .002 min⁻¹ strain rates. The precipitous drop ends at an tangent modulus value of approximately 250 MPa and a strain of 8%, which is a similar tangent modulus value as seen at 25°C. From that point to the peak strain there is a tailing off to the peak strain of 21%.

The 300 MPa curves pressure (Figure 4.27) are in the glassy state, and are characterized by a significant jump in the second maximum value. The difference in modulus between the .2 and .002 min⁻¹ strain rates is quite large at 200 MPa. The precipitous drop is steeper the higher the value of the maximum (6% - 8% strain), dropping to the plateau value of 250 MPa (9% -12% strain), which is the same value noted at 200 MPa at 50°C, and noted at 300 MPa at 25°C. However, the high strain rate curve does not cross over the lower strain rate curves at this point as they did at 25°C. The final descent (12% - 19% strain) shows no strong strain
4.2.2.3 Temperature: 75 °C

In general the curves at 75°C have few features, gently declining to the peak stress. The second modulus maximum appears only at much higher pressures (200 MPa and 300 MPa) and occurs at earlier strains compared with the maximum seen at 50°C and 25°C, never fully developing (i.e. characterized by a steeper drop following the maximum which ends at the shallower slope of the second stage of decline).

All the curves at 0.1 MPa (Figure 4.28) gently decline and approach the abscissa asymptotically (peak strain of 18% - 23%). The strain rate effect is greatest at the beginning.

At 100 MPa (Figure 4.29) the curves show the same shape as at 0.1 MPa, approaching the abscissa asymptotically, with a slight plateau noted in some of the curves from 3% - 5% strain. The effect of strain rate is largest at the start of the test. The curves trail off to a peak strain of 21% - 24%, which is greater than the peak strains at 0.1 MPa.

A second modulus maximum appears in the curves at 200 MPa (Figure 4.30), from 2-6% strain. The strain rate effect is largest at the maximum. The shape of the stress strain curves are similar from 15% strain onward. The same trend was noted as pressures approached and exceeded the pressure-induced glass transition at 50°C and 25°C. The peak strain is larger again than for the lower pressure curves (0.1 MPa and 100 MPa) with a value of 25% - 26%.

At 300 MPa (Figure 4.31), the maximum occurs between 3% - 6% strain. Again, the effect of the strain rate is largest at the maximum. There are suggestions of a section of slightly shallower slope after the maximum, occurring between 8% and 12% strain at 150-200 MPa. This region is also noted in the pre-pressure-induced glass transition regions at the lower temperatures. Following this, there is a gradual slope down to the peak strain of 23% - 26%, with a crossover of the highest strain rate. The effect of strain rate on this portion of the curve is small.
Figure 4.20: Tangent modulus-engineering strain curves for polypropylene. 
T = 25°C and P = 0.1 MPa for various strain rates.
Figure 4.21: Tangent modulus-engineering strain curves for polypropylene. 
T=25°C and P= 100 MPa for various strain rates.
Figure 4.22: Tangent modulus-engineering strain curves for polypropylene. T=25°C and P = 200 MPa for various strain rates.
Figure 4.23: Tangent modulus-engineering strain curves for polypropylene. T=25°C and P = 300 MPa for various strain rates.
Figure 4.24: Tangent modulus-engineering strain curves for polypropylene.

$T=50^\circ C$ and $P=0.1$ MPa for various strain rates.
Figure 4.25: Tangent modulus-engineering strain curves for polypropylene. 
T=50°C and P = 100 MPa for various strain rates.
Figure 4.26: Tangent modulus-engineering strain curves for polypropylene. 
T=50°C and P = 200 MPa for various strain rates.
Figure 4.27: Tangent modulus-engineering strain curves for polypropylene. 
$T=50^\circ C$ and $P=300$ MPa for various strain rates.
Figure 4.28: Tangent modulus-engineering strain curves for polypropylene. 
$T=75^\circ\text{C}$ and $P=0.1$ MPa for various strain rates.
Figure 4.29: Tangent modulus-engineering strain curves for polypropylene. T=75°C and P = 100 MPa for various strain rates.
Figure 4.30: Tangent modulus-engineering strain curves for polypropylene. 
T=75°C and P=200 MPa for various strain rates.
Figure 4.31: Tangent modulus-engineering strain curves for polypropylene. 
T=75°C and P = 300 MPa for various strain rates.
## Tangent Modulus: Second Maximum (MPa)

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Table 4.5: Second Maximum of the Instantaneous Modulus.
5. Discussion

Deformation of semi-crystalline polymers is a complex process, with a number of different mechanisms occurring simultaneously throughout the deformation process. At high pressures, however, conditions are such that certain mechanisms are hindered or restricted until a critical stress threshold is realized. This has two interesting repercussions. The first is that conditions at the threshold can be characterized and this in turn allows specific mechanisms to be assigned. The second is that prior to this stress or strain threshold, other mechanisms are forced to accommodate the additional deformation. The forced response is often exaggerated and characteristic of a particular mechanism. In other words, the mechanisms prior to the stress threshold are also revealed.

With the application of pressure there were two transitions observed in the tensile response of polypropylene, one speculated to be associated with the crystalline component and the other with the amorphous component. With increasing pressure there is the development of a distinct bend in the stress-strain curve to lesser slope prior to the stress maximum. It is suggested that this is the yield transition which is associated with the onset of crystalline flow. The second transition is a jump in the tensile response at a particular pressure. This was determined to be due to a pressure-induced rubber-to-glass transition of the amorphous component. In other words, the amorphous phase, which is in the rubbery state at low pressure, undergoes a transition to the glassy state at a particular pressure \( P_g \) (the glass transition pressure). Comparing the tensile response across these two transitions results in a model of the deformation mechanisms operating during the high pressure deformation process of polypropylene. This analysis is contained in Section 5.3.

The initial objectives of the doctorate were to determine the effect of temperature on the modified-Coulomb yield criterion for polypropylene deformed in tension and to determine the effect of pressure on the shear activation volume for polypropylene at various temperatures. Both objectives are based solely on the accurate determination of the stress maximum. It will be determined that the temperature has a significantly effect on the linear yield-pressure relationship given by the modified-Coulomb yield criterion. This is covered in Section 5.2. Finally, based on the Eyring flow model, the shear activation volume was determined for various pressures and temperatures. It was
observed that the shear activation volume-pressure relationship changes abruptly across the glass transition pressure. This is discussed in Section 5.4 along with the flow mechanisms involved.
5.1 Validation of the High Pressure Tensile Testing System

The initial objectives of the doctorate were to determine the effect of temperature on the modified-Coulomb yield criterion for polypropylene, and to determine the effect of pressure on the shear activation volume for polypropylene at various temperatures. The high pressure tensile testing machine was designed and fabricated for this purpose.

Upon completing the fabrication of the high pressure tensile testing machine, consideration was given to determining the reproducibility, sensitivity and accuracy of the tensile tests. A comparison of the peak stresses for polypropylene between this study and that of Mears, Pae and Sauer [1] for a strain rate of 0.200 min\(^{-1}\) is shown in Figure 5.01. The tensile yield stress in polymers is commonly defined as the peak stress (i.e. the stress maximum). There is usually no distinguishing feature before this stress maximum which can be associated with yielding. However, with the application of high pressure there is the emergence of a feature fitting this yield criteria, and thus the term peak stress is used here to describe the stress maximum and to distinguish it from the yield stress.

The data from Mears et al. were obtained at room temperature. The present work was carried out at 25\(^{\circ}\)C. In this work, the engineering stress is defined as the load divided by the initial cross-sectional area of the sample determined at 25 \(^{\circ}\)C and at atmospheric pressure. No attempt is made to compensate for cross-sectional changes due to subsequent pressurization or heating of the sample. There is no mention in the work of Mears et al. of any adjustment to the engineering stress values to compensate for changes in gauge cross-sectional area due to pressure.

In our study, two tests were carried out at each pressure. The two results at 100 MPa pressure were virtually identical and overlap one another to such an extent they are not distinguishable on the graph. The same is also true at 200 MPa pressure. The scatter in the Mears et al. data is due to the relative insensitivity of their load sensing device. Their actuating piston was hollowed out along the central axis and a strain gauge inserted past the point where the pressure seals would act. The advantage of the technique is that the strain gauge is at atmospheric pressure and no electrical signal feedthrough from the high pressure environment is required. However, in order to withstand the high pressures, the wall thickness of the actuating piston must be relatively large, and thus
the sensitivity of the load sensing device is significantly reduced.

In this work, the load cell was mounted inside the pressure vessel. As well, the design of the load cell was optimized for the lighter loads required to extend the polypropylene sample only.

The pressure is seen to have a profound effect on the peak stress of the polypropylene, and the relationship is seen to be linear, or nearly so. The linear relationship between stress and pressure is known as the modified-Coulomb criteria for yield and for the case of a tensile engineering stress is given by the following equation.

\[ \sigma = \sigma_{atm} + \phi P \]

where \( \sigma \) is the engineering tensile peak stress (defined as the load divided by the initial cross-sectional area), \( \sigma_{atm} \) is the tensile peak stress at atmospheric pressure, and \( \phi \) is the pressure coefficient.

| Table 5.01: Linear Regression of the Peak Stress as a Function of Pressure (MPa) |
|---------------------------------|-----------------|-----------|
| Strain Rate = 0.200 min⁻¹.      | Coulomb's Criteria (MPa) | R-value  |
| This study (25°C)               | \( \sigma = 27.33 + 0.226 P \) | .998      |
| Mears, Pae, & Sauer (RT)        |                               |           |
| (0-300 MPa)                     | \( \sigma = 30.12 + 0.197 P \) | .944      |
| (0-690 MPa)                     | \( \sigma = 30.11 + 0.206 P \) | .972      |

Regressions of the two sets of data relating peak stress and pressure are given in Table 5.01. The Mears et al. regression include regressions done over the same pressure interval as this work, as well as their whole data set (not displayed in Figure 5.01). In spite of the large scatter in the Mears et al. data, the regressions have quite similar intercepts and slopes.

The R-value for the linear regression given for this work is 0.998, assuming that the
relationship between peak stress and pressure is indeed linear. (In fact, there is a pressure-induced rubber to glass transition which occurs between 100 and 200 MPa which causes a slight discontinuity in the peak stress-pressure curves. This transition will be referred to as the pressure-induced glass transition, and will be discussed in the following section on the modified-Coulomb yield criterion). The consistency in peak stress values from one test to another is also evident in the tests carried out at strain rates of 0.020 and 0.002 min$^{-1}$. The sensitivity of the high pressure machine allowed significant additional information to be determined: the pressure-induced glass transition is evident from the peak stress results; the shear activation volume at elevated pressures can be determined from peak stress differences due to strain rate changes; and curves based on the change in slope of the stress-strain curves prior to the peak stress can be constructed and associated with specific deformation events.

In summary, the reproducibility and sensitivity of the peak stress results from the high pressure tensile testing machine were exceptionally good. The values for the peak stress match up extremely well with those available from the literature, which is one measure of the accuracy of the tests.
Figure 5.01: Peak stress as a function of pressure. A comparison between this study and that of D.R. Mears, K.D. Pae and J.A. Sauer, [J. Appl. Phys., 40, 4229 (1977)].

The temperatures are 25°C and room temperature respectively.

The strain rate is 0.2 min⁻¹ in both works.
5.2 Effect of Temperature on the Modified-Coulomb Yield Criterion for Polypropylene

5.2.1 Introduction

Pressure exerts a significant effect upon the deformation behaviour of polymers. Not only does the yield stress increase with increasing pressure, but the modulus is also similarly affected. At pressures where polymers exhibit this pronounced pressure response, the onset of yielding of metals remains virtually unaffected by the pressure. This is due to the fact that the plastic resistances of polymers are relatively high compared with their moduli, the ratio being 2-3 orders of magnitude greater than that for metals. However, for very high strength steels, where the plastic resistance is a substantial portion of the moduli, a similar pressure-yield relationship is observed for metals as well.

The relationship between the yield strength of polymers and pressure is linear, described by an empirically determined equation known as the modified-Coulomb yield criterion. In tension, this is given by

\[ \sigma = \sigma_{atm} + \phi P \]  \hspace{1cm} (5.1)

where \( \sigma \) is defined as the tensile yield stress at pressure \( P \), \( \sigma_{atm} \) is the tensile yield stress at atmospheric pressure, and \( \phi \) is the pressure coefficient.

Presently, there is little understanding of the molecular factors which affect \( \phi \). Virtually all studies of the pressure effect on polymer deformation have been carried out at room temperature. Comparison of \( \phi \) among polymers have been made with the implicit assumption that \( \phi \) is constant. However, the consequences of this assumption often lead to erroneous conclusions and makes any attempt at relating \( \phi \) with molecular factors difficult.

Aside from the linear yield stress dependency in polymers, increasing pressure can also cause other transitions which have a pronounced effect on the tensile deformation response. In particular, increasing pressure may cause transitions in both the amorphous
component, from the rubbery to the glassy state, as well as the crystalline component, due to changes in crystal structure. It will be seen that the amorphous component of polypropylene undergoes a transition at both 25 °C and 50 °C at elevated pressures.

The next section will first address the transition of the amorphous component. This will be followed by an examination of the effect of temperature on the modified Coulomb yield criterion, and consequently the pressure coefficient, $\phi$, for polypropylene.
5.2.2 Results

The peak stress-pressure relationship at 25 °C, shown in Figure 5.01, is close to linear. However, it was later noted that a marked transition in the tangent modulus-pressure curve occurred between 138 MPa and 200 MPa (Figure 5.11). Upon re-examination of the peak stress results it was noted that the transition was clearly evident here as well, although it is not as pronounced. In order to see this transition more clearly, the first set of data, in which 69 MPa pressure intervals were used, is included (Figure 5.02). At 25°C, the curve is divided into two linear sections, with a transitional jump in peak stress value between pressures of 138 and 207 MPa pressure.

At 50 °C, a transitional jump also occurs in the tangent modulus maximum-pressure curves at 50 °C between 200 and 300 MPa pressure (see Figure 5.13). Again, close examination of the peak stress-pressure curve shows that the curve is linear to 200 MPa pressure, with a transitional jump between 200 and 300 MPa pressure.

At 75 °C, the curve is linear throughout the pressure range tested, with no transitional jump evident. In this case, the tangent modulus maximum-pressure curve shows no transitional jump over the same pressure interval.

The slopes of the curves in the peak stress-pressure graph shown in Figure 5.02 are seen to decrease, in the rubbery state, with increasing temperature. Linear regressions were carried out and the resulting modified-Coulomb yield equations are shown in Table 5.02. Both the atmospheric peak stress, $\sigma_{\text{atm}}$, and the pressure coefficient, $\phi$, are seen to decrease with increasing temperature. Plotting both as a function of temperature in Figure 5.03, it is evident that the atmospheric peak stress decreases at a faster rate than the pressure coefficient (the y-axes were chosen to illustrate this). This may be expected to be the case for all polymers. As the temperature approaches the melt temperature, the atmospheric peak stress tends to zero. However, since the melt temperature increases with pressure, the pressure coefficient at the atmospheric melt temperature will not be zero, but a finite positive value. Therefore the rate of decrease in the atmospheric peak stress would be expected to be greater than that of the pressure coefficient as the melt temperature is approached.
The ratio $\phi/\sigma_{\text{atm}}$, the normalized pressure coefficient, is examined as a function of temperature in Figure 5.04. The ratio increases only slightly as the temperature increases, from 0.0076 MPa$^{-1}$ at 25 °C to 0.0091 MPa$^{-1}$ at 75 °C. For the temperature range examined, the room temperature ratio $\phi/\sigma_{\text{atm}}$ gives a fair approximation of the ratio at 50°C and 75°C.
Figure 5.02: Peak stress as a function of pressure for polypropylene. Temperature = 25°C, 50°C and 75°C. Strain rate = 0.02 min⁻¹. Set I data included.
The modified-Coulomb yield equation was determined from the peak stress.

Figure 5.03: The atmospheric peak stress, $\sigma_{\text{atm}}$, and pressure coefficient, $\phi$, as a function of temperature, from the modified-Coulomb yield equation for polypropylene.
Figure 5.04: The effect of temperature on the ratio $\phi/\sigma_{\text{at}}$ for PP in the rubbery state. $\phi$ is the pressure coefficient and $\sigma_{\text{at}}$ is the atmospheric peak stress, from the modified-Coulomb yield criterion.
5.2.3 Discussion

5.2.3.1 The Pressure-Induced Rubber-to-Glass Transition

The cause of the transitional jump in the peak stress with increasing pressure can be attributed to either the pressure-induced rubber-to-glass transition of the amorphous component or to a pressure-induced phase transformation of the crystalline component.

The pressure interval over which the transitional jump occurs at 25 and 50 °C is plotted against the temperature in Figure 5.05. The line drawn through these intervals close to their mid-points can be extrapolated back to atmospheric pressure (P = 0.1 MPa) where the transition temperature is determined to be approximately -20°C, or the glass transition temperature for polypropylene at atmospheric pressure. In other words, the transitional jump in value is due to the pressure-induced glass transition of the amorphous phase. The pressure acts to increase the rubber-to-glass transition temperature.

In the Background section it was noted that a pressure increase results in an increase in the rubber-to-glass transition for the polymers examined. Typical values of dT_g/dP for a variety of polymers were 15-35 °C/100 MPa (15-35 °C/kb). From Figure 5.05 the change in the glass transition temperature with pressure, dT_g/dP, is determined to be approximately 28°C/100 MPa, which is within the anticipated range for such a transition. The predicted transition at 75 °C would occur at 340 MPa, which is beyond the range examined. As expected, there is no jump in maximum values noted at 75 °C in the pressure range studied.

Similar transitions have been noted in other high pressure studies of polypropylene. The shear modulus of polypropylene showed a glass transition at about 160 MPa [2] and the compression modulus of polypropylene showed a glass transition at about 210 MPa [3]. The shear modulus reported falls within the transition interval determined by this work for the tensile modulus.

An interesting aspect of the polypropylene response with the amorphous component in the glassy state at high pressure is that deformation is not brittle in nature, as it is at atmospheric pressure (for T < T_g), but ductile.
The Effect of Temperature on the Modified-Coulomb Yield Criterion

It was determined that the ratio $\Phi/\sigma_{atm}$ at 50 and 75 °C was similar to the value at 25°C (Figure 5.04). We can use this observation to generate peak stress-pressure curves at elevated temperatures using only atmospheric temperature tests and room temperature pressure tests. (This would allow reasonable estimates to be made of the peak stress at high temperature and pressure using an unheated high pressure testing machine.) The assumption is made that the normalized pressure coefficient, $\Phi/\sigma_{atm}$, determined at room temperature, is the same at elevated temperature. This approximation was applied to the polypropylene data in the rubbery state for temperatures of 50°C and 75°C in Figure 5.06. It can be seen that although the approximation underestimates the peak stress/pressure curve, it does offer a fair estimation of the elevated pressure/temperature data.

5.2.3.2 Molecular Factors Affecting the Relative Pressure Coefficient, $\Phi/\sigma_{atm}$

Much of the interpretation of the pressure coefficient $\Phi$ is based upon the analogy with the original Coulomb relationship between the normal stress and soil strength[4]. This states that the critical shear stress, $\tau$, necessary for yielding in a plane varies linearly with the stress normal to this plane.

$$\tau = \tau_c + \lambda \sigma_N$$  \hspace{1cm} 5.2

where $\tau_c$ is the "cohesion" of the material
$\lambda$ is the coefficient of friction
and $\sigma_N$ is the normal stress on the yield plane.

The form of this equation has been applied to semi-crystalline polymers to describe the plastic resistance along preferred crystallographic planes and directions for quasi-single crystal textures in conjunction with the Schmidt equation. By quasi-single crystal it is meant that the polymer has been oriented by certain types of deformation processes (e.g. plane strain compression in a channel die) such that the resulting texture is highly oriented in both the chain direction as well as in the crystal directions normal to the chain direction. In this case the Schmidt equation, which was derived to describe the
onset of yielding in metal single crystals, is modified to include a normal stress term. The original Schmidt relationship states that yielding occurs in a particular slip direction on a particular slip plane when the resolved shear stress reaches a critical value. For an applied uniaxial stress of $\sigma$ (either tension or compression) in which slip occurs on a plane whose normal makes the angle $\phi$ with the applied stress direction, and for which the angle between the slip direction and loading direction is given by $\theta$, the resolved shear stress, $\tau$, is given by the relation

$$\tau = \sigma \cos \phi \cos \theta$$

Similarly, the normal stress, $\sigma_N$, is described as

$$\sigma_N = \pm \sigma \cos \phi \sin \theta$$

where $\sigma_N$ is positive in tension and negative in compression.

The resulting form of the Schmidt equation is the same as the Coulomb equation, but the terms are different.

$$\tau = \tau_c + k \sigma_N \quad 5.3$$

where $\tau$ is the shear stress resolved in the shear plane, $\sigma_N$ is the resolved stress normal to the shear plane, $\tau_c$ is the critical shear stress required to activated slip in simple shear and $k$ is the coefficient of the normal stress component. It was found for some slip systems that this relationship described well the response of quasi-single crystal polyethylene [5] and nylon 6 [6].

Based on the similarity of Equations 5.2 and 5.3, it is conceptually easy to infer the same mechanisms between soils and polymers, and that the flow of the polymer chains past one another is a direct indication of their chain conformation. The more irregular the chain conformation, the "rougher" the polymer, the greater the "friction" coefficient [7]. In other words, the "friction" coefficient reflects the structure of the polymer chain. For example, it has been reported that the pressure coefficient for nylon 6 [6] is greater than for polyethylene at room temperature, and that this was attributed to a greater degree
of "roughness" in the nylon [8], the roughness being due to the presence of out-of-plane C=H, N=H and C=O groups of the nylon 6 crystals.

There is some difficulty with this view. The friction analogy infers that \( \tau_{c} \) and \( k \) are constants, implying that the two factors are independent of one another (so that direct comparison between polymers may be carried out solely based on the one factor or the other).

The modified-Coulomb yield equation used for this work (Equation 5.1) uses pressure rather than the normal stress component as the variable (Equation 5.3). The normal stress component form of the Coulomb equation is seen as a limiting case of the more general pressure form, where the factor \( k \) corresponds to the pressure coefficient \( \phi \), and the factor \( \tau_{c} \) corresponds to \( \sigma_{atm} \).

Since both \( \phi \) and \( \sigma_{atm} \) decrease as the temperature increases for PP, they are not independent variables. Since \( \phi \) varies with temperature, direct comparisons of \( \phi \) for different polymers cannot be carried out since they will depend upon the temperature at which the comparison is made. As a result, the values of \( \phi \) (or \( k \)) cannot be taken as a direct indication of chain structure differences between polymers.

Since \( \sigma_{atm} \) and \( \phi \) are not independent variables, the question then posed is whether one can isolate those factors which affect \( \phi \) to a greater or lesser extent than their effect on \( \sigma_{atm} \). A measure of this is given by the ratio \( \phi / \sigma_{atm} \), the normalized pressure coefficient. The relative insensitivity of the ratio \( \phi / \sigma_{atm} \) to changes in temperature, noted here for polypropylene, suggests that this ratio may be a better indicator than \( \phi \) of the relationship between those factors affecting the pressure response of different polymers. Differences in the \( \phi / \sigma_{atm} \) ratio between similar polymers may give some indication of those factors which determine the relative pressure sensitivity of a polymer.

The increase in the plastic resistance of polymers due to pressure suggests that as the polymer becomes more compressed, the conditions necessary for the onset of plastic deformation of the crystalline component become increasingly difficult. If the polymer is more sensitive to this compression, it would be expected to show an increased relative pressure sensitivity.
At the molecular level, it is anticipated that the relative pressure sensitivity of a particular polymer would be affected by those factors which would promote a decrease in density. Two factors affecting the density in a polymer are the relative amount of the amorphous component and the packing efficiency of the molecular chain. Those polymers with lesser density would be expected to show a greater relative pressure sensitivity. These are examined by comparisons between MDPE, LDPE, and PP (medium density polyethylene, low density polyethylene, and polypropylene, respectively), using MDPE as the standard for comparison.

Table 5.03a compares the density, crystallinity, $\sigma_{\text{atm}}$, $\phi$, and $\phi/\sigma_{\text{atm}}$ for MDPE, LDPE, and PP. The results are based upon the peak stress as determined from tensile testing, and apply only to the rubbery state for each polymer.

Table 5.03a  Comparison of the Pressure Response of Similar Semi-Crystalline Polymers With Different Void Volumes (Room Temperature)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density (Mg/m³)</th>
<th>Crystallinity (%)</th>
<th>Strain Rate (min⁻¹)</th>
<th>$\sigma_{\text{atm}}$ (MPa)</th>
<th>$\phi$</th>
<th>$\phi/\sigma_{\text{atm}}$ (1/MPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDPE</td>
<td>.9473</td>
<td>67.7</td>
<td>0.2</td>
<td>26</td>
<td>.098</td>
<td>.0038</td>
<td>[9]</td>
</tr>
<tr>
<td>LDPE</td>
<td>.9231</td>
<td>51.6</td>
<td>-</td>
<td>12</td>
<td>.081</td>
<td>.0067</td>
<td>[10]</td>
</tr>
<tr>
<td>PP</td>
<td>.905</td>
<td>63</td>
<td>0.2</td>
<td>28.5</td>
<td>.192</td>
<td>.0067</td>
<td>This study</td>
</tr>
</tbody>
</table>

The effect of crystallinity was determined by comparing LDPE, which is 52% crystalline, with MDPE, which is 68% crystalline. LDPE has the same intermolecular bonding (van der Waals) as MDPE, but with a greater amorphous content and therefore lower density. It would be expected that the pressure would have a greater effect on the less dense LDPE. Comparison only of their respective pressure coefficients, $\phi$, would lead to the conclusion that the MDPE is more pressure sensitive than the LDPE ($\phi$=0.098 vs. 0.081 respectively). However, for both LDPE and MDPE, it is seen that both $\sigma_{\text{atm}}$ and $\phi$ decrease as the percent crystallinity decreases. Clearly $\phi$ is not independent of $\sigma_{\text{atm}}$. The relative effect of pressure on the yield strength (i.e. peak stress) is given by the ratio $\phi/\sigma_{\text{atm}}$. In this case, $\phi/\sigma_{\text{atm}}$ for LDPE is greater than for MDPE (0.0067 vs. 0.0038 MPa⁻¹). In other words, the decreased density affects both $\sigma_{\text{atm}}$ and $\phi$, but the effect upon $\phi$ is greater and this is reflected in the greater $\phi/\sigma_{\text{atm}}$ ratio for LDPE. What is important is the relative effect of pressure on the yielding mechanisms, and since there is a substantial
difference in $\sigma_{\text{atm}}$, the ratio $\phi/\sigma_{\text{atm}}$ takes this into account.

The effect of the packing efficiency of the molecular chain can be examined by comparing the pressure response of the PP with that of MDPE. Both polymers have similar constituent molecules and morphology, and the interchain bonding (van der Waals) is the same for both. As well, the degree of crystallinity for both is similar. The chain conformation of PP is a 3, helix, rather than the planar zig-zag conformation of the MDPE. The theoretical densities of the crystalline phases are $1.000 \text{ Mg/m}^3$ for PE and $0.937 \text{ Mg/m}^3$ for PP. This results in a lower density for the PP and accounts for its greater compressibility. The PP has a considerably larger value for $\phi/\sigma_{\text{atm}}$, and it is suggested that this reflects the looser packing of the 3, helix.

Another factor which may be expected to show a relative pressure response is the interchain bond strength. In this case, the onset of plastic deformation of the crystalline phase would be expected to be more difficult if a critical transient dilation is required to initiate yielding. Again, the ratio $\phi/\sigma_{\text{atm}}$ is used to determined the relative effect of pressure on differences in interchain bond strength. POM (polyoxymethylene) and nylon 6, in which some of the interchain bonds are polar, are compared with polyethylene, which has only the weaker van der Waals interchain bonds.

The chain conformation of the POM (-CH$_2$O-) is a 9/5 helix. The "heavier" oxygen atom in alternate main chain positions as well as a shorter backbone length per mer than MDPE accounts for its greater density. The stronger polar bond is due to the oxygen atoms present in the main chain. This results in both the greater peak stress at atmospheric pressure of POM than MDPE (82 MPa vs 26 MPa respectively), as well as an increase in the pressure coefficient $\phi$ (0.166 vs 0.098 respectively) as shown in Table 5.03b. Comparison of $\phi$ only between POM and MDPE as an indication of the pressure sensitivity of these polymers would lead to the conclusion that POM is more pressure sensitive than MDPE.

However, the relative change of peak stress with pressure, indicated by the ratio $\phi/\sigma_{\text{atm}}$, of POM is half that of MDPE (0.0020 vs. 0.0038 MPa$^{-1}$ respectively). As the interchain bond strength increases, the relative pressure sensitivity, as represented by $\phi/\sigma_{\text{atm}}$, decreases. This suggests that the stronger the interchain bond strength, the greater the resistance to formation of a transient dilation necessary to initiate yielding, thus resulting in the
decreased relative sensitivity to the pressure.

Table 5.03b Comparison of the Pressure Response of Similar Semi-Crystalline Polymers with Different Interchain Bond Strengths

| Polymer | Density (Mg/m³) | Crystallinity (%) | Strain Rate (min⁻¹) | σ₁₀₀ (MPa) | φ | \(\phi/\sigma_{
|---------|----------------|------------------|----------------------|------------|---|\)
|---------|----------------|------------------|----------------------|------------|---|\)
| MDPE    | 0.9473         | 67.7             | 0.2                  | 26         | .098 | .0038 | [9]          |
| POM     | 1.425          | 74               | -                    | 82         | .166 | .0020 | [12]         |

By analogy, the same arguments used to relate interchain bond strength effects for POM and MDPE can be extended to studies on the critical resolved shear stress, \(\tau_c\), and the normal stress sensitivity factor, \(k\), given by Equation 5.3. Quasi-single crystal textures for HDPE [5] and nylon 6 [6] were generated using channel die compression, which results in plane strain compression. After identification of the principal slip systems, mechanical tests determined the resistance to plastic deformation of those slip systems.

HDPE and nylon 6 both have a planar zig-zag crystal chain conformation with the cross-sectional area/chain being almost identical (18 Å²). Both have van der Waals interchain bonds. In addition, the nylon 6 has some interchain polar bonds associated with the oxygen atom of the carboxyl group.

Table 5.03c Comparison of the Normal Stress Response of Similar Semi-Crystalline Polymers with Different Interchain Bond Strengths

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Density (Mg/m³)</th>
<th>Crystallinity (%)</th>
<th>Strain Rate (min⁻¹)</th>
<th>Slip System</th>
<th>(\tau_c) (MPa)</th>
<th>(k)</th>
<th>(k/\tau_c) (1/MPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>0.963</td>
<td>70-75</td>
<td>.025</td>
<td>(100)[001]</td>
<td>7.2</td>
<td>.11</td>
<td>0.0153</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(010)[001]</td>
<td>15.6</td>
<td>.20</td>
<td>0.0128</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(100)[010]</td>
<td>12.2</td>
<td>.17</td>
<td>0.0139</td>
<td></td>
</tr>
<tr>
<td>Nylon 6</td>
<td>1.151</td>
<td>43.4</td>
<td>.1</td>
<td>(001)[010]</td>
<td>16.24</td>
<td>.13</td>
<td>0.0080</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(100)[010]</td>
<td>23.23</td>
<td>.28</td>
<td>0.0121</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(001)[001]</td>
<td>23.18</td>
<td>.13</td>
<td>0.0056</td>
<td></td>
</tr>
</tbody>
</table>

The main slip systems are identified in Table 5.03c along with their respective critical resolved shear stresses and normal-stress sensitivity factors. The chain direction is [001]
for HDPE and [010] for nylon 6. In both HDPE and nylon 6 there is one slip system with significantly less resistance than the others, and in both of these cases this is in the chain direction. Although one can average the respective ratios of $k/\tau_c$ MPa$^{-1}$ (and achieve the same result) comparison will be done only on those slip systems with the least resistance (these predominate the plastic deformation process of the crystalline component). It is seen that the greater interchain bond strength of the nylon 6 results not only in a greater critical resolved shear stress, $\tau_c$, than for HDPE (16.24 vs 7.2 MPa respectively), but also a slightly greater normal stress sensitivity factor, $k$, (0.13 vs 0.11). Again, comparison only of the normal stress sensitivity factor, $k$, would lead to the conclusion that the nylon 6 was slightly more sensitive to the normal stress than HDPE. However, the relative normal stress sensitivity factor, given as the ratio $k/\tau_c$, shows that the ratio for nylon 6 is nearly half that of the HDPE (0.0080 vs 0.0153 MPa$^{-1}$ respectively). The relative normal stress sensitivity of the nylon is significantly less than that for MDPE. In other words, the greater the interchain bond strength of the polymer, the relatively more resistant it is to an increase in the normal stress. This is, of course, the same observation made with respect to the pressure in comparisons between MDPE and POM.

Whether the pressure or normal stress form of the equation is used, the trends are the same. Factors contributing to decreased density have the same relative effect on the normalized pressure coefficient, $\phi/\sigma_{sm}$, and the normalized normal stress coefficient, $k/\tau_c$, namely that a decrease in density results in an increase in both ratios. As well, factors which would resist the formation of a transient dilation necessary to initiate plastic deformation of the crystalline phase, such as an increase in the interchain bond strength, also have a similar effect on these normalized ratios. In this case, an increase in the resistance to void formation results in a decrease in the normalized ratios, $\phi/\sigma_{sm}$ and $k/\tau_c$.

Studies have shown that the yield stress in semi-crystalline polymers is predominantly influenced by the plastic resistance of the crystalline component [13],[14]. The effect of lesser density and the relative resistance to formation of a transient dilation on the normalized pressure coefficient, $\phi/\sigma_{sm}$, suggests that yielding is due to the ability to generate the critical dilation necessary to nucleate dislocations in those crystallographic planes and along those directions of the minimum resolved shear stress.
Figure 5.05: The glass transition temperature as a function of pressure for polypropylene.
Approximation of the peak stress at elevated pressures and temperatures based on atmospheric data and room temperature-elevated pressure data.

\[
\frac{\Phi}{s_{atm}}_T = \left(\frac{\Phi}{s_{atm}}\right)_{298\, K}
\]
5.2.4 Conclusion

1. There is a pressure transition, noted from the peak stress and the second maximum of the tangent modulus, which is due to the pressure-induced rubber-to-glass transformation.

2. The glass transition pressure is increased as the temperature increases. This ratio was determined to be approximately 28°C / 100 MPa.

3. The pressure coefficient, φ, for polypropylene in the rubbery state is not constant, but decreases with increasing temperature.

4. For polypropylene the factors σ_{atm} and φ, from the modified Coulomb yield equation, are similarly affected by temperature, and therefore are not independent variables. Both decrease with increasing temperature, and their ratio, φ/σ_{atm}, is approximately constant in the temperature range examined.

5. The similar temperature response of the normalized pressure coefficient, φ/σ_{atm}, suggests that molecular factors, such as decreased density and interchain bond strength have an affect on both σ_{atm} and φ. Based on the polymers examined, φ/σ_{atm} increases with decreasing density (due to the relative amount of amorphous phase, or the packing efficiency of the molecular chain). In addition, the ratio φ/σ_{atm} is inversely proportional to the interchain bond strength. This suggests that a greater interchain bond strength increases the resistance to formation of a transient dilation necessary for the onset of plastic deformation.
5.3 The Shear Activation Volume and Flow Mechanisms at High Pressure

5.3.1 Introduction

The effect of pressure on the plastic deformation of polymeric solids is pronounced, with both the peak stress and modulus increasing with increasing pressure. Although yield criterion have been developed to describe the pressure dependence of the peak stress, there is still little understanding of the flow mechanisms accounting for this pressure effect.

Much of the effort undertaken to understand the deformation process of polymers has been based on characterizing the morphological and textural development, using electron microscopy and x-ray techniques. Recently, comprehensive work utilizing these techniques in tandem on quasi-single crystal semi-crystalline polymer has been carried out to identify slip systems within the crystalline component and to quantify their relative contribution to tensile deformation \[8\][15][5][16][6][17][13]. However, a full understanding of the actual deformation mechanisms is still not clear. Yielding in semi-crystalline polymers involves elastic and plastic deformation of both the amorphous and crystalline phases. Which of these governs the rate limiting step at the onset of plastic deformation and how they interact with one another are two points which are not well understood.

Polymer deformation is a thermally activated process described by an Arhenius-like relationship between strain rate and stress. The flow model most often used to account for this relationship is that proposed by Eyring. In this model, the rate at which a mobile species will jump to another lattice position is dependent upon the potential energy barrier. In the absence of an applied stress, the rate of flow in the forward and backward directions is the same, so there is no net flow. Application of stress linearly reduces the potential energy barrier in the stress direction. (This assumes that the magnitude of the applied stress is sufficient so that the probability of a reverse jump is negligible). With the further assumption that the change in entropy is also negligible, one obtains the following relationship

\[
\dot{\gamma} = \dot{\gamma}_0 \exp \left[ -\frac{\Delta H - \tau V}{kT} \right]
\]
where $\dot{\gamma}$ is the shear strain rate, $\dot{\gamma}_0$ is the pre-exponential factor assumed constant, $\Delta H$ is the activation enthalpy, $\tau$ is the shear stress, $V$ is the shear activation volume, $k$ is the Boltzman constant and $T$ is temperature. Deformation is then viewed as the surmounting of a potential energy barrier by the mobile molecule with approximate dimensions given by the factor $V$, the shear activation volume.

There are limitations with this model when applied to long linear-chained molecules. In this case, the linear relationship of the activation energy with the applied stress is not exactly linear, and is inadequate to describe the relationship over large ranges of strain rate. This can be attributed mainly to the dual nature of the atomic bonding inherent in polymeric materials. In this case local interactions on the atomic scale are not solely influenced by the relatively weak intermolecular bonding. The covalent main chain bonding introduces not only restrictions to local mobility, but can transfer stresses over distances many times larger than that of an atomic radius. This introduces deviations from equilibrium, as defined solely by the weak interchain bonds, which can exist locally over dimensions significantly greater than an atomic radius.

In spite of these obvious limitations, the form of this equation has some advantages. First, it is relatively simple in form, requiring the measurement of either the strain rate or the stress. And second, one obtains two parameters, the activation enthalpy and the shear activation volume, $V$. Both can act as markers for transitional changes in deformation mechanisms. Identifying commonalities in these transitions under varying conditions and between different polymeric solids can help in determining these deformation mechanisms.

To account for the linear pressure dependency of the stress evident in polymers it has been suggested [18] that the Eyring equation be further modified in the following manner:

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left[\frac{-(\Delta H + P V^*) + \tau V}{kT}\right]$$

where $V$ is the shear activation volume, $P$ is the pressure, and $V^*$ is the pressure activation volume. For conditions where the pressure is zero (approximately true at atmospheric pressure, where the pressure is much less than the tensile stress), the equation reduces to the usual atmospheric form of the Eyring equation. The interpretation often given is that $P V^*$ represents the work which must be done against hydrostatic pressure, and the term $\tau V$ represents the work done by the applied stress in
surmounting the energy barrier.

The form of the modified-Coulomb yield criteria can be derived from this equation quite easily. Taking the natural logarithm and rearranging, the following is obtained.

\[
\tau = \left[ \frac{\Delta H}{V} + \frac{kT}{V} \ln \left( \frac{\dot{\gamma}}{\dot{\gamma}_0} \right) \right] + \left( \frac{V^*}{V} \right) P \tag{5.5}
\]

This is the same form as the modified-Coulomb equation, \( \tau = \tau_{\text{sim}} + \phi P \). The term \( \tau_{\text{sim}} \) is equal to the square bracketed term, and is constant for a given strain rate. (The modified-Coulomb yield criteria is implicitly assumed to be defined at constant strain rate and room temperature.) The pressure coefficient, \( \phi \), is then seen to equal the ratio of the pressure to shear activation volumes. Therefore, the shear activation volume and the pressure activation volume are related by \( V^* = \phi V \).

To determine the shear activation volume, \( V \), the Eyring equation is further rearranged as follows:

\[
\frac{\tau}{T} = \frac{k}{V} \ln \dot{\gamma} + \left[ \frac{\Delta H + PV^*}{TV} \right] \frac{k}{V} \ln \dot{\gamma}_0 \tag{5.6}
\]

For conditions of constant pressure and temperature, and assuming that the pressure activation volume is not a function of the strain rate, it is seen that the term \( (\Delta H + PV^*) \) is constant, and consequently the bracketed term is also constant. The shear activation volume, \( V \), can then be determined from strain rate tests carried out at constant temperature and pressure. Plotting \( \tau/T \) (\( \sigma/T \) in tension) as a function of the natural logarithm of the strain rate gives a straight line (at a given temperature) with slope \( k/V \).

(Ideally, the shear and pressure activations volumes are determined from jump experiments, where the jump in the strain rate or the pressure results in an effect on the flow stress at a given standard reference state (same structure). The equations used in this approach are given in the following discussion section. Jump experiments were not performed in this work. Instead, two assumptions are made. The first is that, for a constant temperature and pressure, the structure at the onset of necking (the peak stress) is essentially the same for varying strain rates. The second is that the dependence of the yield stress on strain rate changes is essentially the same as that of the peak stress. This latter point seems to be confirmed in the experimental results.)
At present, little work has been carried out on the effect of pressure on the deformation mechanisms of linear semi-crystalline polymers. The substantial effect of pressure on both the yield stress and modulus indicates a fundamental relationship with yielding mechanisms. In this work, the effect of pressure on the deformation of polypropylene is examined with the aim of understanding the basic mechanisms which are rate controlling.

5.3.2 Results

The peak stress as a function of pressure at 25°C is shown in Figure 5.07 for strain rates of 0.2, 0.02, and 0.002 min⁻¹. As noted previously, there is a transition occurring between 138 and 200 MPa pressure associated with the pressure-induced rubber-to-glass transition. On either side of this transition, the relationship was noted to be linear. Consequently, the curves drawn in the rubbery regime in Figure 5.07 are extended from 100 to 138 MPa pressure. Although the strain rate increases exponentially by a factor of 10, it is seen that the stress interval between those strain rates is constant (i.e. the stress interval between 0.002 and 0.02 min⁻¹ strain rates is equal to the stress interval between 0.02 and 0.2 min⁻¹ strain rates). This is characteristic of a thermally-activated process.

As mentioned, one can determine the pressure activation volume, as described by the Eyring equation, from the slope of the ratio of the tensile peak stress divided by the absolute temperature, \( \sigma/T \), plotted against the natural logarithm of the tensile strain rate, \( \dot{e} \), according to Equation 5.6. This has been carried out for the 25°C data, and is shown in Figure 5.08. It is noted that the relationship is linear.

The shear activation volume, \( V \), is obtained from the slope of these curves, the slope being equal to \( k/V \). The shear activation volumes, calculated from these slopes are tabulated in Table 5.04 for 25°C. Also included are the results from testing done at 50 and 75 °C.

<table>
<thead>
<tr>
<th>Table 5.04 Shear Activation Volumes (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>298 K</td>
</tr>
<tr>
<td>323 K</td>
</tr>
<tr>
<td>348 K</td>
</tr>
</tbody>
</table>
This is plotted as a function of pressure for various temperatures in Figure 5.09. The shear activation volume is seen to decrease with increasing pressure. At 25 °C, the rate of decrease is quite rapid at first, from a value of 2437 Å³ at atmospheric pressure down to 1804 Å³ at 100 MPa, and appears to approach a limiting value of approximately 1650 Å³ at pressures greater than the pressure-induced glass transition pressure (200 MPa and 300 MPa). This is consistent with the compressibility response of polymers, where the rate of compression decreases with increasing pressure. Also included in Figure 5.09 are the shear activation volumes determined at 50 and 75 °C. The magnitude of the decline in shear activation volume is more pronounced at the higher temperatures. At a given pressure, the shear activation volume increases with increasing temperature in an intuitively acceptable manner consistent with thermal expansion and free volume theories.

At 50 °C, the shear activation volume declines from a value of 4013 Å³ at atmospheric pressure to a value of 1908 Å³ at 200 MPa, where it too appears to approach a limiting value at pressures greater than the pressure-induced glass transition. Here the value of the shear activation volume in the glassy state is slightly greater (1731 Å³ ) than that observed at 25 °C (~1650 Å³ ). The rubber/glass transition line drawn in the figure crosses the 25 and 50°C curves at their predicted glass transitions based on $dT_g/dP = 28°C/100$ MPa (see section 5.2.3.1 The Pressure-Induced Rubber-to-Glass Transition).

The shear activation volume values at 75 °C are greater at every pressure than those at 50 °C, decreasing from a value of 6049 Å³ at atmospheric pressure to 2315 Å³ at 300 MPa pressure. The values do not appear to approach a constant value at high pressure, which is consistent with the fact that the glassy state is not realized for this temperature at the pressures tested.
Figure 5.07: The effect of strain rate on the peak stress-pressure curve at 25 °C.
Figure 5.08: Peak stress/temperature versus the natural logarithm of strain rate for various pressures. Temperature is 25°C.
Figure 5.09: The shear activation volume as a function of pressure, for temperatures of 25, 50 and 75°C.
5.3.3 Discussion

In this section, the polypropylene results will be compared with data for high molecular weight polyethylene from the literature. Following this, the mechanisms associated with the shear activation volume will be addressed.

5.3.3.1 Shear Activation Volume

According to the Eyring flow model, in a situation where only one mechanism is operative, the shear activation volume is interpreted as the transient change in volume during a deformation event which allows the mobile group to move from one position to another. For intricate structures, such as semi-crystalline polymers, the situation is complex, particularly under conditions where the amorphous component is in the rubbery rather than the glassy state. In this case, multiple mechanisms may be operative, and the interactions between mechanisms makes a direct interpretation of the parameter $V$ difficult. Investigation of those conditions which minimize the number of active mechanisms provides a suitable starting point.

Aside from low temperatures, the amorphous component can exist in the glassy state at pressures greater than the pressure-induced glass transition. From this work it is observed that there is a transition in the shear activation volume at the pressure-induced glass transition. The shear activation volume decreases significantly with increasing pressure in the rubbery state, and then becomes approximately constant in the glassy state. This transition occurs at various temperatures (25 and 50 °C), and the value of the shear activation volume in the glassy state at those temperatures is similar.

Based on the observation of a critical value of the shear activation volume characteristic of the pressure-induced glass transition in polypropylene at different temperatures, it may be asked if this same response is noted at the glass transition in other semi-crystalline polymers. Work has been carried out by Davis and Pampillo [19] of the effect of pressure on the pressure shear activation volume, $V^*$, for high molecular weight polyethylene (HMWPE). In their work, rather than the shear activation volume, $V$, they instead determine the pressure activation volume, $V^*$. Davis and Pampillo interpret the pressure activation volume as the transient increase in volume of the material when one activation event occurs.

In order to compare the two works it is necessary to convert the pressure activation
volume, \( V^* \), determined at strains greater than the Lüders strain, to the shear activation volume, \( V \), determined at the peak stress, which is used in this work.

In the work of Davis and Pampillo, high molecular weight polyethylene powder (\( M_w = 2.8 \times 10^6 \)) was compression moulded followed by quenching in ice. This produced a poorly defined microspherulitic structure which resulted in a very small yield drop, and virtually no non-uniform strain region (no neck formation). The uniform strain regime began by 50% engineering strain over the pressure range from 277 to 831 MPa. At lower pressure the uniform strain regime began later, increasing to 90% strain at atmospheric pressure.

Davis and Pampillo define the pressure activation volume (in tension) as

\[
V^* = kT \left( \frac{\delta \ln \dot{\varepsilon}}{\delta P} \right)_{T, \sigma, \varepsilon}
\]

The derivative is defined at constant temperature, stress, and strain. This equation can be applied to creep conditions where the stress is kept constant and the strain rate measured. The assumption of constant strain implies that the structure at that particular strain is the same and by inference, that the deformation mechanisms are similar.

Davis and Pampillo redefine the pressure activation volume so that it can be applied to the case of constant tensile strain rate.

\[
V^* = kT \left( \frac{\delta \ln \dot{\varepsilon}}{\delta \ln \sigma} \right)_{T, \sigma, \varepsilon} \left( \frac{\delta \ln \sigma}{\delta P} \right)_{T, \sigma, \varepsilon}
\]

The advantage of this approach is that the shear activation volume can be determined at various strains, provided that deformation is uniform (no continued localized "necking"). Since there was little necking in the ice-quenched high molecular weight polyethylene, the shear activation volume could be determined, starting from 50-90% strain to the failure strain. It was shown that \( V^* \) is not a function of strain at high pressure, and is only a slight function of strain at lower pressures. Given that the uniform strain began as early as 50% strain (the transformation to the fibrillar structure is very gradual and has just started at this point), and that \( V^* \) is relatively insensitive to strain, we make the reasonable assumption that \( V^* \) is similar in value at the yield point (where the strain is approximately 20-30%).
This assumption allows the $V^*$ data to be converted to $V$, the shear activation volume, since the yield stress-pressure relationship is available from their paper. First, Davis and Pampillo defined the shear activation volume, $V$, as

$$V = kT \left( \frac{\delta \ln \dot{\varepsilon}}{\delta \sigma} \right)_{T,P,\varepsilon}$$

Redefining the pressure activation volume, $V^*$, by replacing $\delta \ln \sigma$ in Equation 5.7 with $\delta \sigma$, one obtains

$$V^* = kT \left( \frac{\delta \ln \dot{\varepsilon}}{\delta \sigma} \right)_{T,P,\varepsilon} \left( \frac{\delta \sigma}{\delta P} \right)_{T,\varepsilon}$$

It can be readily seen that $V^*$ and $V$ are related by

$$V^* = V \left( \frac{\delta \sigma}{\delta P} \right)_{T,\varepsilon}$$

Although Davis and Pampillo fit their yield stress versus pressure data to a quadratic, a linear function shows an excellent fit to the data to 7 kbar pressure (700 MPa). Given the form of this relationship as

$$\sigma = \sigma_{adm} + \phi P$$

we can place this value for $\sigma$ into the previous equation ($\delta \sigma/\delta P$) to obtain the general relationship $V^* = V\phi$. This, then, allows conversion of the pressure activation volume, $V^*$, to the shear activation volume, $V$, by multiplying their pressure activation volume by the factor $1/\phi$. From their yield-pressure data the pressure coefficient, $\phi$, was determined to be 0.078, which is a value in keeping with other results for medium density polyethylene [9].
Figure 5.10: Shear activation volume as a function of pressure for polypropylene and polyethylene. Temperature is 25°C.
The resulting shear activation volume for polyethylene at room temperature is shown in Figure 5.10 along with the 25°C data of polypropylene from this study. The curve shown for polyethylene from Pampillo and Davis [20] was determined at $\varepsilon = 1.25$. The PE is seen to decrease from a value of 3350 Å$^3$ at atmospheric pressure to an approximate value of 1700 Å$^3$ at pressures of 600 MPa and greater. This transition at 600 MPa pressure has a marked similarity to that noted for polypropylene at the pressure-induced rubber-to-glass transition. It therefore seems possible that the same deformation mechanisms are operative in both materials.

It is also evident that the value of the shear activation volume at the transition is similar for both PE and PP. In the case of polypropylene, this transition in the value of the shear activation volume coincided with the pressure-induced glass transition. Pampillo and Davis make no such association. However, for polyethylene, bulk modulus measurements by Heydemann and Houck [21] show a bend in the bulk modulus-pressure curve at 6 kbar (600 MPa) which they attribute to the pressure-induced glass transition. They also cite NMR work by Cleron et. al. [22] which shows broadening of the NMR line width at the same pressure. The NMR broadening indicates decreased mobility of the protons attached to the carbon chain. Thus, the transition in slope of the shear activation volume noted at 600 MPa pressure is due to the rubber to glass transition. This response is identical to the one noted in this work for PP.

There is a difference in values of the shear activation volumes at atmospheric pressure, the shear activation volume of PE being greater than that of PP. This can be attributed to the temperature difference between the test temperature and the glass transition temperature ($T - T_g$). The PE is 135°C above its glass transition temperature, $T_g$ (-110°C), compared with PP which is just 45°C above its glass transition temperature, $T_g$ (-20°C). Given that the shear activation volume is approximately constant in the glassy state, then the larger relative temperature difference of the PE could result in the larger shear activation volume, provided $\Delta V/\Delta T$ (in the rubbery state) for both PE and PP is not too dissimilar in value.

The shear activation volume, $V$, for PP in the glassy state at 25°C and 50°C was similar in value (1654 Å$^3$ and 1731 Å$^3$ respectively). This suggests that there is a critical value for the shear activation volume when the amorphous component is in the glassy state which is only slightly dependent on temperature and pressure. The pressure activation volume, $V^*$, for the same conditions does not display a constant value in the glassy state. This is due to the fact that the pressure coefficient for PP at these two temperatures is
significantly different ($\phi_{298K} = 0.185$, $\phi_{323K} = 0.135$), and consequently conversion to the pressure activation volume using the relation $V^* = \phi V$ results in significantly different values in the glassy state (307 Å$^3$ at 25°C and 234 Å$^3$ at 50°C). Intriguingly, the shear activation volume, $V$, in the glassy state at room temperature for PE and PP is similar in value ($1700 \text{ Å}^3$ for PE and 165 Å$^3$ for PP). Conversion of the PP data to $V^*$, the pressure activation volume, (again using the relation $V^* = \phi V$) would result in much different values for the glassy state, since the pressure coefficient of stress for PP is not the same as for PE ($\phi_{PP} = 0.185$, $\phi_{PE} = 0.078$).

The similarity in shear activation volumes above the glass transition pressure for PP at 25 °C for various pressures and at various temperatures (25 °C and 50 °C) suggests that there is a critical value of the shear activation volume, $V$, defined by the glassy state. There is no such critical threshold evident using the pressure activation volume, $V^*$. 
5.3.3.2 Flow Mechanisms

Glassy State

The deformation of polypropylene at \( P > P_g \) takes place in discrete stages (this is discussed in Section 5.4). This, and the fact that the shear activation volume is approximately constant at various pressures and temperatures suggests that a single mechanism is rate limiting.

Polypropylene deformation at \( P > P_g \) is viewed as comprising five basic mechanisms: the creation of a transitory dilation volume (TDV) for flow of the amorphous component; flow of the amorphous component; the nucleation of dislocations; the propagation of dislocations; and chain scission.

It should be kept in mind that the shear activation volume is determined from the peak stress, and as such reflects those mechanisms operative at that point in the deformation. Previous deformation stages, if already terminated, will not necessarily influence this value. The attempt here, then, is to identify possible mechanisms which can account for the increase in stress due to an increase in strain rate (the parameters that determine the shear activation volume). Consideration will be given to each of the proposed mechanisms in turn, beginning with the mechanisms governing the deformation of the amorphous component.

Tensile deformation in semi-crystalline polymers begins with the deformation of the amorphous phase, which is predominantly elastic in nature. The onset of plastic deformation is generally associated with the deformation of the crystalline phase. For polyethylene at room temperature, the onset of plastic deformation has been reported to commence at about 5% strain [5] and is attributed to the onset of plastic deformation of the crystalline component. In the case of polypropylene, as reported in this work (Section 5.4), there appears a transition in the initial pre-peak stress portion of the stress-strain curve that is particularly prominent in the glassy state. Although less prominent at pressures below the glass transition, the transition is observable at pressures down to 69 MPa at 25 °C. The transition is manifest by a bend to lesser slope, and occurs at about 7% strain at 69 MPa pressure. As the pressure is further increased, the transition becomes more prominent and occurs at increasing strains until the glass transition pressure is reached, at which point the transition strain becomes constant at 9%. It has been suggested in this study (Section 5.4) that this transition is associated with the onset
of plastic deformation of the crystalline component as well. Deformation to that point is attributed mainly to the weaker amorphous component.

The amorphous component exists as a thin interlayer between adjacent crystalline lamellae. The points at which the tie molecules within the amorphous interlayer enter the lamellae effectively act as crosslinks (until the onset of crystalline deformation). In this regard, the amorphous component acts more as an elastomeric polymer than as a purely amorphous one, and it is illustrative to examine the deformation response of elastomers to pressure, particularly through the pressure-induced glass transition.

The stress-strain response of a polyurethane (PUR) elastomer at varying pressures is shown in Figure 2.13 [23]. At pressures of 3 kbar and below, the elastomer is in the rubbery state, and shows a typical elastomeric deformation response. The increase in pressure increases the level of the stress-strain curve, with the stress interval between 1 and 2 kbar being similar in magnitude to the stress interval between 2 and 3 kbar. Between 3 and 4 kbar, the PUR elastomer undergoes a pressure-induced glass transition. The stress interval across the glass transition is seen to be larger than the increases due to pressure in either the rubbery or glassy states. (In the glassy state the PUR is, of course, no longer elastomeric).

There are three additional responses of the PUR elastomer that are significant, and pertinent to the discussion of the initial elastic/elastomeric response of the amorphous component of polypropylene, two of which cannot be interpreted directly from the stress-strain curve. First, in the glassy state, there is the appearance of a stress maximum at low strains, followed by a region of constant reduced stress. The form of the stress-strain curve is similar to that for many amorphous polymers in the glassy state at high pressure, where the superposed hydrostatic pressure inhibits premature brittle fracture.

However, there is an important difference between the response of the glassy PUR "elastomer" and ductile amorphous polymers in the glassy state (the second response mentioned). Unlike the amorphous polymers, the PUR elastomer does not form a localized reduced section, or neck, but continues to deform homogeneously. Apparently the stress is sufficiently homogeneously distributed throughout the reduced gauge section so as to prevent localized softening and neck formation. Orientation strengthening, which causes the neck to stabilize in amorphous polymers, still occurs in the PUR elastomer, but gradually over much larger strains.
The third response is that upon release of the load when in the glassy state, the PUR slowly retracts. Flow is still possible in the glassy state, and the drive to retract is not elastomeric but due to the elastic chain extension of the main chain bonds.

Given this response of the PUR elastomer in the glassy state, can the Eyring flow model be related to the flow response following the stress maximum? A number of points can be made in this regard. First, the stress maximum in the glassy state occurs at low strain and at the same strain regardless of the pressure. It is suggested that a critical transitory dilation volume must be created within the glassy PUR before amorphous flow can occur. This occurs at a critical tensile strain and requires a greater stress level than is required to sustain flow. Now, if one measured the flow stress response in the region following the stress maximum due to changes in the strain rate, would those changes be influenced by the stress maximum? It is speculated here that it would not. In other words, it is suggested that the flow stress response to changes in strain rate would reflect only those processes involved in flow of the amorphous component. If this is the case, the shear activation volume, based on the Eyring model, would represent amorphous flow only, and not be affected by the stress maximum. Consequently, the rate limiting step at the point in the deformation process after the stress maximum is interpreted as being due to flow of the amorphous phase, even though the flow stress is less than the stress required to create the critical transitory dilation volume for amorphous flow to begin. This could be verified experimentally by determining the shear activation volume at various pressures above the glass transition. A constant shear activation volume for various pressures in the glassy state would indicate that it is not affected by the stress required to create the critical transitory dilation volume for amorphous flow to initiate.

Extending this analysis to PP, the deformation in the glassy state prior to the plastic deformation of the crystalline component is interpreted as a two step process; the creation of sufficient transitory dilation volume for flow in the amorphous phase to occur, followed by amorphous flow. Flow proceeds, however, not at a constant flow stress, but at increasing stress, similar to the response of the PUR elastomer as its limiting strain is approached. In the case of PP, until plastic deformation of the crystalline component begins, the tie molecules of the amorphous interlayer are temporarily fixed at their point of entry into the adjacent lamellae, and their extension is severely limited. As a result, the stress continues to increase. Stress differences due to changes in strain rate, to the onset of crystalline flow, are attributed solely to flow of the amorphous component.

The flow response is, however, not permanent. The driving force for amorphous flow in
both cases is the relieving of the elastic chain extension of the tie molecules (i.e. local high strains within the extended chain are redistributed gradually along the chain). If the external load is released, this redistributed elastic strain along the chain would generate a localized elastic stress which is retractive in nature, and which then acts as the driving force for reverse amorphous flow and the gradual contraction of the polypropylene (and the PUR elastomer) to its original dimensions.

To summarize, this analysis begins with the assumption that the response of the amorphous component in polypropylene prior to the onset of crystalline flow is similar to the response of a PUR elastomer in the glassy state. Amorphous flow is seen as redistributing stresses along the elastically extended tie molecules, and is initiated upon generation of a critical transitory dilation volume within the amorphous component, which occurs at a critical strain. From this, it is proposed that differences in the stress past the point where a critical transitory dilation volume is generated (but prior to the onset of plastic deformation of the crystalline component), due to varying strain rate, are due to the flow of the amorphous component only, and are unaffected by the larger stress necessary to create the transitory dilation volume necessary to start that amorphous flow. Derived values, such as the shear activation volume, are therefore seen as a measure of this amorphous flow response until the onset of plastic deformation of the crystalline component. Amorphous flow is also anticipated to continue past the onset of plastic deformation of the crystalline component and is operative at the stress maximum.

Next we consider those mechanisms affecting the deformation of the crystalline component: nucleation and propagation of dislocations. The nucleation of dislocations requires both the creation of its own transitory dilation volume and the presence of a critical shear stress. The creation of a critical transitory dilation volume is dependent on two factors: the elastic stress state which generates a triaxial tensile stress state at the crystalline-amorphous interface and the flow of the amorphous component. It will be noted in Section 5.4 that factors which restrict amorphous flow, such as the transition from the rubbery to the glassy state, hinder the formation of a critical dilational volume for nucleation of dislocations, and require a greater triaxial tensile stress state at the interface. Similarly, increases in the second maximum of the tangent modulus with increasing strain rate were seen to delay the onset of yield to slightly greater strains (Figures 4.23 and 4.27, 300 MPa pressure at 25 and 50 °C), and consequently greater stresses are required at yield. Consequently, the restricted flow of the amorphous component hinders the creation of the critical transitory dilation volume for dislocation.
nucleation, and is seen as the rate limiting step for this process.

The nucleation of dislocations requires not only a critical transitory dilation volume, but the presence of a critical shear stress as well. The magnitude of this shear component is significantly less than the hydrostatic component under conditions of high pressure. The modified-Coulomb yield criterion gives some indication of this \( \tau = \tau_0 + \phi P \). At \( P > P_s \), most of the yield stress is due to the hydrostatic component \( \phi P \). Given the severe elastic stress state present at the crystalline-amorphous interface, it is anticipated that there is more than sufficient shear stress present, and that the nucleation process happens readily once the critical transitory dilation volume necessary to nucleate dislocations is created. Consequently, amorphous flow is seen as the rate limiting step for the nucleation of dislocations.

The rate dependence of dislocation motion in the crystalline component is not considered to be a major factor for a spherulitic morphology. Dislocation flow is restricted to slip directions which do not sever the main chain. This is along planes parallel to the chain direction. Since the chain direction is normal to the lamellar surface (or close to it), slip can occur either in the thickness direction or the width direction. The lamellar thickness is extremely small, of the order of 200 Å. In this case there is little to impede the travel of dislocations. The lamellar width, although significantly greater than the thickness, is also of limited dimension, and again there is little to restrict dislocation motion in this direction. In either case, dislocation flow should occur with relative ease, and not be a limiting step in the deformation process.

However, for other morphological structures, it has been shown that there is a rate dependence of dislocation motion. In particular, work has been carried out on quasi-single crystal morphology for nylon 6 [6]. In this case, initially spherulitic nylon was textured into a quasi-single crystal morphology by plane strain compression at 170 °C in a deep channel die to a compression ratio of 4.0. As a result the amorphous component became indistinguishably distributed into a textured material with long range structural coherence. The rate dependence measured came from the simple shear rate along the principal crystallographic planes, and was interpreted as a problem of thermally assisted dislocation glide. In this case, the "lamellar" thickness and width are substantially longer than in the case for a spherulitic morphology.

Finally, chain scission is considered. Evidence of C-C bond breakage was determined from EPR (electron paramagnetic resonance) experiments on oriented semi-crystalline
polymers [24]. Bond breakage was noted at strains greater than the Lüders strain. At strains smaller than this, during yielding and necking of the specimen, there is no detectable EPR signal [25]. It was also determined that the molecules were broken throughout the specimen, and thus chain scission results from plastic deformation rather than just at the fracture surface. In this work, the situation is somewhat different. The polypropylene has a spherulitic unoriented morphology, and the amorphous component is in the glassy rather than rubbery state. The amorphous component in the glassy state is much stronger and deformation of the amorphous interlayer is more homogeneous than in the rubbery state. Tie molecules bridging adjacent rigid lamellae can transfer the stress effectively to adjacent molecules. In contrast, in the rubbery state, the tie molecules cannot transfer this stress and effectively carry most of the stress between adjacent lamellae. As well, other non-tie molecules within the amorphous component cannot as effectively transfer stress across the crystalline-amorphous interface. As a result, the critical stress required for chain scission of the tie molecules at the crystalline/amorphous interface is more easily achieved in the rubbery state. Thus, it would be expected that, if chain scission were to have an effect, it would more likely be at pressures less than the glass transition pressure where the polypropylene is in the rubbery rather than glassy state.

A similar conclusion was made in low temperature studies on PE by Davis and Pampillo [26]. They proposed that the two major deformation mechanisms of amorphous flow and chain scission were operating in series. At temperatures below the glass transition temperature, amorphous flow was proposed as the dominating mechanism. At temperatures above the glass transition temperature, it was suggested that chain scission at the amorphous/crystalline interface becomes the dominating mechanism. In this work it was observed that the shear activation volume, V, in the glassy state is similar at 50°C to the values at 25°C. However, the yield strain is markedly different, being 9% strain at 25°C (300 MPa pressure) and 7% at 50°C (300 MPa pressure). In other words, the degree of chain extension of the tie molecules is much different at the two temperatures. Since chain scission is anticipated to occur at the point of entry of the extended tie molecules into the lamellae, it would be expected that the greater extensions realized at 25°C should generate more chain scission events (if it is occurring) than at 50°C. But there is little difference in the shear activation volumes in the glassy state at these two temperatures, which suggests that chain scission is not a rate limiting mechanism.
Of the five mechanisms proposed, only flow of the amorphous component is seen as a possible mechanism accounting for the stress differences due to changes in strain rate for polypropylene in the glassy state. Amorphous flow is seen acting in two critical ways. First, amorphous flow acts to redistribute high local stress concentrations due to non-homogeneous extension of the tie molecules. And second, amorphous flow is the rate limiting step in the creation of the critical transitory dilation volume for dislocation nucleation. Thus, the approximately constant value for the shear activation volume in the glassy state is attributed to the flow volume of the amorphous component.
Rubbery State

Interpretation of the mechanisms operative in the rubbery state is more difficult, since more mechanisms are operative. The brief exercise which follows goes no further than to suggest possible mechanisms which are operative.

In the rubbery state, we begin by making a distinction between the response at high pressure and at low pressure. At high pressures in the rubbery state, more stress is transferred by the tie molecules (less stress is transferred by the surrounding amorphous molecules). There are still high strains at the crystalline-amorphous interface due to the inhibiting effect of pressure on the formation of a transitory dilation volume for amorphous flow, which is evident from the delayed strains at yield. Conditions are better for chain scission of tie molecules at their entry points into the adjacent lamellae. In the rubbery state, the tie molecules cannot transfer the stress as effectively to the surrounding amorphous molecules as would be the case when in the glassy state. As well, the stress transfer between the other amorphous molecules and the crystalline lamellae across the interface is less effective. Consequently, more stress is taken by the tie molecules bridging adjacent lamellae, and the tie molecule itself is more severely strained at its point of entry into the lamellae (the location where chain scission takes place). Thus, in addition to amorphous flow, chain scission may also be a factor in affecting the shear activation volume. This effect may manifest itself in slope changes in the shear activation volume-pressure curve. However, the pressure increments examined in this work were not fine enough to discern any effect. As previously mentioned, this possible mechanism was also suggested by Davis and Pampillo.

At low pressures, formation of a transitory dilation volume for nucleation of dislocations will occur with relative ease (or may already be present) with yielding of the crystalline component beginning at earlier strains. As a result there is less chance of chain scission occurring since the elastic strains at the crystalline-amorphous interface would be less. A number of different mechanisms involving amorphous flow are now activated, with the shear activation volume for these increasing with increasing temperature and decreasing pressure. Much of the change in the shear activation volume, noted in Figure 5.10 is no doubt due to this. However, the relative contributions of each of these mechanisms cannot be further determined from these results. Again, it may be that subtle changes in the slope of the shear activation volume versus pressure curves could be discerned if the pressure interval was finer.
5.3.4 Conclusions

**Glassy State**

1. The shear activation volume for polypropylene when the amorphous component is in the glassy state is approximately constant at various pressures (1654 Å$^3$ and 1623 Å$^3$ at 200 and 300 MPa respectively (temperature=25°C)), as well as at various temperatures (1623 Å$^3$ and 1731 Å$^3$ at 25°C and 50°C respectively (pressure=300 MPa)).

2. In the glassy state, of the five mechanisms proposed, only flow of the amorphous component is seen as a possible mechanism accounting for the stress differences due to changes in strain rate for polypropylene in the glassy state. Amorphous flow is seen acting in two critical ways. First, amorphous flow acts to redistribute high local stress concentrations due to non-homogeneous extension of the tie molecules. And second, amorphous flow is the rate limiting step in the creation of the critical transitory dilation volume for dislocation nucleation. Thus, the approximately constant value for the shear activation volume in the glassy state is attributed to the volume necessary for flow of the amorphous component.

**Rubbery State**

3. In the rubbery state, the shear activation volume for polypropylene decreases as the pressure increases. This response was also noted from the work of Davis and Pampillo for high molecular weight polyethylene.

4. In the rubbery state, amorphous flow is seen as the dominant influence on the shear activation volume value. However, as well as multiple mechanisms for amorphous flow being activated, the possibility exists that other mechanisms are also involved.
5.4 The Tensile Deformation Process at High Pressure

5.4.1 Introduction

The linear pressure dependency of the stress in polymers, described by the modified-Coulomb yield criterion, has been well documented [27]. The modulus also shows a pressure response, increasing with increasing pressure, but not necessarily in a linear fashion.

Although a significant amount of work has documented the mechanical response to pressure of polymers, there is yet no satisfactory mechanistic explanation to the linear pressure dependence of the yield stress, or to the increase in the modulus with pressure of polymers.

In this work, there was a unique and complex tensile response observed during the initial stages of deformation which becomes prominent at high pressures. The observation was made possible due to two factors; the sensitivity of the high pressure tensile testing machine, and the change in the tensile response of the polypropylene as the pressure increases through the glass transition pressure.

It is the purpose of this section to identify the actual molecular mechanisms contributing to the initial elastic response of the polypropylene, as well as the onset of plastic deformation, and to relate how the pressure affects both of these deformation responses.
5.4.2 Results

The sensitivity of the high pressure tensile testing machine allowed the initial portion of the stress-strain curve, prior to the peak stress, to be examined closely. Under conditions of high pressure the stress-strain curve showed some distinct features. The challenge faced was to first characterize these features, to determine how they were affected by the pressure, temperature and strain rate, and then, if possible, to associate mechanisms with some of those features. It was found that the derivative of the stress-strain curve (the tangent modulus) was a much more sensitive indicator of these changes. This will be examined first.

It will be seen that there is a marked transition in the tangent modulus-strain curve occurring between 4 and 8 % strain. At high pressures this transition is quite evident in the stress-strain curves, being marked by a sudden change to lesser slope. The tangent modulus-strain curves allow this transition to be tracked under less optimal conditions. This transition and how it is affected by pressure, temperature and strain rate is examined next in the section on yield stress.

The Tangent Modulus

In this work the tangent modulus, defined as the slope at various points along the stress-strain curve, was determined. The features of the tangent modulus-strain curve were described in depth in the Results section. The 25 °C data will be briefly summarized.

At atmospheric pressure the tangent modulus values decrease from an initial high value at strains less than 1% to a value of zero at the peak strain (Figure 4.20). However, as the pressure is increased, a second maximum soon appears, occurring at strains of 4% at low pressure and increasing to 8% at and above the glass transition pressure. The second maximum becomes more prominent as the pressure is further increased. At high pressures (P > 200 MPa), the interval between the second maximum and the peak strain can be divided into three sections (Figures 4.22 and 4.23). The first section features a precipitous drop in the tangent modulus value over a narrow strain interval (8-10%) immediately following the maximum. The second section is either constant in value or declines modestly. The third section is marked by a gradual and continuous decline to a value of zero. At pressures of 200 MPa and above, these three sections are remarkably similar in shape and value for various pressures.
The second maximum of the tangent modulus occurs between 4 and 8% strain, and is most prominent at high pressures. The maximum is plotted as a function of pressure in Figure 5.11, for a temperature of 25°C and a strain rate of 0.020 min⁻¹.

There was a transition in the second maximum values noted between 100 MPa and 200 MPa. Since the pressure interval was smaller for the first set of tests, those data are included. The slightly lower slope of the first set was determined to be due to a slight decrease in pressure occurring during the testing procedure. This situation was remedied for the second set of tests.

The second maximum, which is a major feature at high pressures, gradually decreases in value and prominence as the pressure is reduced. At atmospheric pressure there is no second maximum following the initial maximum. As the pressure is increased there is a sizeable increase in the second tangent modulus maximum, with two approximately linear sections, one from 0 - 138 MPa, and another from 200 - 350 MPa pressure. Between 138 and 200 MPa the modulus value jumps significantly. The jump in value is due to the pressure-induced glass transition of the amorphous phase. As previously noted, the glass transition has been reported in other high pressure studies of polypropylene. The shear modulus of polypropylene showed a glass transition at about 160 MPa [2] and the compression modulus of polypropylene showed a glass transition at about 210 MPa [1].

The glass transition has no effect on the crystalline phase, affecting only the amorphous phase. Thus, the straining of the amorphous phase is a component of deformation contributing to the maximum value.

The effect of strain rate on the tangent modulus maximum/pressure curves for a temperature of 25°C is shown in Figure 5.12. A series of parallel curves are observed, with the tangent modulus maximum increasing as the strain rate is increased at a given temperature. (The lower pressure portion of the curve is extended to 138 MPa since the first data set show approximate linearity to that point). Thus the maximum cannot be characterized as being entirely elastic in nature, but has a flow component as well. This plastic strain need not be large to have a pronounced effect on the modulus value. Discrimination between flow due to the amorphous phase, or the crystalline phase, or both cannot be made based on the data presented thus far.
The effect of temperature on the second maximum of the tangent modulus is shown in Figure 5.13 for temperatures of 25, 50 and 75 °C and a strain rate of 0.020 min\(^{-1}\). There is a jump in maximum values noted at 50°C occurring between 200 and 300 MPa. The same discontinuity was noted over the same pressure interval in the peak stress results. The jump in maximum values is again associated with the pressure-induced glass transition. The predicted transition at 75 °C would occur at 340 MPa, which is beyond the range examined. As expected, there is no jump in maximum values noted in the range studied.

### Table 5.05  Tangent Modulus Maximum vs Pressure (MPa)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(P&lt;P_d)</th>
<th>(P&gt;P_d)</th>
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<tbody>
<tr>
<td>25°C</td>
<td>(E = 212 + 1.64 P)</td>
<td>(E = 330 + 1.85P)</td>
</tr>
<tr>
<td>50°C</td>
<td>(E = 110 + 1.33 P)</td>
<td></td>
</tr>
<tr>
<td>75°C</td>
<td>(E = 88 + 0.57 P)</td>
<td></td>
</tr>
</tbody>
</table>

Linear regressions were carried out on the curves in Figure 5.13 and are tabulated in Table 5.05. The second set of tests carried out at 25°C were used for that regression. The intercept value (projected to atmospheric pressure) decreases as the temperature increases as expected. The slope of the curves decreases with increasing temperature. At 25 °C the pressure dependence of the modulus above and below the glass transition does not change significantly (1.85 versus 1.64). The temperature dependency of the second tangent modulus maximum is a further indication that there is a flow component to the tangent modulus.

In summary, the second maximum of the tangent modulus is linearly dependent upon the pressure. There is a jump in value at the pressure-induced glass transition which associates the second maximum with the amorphous phase. The pressure-induced glass transition occurs between 138 and 200 MPa pressure at 25 °C and between 200 and 300 MPa pressure at 50°C. And finally, the temperature and strain rate dependency of the second maximum is evidence that there is a flow component associated with this tangent modulus maximum, in addition to the elastic component one usually associates with modulus values.
The Yield Stress

The stress-strain curves at 200 and 300 MPa pressure and 25 °C show a distinct bend which occurs at 60-70% of the peak stress (Figures 4.07 and 4.08). This bend corresponds to the sudden drop in the tangent modulus-strain curve, marking the initiation of a new deformation mechanism and, in contrast to the peak stress, represents a true yield point.

Determination of stress at this bend from the stress-strain curve is sometimes difficult since the bend occurs over a small range of strain. A more sensitive measure of this transition is obtained from the tangent modulus-strain curve (Figure 4.17). Here the bend in the stress-strain curve coincides with the steep decline in the value of the tangent modulus immediately following the second maximum. The decline in the value of the tangent modulus with strain in the high pressure glassy state actually exhibits three discrete stages; an initial steep decline; a second stage where the tangent modulus value declines slightly, if at all; and a final third stage where the value of the tangent modulus declines steadily and continuously to a value of zero at the peak strain. The initial decline is most prominent at pressures greater than the pressure-induced glass transition. It is characterized by a rapid decrease in modulus over a limited strain interval (8-10% strain) from a point near the modulus maximum to a tangent modulus value of 200 to 250 MPa.

The stress corresponding to the strain at the mid-point of the initial steep decline in modulus was defined as the yield stress. Using this definition, the yield stress was determined by plotting simultaneously the stress-strain and modulus-strain curves on the same strain axis (Figure 5.14).

The yield stress data are presented in Table 5.07. The 25 °C data is plotted as a function of pressure in Figure 5.15. The peak stress is plotted as well for comparison. The linear dependency upon the pressure, noted with the peak stress, also holds true for the yield stress as defined here. The yield stress-pressure curve consists of two linear sections separated by the glass transition. In the glassy state, the yield stress curve closely parallels that of the peak stress. Linear regressions done on the rubbery and glassy lines of the yield stress are listed along with the linear regression for the peak stress in Table 5.06. The pressure coefficient for the yield and the peak stress in the glassy state are the same (.207 and .211 respectively). This is a direct consequence of the previously noted similarity in the tangent modulus-strain curve, where the shape and magnitude of the curves of the second and third stage decline are the same. This suggests that the
same deformation mechanisms are operative from the onset of yield to peak for all curves in the glassy state. There is no increase in the separation of the curves with increasing pressure, and it can be concluded that flow over this strain interval is not dependent on the pressure.

Table 5.06: Linear Regression of Yield and Peak Stress as a Function of Pressure (MPa)

<table>
<thead>
<tr>
<th></th>
<th>( P &lt; P_g )</th>
<th>( P &gt; P_g )</th>
</tr>
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<tbody>
<tr>
<td>Yield</td>
<td>( \sigma = 13.23 + .141 P )</td>
<td>( \sigma = 8.02 + .207 P )</td>
</tr>
<tr>
<td>Peak</td>
<td>( \sigma = 24.42 + .181 P )</td>
<td>( \sigma = 24.96 + .211 P )</td>
</tr>
</tbody>
</table>

In the rubbery state, the yield stress is also linearly dependent upon the pressure. The slope of the yield curve in this region is less than that for the peak. Yielding occurs at earlier strains as the pressure decreases and over a larger strain interval, and this accounts for the decreased interval between the yield and peak stresses as the pressure decreases. The stress interval between the yield and the peak stress at pressures on adjacent sides of the glass transition is the same (27 MPa). In other words, after yielding has occurred, the deformation path from yield to the stress maximum is not affected by the state of the amorphous component.

The yield stress also jumps in value over the glass transition, and in a more noticeable fashion than the peak stress. This is an important point, since it establishes that the state of the amorphous phase, either rubbery or glassy, plays a significant role in determining the deformation conditions for yield.

At 50°C, the features of the tangent modulus-strain curve which define the yield point are evident at 100, 200 and 300 MPa pressure (Figure 4.18). The yield stress-pressure relationship is plotted in Figure 5.12. The peak stress is plotted as well for comparison. In the rubbery state (100 and 200 MPa pressure) the yield and peak stress lines are close to parallel. The jump in yield stress at the pressure-induced glass transition, noted in the 25°C data, is also distinctly evident here.

At 75°C, at pressures of atmospheric and 100 MPa, the tangent modulus-strain curves are relatively featureless (Figure 4.19). At pressures of 200 and 300 MPa, the modulus maximum becomes apparent, and occurs at earlier strains than that observed at 50°C and 25°C. The features of the tangent modulus-strain curve which define the yield point were not distinct enough at these pressures to derive a yield stress.
Table 5.07: Yield Stress at 25 and 50°C for Various Pressures and Strain Rates
Necking occurred in the polypropylene under all conditions of high pressure, even above the pressure-induced glass transition. During formation of the neck and subsequent drawing, there is a continuous transformation from the spherulitic structure, which has begun breaking down at the peak strain, to the fibrillar structure. The fibrillar structure continues to deform and, with increasing orientation of the molecular chains, increases in strength until the reduced section becomes strong enough to resist further deformation. Subsequent deformation occurs in a localized region between the now stable reduced section (neck) and the unreduced section. The process is not affected by the state of the amorphous component (either glassy or rubbery), being mainly dependent upon flow of the crystalline component.

The effect of pressure on the draw stress for temperatures of 25, 50 and 75 °C is shown in Figure 5.17. The draw stress increases linearly with pressure at 25 °C. There is no jump in the value of the draw stress over the pressure-induced glass transition, which was noted in the peak stress results. Once flow has been initiated, plastic deformation of the crystalline component predominates the overall necking process. Whether the amorphous phase is in the glassy or rubbery state has little effect on the draw stress level. The same insensitivity of the draw stress across the pressure-induced glass transition is also noted at 50 °C where the transition occurs between 200 and 300 MPa pressure.

There was greater variability in the draw stress values than the peak stress values. Neck formation is inherently unstable, and it can be concluded that neck geometry has a critical effect on the draw stress level and the final structure realized.

In summary, the draw stress is a linear function of the pressure. It is not affected by the pressure-induced glass transition, which is indicative that the amorphous component does not play a critical role during necking. Necking itself is indicative of large scale crystalline flow. There is some evidence that chain scission is occurring at high pressure at the onset of necking. At pressures of 345 MPa, fracture occurs before development of the neck is fully completed.
Figure 5.11: The second maximum of the tangent modulus as a function of pressure. The temperature is 25°C. The strain rate is 0.02 min⁻¹.
Figure 5.12: The effect of strain rate on the second maximum of the tangent modulus. The temperature is 25°C. The strain rates are 0.2, 0.02, and 0.002 min⁻¹.
Figure 5.13: The effect of temperature on the pressure response of the second maximum of the tangent modulus.
Temperatures are 25, 50 and 75°C. Strain rate is equal to 0.02 min\(^{-1}\).
Figure 5.14: Tensile stress and tangent modulus as a function of strain. The temperature is 25°C. The strain rate is .02 min⁻¹.
Figure 5.15: The yield and peak stress as a function of pressure. Temperature is 25°C. Strain rate is .02 min⁻¹.
Figure 5.16: The yield and peak stress as a function of pressure. Temperature is 50°C. Strain rate is .2 min⁻¹.
Figure 5.17: Draw stress as a function of pressure for temperatures of 25, 50 and 75°C. Strain rate is 0.020 min⁻¹.
5.4.3 Discussion

With increasing pressure, the tangent modulus-strain curves develop two distinct features not observed at atmospheric pressure. The first feature is the development of a second maximum which occurs between 4% and 8% strain, depending on the pressure. The maximum increases with increasing pressure in a linear fashion, with a jump in value across the glass transition. The second feature is a rapid decline in value immediately following the maximum. The strain at which the rapid decline occurs increases from 6% at low pressures to 10% at the glass transition pressure. Further increases in pressure above the glass transition do not increase this strain. The deformation mechanisms involved in this rapid decline will be addressed first.

5.4.3.1 The Yield Transition

At high pressure the rapid decline in the tangent modulus after the second maximum marks a transition in the deformation process. This corresponds with the bend to lesser slope of the pre-peak portion of the stress-strain curve. This rapid decline is observed to become greater in magnitude and smaller in strain interval as the pressure is increased (Fig.4.17). As well, the stress associated with the transition is linearly dependent upon the pressure.

This response poses two significant questions:
1. What is the cause of the transition?
2. Why is the stress associated with this transition linearly dependent on the pressure?

Before addressing the first question, it should be pointed out that such a sudden transition suggests that the yielding process is occurring simultaneously over a substantial portion of the spherulite. This in turn requires that the stress be homogeneously distributed throughout the spherulite. It would be expected that the stress distribution would be more homogeneous when the polymer is under high pressure with the amorphous component in the glassy state. The amorphous phase is much stronger in the glassy rather than rubbery state with a greater amount of stress being transferred between adjacent molecular chains. Thus the amorphous phase in the glassy state locks the structure together more effectively, resulting in greater homogeneity in the stress distribution.
The cause of the transition can be considered to be due to three possible mechanisms:

1. The onset of flow of the amorphous component.
2. The onset of flow of the crystalline component.
3. The occurrence of a mass scission event.

Considering each in turn allows us to eliminate those mechanisms whose response is not consistent with the observed results. Flow of the weaker amorphous component occurs at lower stress levels than flow of the crystalline component. The question then asked is whether the transition represents the onset of amorphous flow. Evidence of flow prior to the transition comes from the strain rate results, where it is observed that for a given pressure and temperature the second maximum of the tangent modulus increases with increasing strain rate. Since this maximum occurs earlier in the deformation process that the transition indicates that there is some flow occurring prior to the transition, and it is suggested that this flow is due to the amorphous component. If this is the case then the transition is not due to the onset of amorphous flow.

Next, consideration is given to the occurrence of a mass scission event as the cause of the sudden and rapid transition. Chain scission is envisioned as occurring at the point where a tie molecule enters the crystalline lamellae. The first problem with this view is that the tie molecules are not all the same length and they would not all be pulled taut and reach the same critical stress to break in a co-operative fashion. A second problem with this view is that it cannot adequately explain the pressure dependency of the yield stress. Given a mass scission event at high pressures where the tie molecules are all extended to a limiting strain, begs the questions of what happens at lower pressures, which are characterized by a lower modulus maximum, yield stress as well as slightly lower yield strain. The tie molecules would not be extended to the same limiting strain at the lower pressure, and conditions for a mass scission event would not be satisfied. Thus, the transition cannot be associated with a mass scission event.

This indirect argument leaves only the onset of crystalline flow as the possible cause of the transition. We know that crystalline flow is possible at high pressure. Even within the glassy state (e.g. 300 MPa and 25 °C), the polypropylene is still able to form a neck, indicating that widespread crystalline deformation is occurring as the structure transforms from a spherulitic to fibrillar morphology.
There is also evidence from the literature which supports the concept that the onset of flow of the crystalline component is the cause of the transition. As reported by Bartczak et al. [5], the strain range for the onset of plastic deformation of the crystalline component for polyethylene is similar to those reported in this work for polypropylene. In the work of Bartczak et al., the plastic component of deformation was determined using polyethylene with a quasi-single-crystal morphology. This morphology was produced by plane strain compression using a channel die and resulted in the molecular chains aligning in the flow direction. Mechanical testing at various angles to the chain direction, along certain slip planes (determined using X-ray techniques) allowed the determination of slip systems, their relative resistances and the onset of plastic deformation. Plastic deformation for polyethylene was determined to begin at atmospheric pressure and room temperature between 4 and 5% strain and reached a steady state condition (i.e. the plastic deformation vs. total deformation curve is linear) by 9-10% strain for various orientations to the (010)[001] slip system (slip in the [001] chain direction along the (010) plane). This plastic deformation was determined to be due to the deformation of the crystalline component from X-ray techniques. This is the same strain range noted in this study for the high pressure deformation of polypropylene. At atmospheric pressure the onset of the yield transition in polypropylene is similar to that noted for polyethylene (4-5% strain). At high pressures, the onset of the yield transition for polypropylene coincides with the beginning of the steady state plastic deformation condition in the polyethylene (9-10% strain).

The arguments given are not, in themselves, conclusive on the issue, but do strongly suggest that the sudden transition is due to the onset of crystalline flow.

The second question of why there is a linear relationship between the transition stress and the pressure is now addressed. One possible mechanism which would account for this relationship is the formation of a void. To form a void in a material requires a triaxial state of tensile stress. What would then be the effect on void formation if the material had a triaxial compressive stress (due to hydrostatic pressure) superposed upon it? The answer is that for the void to form there must be generated an additional triaxial tensile stress to overcome this triaxial compressive stress. For a sufficiently soft material (i.e. with an atmospheric tensile strength much less than the hydrostatic pressure) the relationship between the triaxial tensile stress and pressure (a triaxial compressive stress) would be close to linear. Thus, a void formation mechanism could satisfy the linear dependency between the yield stress and pressure. This is an important point.
Thus, it is proposed that there is a direct relationship between the empirically determined modified-Coulomb yield criterion and a microscopic deformation mechanism; the formation of a critical void volume results in the pressure dependence of the yield stress. The formation of this void within the material requires a triaxial tensile stress state which must overcome not only the atomic coherency of the polymer, but also the superposed triaxial compressive stress due to the external hydrostatic pressure. If the atomic coherency stresses are small compared with the hydrostatic pressure, then it would expected that the relationship between the yield stress and pressure would be linear.

In other words, the triaxial tensile stress required for void formation is directly proportional to the superposed pressure, and accounts for the linearity between the yield stress and pressure, shown in Figure 5.11, described by the modified-Coulomb yield criterion. It is emphasized here that the relationship is not with the peak stress, but with the yield stress, which is defined at the strain at the mid-point of the rapid drop in the tangent modulus.

A final piece of the puzzle falls into place when one links the onset of crystalline deformation with the formation of a void. It is proposed that the critical void volume for crystalline flow is that required to form a nucleation site for dislocation generation. The onset of crystalline flow is inhibited until a critical stress is realized which is linearly dependent upon the pressure. The effect of pressure is to inhibit this void formation and delay the onset of yield to greater strains.

One additional point can be made to this void nucleation model. The formation of void would require loss of intermolecular contact across the cavity, for which there is little evidence. What is likely to be the case is the production of transitory dilation volume (TDV) allowing segmental mobility, which reduces the intermolecular segmental interaction but does not eliminate it. In the balance of the argument, TDV will be used only.

To summarize, it is proposed that the yield transition marks the onset of flow of the crystalline component. The mechanism associated with this is the nucleation of dislocations in the crystalline lamellae. Formation of this volume requires a triaxial tensile state of stress which is linearly dependent upon the externally applied pressure (a triaxial compressive state of stress). Thus the nucleation event is associated with a
critical stress. In contrast, flow models predict that deformation will occur even at minute stress levels. At high pressure a critical stress is evident from the bend in the stress-strain curve, even though there is a distribution of lamellar orientations. For such a sudden transition to be evident indicates that yielding is occurring over large regions of the spherulite. This requires that the stress be homogeneously distributed throughout the spherulite, and this in turn requires that strains be largely elastic at the point of yielding. This is readily apparent in the glassy state. The yield transition becomes less pronounced as pressure decreases below the glass transition as the strains become more plastic in nature due to flow of the amorphous phase.

The model proposed still has a significant piece of the puzzle missing, and that is how a sufficiently large triaxial tensile stress is generated, one that is large enough to overcome the hydrostatic pressure, to form a transient dilation volume for dislocation nucleation. The answer to this requires looking at the elastic response of the polypropylene to pressure. This is addressed in a following section on deformation before crystalline yield which follows the next two sections.

**Nucleation Site**

A number of nucleation sites and types of sources have been suggested, both within the lamellae at chain ends[28], and at the thinned-edge of the lamellae at the crystalline-amorphous interface as screw dislocations [29],[30]. However, the matter is still unclear.

In this work, the yield transition has been interpreted as being due to the onset of crystalline flow of the lamellae. However, there is also observed a jump in the yield stress value over the glass transition pressure. This seems to contradict the interpretation that the yield point is a dislocation nucleation related event since only the amorphous phase should be affected by the rubber to glass transition. How can a crystalline yield process be influenced by the state of the amorphous phase? The seeming discrepancy actually leads to an important conclusion. It locates the nucleation site at the crystalline-amorphous interface. The critical TDV for dislocation nucleation is most easily created in the amorphous component at the crystalline-amorphous interface. The jump in the yield stress at the glass transition pressure is due to the decreased mobility of the amorphous component in the glassy state. In other words, the
reduced mobility of the amorphous phase in the glassy state adds an additional obstacle to nucleation at the interface, and a greater amount of stress is therefore required to initiate yielding in the glassy state. This accounts for the jump in the yield stress across the pressure-induced glass transition.

It should be pointed out that the argument presented does not exclude the possibility of other concurrent nucleation sites located within the crystalline lamellae, only that nucleation does take place at the amorphous/crystalline interface.

**Propagation of Dislocations**

In the glassy state, the tangent modulus-strain curve following the rapid decline is characterized by a plateau for an interval of about 3% strain followed by a gradual decline to a value of zero at the peak stress. These final two stages are similar in shape and magnitude for various pressures (Figures 4.22 and 4.23). A direct result of this similarity is that the stress interval between the yield and peak stresses is constant as the pressure increases. This suggests that the deformation path from the yield to peak strains is essentially the same in the glassy state. There is now massive crystalline flow, and propagation of dislocations occurs with relative ease.

The transition between the first and second stages marks the completion of the creation of the nucleation sites. The invariance in the stress interval between the yield and peak stresses with pressure suggests that dislocation propagation is not the rate limiting step. Also it infers that, since amorphous flow is pressure sensitive, the amorphous phase does not play a significant role once crystalline flow has begun. (This follows from the observation that the second and third stages of decline in the tangent modulus-strain curve are invariant for varying strain rates). The same conclusion based upon the insensitivity in the critical resolved shear stress and the flow stress to a transition in the shear modulus value at 310 K has also been made [8]. (It should be noted however, that this work showed that there is a difference in flow stress level across the pressure-induced rubber-to-glass transition which is observable if the apparatus is sensitive enough. Notwithstanding this, this transition has a much greater effect on the modulus than on the flow stress, and the general conclusion made that the amorphous component does not play a significant role once crystalline flow has begun remains valid.)
Given that plastic deformation of the crystalline lamellae does not occur until the yield transition and that the stiffness of the lamellae is greater than that for the amorphous phase means that most of the strain prior to yield, both elastic and plastic, occurs in the amorphous phase. As a result, the initial modulus and its sensitivity to strain rate and pressure is a reflection mostly of the stiffness and flow properties of the amorphous phase. This will be addressed in the following section.

5.4.3.2 Deformation Before Crystalline Yield

We have seen that there is an unusual initial deformation response which becomes prominent at high pressures where the polypropylene approaches and surpasses the glass transition pressure. Although some features of this response are observed directly from the stress-strain curve, it is the derived tangent modulus-strain curve that displays these features with exceptional sensitivity. Specifically, at high pressure, and in the glassy state, there is the appearance of a second maximum at finite tensile strains. This was followed by a rapid decline which was interpreted in the previous section as the onset of crystalline deformation. This allows crystalline flow prior to yield to be eliminated as a contributor to this deformation.

One of the consequences of the rapid yield transition and the attendant delay in the yield is that deformation mechanisms occurring prior to yield are forced to take up the extra strain. This results in a deformation response which is considerably exaggerated and allows specific mechanisms to be identified with this response. It will be seen that the pre-yield response is largely elastic and that a measure of this, the tangent modulus, is dependent on the pressure. The pressure dependence of the modulus in polymers has been well documented in the literature. However, it is not well understood.

In this section, the development of the second maximum of the tangent modulus with increasing pressure will be examined. Prior to crystalline yield between 9 and 10% strain, deformation is observed to be largely elastic. The possible elastic mechanisms for this response will be discussed. Next to be addressed will be deformation prior to the second maximum, namely the initial maximum, the subsequent decline and rise to the second maximum. Can these features be associated with specific deformation mechanisms? Understanding the mechanisms involved can explain the following mechanical responses: first, the increase in the second maximum of the tangent
modulus with pressure; second the increase in the second maximum with strain rate: and third, the jump in value of the second maximum across the glass transition pressure.

Types of Elastic Response

The elastic response of metals and ceramics is characterized by no permanent flow. All of the energy of deformation is stored, and is usually assumed to be instantly reversible. The modulus is associated with the fractional interatomic displacement resulting from an applied stress, and consequently is determined as the strain tends to zero. The modulus also tends to be linear with strain, or is a slightly decreasing function of strain.

In the case of polymers, significant extensions and exceptions to the above must be made, due to the fact that there are now two types of bonds operative; relatively weak intermolecular bonding and relatively strong main chain bonding. For semi-crystalline polymers, one can then characterize four different types of elastic response. Within the amorphous component there is; fractional intermolecular displacement, rubbery elasticity, and main chain extension causing distortion of the main chain bonds. In the crystalline component there is distortion of the unit crystal cell. Elastic energy can also be stored collectively by larger morphological units, such as the extension, bending and twisting within lamellae and separation (normal to the lamellar surface), shear and twisting between lamellae. Basically these are just an extension of the previous elastic deformation modes and will not be considered separately.

Fractional intermolecular displacement of the amorphous component. In the rubbery state, the modulus, classically defined as an elastic and instantaneously reversible response with no permanent flow, for the amorphous component, due solely to the weak interchain bonds, is zero. In other words flow occurs at infinitely small stress levels.

In the glassy state, although flow is exceptionally difficult, it is still possible. Given sufficient time, the response to stress would be similar to that in the rubbery state: that is, flow would occur at infinitely small stress levels. Modulus measurements made at finite strains are due mainly to the distortion of the main chain bonds, and are not elastomeric. Time and temperature effects on the modulus values, observed given sufficient time, are due to the weaker interchain bond energy.
Rubbery elasticity of the amorphous component.
In the rubbery state, the amorphous component can store elastic energy of a completely different type. In this case the thermal vibrations exert a line tension on a length of molecular chain which is fixed at it's ends. These fixed ends may be permanent (crosslinks) or temporary (entanglements, entry points into crystalline regions). The restoring force is proportional to the difference in length between the actual average end to end chain length and the root mean square of that chain length. Elastomeric extension can be effective to several hundred percent strain depending upon crosslink density, and therefore energy can be stored to those high extensions. In the case of semi-crystalline polymers, the amorphous phase is relatively thin, with the tie molecules, linking adjacent lamellae, acting as elastomeric units. The tie molecules are constrained at their points of entry into the adjacent lamellae which act effectively like crosslinks. Total extension is limited by the relatively short lengths of the tie molecules. Thus, the maximum strain possible in which elastomeric energy can be stored is limited.

In the glassy state, elastomeric extension is not possible.

Main chain extension causing distortion of the main chain bonds
Straightening of the amorphous chain in the rubbery state will result in an elastomeric retractive force. Extensions beyond this will cause distortion of the main chain bonds. In the main chain direction, the modulus is very high, and the amount of strain before chain scission occurs can be significant. For polymers characterized with a planar zig-zag structure, such as polyethylene, strain in the main chain direction can be attributed to two types of bond deformation: bond extension and bond angle opening. For helically wound polymers such as polypropylene, an additional bond deformation type must be included: bond torsion. The combination of a high modulus with a high strain before chain scission results in a tremendous amount of stored energy in the main chain direction. Thus, the amount of elastic strain that can be taken up by the tie molecules due to main chain bond distortion is substantial. The elastic strains from this deformation mode contribute at significant finite strains, and are not limited to infinitely small strains.

Distortion of the unit crystal cell
The mechanical properties of polymer crystals are not straightforward. A distinction must now be made between those directions governed solely by the relatively weak intermolecular bonds (which affect the tensile (compressive) moduli acting normal to
the chain direction, and shear moduli acting parallel to the chain direction), those
directions governed solely by the strong main chain bonds (tensile (compressive) moduli
in the chain direction) and those moduli directions governed by both types of bonding
(e.g. shear moduli acting in directions normal to the chain direction).

Not only is it important to determine the yield stress in various crystal directions, but the
yield strain. In other words, the elastic energy which can be stored in the various crystal
directions is important. In those directions governed by the relatively weak
intermolecular bonds, the strain before yield is small, and this coupled with a relatively
low modulus results in a low capacity to store elastic energy. Modulus due to this is
measured as the strain tends to zero. The interatomic spacing is defined by the crystal
structure, and flow will not occur until a critical stress is reached.

In the chain direction, the modulus is very high, and the amount of strain before chain
scission can be significant. Combining both the high modulus and high strain before
chain scission results in a tremendous capacity to store elastic energy in the main chain
direction.
Elastic Deformation of Polypropylene in the Glassy State at Finite Strains

Examination of the stress-strain response of the polypropylene in the glassy state indicates that the initial deformation is largely elastic. At 300 MPa pressure and 25°C temperature, where the polypropylene is in the glassy state (Figure 4.08) it is observed that there is little deviation in the stress strain curve for various strain rates to 55 MPa, or over 60% of the peak stress. This tensile response is largely elastic to relatively high extensions of 9% strain.

Of the elastic deformation modes discussed, the only mode capable of this extension is that involving main chain extension. Prior to the onset of crystalline flow, most of the strain will be taken up by the weaker amorphous interlayer. This strain will be taken up by the tie molecules in the amorphous interlayer by chain extension. Since lamellar thicknesses are greater than the amorphous interlayer between them, chain extension of the tie molecules must exceed the overall yield strain substantially. The question then is whether the required yield strain is possible by chain extension of the tie molecules? The total extension a tie molecule may be strained before chain scission depends on a number of factors: the length of the tie molecule; the orientation of the end points of the tie molecule (points of entry into the lamellae) with respect to the local deformation paths of those end points; and the total extension of the tie molecule prior to chain scission (this includes the amount of slack in the tie molecules as well as the amount the straightened chain can be extended prior to chain scission).

In the case of polypropylene, the helical conformation allows substantially greater extension of its main chain than the planar zig-zag conformation of the polyethylene. With increasing strain the polypropylene helix uncoils, and the main chain stiffness should approach that for polyethylene. Both polymers have a main chain C-C bond length of 1.54 Å, and a bond angle of 109.5°. The 3, polypropylene helix results in a c-axis distance of 6.488 Å, which would have to be extended 16.3% to reach the planar zig-zag length for an equivalent number of polyethylene mer units. The polyethylene chain is itself extensible; theoretical estimates of its elongation before scission are 33% [31]. Thus a conservative approximation of the total extension of the polypropylene chain prior to chain scission (neglecting the effect of defects) is greater than 33%. Still further strain of the amorphous interlayer can be effected by chain scission of those tie molecules with shorter lengths. Therefore, the largely elastic response of the polypropylene at high pressure to the yield point at 9% strain can be attributed in large
part to the chain extension of the tie molecules within the amorphous interlayer.

There are other contributors to the overall elastic response. The first to be mentioned is the elastic deformation in the chain direction of the crystalline lamellae. Since the lamellae are structurally much stronger than the amorphous interlayer, the elastic strain is not expected to be significant relative to that experienced in the amorphous interlayer. However, the elastic energy stored may be considerable. As well, because of locking between adjacent molecular chains within the amorphous interlayer which is in the glassy state, there may also be a significant elastic contribution due to main chain bond distortion of molecules which are not tying adjacent lamellae together.

In the rubbery state, the same interpretation applies, with the exception of the contribution from non-tie molecules within the amorphous interlayer. The contribution of elastomeric extension of the tie molecules to the total elastic response is limited. Soon after strain has begun the slack in the tie molecules is taken up and chain extension is initiated.

To conclude, given that no plastic flow of the crystalline component occurs prior to yield and that the lamellar modulus is much greater than that of the amorphous interlayer, determines that most of the strain before yield occurs within the amorphous interlayer. Since the amorphous component is in the glassy state at these pressures, amorphous flow is difficult. Deformation is largely elastic and the elastic energy is stored mainly by the tie molecules within the amorphous interlayer by extension of the molecular chains.
The Elastic Component of Deformation Before Crystalline Yield

In the glassy state, the tangent modulus is seen to have an initially high modulus value followed by a strain interval of reduced modulus, and then increases to a second maximum before dropping precipitously at the yield point (Figure 4.22). Using crosshead displacement to determine strains, there is good reproducibility of the tangent modulus-strain curves above 2-3% strain. To understand the initial deformation at strains less than this, it is illustrative to consider work carried out by Questad et al. on the high pressure tensile deformation of a polyurethane elastomer [23]. Since plastic deformation of the crystalline component in polypropylene does not occur until 9% strain, most of the deformation prior to this takes place in the amorphous interlayer. This amorphous interlayer is highly constrained by the adjacent lamellae and by the tie molecules linking adjacent lamellae. The points of entry of the tie molecules into the crystalline lamellae can be considered to act as crosslinks until the onset of crystalline flow. It is suggested that a high pressure analogue for this amorphous interlayer is found in the high pressure response of a crosslinked elastomer rather than an amorphous polymer.

In the high pressure tensile deformation of the polyurethane elastomer, it was observed that there is a glass transition between 3 and 4 kb pressure. Below that pressure the tensile response was typically elastomeric, with the stress level of the stress-strain curve increasing linearly with pressure. Above the glass transition pressure, (where the polymer is no longer elastomeric since it is now in the glassy state) the stress-strain curve displays an initial high modulus, with the stress increasing to a stress maximum, followed by a reduced stress level of constant value (see Figure 2.13). Unlike the stress-strain curve of semi-crystalline polymers, which have a similar shape, the reduced stress level was not associated with a localized necking instability, but a homogeneous reduction in the cross-sectional area throughout the gauge section. In other words, flow occurs in the glassy state after an initial resistance. It has been suggested here that the initial stress maximum is the stress required to form a transitory dilation volume for flow of the amorphous "elastomer" now in the glassy state. Once this transitory dilation volume is formed, glassy flow can proceed at constant stress.

This interpretation of the glassy response of the polyurethane elastomer is now applied to the glassy response of the amorphous interlayer of polypropylene. Using this analogy, it is conjectured that the initial resistance to flow by the glassy amorphous component is characterized by a high initial modulus. Upon reaching a critical yield stress (which
for the amorphous component is substantially less than that of the crystalline component) flow begins. However, unlike the glassy elastomeric response, there is no stress maximum observed since the tie molecules have already begun to take up the stress. The stress continues to increase due to elastic extension of the molecular chains. In other words, there is an overlap between the yielding of the amorphous component and chain extension of the tie molecules. In this situation, it is possible for the tangent modulus to decrease (due to the onset of glassy amorphous flow) and at the same time for the stress to continue to increase (due to the initiation of chain extension of the tie molecules). This would account for the minimum in the tangent modulus-strain curve between the first and second maximums.

Following the minimum, there is a subsequent rise in the tangent modulus to the second maximum. There are two contributions which can increase the modulus with increasing strain. First, there is an increase with strain in the number of chain extended tie molecules. Before extension of the tie molecules begins, they carry relatively little stress. The slack has to first be taken up by the initial lengthening of the tie molecule. The slack is taken up differentially (due to varying slack lengths), increasing with strain and resulting in an increase in the modulus. As in the case of elastomers in the last stages of extension prior to failure, the stress increases asymptotically as the limiting strain is approached. This is suggested to be the major contributor to the increase in tangent modulus with increasing strain.

A second contribution is due to the chain conformation of the polypropylene molecule. The modulus-strain response of the helically-wound polypropylene chain actually increases with increasing strain over the strain interval between 0 and 8% strain. Work by Wool and Boyd [32] compared stress infrared results on ultra-oriented polypropylene with single chain deformation calculations. A non-linear stress-strain curve was determined, in which the initial chain modulus (as the strain tends to zero), calculated to be 30 GPa, was significantly less than the average chain modulus (determined between 0 and 8% strain) of 40 GPa. The result was a stress-strain curve which swept upwards (See Figure 2.2). Both of these contributions can lead to an increase in the tangent modulus with increasing strain, and it is suggested that this accounts for the rise to the second tangent modulus maximum.

To summarize, the tangent modulus response is quite unusual. The initial deformation process is complex, and the resulting modulus values are not a simple function of strain.
After a high initial modulus, flow of the amorphous component begins and the modulus decreases. Concurrently, stress is taken up increasingly by the tie molecules. With further deformation the modulus increases, due to the increasing number of tie molecules being extended, and to the increase in modulus with strain inherent in the helically-wound structure of the polypropylene chain. The tangent modulus and the stress increase until a critical tensile stress is reached (i.e. the tensile stress required to generate a triaxial tensile stress state in which to form a critical transitory dilation volume sufficient for dislocation nucleation), at which point crystalline yielding begins, and the tangent modulus drops off precipitously. (Once crystalline flow has begun, the tie molecules are no longer fixed at their points of entry into the crystalline lamellae. This results in relieving the extended state of the tie molecules, and consequently the precipitous drop in modulus.)

Yielding occurs in the glassy state at about 9% strain, and the deformation to that point is largely elastic in nature. The pressure dependence of the tensile modulus at finite strains is a direct consequence of the critical tensile stress required for formation of a transitory dilation volume for dislocation nucleation at crystalline yield coupled with the deformation response of the tie modulus which are in the final stage of elastomeric extension. Put another way, the tie molecules, which are in the latter stages of extension, will increase their carrying stress as an asymptotically increasing function of strain. Once the critical stress is realized crystalline flow begins. This is another important point. Since the force carried by the tie molecules increases asymptotically at their limiting strain, it would be easy to infer a critical strain criteria instead. However, such a critical strain model cannot account for the linearity noted between the yield stress and pressure. (This has important repercussions for yield models which have a modulus/yield stress factor (or elastic strain) in their equations.)

It is interesting to note that two yielding events occur in this glassy, but ductile, semi-crystalline polymer: an almost immediate yielding of the amorphous phase; and yielding of the crystalline lamellae at about 9% strain. Formation of a transitory dilation volume will occur first in the amorphous component, to initiate amorphous flow and second, at the amorphous-crystalline interface to initiate crystalline flow.
The Plastic Component of Deformation Before Crystalline Yield

Thus far we have concentrated on the elastic component of deformation prior to crystalline yield. However, there is also a flow component as noted from the strain rate sensitivity of the second maximum of the tangent modulus. Considering the mechanisms involved in this flow gives an insight into this strain rate dependency of the second maximum of the tangent modulus.

In the final stages of elastomeric extension, just prior to failure, the stress increases asymptotically to a limiting strain. Consequently, the tangent modulus will also increase with strain during this final stage of extension. The same elastomeric response is expected in the amorphous interlayer prior to the onset of crystalline flow. The critical strain in this case is not defined by specimen failure but by the formation of a transitory dilation volume sufficient to allow dislocation nucleation to take place. If the formation of a critical transitory dilation volume is dependent upon flow of the amorphous component (dislocation nucleation cannot occur until that point) then factors that inhibit this flow, or do not allow sufficient time for flow in the case of the strain rate, will delay formation of this transitory dilation volume until slightly greater strains. As a result, there will be a substantial and asymptotic increase in the stress and consequently an increase in the tangent modulus. The effect of this is plainly seen across the pressure-induced glass transition. Flow of the amorphous component in the glassy state is now severely restricted, and the tangent modulus jumps in value across this transition. Formation of a transitory dilation volume will be delayed to slightly greater strains. Because of the limited extension remaining in the already stretched tie molecules which exhibit the final stage of the elastomeric extension response, the stress increases asymptotically and consequently the second maximum of the tangent modulus is also seen to increase.

Thus, formation of a transitory dilation volume is dependent not only on a critical triaxial tensile stress, but upon the flow of the amorphous component as well.
5.4.3.3 The Constrained Ductile Interlayer

It was proposed in Section 5.4.3.1 (The Yield Transition) that a transitory dilation volume formation mechanism could explain the linearity between the yield stress and the pressure. The triaxial tensile stress required for this TDV formation is directly proportional to the superposed pressure (a triaxial compressive stress). For a material in which the atmospheric yield stress is substantially less than the hydrostatic pressure, the relationship between the yield stress and pressure would be expected to be close to linear.

It was also noted that a significant piece of the puzzle was still missing, and that is how a sufficiently large triaxial tensile stress is generated. In this regard, there is a geometry which can generate large triaxial tensile stresses in a two phase material called a constrained ductile interlayer. It will be first shown how this geometry generates a triaxial state of stress and then that geometry will be associated with a specific structure within the semi-crystalline polypropylene.

A constrained ductile interlayer is shown in Figure 5.18. The compliant ductile interlayer is sandwiched between two stiffer and more rigid blocks. A tensile stress is applied normal to the plane containing the ductile interlayer. Upon tensile extension, the less stiff and ductile interlayer will be strained in the tensile direction to a much greater degree than the stiffer and more rigid blocks on either side. It will also want to contract laterally. Prior to flow of the ductile interlayer, the contractive strain in the ductile interlayer, normal to the tensile stress, is related to the tensile strain according to the Poisson relationship \( e_{\text{normal}} = -v e_{\text{tensile}} \). After flow of the ductile interlayer has begun, the amorphous interlayer will wish to contract normal to the tensile strain in keeping with a constant volume criterion \( e_{\text{normal}} = -0.5 e_{\text{tensile}} \). The rigid blocks will also contract laterally according to the Poisson relationship (it's pre-yield response is elastic) but, since it is significantly stiffer, it's tensile extension (and consequent lateral Poisson's strain) is much smaller than that of the ductile interlayer. As a result, the ductile interlayer will wish to contract laterally to a much greater extent than the adjacent rigid block. However it is prevented, or constrained, from doing so at the interface with the stiffer, more rigid block. This generates a biaxial tensile stress in the ductile interlayer at the interface, in the direction normal to the applied tensile stress. Since this biaxial tensile stress is coupled with the original applied tensile stress, a triaxial tensile stress is generated in the ductile interlayer at the interface with the rigid block.
Figure 5.18: A model of a constrained ductile interlayer. Upon application of a tensile load, a triaxial tensile stress state is developed in the ductile and less stiff interlayer at the interface with the stiffer and more rigid blocks.
Next, we identify a possible structure and geometry within the semi-crystalline polypropylene which can generate a constrained ductile interlayer condition. In this case, the "ductile" amorphous interlayer is sandwiched between the "rigid" lamellar blocks (Figure 5.19). Upon application of a tensile stress normal to the plane of the amorphous interlayer, the interlayer will want to contract laterally. This lateral contraction will have both an elastic strain component (-ve$_{\text{tensile}}$) as well as a plastic strain component (-0.5 e$_{\text{tensile}}$). The elastic tensile extension of the rigid lamellae is significantly less than that of the amorphous interlayer due to its greater stiffness, and consequently the elastic lateral contraction will also be less. The amorphous interlayer, wishing to contract laterally to a greater extent than the rigid lamellae, is constrained from doing so at the interface with the lamellae due to both intermolecular bonding across the interface and the molecular constraint of the tie molecules connecting adjacent lamellae. This will generate biaxial stresses within the amorphous interlayer at the interface, which, coupled with the applied tensile stress, creates a triaxial tensile stress state.

This puts the last piece of the puzzle in place. The triaxial tensile stresses necessary for void formation can be generated within the amorphous interlayer at the interface with the rigid lamellae. The key to realizing how the extremely high triaxial tensile stresses necessary are generated is the role played by chain extension of the tie molecules. Tremendously high stresses can be transferred along the molecular chains of the tie molecules due to chain extension. This results in regions of extremely high stress gradients with dimensions measured in atomic radii. At high pressure, these regions of high stress gradients cannot equilibrate easily, and the conditions for yield are defined at this atomic scale.

The important point here is that it is the combination of chain extension and the morphological geometry which defines the triaxial tensile stress state at the amorphous-crystalline interface where formation of a transitory dilation volume for dislocation nucleation takes place. The stress state conditions necessary for nucleation of dislocations are created in the amorphous interlayer at the interface with the crystalline lamellae. Figure 5.19 also suggests a possible nucleation site located at the thinned-edge of the lamellae at the crystalline-amorphous interface. This has been proposed as the nucleation site for screw dislocations [29],[30].
Triaxial Tensile Stress State

Amorphous Interlayer

Crystalline Lamella

Tensile Stress

Figure 5.19: Model describing conditions within the semi-crystalline structure which satisfy a constrained ductile interlayer condition. Triaxial tensile stresses are generated within the amorphous interlayer at it's interface with the crystalline lamellae. These triaxial tensile stresses are necessary for creating the transitory dilation volume for nucleation of dislocations.
5.4.3.4 A Deformation Model Accounting for the Pressure Response of Polypropylene

Putting all the pieces of a very complicated puzzle together, one finally obtains a comprehensive model which explains the high pressure response of polymers. The model draws upon a detailed examination of the initial tensile deformation response of polypropylene to variations in pressure, temperature and strain rate. Critical to its success is the fact that, serendipitously, there were two transitions apparent at high pressure, one which is suggested to be associated with the crystalline component (the yield transition), the other with the amorphous component (the pressure-induced glass transition). This provided a unique opportunity to unravel a complex deformation process of an equally complex structure.

Crystalline Yield

As the pressure is increased there develops some striking and unusual features in the tensile stress-strain and tangent modulus-strain curves for polypropylene. Pivotal is the observation that there is a bend in the stress-strain curve to lesser slope prior to the peak stress. This point marks the yield point and is associated with the onset of plastic deformation of the crystalline component.

The derived tangent modulus-strain curve was found to be a more sensitive indicator of the various stages of deformation. Of particular note was the development of a second maximum at finite strains (6-7%) followed by a rapid drop in value corresponding to the bend to lesser slope of the stress-strain curve. The yield point was defined at the midpoint of the rapid drop in the tangent modulus following the second maximum.

It was found that the yield stress was also a linear function of pressure. It was also noted that formation of a transitory dilation volume within a material requires a triaxial tensile stress state. Thus the linearity between the stress and pressure, given by the empirically determined modified-Coulomb yield criteria, can be linked to a transitory dilation volume (TDV) formation process. It is proposed that the triaxial tensile stress state required to from this TDV is directly proportional to the triaxial compressive stress state due to the hydrostatic pressure. Combining this with the association of the onset of crystalline flow with the yield stress leads to the interpretation that the TDV volume formed at the yield
point is the volume required to nucleate dislocations.

The yield stress is noted to jump in value across the glass transition, indicating that the yielding process involves the amorphous component. This seems to contradict the interpretation that the yield point is associated with the onset of crystalline deformation. An answer which satisfies both conditions is a situation in which the nucleation site is located at the crystalline-amorphous interface.

It is proposed that prior to the onset of crystalline flow, most of the strain is elastic in nature, and occurs within the weaker and less stiff amorphous interlayer. This interlayer is bounded on both sides by the stronger and stiffer lamellae. This structure defines a constrained ductile interlayer. If a tensile stress is applied normal to the interlayer, the amorphous interlayer will be extended in the tensile direction and will wish to contract laterally to a greater extent than the adjacent lamellae. The constraint imposed at the interface with the adjacent lamellae will result in a biaxial tensile stress in the plane of the interlayer at that interface which, coupled with the applied tensile stress, will generate a triaxial tensile state of stress.

The triaxial tensile stress state required to create a transitory dilation volume sufficient in size to nucleate dislocations is directly proportional to the triaxial compressive stress state due to the hydrostatic pressure. For conditions where the hydrostatic pressure is significantly greater than the atmospheric yield stress, the tensile yield stress will be linearly dependent on the pressure. This links the linearity observed between the yield stress (as defined here) and the pressure, described by the modified-Coulomb yield criterion, with a specific mechanism. Upon reaching a critical tensile stress (defined by the modified-Coulomb yield criteria) a TDV is formed within the amorphous interlayer at the crystalline interface of sufficient size to nucleate a dislocation.

One of the implications of this proposed mechanism is that the morphological structure (the thicknesses of the amorphous interlayer and the lamellae) will have a significant effect upon the resulting triaxial tensile stress state, since this will change the constraint conditions at the interface. In other words, the modified-Coulomb yield criterion may vary significantly due to the geometry at the yielding interface (e.g. the difference in the normalized pressure coefficients of LDPE and MDPE discussed in Section 5.2).

In tension, at high pressure, yield has two stress components: a critical triaxial tensile
stress for formation of a transitory dilation volume for nucleation of dislocations; and a critical shear stress to create dislocations. The critical triaxial tensile stress requires a sufficiently high elastic tensile stress and a structural geometry (such as a ductile interlayer). The high elastic tensile stress is generated through chain extension of the tie molecules.

**Tangent Modulus**

In tension, as pressure increases above atmospheric, there appeared a second maximum in the tangent modulus strain curves just prior to the yield point. This second maximum increased with pressure, jumping in value across the pressure-induced glass transition. The deformation mechanism proposed to account for the second maximum was chain extension of the tie molecules in the amorphous interlayer. Although deformation to the second maximum was predominantly elastic, some amorphous flow is possible, as seen from the strain rate sensitivity of the second maximum.

A model was proposed in which the tie molecules are seen as effectively fixed at their points of entry into the adjacent lamellae, prior to the onset of crystalline flow, and that they respond in a similar fashion to an "elastomeric" polymer in the final state of extension, where the stress increases asymptotically to a limiting strain. The limiting strain in this case was not specimen fracture but formation of a transitory dilation volume large enough to allow dislocation nucleation. This response would account for the experimentally observed increase in the tangent modulus with strain to the second maximum.

The pressure dependence of the tensile modulus at finite strains is a direct consequence of the critical tensile stress required for formation of a TDV for dislocation nucleation at crystalline yield coupled with the deformation response of the tie modulus which are in the final stage of elastomeric extension. The relationship between the tensile modulus and pressure, therefore, is not necessarily linear.

Both the jump across the glass transition pressure and the strain rate sensitivity of the second maximum can be explained by flow of the amorphous component. Flow of the amorphous component can occur even in the glassy state, as evident in the strain rate sensitivity of the second maximum of the tangent modulus. Factors which inhibit or
restrict amorphous flow delay the creation of the TDV of sufficient size necessary for nucleation of dislocations, resulting in a slight increase in the applied strain. Since the amorphous interlayer responds as if in the final stage of elastomeric extension, the slight increase in strain results in a significant increase in stress, with a consequent increase in the second maximum of the tangent modulus. This would account for the jump noted at the glass transition pressure as the amorphous component undergoes the pressure-induced rubber-to-glass transition. Flow of the amorphous component is significantly hindered in the glassy state and consequently formation of the TDV is delayed slightly. In other words, the TDV formation process is affected by two factors: the main one is the creation of a triaxial tensile stress state at the crystalline-amorphous interface; and the second is due to flow of the amorphous component during the TDV formation process. In the case of the strain rate sensitivity of the second maximum, at the increased strain rates there is insufficient time for amorphous flow to form TDV's for dislocation nucleation. As a result, the yield strain increases slightly, and the second maximum will also increase due to the limited chain extension remaining of the tie molecules, resulting in the observed jump in the yield stress value.

Extensions and Implications of the High Pressure Deformation Model

To extend the analysis to shear and compressive deformation is not straightforward. In tension, at high pressure, yield has two stress components: a critical triaxial tensile stress for void formation; and a critical shear stress to create dislocations in the newly created critical void volume. The critical triaxial tensile stress requires a sufficiently high elastic tensile stress and a structural geometry (such as a ductile interlayer). The high elastic tensile stress is generated through chain extension.

In compressive or shear deformation, in which the amorphous phase is in the high pressure glassy state (where amorphous flow is difficult), deformation is predominantly elastic. As a result chain extension will occur almost immediately upon straining. Chain extension will transfer a tensile stress along the molecular chain. The inhomogeneity of the morphological structure and the anisotropic properties of the molecular chain will create local regions where a triaxial stress state will be generated. In other words, one of the yield stress criteria, that of a critical triaxial tensile stress state, will be met in both shear and compressive deformations. As a result, there will be a drive to nucleate a TDV. In compression, the elastic compressive strains are limited before yield occurs.
Lamellae oriented normal to the applied stress will buckle and splay apart, generating triaxial tensile stresses between those buckled or splayed regions. In directions normal to the applied compressive stress, chain extension occurs almost immediately. In this case, the morphological structure coupled with the chain extension will create localized conditions of triaxial tensile stress.

The ease of creating local regions of triaxial tensile stress would be thought to be greatest in tension, and least in compression, with torsion in between. This is the actual trend seen in the calculated octahedral shear stresses at atmospheric pressure [33].

As mentioned, deformation requires both a critical triaxial tensile stress state to create the transitory dilation volume for nucleation, and a critical shear stress to effect plastic flow of the crystalline component. At high pressure, the triaxial tensile component is large, having to overcome the externally applied hydrostatic pressure. At atmospheric pressure, the relative influence of the shear stress will be larger.

There are some fundamental ramifications of this stress criteria. The first criterion, that of a critical triaxial stress, predominates under conditions of high pressure. This critical triaxial stress requires that a sufficiently high tensile stress be generated, which is mechanistically accomplished by chain extension. Since chain extension is inherently tensile in nature, the best measures of this response are the tensile stress and the tensile modulus. The second criterion, that of a critical shear stress, is the major criterion at atmospheric pressure. In this case, the shear properties are a necessary measure to determine the yield criterion.

In other words, the dual nature of polymeric chains, with strong main chain bonds and relatively weak interchain bonds, has to be accounted for in any model of deformation. The main chain bonds are capable of high tensile loading and can transfer these stresses along the chain over distances many times greater than an atomic radii. This will create highly localized non-equilibrium conditions within the polymer. In contrast with this, the interchain bonding is highly localized, with its sphere of influence not much greater than an atomic radii. In those directions where bonding is governed mainly by these interchain bonds, the shear modulus is a valid macroscopic measure. However, to consider the shear interactions alone in any polymeric deformation model is incorrect.

The pressure dependency of the shear modulus is often reported in the literature. This
begs the question of what is being measured since chain extension occurs almost immediately upon straining, and this is fundamentally a tensile response. At a fundamental level, should the shear modulus be a function of the pressure? The answer is generally no, except in the case where the magnitude of the pressure approaches that of the modulus. In this case there is an expression by Birch [34] relating the modulus to the pressure.

A model of amorphous yield in the glassy state has been proposed by Argon [35]. In the model the shear stress, the shear modulus and the shear strain are the measured parameters used. The model allows the shear modulus to change with temperature, and presumably pressure, but also includes a separate pressure term. The basis for this was the experimentally determined response of the shear stress to pressure. The shear modulus of some polymers showed a strong pressure dependency, while others did not. It is suggested here that recognizing the two stress criterion for yield could clarify this apparent contradictory response of polymers considerably. Clearly, the shear properties cannot be used exclusively to model yielding, particularly under conditions of high pressure. In fact, in the case of high pressure, it can be argued that the tensile properties could be used exclusively to model yielding without significant error.
5.4.4 Conclusions

Yield

1. At high pressure, a bend to lesser slope appears in the stress-strain curve of polypropylene prior to the peak stress. This bend was defined as the yield point. The yield stress varied linearly with the pressure.

2. Given that a triaxial tensile stress state is required for formation of a transitory dilation volume, the linearity of the yield stress with pressure suggests a transitory dilation volume formation mechanism. The triaxial tensile stress state required for formation of a transitory dilation volume must overcome the triaxial compressive stress state due to the hydrostatic pressure. This associates a specific mechanism with the empirically determined modified-Coulomb yield criterion.

3. The observed yield point in polypropylene was associated with the onset of crystalline deformation. It is proposed that the yield transition is due to the formation of a transitory dilation volume of sufficient size to allow the nucleation of dislocations.

4. The yield stress jumps in value as the pressure increases through the glass transition pressure, indicating that the amorphous component is involved in yield. Given the proposed association of yield with the onset of crystalline flow suggests that the dislocation nucleation site is at the crystalline-amorphous interface.

5. The tangent modulus, prior to the yield point, is strain-rate sensitive, increasing in value with increasing strain rate. The interpretation given is that amorphous flow has started prior to yield.

6. The model proposed to define the stress state at the crystalline-amorphous interface is based on a constrained ductile interlayer. Upon tensile straining in a direction normal to the interface, the compliant (low modulus) and weak (already flowing) amorphous interlayer is constrained from contracting in the direction normal to the tensile strain by the adjacent stiffer (greater modulus) and rigid (not as yet flowing) crystalline lamellae. This generates a biaxial tensile stress within the amorphous interlayer which, when coupled with the applied tensile stress, results in a triaxial tensile stress state.
7. Crystalline flow begins when the triaxial tensile stresses within the amorphous interlayer required to form a transitory dilation volume sufficient in size to nucleate dislocations, overcomes the triaxial compressive stress state due to the hydrostatic pressure. This accounts for the linearity observed between the yield stress and pressure in polymers.
Elastic Deformation before Yield

1. As pressure increases above atmospheric, there appeared a second maximum in the tangent modulus strain curves just prior to the yield point. This second maximum increased in an approximately linear fashion with pressure, jumping in value across the pressure-induced glass transition. The deformation mechanism proposed to account for this elastic response was chain extension of the tie molecules in the amorphous interlayer.

2. A model was proposed in which the tie molecules are seen as effectively fixed at their points of entry into the adjacent lamellae, and that prior to the onset of crystalline flow, respond in a similar fashion to an elastomeric polymer in the final state of extension, where the stress increases asymptotically to a limiting strain. The limiting strain in this case was not specimen fracture but formation of a transitory dilation volume large enough to allow dislocation nucleation. This response would account for the experimentally observed increase in the tangent modulus with strain to the second maximum.

3. The pressure dependence of the tensile modulus at finite strains is a direct consequence of the critical tensile stress required for formation of a transitory dilation volume for dislocation nucleation at crystalline yield coupled with the deformation response of the tie molecules which are in the final stage of elastomeric extension.

Plastic Deformation before Yield

1. Although deformation to the second maximum was predominantly elastic, some amorphous flow is possible, as seen from the strain rate sensitivity of the second maximum.

2. The elastomeric model can be extended to qualitatively accounts for both the jump across the glass transition pressure and the strain rate sensitivity of the second maximum. Flow can occur even in the glassy state, as evident in the strain rate sensitivity of the second maximum. Factors which inhibit or restrict amorphous flow delay the creation of the transitory dilation volume required for crystalline flow, resulting in a slight increase in the applied strain. Since the amorphous interlayer responds as if
in the final stage of elastomeric extension, the stress increases asymptotically for a further slight increase in strain, with a consequent increase in the second maximum of the tangent modulus. This would account for the jump noted in the value of the second maximum as the amorphous component undergoes the pressure induced rubber-to-glass transition. Flow of the amorphous component is significantly hindered in the glassy state and consequently TDV formation is delayed slightly. In other words, the TDV formation process is affected by two factors: the main factor is the creation of a triaxial tensile stress state at the crystalline-amorphous interface (which must overcome the pressure); and the second is due to flow of the amorphous component during the TDV formation process. In the case of the strain rate sensitivity of the second maximum, at the increased strain rates there is insufficient time for amorphous flow to form TDV’s for dislocation nucleation. As a result, the yield strain increases slightly, and the second maximum of the tangent modulus will also increase due to the limited chain extension remaining in the tie molecules.


34. F. Birch, *J. Appl. Phys.*, **9**, (1938) 4

6. Conclusions

Glass Transition Pressure

1. There is a pressure transition, noted from the peak stress and the second maximum of the tangent modulus, which is due to the pressure-induced rubber-to-glass transformation.

2. The glass transition pressure is increased as the temperature increases. This ratio was determined to be approximately \( 28^\circ C / 100 \text{ MPa} \).

Effect of Temperature on the Modified-Coulomb Yield Criterion

3. The pressure coefficient, \( \phi \), for polypropylene in the rubbery state is not constant, but decreases with increasing temperature.

4. For polypropylene the factors \( \sigma_{\text{atm}} \) and \( \phi \), from the modified Coulomb yield equation, are similarly affected by temperature, and therefore are not independent variables. Both decrease with increasing temperature, and their ratio, \( \phi/\sigma_{\text{atm}} \), is approximately constant in the temperature range examined.

5. The similar temperature response of the normalized pressure coefficient, \( \phi/\sigma_{\text{atm}} \), suggests that molecular factors, such as decreased density and interchain bond strength have an affect on both \( \sigma_{\text{atm}} \) and \( \phi \). Based on the polymers examined, \( \phi/\sigma_{\text{atm}} \) increases with decreasing density (due to the relative amount of amorphous phase, or the packing efficiency of the molecular chain). In addition, the ratio \( \phi/\sigma_{\text{atm}} \) is inversely proportional to the interchain bond strength. This suggests that a greater interchain bond strength increases the resistance to formation of a transient dilation necessary for the onset of plastic deformation.
Shear Activation Volume

**Glassy State**

1. The shear activation volume for polypropylene when the amorphous component is in the glassy state is approximately constant at various pressures (1654 Å$^3$ and 1623 Å$^3$ at 200 and 300 MPa respectively (temperature = 25°C)), as well as at various temperatures (1623 Å$^3$ and 1731 Å$^3$ at 25°C and 50°C respectively (pressure = 300 MPa)).

2. In the glassy state, of the five mechanisms proposed, only flow of the amorphous component is seen as a possible mechanism accounting for the stress differences due to changes in strain rate for polypropylene in the glassy state. Amorphous flow is seen acting in two critical ways. First, amorphous flow acts to redistribute high local stress concentrations due to non-homogeneous extension of the tie molecules. And second, amorphous flow is the rate limiting step in the creation of the critical transient dilational volume for dislocation nucleation. Thus, the approximately constant value for the shear activation volume in the glassy state is attributed to the volume necessary for flow of the amorphous component.

**Rubbery State**

3. In the rubbery state, the shear activation volume for polypropylene decreases as the pressure increases. This response was also noted from the work of Davis and Pampillo for high molecular weight polyethylene.

4. In the rubbery state, amorphous flow is seen as the dominant influence on the shear activation volume value. However, as well as multiple mechanisms for amorphous flow being activated, the possibility exists that other mechanisms are also involved.
Yield

1. At high pressure, a bend to lesser slope appears in the stress-strain curve of polypropylene prior to the peak stress. This bend was defined as the yield point. The yield stress varied linearly with the pressure.

2. Given that a triaxial tensile stress state is required for formation of a transitory dilation volume, the linearity of the yield stress with pressure suggests a transitory dilation volume formation mechanism. The triaxial tensile stress state required for formation of a transitory dilation volume must overcome the triaxial compressive stress state due to the hydrostatic pressure. This associates a specific mechanism with the empirically determined modified-Coulomb yield criterion.

3. The observed yield point in polypropylene was associated with the onset of crystalline deformation. It is proposed that the yield transition is due to the formation of a transitory dilation volume of sufficient size to allow the nucleation of dislocations.

4. The yield stress jumps in value as the pressure increases through the glass transition pressure, indicating that the amorphous component is involved in yield. Given the proposed association of yield with the onset of crystalline flow suggests that the dislocation nucleation site is at the crystalline-amorphous interface.

5. The tangent modulus, prior to the yield point, is strain-rate sensitive, increasing in value with increasing strain rate. The interpretation given is that amorphous flow has started prior to yield.

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2. A model was proposed in which the tie molecules are seen as effectively fixed at their points of entry into the adjacent lamellae, and that prior to the onset of crystalline flow, respond in a similar fashion to an elastomeric polymer in the final state of extension, where the stress increases asymptotically to a limiting strain. The limiting strain in this case was not specimen fracture but formation of a transitory dilation volume large enough to allow dislocation nucleation. This response would account for the experimentally observed increase in the tangent modulus with strain to the second maximum.

3. The pressure dependence of the tensile modulus at finite strains is a direct consequence of the critical tensile stress required for formation of a transitory dilation volume for dislocation nucleation at crystalline yield coupled with the deformation response of the tie molecules which are in the final stage of elastomeric extension.

Plastic Deformation before Yield

1. Although deformation to the second maximum was predominantly elastic, some amorphous flow is possible, as seen from the strain rate sensitivity of the second maximum.

2. The elastomeric model can be extended to qualitatively accounts for both the jump across the glass transition pressure and the strain rate sensitivity of the second maximum. Flow can occur even in the glassy state, as evident in the strain rate sensitivity of the second maximum. Factors which inhibit or restrict amorphous flow delay the creation of the transitory dilation volume required for crystalline flow, resulting in a slight increase in the applied strain. Since the amorphous interlayer responds as if
in the final stage of elastomeric extension, the stress increases asymptotically for a further slight increase in strain, with a consequent increase in the second maximum of the tangent modulus. This would account for the jump noted in the value of the second maximum as the amorphous component undergoes the pressure induced rubber-to-glass transition. Flow of the amorphous component is significantly hindered in the glassy state and consequently TDV formation is delayed slightly. In other words, the TDV formation process is affected by two factors: the main factor is the creation of a triaxial tensile stress state at the crystalline-amorphous interface (which must overcome the pressure); and the second is due to flow of the amorphous component during the TDV formation process. In the case of the strain rate sensitivity of the second maximum, at the increased strain rates there is insufficient time for amorphous flow to form TDV's for dislocation nucleation. As a result, the yield strain increases slightly, and the second maximum of the tangent modulus will also increase due to the limited chain extension remaining in the tie molecules.
Recommendations

A number of points with respect to the proposed high pressure deformation model remain speculative at this point.

1. The distinct bend in the stress-strain curve prior to the peak stress at high pressure has been associated with the onset of crystalline plastic deformation.

2. The appearance of a second maximum in the tangent modulus-strain curve has been associated with the elastic chain extension of the tie molecules.

3. The criteria for the onset of crystalline plastic deformation has been suggested to be the formation of a critical transitory dilation volume (TDV) of sufficient size to nucleate dislocations. This point is critical in connecting the empirically-based modified Coulomb yield criterion with a specific mechanism (i.e. the triaxial tensile stress necessary for formation of a critical TDV sufficient to nucleate dislocations). The geometry and morphology which is capable of generating a triaxial tensile stress characteristic of a constrained ductile interlayer is the lamellar/amorphous sandwich positioned such that the lamellar normal is in the same direction as the tensile stress.

The first point can be verified in two ways. The first is to deform the PP to various strains, remove the load and determine the net plastic deformation. There should be no plastic deformation to the point of the bend in the stress-strain curve. This will determine the onset of plastic deformation. The second test is to determine changes in crystalline orientation using WAXD to establish the onset of plastic deformation of the crystalline component. Both of these tests should verify the onset of crystalline deformation with the bend in the stress-strain curve (and of course the precipitous decline in the tangent modulus-strain curve).

The second point is more difficult experimentally. The best method is an in-situ SAXS during the high pressure tensile test. The lamellar spacing along equatorial regions should increase dramatically to a maximum at the second maximum in the tangent modulus-strain curve.

The third point can be verified in two ways. At atmospheric pressure, deformation within the spherulite occurs first in the central core of the spherulite and spreads out along the equatorial regions to the spherulitic boundary (the tensile direction is through the
spherulitic N/S poles). It so happens that the lamellae are suitably oriented in these equatorial regions to satisfy a constrained ductile interlayer geometry. Similar analysis of the deformation within the spherulite at high pressure should be carried out to verify that the equatorial region does deform first.

The second method deals with creating a simpler structure where relationships are more straightforward. A structure in which the growth direction of the lamellae was all in one direction would be ideal. This structure could be created by solidification of the PP on a long copper bar which is heated underneath the one end and cooled underneath the other. By moving the copper bar along these two heating/cooling courses, a unidirectional solidification front could be created such that a structure with only one lamellar direction exists. Testing at various orientations to that growth direction (at various pressures) should allow analysis of the stress states at the amorphous interlayer and how yielding is affected (i.e. the triaxial tensile stress state should be quantifiable, and thus its relationship to yielding established.)

The shear activation volume was noted to become constant in the glassy state. This constant value was associated with flow of the amorphous component. This could be verified with the oriented structure described above, as well as with quasi-single crystall structures. In the latter case, it has been shown in work on nylon 6 [1], in which the amorphous component becomes indistinguishably distributed into a textured material with long range structural coherence, the rate dependence measured came from the simple shear rate along the principal crystallographic planes, and was interpreted as a problem of thermally assisted dislocation glide. How this rate limiting step changes with increasing pressure, and determination of the associated activation volume, are two important areas for study.

APPENDICES
APPENDIX A

Stress Equations for Internally Pressurized Cylindrical Vessels

Pressure vessels, by nature of their function, operate at the limits of the mechanical properties of their materials of construction. It is therefore important to have an understanding of how these stresses are distributed and how vessel geometry (i.e. the ratio of the outer to inner diameter of the cylindrical vessel) affects this stress distribution in order to optimize design. First to be examined is the stress distribution of the pressure vessel operating within the elastic limit of the material. Equations will be derived which can then be used in the design of the pressure vessel. The second section on the burst limit examines what occurs to the vessel upon reaching the elastic limit and begins to deform. The approach used in this case is to examine the elastic-plastic response of a cylindrical pressure vessel constructed of a simple material (elastic up to the yield stress, then perfectly plastic). It is a straightforward model which quickly gives a feel for the dynamics between pressure, vessel geometry and material response.

Elastic Limit

An equation relating the stress components to the internal pressure and radius of a cylindrical vessel with varying wall ratios will be derived. From this will follow the derivation of the pressure-yield stress-vessel geometry relationship. This relationship will allow one to design a pressure vessel to operate entirely within the elastic regime of the material.

The derivation is divided into the following steps.

1. Stress equations for a cylinder.
   These equations will not be used in the derivation directly, but will be used to check the derived relationship.

2. Strain equations for a cylinder.
   The start of the derivation involves a given general relationship between the radial displacement and the radius.

3. Hooke’s law.
   The strains will be inserted into the Hooke’s law relationship to derive equations for the stress components.

4. Boundary conditions.
   The pressures at the inner and outer radii of the cylinder will be inserted into the stress equations to eliminate two constants from the displacement equation.

   Using the distortion energy theory of yielding the relationship between pressure and yield strength for a cylindrical vessel of varying wall ratios will be derived.

It is assumed that the longitudinal stress distribution is uniform.
First, consider the element from the wall of a cylinder shown in Figure A.1. Summing the forces in the direction of the bisector of the angle dφ, one obtains

\[ \frac{\sigma_r}{2} \frac{d\phi}{dr} + \frac{\sigma_r}{2} \frac{d\phi}{dr} = \sigma_r r d\phi - (\sigma_r + \frac{\delta \sigma_r}{\delta r} (r + dr) d\phi) = 0 \]

where \( \sigma_r \) is the tangential stress and \( \sigma_r \) is the radial stress. Simplifying, and neglecting higher order terms we obtain

\[ \sigma_r - \sigma_r - r \frac{\delta \sigma_r}{\delta r} = 0 \] (A.1)

This stress equation follows from the force equilibrium equation and must be met by the derived equations to follow.

Second, the radial displacement of a cylindrical vessel stressed elastically is given by

\[ u = Ar + \frac{B}{r} \] (A.2)

where \( u \) is the radial displacement, \( r \) is the radius and \( A \) and \( B \) are constants.

To derive the radial and tangential strains, consider the element shown in Figure A.2. The longitudinal displacement is omitted for clarity. The radial displacement of the cylindrical surface of radius \( r \) is \( u \). The radial displacement of the cylindrical surface of radius \( (r + dr) \) is \( u + (\delta u/\delta r)dr \). Therefore the total radial elongation of length \( dr \) is \( (\delta u/\delta r)dr \) and the unit strain is

\[ \epsilon_r = \frac{\delta u}{\delta r} \]

In the tangential direction, the strain is given as

\[ \epsilon_r = \frac{(r + u) d\phi - r d\phi}{r d\phi} = \frac{u}{r} \]

Third, we insert these strain values into the Hooke's law relation.

\[ E \epsilon_r = E \left\{ A - \frac{B}{r^2} \right\} = \sigma_r - \nu (\sigma_r + \sigma_z) \] (A.3)

\[ E \epsilon_t = E \left\{ A + \frac{B}{r^2} \right\} = \sigma_t - \nu (\sigma_z + \sigma_r) \] (A.4)

\[ E \epsilon_z = \sigma_z - \nu (\sigma_z + \sigma_r) \] (A.5)

where \( \nu \) is Poisson's ratio.
Figure A.1: Stress element of a cylinder.

Figure A.2: Strain element of a cylinder.
Rearranging to obtain equations in terms of the stress components, we obtain

\[
\sigma_r = \frac{(1 + v)(1 - 2v)}{E} = A - (1 - 2v) \frac{B}{r^2} + v \epsilon_z \quad (A.6)
\]

\[
\sigma_T = \frac{(1 + v)(1 - 2v)}{E} = A + (1 - 2v) \frac{B}{r^2} + v \epsilon_z \quad (A.7)
\]

\[
\sigma_z = \frac{(1 + v)(1 - 2v)}{E} = 2vA + (1 - v) \epsilon_z \quad (A.8)
\]

Fourth, to eliminate the constants A and B, we introduce boundary conditions. At inner radius \(a\), \(\sigma_r = P\). At outer radius \(b\), \(\sigma_r = 0\). Solving for A and B, we obtain

\[
A = -v \epsilon_z + \frac{P(1 + v)(1 - 2v)}{E(\omega^2 - 1)}
\]

\[
B = \frac{P b^2 (1 - v)}{E(\omega^2 - 1)}
\]

where \(\omega = b/a\).

Inserting into Equations (A.6), (A.7), and (A.8), we obtain

\[
\sigma_r = \frac{P}{\omega^2 - 1} \left( 1 - \frac{b^2}{r^2} \right) \quad (A.9)
\]

\[
\sigma_T = \frac{P}{\omega^2 - 1} \left( 1 + \frac{b^2}{r^2} \right) \quad (A.10)
\]

\[
\sigma_z = E \epsilon_z + \frac{P (2v)}{\omega^2 - 1}
\]

It can be determined that the stress equations for \(\sigma_r\) and \(\sigma_T\), when inserted into Equation (A.1) do meet the force equilibrium criteria.
Before going on to insert the stress components into the distortion energy-yield equation, the longitudinal strain term, $\varepsilon_z$, can be removed from the longitudinal stress component expression. Assuming that the cylindrical vessel is closed at both ends, and remembering that the longitudinal stress is assumed to be constant across the cross-section of the vessel under elastic stress conditions, we obtain

$$\sigma_z = \frac{p}{\omega^2 - 1}$$

from which it can be easily determined that $\sigma_z = (\sigma_r + \sigma_t)/2$.

The radial and tangential stresses are plotted from the inner to outer wall radii in Figure A.3. It can be seen that the largest stresses occur at the inner diameter of the vessel, with the tangential stress being highly tensile. It is therefore at the inner diameter that yielding will first occur. Inserting the values of $\sigma_r$, $\sigma_t$, and $\sigma_z$ into the Distortion Energy Theory of Yielding, given as follows

$$2 Y_o^2 = (\sigma_r - \sigma_t)^2 + (\sigma_t - \sigma_z)^2 + (\sigma_z - \sigma_r)^2$$  \hspace{1cm} (A.11)

(where $Y_o$ is the isotropic yield strength), the inner diameter will yield when the pressure reaches a value

$$p = \frac{Y_o (\omega^2 - 1)}{\sqrt{3} \omega^2}$$  \hspace{1cm} (A.12)

This equation gives the pressure at which the elastic limit of the cylindrical vessel is reached. Greater pressures are sustainable, however the vessel will change dimension as yielding starts from the bore and works outward, causing sealing problems. The contribution of the wall ratio, given by $(\omega^2 - 1) / \omega^2$, approaches unity as the wall ratio becomes infinitely large (The elastic limit curve in Figure A.4). Thus, a vessel with a wall ratio of 3 has a pressure limit 90% $(8/9)$ of that of a vessel with an infinitely large wall ratio. In other words, wall ratios greater than 3 add very little to extending the elastic limit of cylindrical pressure vessels.
Figure A.3: Stress distribution of a cylinder of a wall ratio of 3 due to internal pressure.

Figure A.4: Yield and burst design criteria for a cylindrical vessel.
Burst Limit

The practical design limit of the pressure vessel is that one given by Equation (A.12). The safety limit, defined as the pressure at which the pressure vessel bursts, is significantly greater, and is derived in this section.

The initiation of yielding occurs at the bore of the vessel when a pressure, defined by Equation (A.12) is surpassed. Upon further increase in pressure the plastic zone begins to grow radially outward. To model this easily requires simplifying assumptions to be made. In this derivation, the vessel material is assumed to be elastic-perfectly plastic, as shown in Figure A.5. In this case the pressure can be increased until the plastic zone reaches the outer wall of the vessel, at which point the vessel fails. It should be pointed out that real materials work-harden and, providing that the material has sufficient ductility, would reach greater pressures before failure.

The derivation for determining the burst limit divides the vessel into two regions, an inner region where plastic deformation has taken place (radius a to radius c) and an outer elastically strained region (radius c to radius b), shown in Figure A.6. The derivation will proceed by developing stress equations for both the plastic and elastic regions. Next, boundary conditions are used to resolve the constants present in the stress equations. This will result in an expression relating the pressure to the isotropic yield stress for a cylinder of a given outer diameter/inner diameter ratio and a given elastic-plastic interface diameter/inner diameter ratio.

Three assumptions are made.

1. Principal strain directions coincide with principal stress directions.
2. There is no volume change due to the plastic component of strain. Volume change is due only to the elastic component of strain.
3. The longitudinal strain, $\varepsilon_z$, is uniform across the cross-section of the vessel and the longitudinal stress is given by $\sigma_z = (\sigma_R + \sigma_T) / 2$ in both the elastic and plastic zones.

The stress relations in the plastic zone will be covered first. Substituting the longitudinal stress, $\sigma_z = (\sigma_R + \sigma_T) / 2$, into the yield criteria (Equation (A.11)), we obtain

$$\sigma_{PLASTIC} - \sigma_{RELASTIC} = \pm \frac{2Y_o}{\sqrt{3}}$$

From the force equilibrium equation (A.1)

$$\sigma_{PLASTIC} - \sigma_{RELASTIC} = r \frac{d \sigma_R}{dr} = \pm \frac{2Y_o}{\sqrt{3}}$$

Integrating, we obtain

$$\sigma_{RELASTIC} = \pm \frac{2Y_o}{\sqrt{3}} \ln r + C_1$$
Figure A.5: Elastic-perfectly plastic stress-strain curve.

Figure A.6: Cross-section of a cylindrical pressure vessel showing an inner plastically deformed region surrounded by an elastically deformed region.
The sign of the first term must be positive since the radial stress is highly compressive at the bore (highly negative in sign) and decreases (becomes more positive, or tensile) as the radius increases. Therefore

\[ \sigma_{r_p} = \frac{2 Y_o}{\sqrt{3}} \ln r + C_1 \]  

(A.14)

Inserting this value for \( \sigma_r \) into Equation (A.13), we obtain

\[ \sigma_{\text{PLASTIC}} = \frac{2 Y_o}{\sqrt{3}} (\ln r + 1) + C_1 \]  

(A.15)

The stress relations in the elastic part of the cylinder are assumed similar in form to the completely elastic case (Equations (A.9) and (A.10)) giving the general relationship

\[ \sigma_{R_{\text{ELASTIC}}} = C_2 - \frac{C_3}{r^2} \]  

(A.16)

\[ \sigma_{T_{\text{ELASTIC}}} = C_2 + \frac{C_3}{r^2} \]  

(A.17)

Next, the constants are evaluated from the boundary conditions. At the elastic-plastic interface, the stresses are continuous. Therefore

\[ \sigma_{R_{\text{ELASTIC}}} = \sigma_{R_{\text{PLASTIC}}} \quad \text{and} \quad \sigma_{T_{\text{ELASTIC}}} = \sigma_{T_{\text{PLASTIC}}} \quad \text{at} \quad r = c \]

\[ \sigma_{R_{\text{ELASTIC}}} = 0 \quad \text{at} \quad r = b \]

Substituting into Equations (A.14), (A.15), (A.16), and (A.17), we obtain

\[ C_2 = \frac{Y_o c^2}{\sqrt{3}}, \quad C_2 = \frac{Y_o c^2}{\sqrt{3}} \frac{1}{b^2} \quad \text{and} \quad C_1 = \frac{Y_o}{\sqrt{3}} \left( \frac{c^2}{b^2} - 1 \right) - \frac{2 Y_o}{\sqrt{3}} \ln c \]

\( C_1 \) can also be determined from Equation (A.14) by inserting the boundary conditions \( \sigma_r = -P \) at \( r = a \). This gives

\[ C_1 = -P - \frac{2 Y_o}{\sqrt{3}} \ln a \]  

(A.18)

Equating the two equations for \( C_1 \) gives an expression relating the pressure to the yield stress for a given wall ratio, \( \omega \), and (elastic-plastic interface diameter)/(inner diameter) ratio, \( n = c/a \).

\[ -P - \frac{2 Y_o}{\sqrt{3}} \ln a = \frac{Y_o}{\sqrt{3}} \left( \frac{c^2}{b^2} - 1 \right) - \frac{2 Y_o}{\sqrt{3}} \ln c \]
Simplifying,

\[ P = \frac{2 Y_o}{\sqrt{3}} \left\{ \frac{\omega^2 - n^2}{2\omega^2} + \ln n \right\} \]  \hspace{1cm} (A.19)

This equation represents the pressure required to cause the elastic-plastic interface to grow to a radius \( c \) when \( c = na \). This relationship is plotted in Figure A.7 for a cylinder with a wall ratio, \( \omega \), of 3.

One can see that most of the increase in pressure occurs during the initial growth of the elastic-plastic interface. Two limiting cases can be taken from this equation; first, the yield pressure when plastic deformation begins at the bore, and second, when the plastic deformation reaches the outer diameter of the pressure vessel (the burst pressure). When plastic deformation begins, \( n = c/a = 1 \), and the pressure is

\[ P = \frac{Y_o}{\sqrt{3}} \left( \frac{\omega^2 - 1}{\omega^2} \right) \]

which is the yield pressure developed previously for the elastic limit (Equation (A.12)). When the plastic deformation ends at the outer wall, \( n = b/a = \omega \), or

\[ P = \frac{2 Y_o}{\sqrt{3}} \ln n \]

This equation gives the burst pressure for a cylindrical vessel.

The ratio of the burst pressure to the yield pressure is

\[ \frac{P_{\text{burst}}}{P_{\text{yield}}} = \frac{\ln n}{(\omega^2 - 1) / \omega^2} \]

For a pressure vessel with a wall ratio of three, the ratio of burst to yield pressure is 2.47. In other words, the pressure at which the vessel will burst at is 2.5 times that at which it will yield, according to the elastic-perfectly plastic model. This ratio is evident from Figure A.7 by comparing the pressure at \( c/a = 1 \) with \( c/a = 3 \). It should be kept in mind that this model assumes elastic-perfectly plastic behaviour which leads to a conservative estimate for the burst pressure, since it does not account for work-hardening.
Lastly, let us examine the radial and tangential stress distributions for two cases of elastic-plastic interface position. The values of the constants \( C_1, C_2, \) and \( C_3, \) are inserted into the previously developed general equations, to obtain functions for the stress components in terms of the radius.

In the plastic zone, the radial and tangential stresses are given by

\[
\sigma_{r,\text{PLASTIC}} = -P + \frac{2 Y_o}{\sqrt{3}} \ln \frac{r}{a} \\
\sigma_{t,\text{PLASTIC}} = -P + \frac{2 Y_o}{\sqrt{3}} \left( \ln \frac{r}{a} + 1 \right)
\]

![Graph](image)

Figure A.7 Maximum pressure as a function of the position of the elastic/plastic interface. The wall ratio \((\omega)\) is 3.
In the elastic zone, the radial and tangential stresses are given by

\[
\sigma_r^{\text{ELASTIC}} = -\frac{Y_o n^2}{\sqrt{3} \omega^2} \left( \frac{b^2}{r^2} - 1 \right)
\]

\[
\sigma_t^{\text{ELASTIC}} = \frac{Y_o n^2}{\sqrt{3} \omega^2} \left( \frac{b^2}{r^2} + 1 \right)
\]

The stress distributions for a vessel with a wall ratio of 3 and a c/a ratio of 1.5 are plotted in Figure A.8. In the plastic zone, the tangential stress is initially less than that experienced at the elastic limit, and increases as a function of \(\ln r/a\), reaching a maximum at the elastic-plastic interface, at which point it decreases as \(1/r^2\). The radial stress is more compressive in nature in the plastic zone than that experienced at the elastic limit, becoming less compressive in nature as a function of \(\ln r/a\) to the elastic-plastic interface, from which point there is a further decrease in its compressive nature as a function of \(1/r^2\). The longitudinal stress was assumed to be \(\sigma_z = (\sigma_r + \sigma_t) / 2\). In the plastic zone the longitudinal stress is initially compressive in nature, becoming tensile in nature in the plastic region and having a constant value of tensile stress from the plastic-elastic interface outward.

To examine how the growth of the elastic-plastic interface affects the stress distributions, a similar vessel with a plastic-elastic interface at \(c/a = 2.0\) is plotted in Figure A.9. The tangential stress is seen to reach a greater tensile value at the elastic-plastic interface. At the inner radius \(\sigma_t\) is less tensile in nature than in the case for \(c/a = 1.5\), and the outer region is significantly greater in tensile value. The radial stress becomes more compressive in nature throughout. The longitudinal stress is more compressive in nature at the bore, and is seen to reach a greater constant tensile stress in the elastic region.

In summary, the burst pressure is significantly higher than the elastic limit for a cylindrical pressure vessel of monobloc construction. In the case of a cylindrical pressure vessel with a wall ratio of 3, the burst pressure is 2.5 times that of the pressure at the elastic limit. Further, this value is a conservative one since the model assumes that the pressure vessel material does not work-harden.

**Stress Raisers and Yielding in Cylindrical Pressure Vessels**

Any non-uniformity, due either to machining marks, microstructural defects, or part geometry, will act as a stress raiser. Finishes for the interior wall of pressure vessels are recommended to be 16 εin or better. High strength steels used usually are vacuum-arc-remelted (VAR) or electroslag remelted to reduce the incidence of inclusions. These inclusions become elongated in the transverse direction due to processing and have a detrimental effect on transverse properties. It is the transverse direction which is the greatest tensile component of stress. Lastly, holes drilled through the wall of the cylinder for hydraulic ports or feedthroughs are stress raisers, increasing the local stress by a factor of three. Therefore, where possible, these ports or feedthroughs are better located at the ends of the vessels or through the closures of the pressure vessel.
Figure A.8: Stress distribution for a cylinder with the elastic-plastic interface at $c/a = 1.5$. The wall ratio ($b/a$) is equal to 3.

Figure A.9: Stress distribution of a cylinder with the elastic-plastic interface $c/a = 2.0$. The wall ratio ($b/a$) is equal to 3.
Materials Of Construction

The maximum pressure achievable in pressure vessels, before the onset of plastic deformation, depends upon the design and materials of construction. For monobloc construction, the maximum pressure can be derived using the strain energy yielding criteria, resulting in the following relationship,

\[ P = \frac{Y_o (\omega^2 - 1)}{\sqrt{3} \omega^2} \]

where \( P \) is the maximum pressure, \( Y_o \) is the yield strength of the material, and \( \omega \) is the ratio of the outside diameter to inside diameter.

The maximum achievable pressure varies directly with the yield strength of the pressure vessel material. Besides maximizing the yield strength, the material should also possess a sufficient degree of ductility and fracture toughness.

Material selection begins by considering the family of ultra-high strength steels. Since corrosion is not a factor in this application, stainless steels will not be considered here. The term ultra-high is arbitrary, and is defined here as those steels with yield strengths greater than 1400 MPa (200 ksi). The ultra-high strength steel family is composed of four groups; low alloy, medium alloy, high alloy, and maraging steels. The low-alloy group are medium carbon steels with less than 1.0 wt % of each alloying element. The major low alloy steels are the highly hardenable 4340 and 300M, a modification of the 4340, and the low hardenability 4130 and 4140 steels. The medium alloy steels, such as H11, have 5 wt % chromium and 1-2 wt % molybdenum. The high alloy ultra-high strength steels contain high levels of nickel and cobalt, such as HP9-4-20 steel which has 9 wt % nickel, 4 wt % cobalt and 0.2 wt % carbon. The maraging steels contain low carbon, 18 wt % nickel, 8 wt % cobalt and 4 wt % molybdenum. 'Maraging' is derived from the term martensite age hardening. The major strengthening mechanism of the maraging steels is the precipitation of an intermetallic, based on the Fe₃Ni structure, in a low hardness, low carbon martensitic matrix. A typical aging treatment is carried out at 460 °C for 3 hours. Besides extremely high strengths, the maraging steels exhibit significant increases in toughness as compared with other ultra-high strength steels. As an example, for a given yield strength of 1400 MPa (200 ksi), 300M possesses a fracture toughness of 60 MPa√m compared with 120 MPa√m for the maraging steel.

Materials Properties of 4340 and 300M

Two low alloy ultra-high strength steels were considered for pressure vessel construction; 4340 alloy and 300M alloy. Their respective chemical compositions are shown in Table B1. 4340 exhibits excellent hardenability due to the additions of nickel (1.8 wt %), chromium (0.8 wt %) and molybdenum (0.25 wt %). As a result, oil quench and temper heat treatments result in high uniformity of through section properties in sections up to 5 cm thick (Figure B.1).
TABLE B1: Alloy Chemical Composition

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>V</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>4340</td>
<td>.38-</td>
<td>.65-</td>
<td>1.65-</td>
<td>.70-</td>
<td>.20-</td>
<td>.20-.35</td>
<td>.01</td>
<td>&lt;.01</td>
<td></td>
<td>MIL-S-8844</td>
</tr>
<tr>
<td>300M</td>
<td>.40-</td>
<td>.65-</td>
<td>1.65-</td>
<td>.70-</td>
<td>.35-</td>
<td>1.45-</td>
<td>&lt;.01</td>
<td>&lt;.01</td>
<td>.05</td>
<td>MIL-S-8844</td>
</tr>
</tbody>
</table>

* MIL-S-8844 is vacuum melted.

300M is basically a 4340 alloy modified with silicon addition (1.6%). The major role of the silicon addition is the shifting of the tempered martensite embrittlement (TME) temperature range from 230-400 °C in the 4340 alloy up to 370-480 °C. As a result, lower tempering temperatures of 200-300 °C can be used resulting in greater strengths. Additionally, the yield strength is increased for a given tempering temperature due to the solid solution strengthening of silicon and the grain refinement due to the vanadium addition.

The yield and ultimate tensile strengths for both alloys, seen in Figure B.2 and Figure B.3, shows that the 300M is 200 MPa greater in yield strength and 300 MPa greater in ultimate tensile strength than the 4340 for a given tempering temperature.

The heat treatment for the two alloys involves austenitizing, quenching into heated oil and tempering, as shown in Table B2. In general the austenitizing temperatures for the 300M alloy are greater than for the 4340, reflecting the high temperature strengthening contribution of the silicon and vanadium.

TABLE B2: Heat Treatments

<table>
<thead>
<tr>
<th></th>
<th>4340</th>
<th>300M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardening</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Austenitizing Temperature</td>
<td>800-875 °C</td>
<td>860-885 °C</td>
</tr>
<tr>
<td>Oil Quench Temperature</td>
<td>65 °C</td>
<td>65 °C</td>
</tr>
<tr>
<td>Tempering</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended Temp.Range</td>
<td>175-230 or 400-650 °C</td>
<td>275-330 °C</td>
</tr>
<tr>
<td>TME* Temperature</td>
<td>230-400 °C</td>
<td>370-480 °C</td>
</tr>
</tbody>
</table>

*Tempered Martensite Embrittlement

Toughness as a function of tempering temperature for 4340 and 300M are compared in Figure B.4 and Figure B.5. Charpy tests for the 4340 show a decrease in charpy impact energies experienced between 260-425 °C, illustrating the temper embrittlement experienced. For 300M alloy, the decrease in impact energy occurs at higher temperatures, between 370-600 °C.

Consequently, the tempering temperatures for the two alloys are mutually exclusive. The 300M is tempered in the range of 275-330 °C, providing yield strengths around
1650 MPa, while the 4340 is tempered from 400-650 °C, providing yield strengths in the range of 900-1350 MPa.

In a cylindrical pressure vessel, the largest component of stress is in the transverse radial direction. Because processing of the steel billet imparts a directional component (longitudinal) to the inclusions, the transverse toughness properties in practice are significantly lower than those in the longitudinal direction. Special steelmaking practices, such as vacuum-arc-remelt (VAR), and electroslag remelt reduce this effect. (See charpy results for 4340 in Figure B.4).

As well as microstructural imperfections, it should be pointed out that stress raisers often cause local regions to experience yielding. The key property here is the toughness of the material. The toughnesses of 4340, tempered at 1000°F, is compared with the toughness of 300M tempered at 575°C in Tables B3 and B4. These two tempering temperatures are used to avoid the temper-embrittling of the martensite and are commonly used tempering practices as a result. For both the Charpy-V impact energy as well as the fracture toughness, the values for the 4340 tempered at 1000°F are twice that of the 300M tempered at 600°F. The tradeoff is in the yield strength properties for the two alloys. From Figure B.2, the yield strength of the 4340 tempered at 1000°F (540°C) is 1100 MPa (160,000 psi), whereas the 300M tempered at 575°F (300°C) has a yield strength of 1670 MPa (242,000 psi).

**Material Design**

The design yield strength is given from the following equation

\[ Y_0 = \sqrt{3} P \frac{\omega^2}{\omega^2 - 1} \]

This equation is valid for monobloc construction, where the von-Mises general yield criterion is met at the inner diameter. (It should be pointed out that this is not a burst criteria). The pressure vessel was designed for pressures of 420 MPa (60,000 psi) at temperatures up to 230°C (450°F). The O.D. and I.D. were 5.0" and 1.5" respectively, giving a wall ratio, \( \omega \) (outer diameter/inner diameter), of 3.33. For the designed pressure and geometry conditions, \( Y_0 \), the isotropic yield strength is 800 MPa (115,000 psi).

Since elevated service temperatures would be applied to the pressure vessel, the effect of service temperature on the yield strength of the steel also must be examined. The effect of temperature on yield properties for 4340 is shown in Figures B.6 and B.7. Given a minimum yield strength requirement of 115,000 psi at 450 °F would correspond to a room temperature yield strength of at least 136,000 psi (950 MPa). (The effect of temperature on strength properties for the 300M is also included, and is shown in Figure B.8.)

4340 vacuum-arc remelted alloy was selected. A 5 1/2 inch diameter bar was obtained from Atlas Specialty Steels, Welland, Canada. Heat treatment was carried out by VAC-AERO, Oakville. This involved heating in vacuum to 800 °C, quenching into 55-70 °C oil, followed by tempering at 510 °C. The yield strength cited on the certificate of testing is 180-186 ksi (1750 MPa), at room temperature, corresponding in the measured hardnsses of \( R_c = 37-40 \). The yield strength at 230 °C can be taken from Figure B.7. A steel with a room temperature strength of 180,000 psi, would have a 450°F yield strength of 150,000 psi.
1050 MPa). This is above the yield criteria, and except for local stress raisers, the bulk of the material is strained elastically, and is not plastically deformed. This gives an elastic design safety factor of 1.31 for the most adverse conditions. The safety factor for burst pressure (assuming elastic-perfectly plastic material behaviour) 3.5 times the maximum design pressure.

Finally, a consideration of the yield strength at the bore of the cylinder should be made. From the section on Pressure Vessel Design Equations in Appendix A, it was seen that the yield criteria is met first at the bore, with the stress state falling off rapidly from the bore to the outer wall as $1/r^2$. The concern was that the oil cooling the inner bore would not cool quite as efficiently as the oil on the outside, since the oil is trapped. Therefore the cooling rates would be marginally less than that experienced at the outside diameter. An estimate of this effect can be made by inspection of Figure B1. This shows that the difference between the surface and the centre of a 3" diameter rod is about 4 $R_e$. (This diameter was chosen as a reasonably conservative approximation of the through thickness properties of a 1.75" thick cylindrical wall). Therefore, since the cooling at the bore surface is much greater than that at the mid-wall thickness, its hardness would be virtually the same as that at the outer diameter. Hence, the yield strength at the bore would be that given from the mechanical property data.
Figure B.1: Effect of bar diameter on as-quenched hardness at various depths in bar. Redrawn from Aerospace Structural Metals Handbook, 1989, CODE 1206, Fig. 1.063.
YIELD STRENGTH: 4340 & 300M

![Graph showing yield strength as a function of tempering temperature for 4340 and 300M alloys.]

Figure B.2: Yield Strength for both 4340 (unfilled symbols), and 300M (filled symbols) as a function of tempering temperature.

References
2. Ibid., p 427, Table 9, air melt
3. Ibid., p 427, Table 9, vacuum-arc-remelt
4. Aerospace Structural Metals Handbook, 1989, CODE 1206, Fig 3.0213, Oil Quench from 800°C.
5. Ibid., Oil Quench from 845°C.
6. Engineering Properties of Steels, p.133
8. Ibid., p 429, Table 14, Transverse, air melt.
9. Ibid., p 429, Table 14, Transverse, vacuum-arc-remelt
10. Aerospace Structural Metals Handbook, 1989, CODE 1217, Fig. 3.0211
11. Ibid., Fig. 3.0212
12. Ibid., Fig. 3.0214, vacuum-arc-remelt
13. Ibid., Fig. 3.0214, electroslag-remelt
14. Ibid., Fig. 3.0216
Ultimate Tensile Strength: 4340 & 300M

Figure B.3: Ultimate tensile strength for 4340 (unfilled symbols) and 300M (filled symbols) as a function of tempering temperature.

References
2. Ibid., p 427, Table 9, air melt
3. Ibid., p 427, Table 9, vacuum-arc-remelt
4. Aerospace Structural Metals Handbook, 1989, CODE 1206, Fig 3.0213, Oil Quench from 800°C.
5. Ibid., Oil Quench from 845°C.
6. Engineering Properties of Steels, p.133
8. Ibid., p 429, Table 14. Transverse, air melt.
9. Ibid., p 429, Table 14, Transverse, vacuum-arc-remelt
10. Aerospace Structural Metals Handbook, 1989, CODE 1217, Fig. 3.0211
11. Ibid., Fig. 3.0212
12. Ibid., Fig. 3.0214, vacuum-arc-remelt
13. Ibid., Fig. 3.0214, electroslag-remelt
14. Ibid., Fig. 3.0216
Figure B.4: Effect of tempering temperature and melting practice on impact properties at room temperature for 4340 alloy. Redrawn from ASMH, 1989, CODE 1206, Fig. 3.0233.

Figure B.5: Effect of tempering temperature on the charpy V-notch impact resistance of electroslag remelted and vacuum-arc-remelted forged plate of 300M. Redrawn from ASMH, 1989, CODE 1217, Fig. 3.0232.
### TABLE B3: Charpy V-Notch Impact Energy

<table>
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<tr>
<td>35</td>
<td>CODE 1206 3.0231</td>
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<td>38</td>
<td>3.0232</td>
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<td>30.39</td>
<td>3.0233</td>
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<td>25</td>
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<td>Air melt, vacuum degassed</td>
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<td>33</td>
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<td>Austenitized @ 1590°F</td>
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**300M, 600 °F Temper**

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<td>VAR, Forged Plate</td>
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<td>20.0</td>
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<td>19.7 L, 14.7 LT, 11.2</td>
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<td>Electroslag Remelt</td>
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### TABLE B4: Fracture Toughness

**4340, 1000 °F Temper**

<table>
<thead>
<tr>
<th>Fracture Toughness (ksi/in)</th>
<th>Reference Figure</th>
<th>Comments</th>
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<tr>
<td>140</td>
<td>CODE 1206 3.02723</td>
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<td>82</td>
<td>3.02723</td>
<td>Air-melt</td>
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**300M, 600 °F Temper**

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<th>Comments</th>
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<tr>
<td>60, 60</td>
<td>CODE 1217 3.02721</td>
<td>VAR, Forged Plate</td>
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<td>67</td>
<td>3.02722</td>
<td>VAR Plate, 1600°F Austenitizing</td>
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<td>60, 58</td>
<td>3.02723</td>
<td>VAR 1° Bar, 1600°F Austenitizing</td>
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<tr>
<td>45</td>
<td>3.02724</td>
<td>VAR</td>
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<tr>
<td>45</td>
<td>3.02726</td>
<td>VAR 5° Bar, 1600°F Austenitizing</td>
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</table>
Figure B.6: Effect of elevated temperature on tensile properties of 4340 bar and sheet with yield strengths greater than 140 ksi. Redrawn from ASMH, 1989, CODE 1206, Fig. 3.0315.
Figure B.7: Effect of elevated temperature on the tensile properties of 4340 bar with yield strengths below 140 ksi. Redrawn from ASMH, 1989, CODE 1206, Fig. 3.0316.
Figure B.8: Effect of elevated temperature on the tensile properties of a large forging of 300M, oil quenched and tempered at 575 °F. From ASMH, 1989, CODE 1217, Fig. 3.0313.
APPENDIX C

STRAIN MEASUREMENT

Basic Principles of Strain Gauging  C1
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Strain Measurement

Basic Principles of Strain Gauging

The basic principles of strain gauging will be developed first, followed by a more detailed examination of the factors that must be taken into consideration so that an accurate measure of strain be obtained.

A standard, quantifiable method of strain measurement is resistance strain gauging. The basis for this technique is the linear relationship between strain and resistance change. In this technique, a strain gauge is mounted on the test piece. Strain experienced by the test piece will change the length of the strain gauge and consequently its resistance. For certain metal alloys, this change in resistance is linearly related to the change in length, and therefore the strain, \( \varepsilon \), according to the following equations:

\[
\frac{\Delta R}{R} = p \frac{\Delta l}{l} \quad \text{or} \quad \frac{\Delta R}{R} = F \varepsilon
\]

where
- \( R \) is the initial resistance of the metal conductor
- \( \Delta R \) is the resistance change of the metal conductor upon straining
- \( F \) is the gauge factor
- \( l \) is the original length of the metal conductor
- \( \Delta l \) is the change in length of the metal conductor.

The gauge factor, \( F \), has a constant value under certain conditions. The gauge factor of a particular gauge stated by the gauge manufacturer is determined under uniaxial stress conditions, on a steel substrate, and at room temperature and pressure. Typically, the gauge factor has a value of about 2.

The causes of the resistance change in the conductor are twofold; first, the length, \( l \), and area, \( A \), of the current conductor are changing [ \( R = \rho (l/A) \) ], and secondly, the resistivity, \( \rho \), of the conductor changes as the state of stress within the conductor changes. In the elastic response region, the length of the conductor increases by \( l(1 + \varepsilon) \), and the width and thickness decrease by the factor \( (1 - \nu \varepsilon) \). This would result in a gauge factor of 1.6, which does not account for the total contribution. The stored energy within the material also contributes to the resistivity changes, however in a complex manner. In the plastic response region, volume is conserved, and the length and area contributions to the strain gage factor alone result in a gage factor of 2. The internal stored energy due to the plastic deformation does not contribute significantly to the gauge factor.

Physically, most strain gauges consist of a thin metal foil conductor mounted on a thin polymer backing. The accuracy of the strain gauge is optimized when the length of the conductor is as long as possible. This is accomplished by photo-resist etching a pattern on a metal foil. The conduction path consists of a thin line wound back and forth on the surface of the polymer substrate with the lines running parallel to one another. A polymer backing is used to mount the strain gauge to the surface of the test piece as well as to insulate the metal grid.
Measurement of the resistance changes, which are quite small, is accomplished using a Wheatstone bridge arrangement. At low strains (\( \varepsilon < 0.002 \)), the change in the voltage output from the bridge is linearly related to the resistance change of the strain gauge and hence, from Equation (1), the voltage output is also linearly related to the strain. The strain can thus be derived directly from a voltage signal.

Consider the quarter Wheatstone bridge circuit shown in Figure C.1, in which one of the four resistance arms consists of the strain gauge. The bridge is initially balanced (\( e = 0 \)) and each arm has the same nominal resistance (\( R_1 = R_2 = R_3 = R_4 \)). It can be shown that the change in the output voltage, \( \Delta e \), is linearly related to the change in the strain gauge resistance, \( \Delta R_g \). Therefore under conditions of low strain (\( \varepsilon < 0.002 \)),

\[
\frac{\Delta e}{E} = \frac{\Delta R_g}{4R_g}
\]  

(2)

where \( \Delta e \) is the output voltage

- \( E \) is the excitation voltage for the bridge
- \( \Delta R_g \) is the resistance change of the strain gauge
- and \( R_g \) is the resistance of the strain gauge equal to \( R_1 \).

Combining Equations (1) and (2) together, we obtain

\[
e = \frac{4}{F} \frac{\Delta e}{E}
\]  

(3)

So, by measuring the voltage output \( \Delta e \), and knowing the excitation voltage, \( E \), and the gauge factor, \( F \), the strain experienced by the strain gauge can be determined.

Unfortunately, although the above formulations demonstrate the principles involved in a straightforward way, the actual situation is complicated by the following factors;

1. The non-linearity of the voltage signal from an "unbalanced" bridge.
2. The effect of temperature and pressure experienced by the strain gauge on signal output.
3. The effects of strains transverse to the grid direction of the strain gauge on signal output.

These will now be examined in more detail.

**Wheatstone Bridge Circuit**

The Wheatstone bridge is simply an electrical configuration which allows for the accurate measurement of an unknown resistance. There are two ways in which to do this, using a "balanced" bridge or alternatively, an "unbalanced" bridge. The configuration of the Wheatstone bridge will be looked at first, and the basic relationships developed.
Figure C.1: Wheatstone bridge circuit drawn conventionally.

Figure C.2: Wheatstone bridge circuit drawn in an alternate form, emphasizing the two parallel arms, each with two resistors.
The configuration is depicted in two ways, shown conventionally in Figure C.1 and alternatively in Figure C.2. The bridge is excited by a voltage \( E \). Across points A and B is a voltmeter with infinitely high impedance. As a result the circuit can be considered alternatively as two arms in parallel, each with two resistors, as shown on the right hand side of Figure C.2. Because of the infinitely high impedance, the voltmeter measures the difference in the voltage between point A and point B which are given respectively in the following.

\[
E_A = E \left( \frac{R_1}{R_1 + R_2} \right), \quad E_B = E \left( \frac{R_4}{R_4 + R_3} \right)
\]

Therefore the potential difference between points A and B is given as

\[
e = E_A - E_B = E \left( \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3} \right)
\]

This equation describes the general relationship between the output voltage and the resistances of the Wheatstone bridge.

The Wheatstone bridge is used to accurately determine resistances, using either a "balanced" bridge or an "unbalanced" bridge. We will first consider the "balanced" condition.

**Balanced Bridge**

A balanced bridge refers to the condition where the potential difference across the bridge is zero. Assume that the resistance of the first resistor is unknown. If one of the resistors, say \( R_2 \), is instead a potentiometer, shown in Figure C.3, and its resistance adjusted until the potential difference, \( e \), is zero, then the bridge is said to be balanced. Under these conditions, the relation between resistances is determined, using Equation (5), as

\[
\frac{R_1}{R_2} = \frac{R_4}{R_3} \quad \text{or} \quad R_1 = R_2 \frac{R_4}{R_3}
\]

This relationship can be used to accurately determine an unknown resistance, say \( R_1 \), knowing the potentiometer resistance \( R_2 \) as well as \( R_3 \) and \( R_4 \).

Next consider that the first resistor is instead a strain gauge \((R_1 = R_2)\). Since only one arm of the four has an active gage, this configuration is known as a quarter bridge. This is shown in Figure C.4. After the strain gauge has been strained, its resistance changes by \( \Delta R_2 = \Delta R_1 \), which is related to the strain as shown in Equation (1).
Figure C.3: A potentiometer is adjusted to balance the Wheatstone bridge \( e = 0 \), and a reading of its resistance is used to determine \( R_1 \).

Figure C.4: A quarter bridge circuit. After straining, the pot is readjusted to rebalance the bridge, and the new pot resistance used to determine the resistance change of \( R_i \) due to straining.
Rearranging to obtain the strain results in the following:

\[ e = \frac{1}{F} \frac{\Delta R_2}{R_2} - \frac{1}{F} \frac{\Delta R_1}{R_1} \]  

(7)

It is this relationship between resistance change and length change that is the basis for the resistance strain gauge technique. From this equation it is seen that if \( \Delta R_1 \) can be obtained, then the strain, \( e \), can be determined. The strain gauge now has a resistance of \( R_1 + \Delta R_1 \), and using this value in Equation (5) we obtain

\[ e = E \left( \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2} - \frac{R_4}{R_4 + R_3} \right) \]  

(8)

Re-balancing the bridge circuit by adjusting the potentiometer from \( R_2 \) to \( R_2' \), so that the bridge voltage equals 0, we obtain

\[ \frac{R_1 + \Delta R_1 + R_2'}{R_1 + \Delta R_1} - \frac{R_4 + R_3}{R_4} \]  

(9)

Simplifying to determine \( \Delta R_1 \), we obtain

\[ \frac{R_2'}{R_1 + \Delta R_1} = \frac{R_3}{R_4} \quad \text{or} \quad \Delta R_1 = R_2' \frac{R_4}{R_3} - R_1 \]  

(10)

Therefore the resistance change, \( \Delta R_1 \), can be determined from the known resistances \( R_1, R_3, \) and \( R_4 \), and the adjusted potentiometer setting \( R_2' \).

To summarize, the resistance of the strain gauge, \( R_1 \), in the unstrained state is determined by balancing the bridge, reading the potentiometer and using Equation (6). The gauge is then strained, and the bridge re-balanced to obtain \( \Delta R_1 \) from Equation (10). From the values of \( R_1 \) and \( \Delta R_1 \), the strain is determined from Equation (7).

**Unbalanced Bridge**

The disadvantage of the resistance technique is that the potentiometer must be adjusted to balance the bridge for each reading. If the gauge resistance is continuously and rapidly changing, then data collection is impossible. In this case, voltages can be measured instead of resistances allowing for faster data collection rates. A further advantage is that the analog voltage signal can be converted to a digital signal and logged by computer. However, the relationship between voltage and resistance is not linear, and therefore the use of voltage is not quite so simple nor straightforward. Let us take a look at the voltage-resistance relationship, using the bridge configuration shown in Figure C.5.
Figure C.5: A quarter bridge circuit with no potentiometer. Strain is determined from the change in the voltage output, \( \Delta e \).
The initial voltage output, $e_i$, is given by Equation (5) and restated here as

$$e_i = E \left( \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3} \right)$$  \hspace{1cm} (11)

After straining, the resistance of the strain gauge increases to $R_1 + \Delta R_1$, resulting in a final voltage output, $e_f$, given by Equation (8) and restated here as

$$e_f = E \left( \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2} - \frac{R_4}{R_4 + R_3} \right)$$  \hspace{1cm} (12)

The change in voltage output, $\Delta e$, is given by

$$\Delta e = e_f - e_i = E \left( \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2} - \frac{R_1}{R_1 + R_2} \right)$$  \hspace{1cm} (13)

One can see that the second resistance term of $e_f$ and $e_i$ are the same and cancel out. Simplifying, dividing by $E$, and dividing the numerator and denominator of the right side by $R_1$ we obtain

$$\frac{\Delta e}{E} = \frac{\frac{R_2}{R_1} \frac{\Delta R_1}{R_1}}{\left(1 + \frac{R_2}{R_1}\right)\left(1 + \frac{\Delta R_1 + R_2}{R_1}\right)}$$  \hspace{1cm} (14)

Now, if $R_1 = R_2$, (conditions that occur if the resistances of each arm are initially equal, and hence, the bridge is initially balanced before strain generation), we can simplify further.

$$\frac{\Delta e}{E} = \frac{\frac{\Delta R_1}{R_1}}{4 + 2 \frac{\Delta R_1}{R_1}}$$  \hspace{1cm} (15)

This equation relates the voltage output and the resistance change for a quarter (one of the four arms active) Wheatstone bridge.

Several points are to be noted.

1. Given the $\Delta R_1/R_1$ term in the denominator, the change in voltage is not a linear function of the change in resistance.

2. At very low strains, and hence very low resistance change $\Delta R_1$, the magnitude of the $2\Delta R_1/R_1$ term in the denominator is negligibly small compared to 4. The resultant non-linearity error due to ignoring the $2\Delta R_1/R_1$ term is half the value of the strain. Thus the error at 2000 $\mu e$ ($\varepsilon = .002$) would be approximately 0.1%, for the bridge with one active arm.
3. From Equation 13 the voltage contribution from bridge arms three and four cancel, that is, has no net effect, when determining the voltage difference. In other words the bridge need not be initially balanced. As long as the voltage difference between unstrained and strained conditions is obtained, the strain can be calculated.

4. From Equation (14), the voltage output signal is maximized when \( R_1 = R_2 \).

Remembering that the relationship between strain and resistance change is given by Equation (1), the strain is related to the voltage difference by the following equation:

\[
\frac{\Delta e}{E} = \frac{F \varepsilon}{4 + 2F \varepsilon} \tag{16}
\]

One can see that the non-linearity term \( 2F \varepsilon \) remains. In terms solely of strain we obtain

\[
\varepsilon = \frac{4 \frac{\Delta e}{E}}{F \frac{E}{1 - 2 \frac{\Delta e}{E}}} \tag{17}
\]

This equation gives the strain from the measured voltage output for a quarter Wheatstone bridge.
Wheatstone Bridge Voltage Measurements: Assumptions

Assumptions are made to simplify the equations for the voltage output of the Wheatstone bridge. One assumption is that \( R_1 = R_2 = R_3 = R_4 \), or that the initial resistances of each arm are identical. How identical must they be and what magnitude of error will they cause if they are not equal?

The answer is that if the bridge is initially balanced, slight variances between the resistances do not contribute significantly to the error. This will now be shown.

First, let us redefine the individual resistances as follows:

\[
\begin{align*}
R_2 &= R_1 + R_2' \\
R_3 &= R_1 + R_3' \\
R_4 &= R_1 + R_4'
\end{align*}
\] (18)

Replacing these values in Equation (12) for a quarter bridge (one active arm), gives us

\[
\frac{\Delta e}{E} = \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_1 + R_3'} - \frac{R_1 + R_4'}{R_1 + R_4' + R_1 + R_3'}
\] (19)

Dividing numerator and denominator by \( R_1 \), and creating a common denominator for the two terms on the right hand side of this equation, we obtain

\[
\frac{\Delta e}{E} = \frac{\frac{\Delta R_1}{R_1} + \frac{1}{R_1} \left[ R_3' - R_2' - R_4' - \frac{R_2'R_4'}{R_1} \right] + \frac{\Delta R_1 R_3'}{R_1 R_1}}{4 + 2 \frac{\Delta R_1}{R_1} + 2 \frac{1}{R_1} \left[ R_3' - R_2' + R_4' + \frac{R_2'R_4'}{R_1} \right] + \frac{1}{R_1 R_1} \left[ R_2'R_3' + \Delta R_1 R_3' + \Delta R_1 R_4' \right]}
\] (20)

This is a rather formidable equation, which can be simplified if we consider the bridge to first be balanced. Inserting the redefined resistances above in Equation (18) into Equation (6), we obtain

\[
\frac{R_1 + R_2'}{R_1} = \frac{R_1 + R_4'}{R_1 + R_4'} \quad \text{or} \quad R_3' = \frac{R_2' + R_4'}{R_1} \frac{R_2'R_4'}{R_1}
\] (21)

Inserting into Equation (19) gives us

\[
\frac{\Delta e}{E} = \frac{\frac{\Delta R_1}{R_1} \left[ 1 + \frac{R_3'}{R_1} \right]}{4 + 2 \frac{\Delta R_1}{R_1} + 2 \frac{1}{R_1} \left[ 2R_3' \right] + 0}
\] (22)
The zero in the denominator represents the last three terms from Equation (20), each with an extra $1/R_1$ term, which, in cases where $R_2$, $R_3$, and $R_4 >> 1$, can be approximated to zero. Further simplifying, we obtain

$$\frac{\Delta e}{E} = \frac{\Delta R_3}{R_1} \left[ 1 + \frac{R_3'}{R_1} \right] \quad \text{or} \quad \frac{\Delta e}{E} = \frac{\Delta R_4}{R_1} \frac{1}{4 + 2 \frac{\Delta R_1}{R_1} \left( 1 + \frac{R_3'}{R_1} \right)}$$

(23)

This last equation is quite similar in form to that for the quarter Wheatstone bridge shown in Equation (15). The following points can be made regarding this equation.

1. The non-linearity term is changed by the factor $1/(1 + R_3'/R_1)$. If $R_3$ is close in value to $R_1$, then $R_3' << R_1$, and the effect of slightly unequal resistances between arms of the bridge can be neglected.

2. The derivation assumed that the bridge was initially balanced prior to straining.

Therefore, the initial assumption that $R_1 = R_2 = R_3 = R_4$ is justified.
Signal Augmentation

The voltage output of the Wheatstone bridge can be augmented by a factor of up to four times that generated by a quarter bridge, using additional strain gauges on the other arms of the bridge. The degree of signal augmentation depends upon the type of strain being measured and the configuration of the strain gauges. Since the voltage output is extremely small and must be amplified begs the question of why try to increase the signal in the first place. The answer is that the signal to noise ratio is increased. Another reason, which will be covered in a later section, is to compensate for temperature and pressure effects on the strain gauge.

The effect of additional strain gauges on signal augmentation using a Wheatstone bridge configuration follows two rules:

1. If the change in resistances occurs in opposite arms, the resistance changes are summed, keeping the sense of whether the resistance change has increased or decreased.
2. If the change in resistances occurs in adjacent arms, then the difference between resistance changes is taken, again keeping the sense of whether the resistance change has increased or decreased.

For example, if there was a 1% increase in resistance in one arm and a 1% decrease in resistance in the adjacent arm, with the resistances of the other two arms remaining constant, then one would measure twice the signal output compared with the case where only one of those arms experienced a change in resistance.

The degree of signal augmentation for various strain gauge configurations and strain states is shown in Table C1. Two cases, involving uniaxial stress, will be developed; the half bridge and a full bridge.

Half Bridge

When measuring strains from a uniaxial stress field, the signal output and therefore the signal to noise ratio can be increased by a factor of two. The configuration is known as a half bridge since two of the four arms contain active strain gauges, shown in Figure C.6, Figure C.8. The strain gauges are configured on opposite arms of the bridge, for example arms one and three. Both gauges will experience the same strain. Let us develop the derivation in a general way first, then make simplifying assumptions as we proceed. In the following derivation, the output voltage is "normalized" by dividing by the excitation voltage E.

Prior to straining, the initial voltage output is given as follows:

\[
\frac{e_0}{E} = \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3}
\]  

(24)
<table>
<thead>
<tr>
<th>BRIDGE/STRAIN ARRANGEMENT (Note 1)</th>
<th>DESCRIPTION</th>
<th>OUTPUT EQUATION—$E_o/E$ in mV/V (Notes 2, 3)</th>
<th>ACTUAL STRAIN INDICATED STRAIN $= \frac{\varepsilon}{\varepsilon}$</th>
<th>COMMENTS</th>
</tr>
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<tbody>
<tr>
<td><img src="image" alt="Single active gage in uniaxial tension or compression." /></td>
<td>$E_o/E = \frac{F\varepsilon}{4 + 2F\varepsilon}\times10^{-3}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1 + \frac{F\varepsilon}{2}\times10^{-3}$</td>
<td>Nonlinear. Incremental correction can be read directly from Fig. 2.</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Two active gages in uniaxial stress field—one aligned with max. principal strain, one &quot;Poisson&quot; gage." /></td>
<td>$E_o/E = \frac{F\varepsilon(1 + \nu)\times10^{-3}}{4 + 2F\varepsilon(1 - \nu)\times10^{-3}}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1 + \frac{F\varepsilon(1 - \nu)}{2\times10^{-3}}$</td>
<td>Nonlinear. Apply incremental correction from Fig. 2, using indicated strain equal to $\varepsilon(1 - \nu)$. (Note 4)</td>
<td></td>
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<tr>
<td><img src="image" alt="Two active gages with equal &amp; opposite strains—typical of bending beam arrangement." /></td>
<td>$E_o/E = \frac{F\varepsilon}{2}\times10^{-3}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1$</td>
<td>Linear.</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Two active gages with equal strains of same sign—used on opposite sides of column with low temperature gradient (bending cancellation, for instance)." /></td>
<td>$E_o/E = \frac{F\varepsilon}{2 + F\varepsilon}\times10^{-3}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1 + \frac{F\varepsilon}{2}\times10^{-3}$</td>
<td>Nonlinear. Incremental correction can be read directly from Fig. 2.</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Four active gages in uniaxial stress field—two aligned with max. principal strain, two &quot;Poisson&quot; gages (column)." /></td>
<td>$E_o/E = \frac{F\varepsilon(1 + \nu)\times10^{-3}}{2 + F\varepsilon(1 - \nu)\times10^{-3}}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1 + \frac{F\varepsilon(1 - \nu)}{2}\times10^{-3}$</td>
<td>Nonlinear. Apply incremental correction from Fig. 2, using indicated strain equal to $\varepsilon(1 - \nu)$. (Note 5)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Four active gages in uniaxial stress field—two aligned with max. principal strain, two &quot;Poisson&quot; gages (beam)." /></td>
<td>$E_o/E = \frac{F\varepsilon(1 + \nu)\times10^{-3}}{2}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1$</td>
<td>Linear.</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Four active gages with pairs subjected to equal and opposite strains (beam in bending or shear in torsion)." /></td>
<td>$E_o/E = \frac{F\varepsilon\times10^{-3}}{2}$</td>
<td>$\frac{\varepsilon}{\varepsilon} = 1$</td>
<td>Linear.</td>
<td></td>
</tr>
</tbody>
</table>

**NOTES:**
1. $\frac{U_R}{R_{x_{\text{nom}}}} = \frac{U_R}{R_{y_{\text{nom}}}} = 1$ when two or less active arms are used.
2. Constant-voltage power supply is assumed.
3. $\varepsilon$ and $\varepsilon'$ strains are expressed in microstrains ($\mu\text{in/in} \times 10^6$).
4. With the gage factor dia of the strain indicator set to the gage factor of the gages in use, the indicator will read the quantity: $\varepsilon'(1 + \nu)$. Multiply this by $(1 - \nu)/(1 + \nu)$ to obtain $\varepsilon(1 - \nu)$. Enter Fig. 2 at $\varepsilon(1 - \nu)$ on the abscissa and read the incremental correction from the appropriate curve. Add the correction (always a positive number) algebraically to $\varepsilon(1 - \nu)$ and divide the result by $(1 - \nu)$ to obtain the actual strain, $\varepsilon$.
5. With the gage factor dia of the strain indicator set to the gage factor of the gages in use, the indicator will read the quantity: $2\varepsilon(1 + \nu)$. Multiply this by $(1 - \nu)/(1 + \nu)$ to obtain $\varepsilon(1 - \nu)$. Proceed as in Note 4 to complete the correction.

**Table C1:**

**Relationship Between Strain Gauge Position in Wheatstone Bridge and Ratio of Output Voltage to Excitation Voltage**
Figure C.6: A half bridge circuit. Voltage output is twice that of a quarter bridge.

Figure C.7: A full bridge circuit, configured for uniaxial strain. The voltage output is \(2(1 + \nu)\) times that of a quarter bridge.
After straining, the strain gauges experience a change of resistance of $\Delta R_1$ and $\Delta R_3$ respectively, and the final voltage output is

$$\frac{e_f}{E} = \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2} - \frac{R_4}{R_4 + R_3 + \Delta R_3}$$  \hspace{1cm} (25)$$

To determine the change in voltage output, we take the difference between Equations (24) and (25).

$$\frac{\Delta e}{E} = \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2} - \frac{R_4}{R_4 + R_3 + \Delta R_3} - \frac{R_1}{R_4 + R_2} + \frac{R_4}{R_4 + R_3}$$  \hspace{1cm} (26)$$

Regrouping, we obtain

$$\frac{\Delta e}{E} = \left[ \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2} - \frac{R_1}{R_1 + R_2} \right] - \left[ \frac{R_4}{R_4 + R_3 + \Delta R_3} - \frac{R_4}{R_4 + R_3} \right]$$  \hspace{1cm} (27)$$

Dividing the numerator and denominator of the first two terms by $R_1$, and the numerator and denominator of the second two terms by $R_4$, we obtain

$$\frac{\Delta e}{E} = \left[ \frac{1 + \Delta R_1/R_1}{1 + \Delta R_1/R_1} - \frac{1}{1 + \Delta R_1/R_1} \right] - \left[ \frac{1}{1 + \Delta R_3/R_3} - \frac{1}{1 + \Delta R_3/R_3} \right]$$  \hspace{1cm} (28)$$

Finding a common denominator for each set of terms, and simplifying, results in the following:

$$\frac{\Delta e}{E} = \left[ \frac{\Delta R_2}{R_1} \frac{\Delta R_1}{R_1} \right] + \left[ \frac{\Delta R_3}{R_4} \frac{\Delta R_3}{R_4} \right]$$  \hspace{1cm} (29)$$

This is the general unbalanced equation for a half bridge. This can be simplified by first assuming that the bridge is initially balanced, or that $R_1 = R_2 = R_3 = R_4$.

$$\frac{\Delta e}{E} = \frac{\Delta R_1}{R_1} \left( \frac{2 + \Delta R_1}{R_1} \right) - \frac{\Delta R_3}{R_4} \left( \frac{2 + \Delta R_3}{R_1} \right)$$  \hspace{1cm} (30)$$
Next, we assume that strain gauges one and three are the same, and that the strains each is experiencing are the same, so that their resistance changes are also the same (\( \Delta R_1 = \Delta R_3 = \Delta R_g \)). This gives us the output voltage-resistance change relationship for a half bridge under uniaxial tensile stress.

\[
\frac{\Delta e}{E} = \frac{\frac{\Delta R_g}{R_g}}{2 + \frac{\Delta R_g}{R_g}} \quad (31)
\]

Four points are noted here.

1. The output voltage of the half bridge is twice that of the quarter bridge.
2. For the case of uniaxial stress, both have the same non-linearity relationship between the voltage change and the resistance change (the \( \Delta R_g/R_g \) term in the denominator). The errors due to the non-linearity term are also the same.
3. It was assumed in Equation (31) that the bridge was initially balanced. However, accurately knowing the resistances and assuming that the strain experienced by both strain gauges are identical, one can use Equation (29). Although this equation is long, using computer data acquisition would allow the calculation to be carried out easily, so that an unbalanced initial condition can be used.
4. From Equation (29), it can be seen that the voltage is maximized when \( R_1 = R_2 \) and \( R_3 = R_4 \).

To relate the voltage output to the strain, we use Equation (1) to obtain the following:

\[
\frac{\Delta e}{E} = \frac{Fe}{2 + Fe} \quad (32)
\]

The strain as a function of output voltage for the half bridge strained uniaxially is given by the following equation.

\[
e = \frac{2 \frac{\Delta e}{E}}{1 - \frac{\Delta e}{E}} \quad (33)
\]

**Full Bridge**

A full bridge has active strain gauges on all four arms, and is shown in Figure C.7 configured for uniaxial strain. Using a full bridge configuration for uniaxial strain increases the magnitude of the signal and the signal to noise ratio by a factor of \( 2(1 + \nu) \). Two of the strain gauges are aligned parallel to the direction of applied stress, on opposite arms of the bridge (on arms one and three, for example). These gauges will experience an elongational strain of \( \epsilon \). The other two strain gauges are aligned at right angles to the direction of applied stress, again on opposite arms of the bridge (on arms two and four, for example). These gauges will experience a contracting strain of \( \nu \epsilon \), where \( \nu \) is Poisson’s ratio.

In the following derivation, the output voltage, \( e \), will be "normalized" by dividing by the excitation voltage \( E \).
Prior to straining, the initial output voltage is given as follows:

\[
\frac{e_i}{E} = \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3}
\]  

(34)

After straining, the strain gauges experience a change of resistance, and the final voltage output is given as follows:

\[
\frac{e_f}{E} = \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + \Delta R_2 + \Delta R_3} - \frac{R_4 + \Delta R_4}{R_4 + \Delta R_4 + \Delta R_3 + \Delta R_3}
\]  

(35)

To determine the change in output voltage, the difference between the above two equations is taken.

\[
\frac{\Delta e}{E} = \left[ \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + \Delta R_2 + \Delta R_3} - \frac{R_1}{R_1 + R_2} \right] - \left[ \frac{R_4 + \Delta R_4}{R_4 + \Delta R_4 + \Delta R_3 + \Delta R_3} - \frac{R_4}{R_4 + R_3} \right]
\]  

(36)

Dividing the first two terms by \(R_1\), and the second two terms by \(R_4\) we obtain

\[
\frac{\Delta e}{E} = \left[ \frac{1 + \frac{\Delta R_1}{R_1}}{1 + \frac{\Delta R_1 + \Delta R_2 + \Delta R_3}{R_1 + R_2}} - \frac{1}{1 + \frac{R_2}{R_1}} \right] - \left[ \frac{1 + \frac{\Delta R_4}{R_4}}{1 + \frac{\Delta R_4 + \Delta R_3 + \Delta R_3}{R_4 + R_3}} - \frac{1}{1 + \frac{R_3}{R_4}} \right]
\]  

(37)

Simplifying this gives

\[
\frac{\Delta e}{E} = \frac{\frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_1}}{\frac{R_1}{1 + \frac{\Delta R_1 + \Delta R_2 + \Delta R_3}{R_1 + R_2}}} - \frac{\frac{\Delta R_4}{R_4} - \frac{\Delta R_3}{R_4}}{\frac{R_4}{1 + \frac{\Delta R_4 + \Delta R_3 + \Delta R_3}{R_4 + R_3}}}
\]  

(38)

Now, if the bridge is initially balanced \((R_1 = R_2 = R_3 = R_4 = R_g)\), and if the strain gauges in the direction of the uniaxial stress experience the same strain \((\Delta R_3 = \Delta R_1 = \Delta R_g)\) and if the strain gauges mounted normal to the direction of stress experience the same strain \((\Delta R_4 = \Delta R_2 = -\nu R_1)\), then

\[
\frac{\Delta e}{E} = \left[ \frac{\frac{\Delta R_1}{R_1} - \left( -\nu \frac{\Delta R_1}{R_1} \right)}{2 \left( 2 + \frac{\Delta R_1}{R_1} (1 - \nu) \right)} \right] - \left[ \frac{-\nu \frac{\Delta R_1}{R_1} - \frac{\Delta R_1}{R_1}}{2 \left( 2 + \frac{\Delta R_1}{R_1} (1 - \nu) \right)} \right]
\]  

(39)
Simplifying, we obtain

$$\frac{\Delta R}{E} = \frac{\Delta R_f}{R_f} \left(1 + v\right)$$

From this last equation we note the following:

1. The voltage output of the full bridge for the case of uniaxial tension is \((1 + v)\) times greater than that of the half bridge, and \(2(1 + v)\) times that of the quarter bridge.

2. Equation (40) shows that the output voltage is a non-linear function of the resistance change. However the non-linearity error is \((1 - v)\) times less than for the half bridge and quarter bridge case.

3. An accurate determination of Poisson's ratio \(v\) is now required to convert the voltage change to strain.

4. It is possible to determine the strain even when the bridge is initially unbalanced using Equation (38), and accurately knowing the resistance of each strain gauge as well as the Poisson's ratio \(v\).

The strain as a function of output voltage for the full bridge strained uniaxially is given in the following equation.

$$e = \frac{2 \frac{\Delta \epsilon}{F}}{E} \frac{\frac{\Delta \epsilon}{E}}{\left(1 + v\right) - \left(1 - v\right) \frac{\Delta \epsilon}{E}}$$
**Temperature and Strain Gauging**

Temperature affects strain gauge output in two ways. First, a change in temperature can induce a voltage output even though the material being strain gauged is not strained. Second, a temperature change can modify the relationship between the elongation and resistance of the strain gauge.

**Temperature-Induced Apparent Strain**

Temperature changes affect the strain gauge voltage output, which will result in error unless accounted and/or compensated for. A quarter bridge configuration that is initially balanced at a particular temperature will register a non-zero voltage output if the temperature is changed. The effect is known as temperature-induced apparent strain. The apparent strain is caused by two effects; the differential thermal expansion between the metal grid conductor and the substrate whose strain is being measured, and by the effect that temperature has on the resistivity of the metal grid conductor.

The strain due to differences in thermal expansion between substrate and grid is

\[ \varepsilon_{\text{AAPL}} = \left( \alpha_s - \alpha_g \right) \Delta T \]  

(42)

where \( \varepsilon_{\text{AAPL}} \) = apparent strain due to differential thermal expansion
\( \alpha_s \) = coefficient of thermal expansion of the substrate
\( \alpha_g \) = coefficient of thermal expansion of the grid
and \( \Delta T \) = change in temperature.

Under conditions of no mechanical constraint, the metal grid will expand (or contract) in response to the temperature change according the relationship \( \alpha_g \Delta T \). There will be no change in the voltage output. However, when the metal grid is mechanically locked to the substrate, its expansion (or contraction) will be constrained. The metal grid will be strained even though the substrate itself is not. This strain experienced by the strain gauge is equal to the difference between the unconstrained and constrained thermal expansion (or contraction). This thermally-induced apparent strain therefore is not a true indication of the substrate strain, and can lead to significant error.

The second effect of a change of temperature is upon the resistivity of the strain gauge. The relationship between resistance and temperature is given in the following:

\[ R_{\text{new}} = R \left( 1 + \beta \Delta T \right) \]  

(43)

where \( R_{\text{new}} \) = resistance of the strain gauge upon changing the temperature
\( R \) = resistance of the strain gauge prior to the temperature change
\( \beta \) = the thermal coefficient of resistance
and \( \Delta T \) = temperature change.
Defining $R_{\text{new}} = R + \Delta R$, and dividing through by $R$, we obtain

$$\frac{R + \Delta R}{R} - 1 = \beta \Delta T \quad \text{or} \quad \frac{\Delta R}{R} = \beta \Delta T \quad (44)$$

Next, we recall the relationship between strain and resistance for a strain gauge.

$$e = \frac{1}{F} \frac{\Delta R}{R} \quad (45)$$

Combining both of the above equations results in the relationship between the apparent strain and the temperature change due to a change in the resistivity of the strain gauge.

$$e = \frac{1}{F} \beta \Delta T \quad (46)$$

where $\varepsilon_{\text{app/}} = \text{apparent strain due to the a change in resistivity of the strain gauge}$

$F = \text{gauge factor}$

$\beta = \text{thermal coefficient of resistivity of the metal grid}$

and $\Delta T = \text{temperature change experienced by the strain gauge}$.

Thus the resistance of the strain gauge will change with temperature. Both effects, that due to the differential thermal expansion between metal grid and substrate and that due to the change in resistivity, are additive. Both together describe the temperature induced apparent strain.

$$e = \left[ (\alpha_s - \alpha_G) + \frac{1}{F} \beta \right] \Delta T \quad (47)$$

A third effect of temperature, which will be addressed later, is upon the relationship between the real strain and the resistance change. This has an effect upon the gauge factor $F$, which is usually assumed constant. The gauge factor does, in fact, change with temperature, but usually only in a slight way.
Temperature Compensation

Two methods are used to eliminate the effect of apparent strain due to temperature.

1. Balancing the bridge at elevated temperature prior to applying stress.
2. Strain gauge compensation; the strain gauge is either configured in the proper bridge arrangement to eliminate the apparent strain effect, or manufactured in such a way as to match the substrate properties to cancel out the apparent strain effect.

These two methods are also used to eliminate the apparent strain due to pressure.

Balancing the bridge at the test temperature so that the strain indicator registers zero strain is a simple and straightforward method of eliminating apparent strain. Its only drawback is that if the temperature fluctuates during the test, then the effects of apparent strain will not be eliminated.

Compensation for the apparent strain can be done by either using an additional strain gauge in the Wheatstone bridge arrangement or by using a self-temperature-compensated strain gauge matched to the coefficient of thermal expansion of the substrate. Use of an additional compensating gauge will be addressed first.

The temperature-induced strain can theoretically be removed by using an additional compensating gauge in the adjacent arm of the Wheatstone bridge. The temperature effect on the resistance and degree of constraint due to the differential expansions of both strain gauge and substrate on the one gauge will be the same as on the other and their effects cancel.

A brief derivation follows. Assume that the active gauge is on the first arm and the compensating gauge is on the second arm of the Wheatstone bridge. Upon experiencing a temperature change, both gauge one and two experience a change in resistance of $\Delta R_1$ and $\Delta R_2$ respectively.

\[
\frac{e_1}{E} = \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3} \quad \text{and} \quad \frac{e_2}{E} = \frac{R_4 + \Delta R_1}{R_1 + \Delta R_1 + R_2 + \Delta R_2} - \frac{R_4}{R_4 + R_3}
\]

(48)

The difference between initial and final voltages is

\[
\frac{\Delta e}{E} = \frac{R_1 + \Delta R_1}{R_1 + \Delta R_1 + R_2 + \Delta R_2} - \frac{R_1}{R_1 + R_2}
\]

(49)

in which the second terms of $e_1$ and $e_2$ cancel out.
Creating a common denominator results in

\[
\frac{\Delta e}{E} = \frac{\frac{\Delta R_1 R_2}{R_1 R_2} - \frac{\Delta R_2}{R_1}}{\left(1 + \frac{\Delta R_1}{R_1} + \frac{\Delta R_2}{R_2} + \frac{\Delta R_1}{R_1} \right) \left(1 + \frac{R_2}{R_1} \right)} \tag{50}
\]

If the strain gauges are identical and they experience the same resistance change, then

\[
\frac{\Delta R_1}{R_1} = \frac{\Delta R_2}{R_2} \quad \text{or} \quad \frac{R_2}{R_1} = \frac{\Delta R_2}{\Delta R_1} \tag{51}
\]

Inserting this into the numerator in Equation (50) we obtain

\[
\frac{\Delta R_1 \Delta R_2}{R_1 \Delta R_1} - \frac{\Delta R_2}{R_1} = 0 \tag{52}
\]

Therefore the change in voltage output, \(\Delta e\), is zero. In other words, the induced apparent strain from gauge number one is cancelled out by the same induced apparent strain of the second gauge.

For the apparent strain to be perfectly offset by the second gauge, the following conditions must be met.

1. Both gauges are identical.
2. Both gauges are mounted on the same substrate.
3. Both gauges experience the same temperature.
4. Leadwires to both gauges are identical.

Under these conditions, the resistance changes in adjacent arms of the Wheatstone bridge should be identical and their effects cancel.

The compensating gauge can either be a "dummy", that is, mounted on an unstrained specimen, or "active", in which case it is mounted on the stressed specimen, hopefully in such a way that the strain measured is opposite in sign from the other gauge so that the signals are added.

Drawbacks of compensating in this way are that fully meeting the above criteria is often impossible, and so at great temperature changes a significant apparent strain may result.
Calibration

The output voltage from the Wheatstone bridge due to strain is quite small and is usually amplified. The relationship between the strain and the voltage after amplification would then be affected by the strain experienced by the strain gage, the leadwire resistances, the amplifier as well as other instrumentation effects. Calibration of the strain with the final output signal must be carried out for the following reasons:

1. To determine the relationship between strain and the amplified output signal.
2. To determine if the amplifier/instrumentation is amplifying the input signal linearly.

There are two calibration methods used, direct and indirect. Direct calibration involves mechanically straining the gauged substrate a precisely known amount. For example, if one is sensing a purely tensile strain, one can suspend weights from the strain sensing element and relate this strain to the output signal from the instrumentation. Indirect calibration is used only for verifying the amplifier/instrumentation used. The technique involves applying a simulated strain gauge output to the input terminals of the instrument and relating the input signal to the output signal. Of the two techniques, direct calibration is, of course, best. It is not always possible to carry it out, in which case the indirect technique must be employed.
APPENDIX D

DESIGN SPECIFICATIONS FOR THE HIGH PRESSURE TENSILE TESTING MACHINE

The purpose of the machine is to tensile test polymer samples at pressures up to 400 MPa (60,000 psi) and temperatures up to 200°C. It is composed of five sections.

I. Top pressure vessel and its end closures
II. Bottom pressure vessel and its closure
III. Support structure
IV. Actuation assembly
V. Internal components of the top pressure vessel

The machine is illustrated in Figures D1 & D2. The top pressure vessel contains the sample, tensile gripping assembly, the bayonet connector, and the load cell. The bottom pressure vessel functions to compensate for fluid volume changes in the top pressure vessel as the actuation shaft is withdrawn. It is sometimes referred to as the volume compensator. The support structure aligns the cylindrical axes of the top and bottom pressure vessels. It consists of three 1" thick plates, spaced apart by four 1" diameter shafts. The actuation assembly consists of three pieces: a 29 1/2' long (75 cm) shaft of 3/8" diameter, a component which supports part of the shaft length, clamps onto the 3/8 inch shaft and presents a loading surface for the downward moving crosshead during tensile testing, and a split collar for the return stroke. The internal components of the top pressure vessel include the load cell and bayonet connector, the gripping assembly, and the loading/unloading tube.

Machining was done by shops working in British units rather than metric units. Therefore dimensions used in the design are all in inches.

I. Top Pressure Vessel and Closures

Top Pressure Vessel Figures D3 & D4

Dimensions: Overall length: 25 3/4"
O.D. : 5.0"
I.D. : 1.5" +.0005 -.0000
Surface finish: √16 μ in RMS

Material: 4340 VAR (Vacuum Arc Remelted)
Heat Treated: To 180/186 kpsi (Rockwell C 37-40)
Austenitized at 1550 °F
Quenched in 50 °C oil
Tempered at 950 °F

Comments:
1. Honing of ID done after heat treatment. The tolerance of the inner bore is critical to maintaining a high pressure seal.
2. The external threads and collar had to be concentric with the internal threads at the bottom of the pressure vessel. The alignment of the actuation shaft is critical to minimize the chance of it buckling under the load imposed by the internal pressures of each of the vessels.
**Top Closure** Figure D5

The top closure consists of two pieces: the cover or plug, and the retaining screw. There is a sliding fit between the two pieces.

**Plug**

Material: 4340 VAR  
Heat Treated: To 180/186 kpsi (Rockwell C 37-40)  
- Austenitized at 1550 °F  
- Quenched in 50 °C oil  
- Tempered at 950 °F

**Comments**

1. The critical dimension is the fit with the 1.5" bore of the pressure vessel. This dimension is required for the static seal, composed of a viton "O"-ring and a metal backup ring.
2. There is a 45° shoulder to receive a metallic back-up ring.
3. The material of construction is the same composition and heat treatment as that of the pressure vessel to ensure fits at various temperatures.
4. The top port is a standard 58° male cone on a 60° female cone hydraulic connection for 1/4" 60,000 psi tube.

**Retaining Screw** Figure D5

Material: 4340 VAR  
Heat Treated: To 180/186 kpsi (to Rockwell C 37-40)  
- Austenitized at 1550 °F  
- Quenched in 50 °C oil  
- Tempered at 950 °F

**Comments**

1. The vent hole functions to relieve pressure of any oil that may leak past the seals. Otherwise, if the threads provide a seal, the ensuing build of pressure under the retaining screw will lock it into position.
2. The material of construction is the same composition and heat treatment as that of the pressure vessel to ensure fits at various temperatures.
3. An ordinary coarse thread is sufficient. Some closures employ a buttress thread which is efficient if only two turns of thread can be accommodated (i.e. cannon).

**Metal Back-up Ring** Not shown

**Description:** A metal ring with a triangular cross-section (90°-45°-45°).
Fits the 45° shoulder of the plug, presenting a flat horizontal surface to the viton "O"-ring.  
OD has the same fit as the bore fit of the plug.  
ID is slightly larger than 1.250".
Material should ideally be of the same composition and temper as that of the vessel and plug.  
This will help ensure fits at elevated temperatures.

**"O"-ring** Viton (Fluorocarbon based elastomer)  
Specification: SAE Standard AS-568: # 218  
Temperature Range: -30° C to 200° C  
**Dimensions:**  
- Nominal OD = 1.5"  
- Nominal ID = 1.25"  
- Nominal width = .125" Actual ID = 1.234 (+.006-.006)  
- Nominal width = .139 (+.004-.004)
**Bottom Closure**  Figure D6

Material: 4340 VAR (Vacuum-Arc-Remelted)
Heat Treated: To 180/186 kpsi (Rockwell C 37-40)
- Austenitized at 1550 °F
- Quenched in 50 °C oil
- Tempered at 950 °F

**Comments**

1. The first critical dimension is the fit with the 1.5" bore of the pressure vessel. This dimension is equal to the bore diameter +.0000 -.0005. The close tolerance is required for the static seal, composed of a viton "O"-ring and a metal backup ring.

2. There is a 45° shoulder to receive a metallic back-up ring.

3. The second critical dimension is the internal .625-.626" recess for the placement of the internal seals between the .325" shaft and the bottom closure. This also required a good surface finish of \(\sqrt{32}\) μin RMS.

4. Four blind 1/8" holes, 7/16" off the central axis, each have their own ports. One is for the hydraulic connection, and this ends with a port with a standard 58° male cone- 60° female cone connection for 3/8" diameter, 60,000 psi tube (HF6 in figure). The other three are for electrical feedthroughs. They also have the same type connection as the hydraulic port, except that they are for 1/4" tube instead of 3/8" tube (HF4 in figure).

5. The fifth 1/8" hole is a vent hole. Its function is to relieve any build up of pressure by hydraulic fluid that escapes past the "O"-ring/metal backup ring seal.

**Gland**

Material: 17-4 PH Stainless (17 Cr-4Ni Precipitation Hardened. AMS 5643).
- \(R_c = 34\).

This part is identical to the gland shown in Figure D7. Its function is to retain an aluminum-bronze packing washer for the seals acting between the actuation shaft and the bottom closure. If "Polypak" seals are used, the gland "bottoms out" when screwing in, since these seals do not require tightening (i.e. their length is shorter than the length available in the .625" recess). If Teflon "V"-rings are used, their long dimension is longer than that available in the .625" recess, and tightening the gland tightens the Teflon "V"-rings in this case. The aluminum-bronze packing washer (Part # 2-5853-AMPCO), "Polypak Seals" (Part # B-1373-Molythane) and Teflon "V"-ring seals were purchased from High Pressure Equipment, 1222 Linden Ave., Erie, PA 16505 (814/838-2028).

**Metal Back-up Ring**  Not shown

**Description:** A metal ring with a triangular cross-section (90°-45°-45°).
- Fits the 45° shoulder of the plug, presenting a flat horizontal surface to the viton "O"-ring.
- OD has the same fit as the bore fit of the plug.
- ID is slightly larger than 1.250".
- Material should ideally be of the same composition and temper as that of the vessel and plug.
- This will help ensure fits at elevated temperatures.

**"O"-ring**

**Fluorocarbon (Viton)**

**Specification:** SAE Standard AS-568: # 218
**Temperature Range:** -30°C to 200°C

**Dimensions:**
- Nominal OD 1.5"
- Nominal ID 1.25"  Actual ID = 1.234 (+.006-.006)
- Nominal width = .125"  Actual width = .139 (+.004-.004)
II. Bottom Pressure Vessel (or Volume Compensator) Figure D7

Volume Compensator

Material: 17-4 PH Stainless, $R_C = 34$

The purpose of this piece is two-fold. First, it compensates for the fluid volume lost or gained in the top pressure vessel due to motion of the actuation shaft. And second, it balances the downward thrust on the actuation shaft caused by the pressurized environment of the top pressure vessel.

One of the novel features of this machine is the technique of maintaining pressure during the withdrawal of the actuation shaft. As the shaft withdraws from the top pressure vessel during the course of pulling the sample during the tensile test, fluid volume is created. This fluid volume is equal to the volume of the shaft which has been removed from the pressure vessel during the test. As a result, the pressure will decrease as the tensile test progresses. If, however, the other end of the shaft reenters another pressure vessel, which is hydraulically linked to the first, then the fluid volume created in the one vessel due to shaft movement will be equal to the fluid volume lost in the second. Since the two vessels are connected, the net fluid volume change will be zero, and the pressure maintained constant.

Comments
1. The critical dimension is the internal .625-.626" recess for the placement of the internal seals between the .325" shaft and the volume compensator. This also requires a good surface finish of $\sqrt{32}$ μin RMS.
2. The external machining at the top of the volume compensator should be done at the same time as the internal machining to ensure concentricity. The alignment of the actuation shaft is critical to minimize the chance of it buckling under the load imposed by the internal pressures of each of the vessels.
3. The port at the bottom of the volume compensator is a standard high pressure (60,000 psi) connection for 3/8" diameter tube. The fittings for these hydraulic ports were purchased from High Pressure Equipment, 1222 Linden Ave., Erie, PA 16505 (814/838-2028).

Gland Figure D7

Material: 17-4 PH Stainless (17 Cr-4Ni Precipitation Hardened. AMS 5643). $R_C = 34$.

This gland is identical in design and function as the gland that fits in the bottom closure. The function of the gland is to retain a aluminum-bronze packing washer for the seals acting between the actuation shaft and the bottom closure. If "Polypak" seals are used, the gland "bottoms out" when screwing in, since these seals do not require tightening (i.e. their length is smaller than the length available in the .625" recess). If Teflon "V"-rings are used, their long dimension is longer than that available in the .625" recess, and tightening the gland tightens the Teflon "V"-rings in this case.

The packing washer (Part # 2-5853-AMPCO), "Polypak Seals" (Part # B-1373-Molythane) and Teflon "V"-ring seals were purchased from High Pressure Equipment, 1222 Linden Ave., Erie, PA 16505. (814/838-2028). Since temperatures of up to 200 °C were experienced in the upper pressure vessel, Teflon "V"-ring seals were used in that vessels bottom closure. "Polypak" seals were used in the bottom pressure vessel since they were functioning at room temperature only.

Both the gland in the bottom pressure vessel as well as the gland in the bottom closure of the top vessel, have a 1 1/8" deep recess by 1" diameter, to accommodate the shaft support component. This allows another 2 1/4" of travel for the actuation shaft.
III Support Structure Figures D8 & D9

The function of the support structure is to support the top pressure vessel and align the cylindrical axes of the top and bottom pressure vessels. The support assembly is shown in Figure D8 and the individual components in Figure D9.

The most important design consideration given was the alignment of the actuation shaft. This meant that the shafts separating the first and second plates be positioned identically from the axis of their central bores in each plate. This was not a straightforward machining operation since each of their central bores were of a different diameter. Shaft position was maintained by using shouldered bolts and drilling close tolerance clearance holes for the shoulders in each plate.

The second requirement was to minimize the central deflection of the plates (similar to the deflection of a drum). The 1” plate and the relative distance of the 1” shafts from the centre of the plates ensured minimal deflection.
IV  **Actuation Assembly**  Figure D10

The actuation assembly acts to translate the motion of the Instron crosshead to the tensile sample inside the top pressure vessel. The actuation assembly consists of three components.

1. Actuation shaft.
2. A shaft collar (See Figure D10) which clamps onto the actuation shaft.
3. A split collar which clamps onto the shaft collar.

**Actuation shaft**

Material: 17-4 PH Stainless, \( R_C = 40 \)
Dimensions: .325 " - .326 " diameter
29 5/8 " length

This component is centreless ground to obtain the tolerances and surface finish required for sealing at pressures to 60,000 psi.

**Shaft Collar**

The loads generated on the actuation shaft by the internal pressure of the vessels are substantial. At 60,000 psi, there is a 6,625 lbs load generated on the 3/8 " actuation rod. This meant that the possibility of buckling had to be examined. The Euler formula for the critical load on a long column is

\[
\left( \frac{L}{k} \right)^2 = C \left( \frac{E}{P} \right) \pi^2 A
\]

where \( L \) is the length of the column, \( k \) is the radius of gyration of cross section \( = (I/A)^{1/2} \), where \( I \) is the moment of inertia, \( C \) is a constant factor depending on the constraints at the ends of the column, \( E \) is the tensile modulus, \( P \) is the load, and \( A \) is the cross-sectional area of the column.

Given a 6,625 lbs load on a steel shaft \( (E = 30 \times 10^6 \text{ psi}) \), using a conservative estimate for the end constraint coefficient \( (C=1) \) and \( k = D/4 \), the maximum length of unsupported column that is stable (i.e. will not buckle) is 6.6 inches.

The distance between top and bottom vessels is 16 inches (this is the actual unsupported distance). Therefore, reinforcement was required. Seven inches of this length was due to the height of the Instron crosshead. There is a 1" diameter hole running vertically down the centre of the crosshead. This coincided with the central axes of the two pressure vessels. The challenge was to design a piece that 1) attached securely to the rod, 2) supported the rod to prevent buckling and 3) moved with the moving crosshead. With respect to the third point, it was advantages not to fix the point of attachment to the crosshead, but to allow the component to be pushed only. The reason for this was that the central axis of the crosshead motion might not coincide with that of the central axes of the two vessels. Any misalignment may have resulted in high lateral forces due to bending of the shaft which would occur at either end of its travel. By being pushed, any major lateral forces would shift the shaft's position on the "floating" surface of the crosshead.

Figure D10 shows the solution found. It is a hollow cylinder 9 3/4 " long, with an OD of 7/8 " and an ID of 3/8". The cylinder is split to allow clamping to the 3/8" shaft. The OD is smaller than the 1" hole in the crosshead to allow for movement due to misalignment. The 9 3/4" length gives sufficient support to the shaft to prevent buckling. And the 2" diameter section presents a flat surface for the crosshead to push, as well as housing the bolts used to clamp the split collar to the shaft.

**Split Collar**

A split collar with an internal diameter of 7/8 " was clamped to the top of the shaft collar. This provided a secure horizontal "pushing" surface for the return stroke.
Internal Components of the Top Pressure Vessel

The internal components comprise the following:

1. Loading and gripping assembly.
2. Cylindrical load cell.

Loading and Gripping Assembly  Figure D11

The design of the grips had to contend with two major problems: aligning and gripping the sample inside the 1.5" internal diameter of the pressure vessel and how to load the sample inside the vessel. The features of this grip design are:

1. The universal joint system at both ends for sample alignment
2. The wedge grip design with a serrated surface for secure gripping.

Alignment is crucial for brittle materials, such as uniaxially oriented polymers. Also included in this group are materials which undergo a ductile to brittle transition due to high pressures.

The wedge grip design is self-tightening, in that as the sample pulls the grips towards itself during extension, the grips are pulled with greater force into the sample. What is critical is that the mating surfaces of the wedge grips be parallel, and that the serration pattern (i.e. pyramidal on 45°) be evenly machined across the entire surface of the grips.

Loading of the sample is accomplished using a bayonet connector. As shown in the front plan view of Figure D11, the bayonet connector is the component at the bottom, partly hidden behind the loading tube (shown by the dashed lines). The bayonet connector is cylindrical, attached to the cylindrical load cell beneath (not shown). As can be seen, there is a backward "J"-shaped insert at the top of the connector. There is a matching insert on the other side, not seen. Into this insert fits a 1/4" rod, mounted sideways through the lower grips. A 1/4 turn positions the 1/4" rod so that it will engage the bayonet connector as the connector is moved downward. To effect the 1/4 turn, a thin-walled tube extended down around the gripping assembly from the top closure is employed. It has a recess along the bottom edge on both sides of the tube. It is designed to effectively move the 1/4" rod laterally without subsequent interference with the tensile test. Upon engagement of the bayonet connector with the 1/4" rod, the rod is pulled away from the thin-walled tube, and no sliding interference can take place.

The maximum design load for the gripping assembly is 1000 lb. All of the gripping components were machined from Ultima® steel with a yield strength of 70,000 psi.

Cylindrical Load Cell  Figure D12

Material:  Ti-6Al-4V
Heat treated at 1200 °C for 2 hours to \( R_C = 30/31 \) (YS = 123,800 psi)
Young's Modulus: 16 x 10⁸ psi
Elongation (longitudinal) = 18 %

The design considerations for the load transducer were to be mechanically stable and at the same time sensitive enough to measure low loads. The ratio of length to diameter is 3.6, which allows the stresses to be more homogeneous at the centre of the reduced section where the strain gauges are placed. The wall thickness of the tube is .012" to allow for the sensitivity necessary. Initially, the compensation gauges were mounted transversely on the tube. A later design added a 5/8" diameter flange at the bottom (using the same material) where no load is transmitted, and the compensation gauges mounted there. A more complete analysis of the load cell is given with the load cell specifications.
Figure D1: High pressure tensile testing machine - Schematic detail.
Figure D2. High pressure tensile testing machine - front and side sections.
Figure D3. Pressure vessel and internal components - sectional detail.
Figure D4. Top pressure vessel - section dimensions.
RETAINING SCREW

PLUG

1/4" dia hole
1/4" deep

1/8" vent hole

1/16" radius.

To fit 1.5" bore ±.0005

- .0005

2.140"

3/4"

45°

1.5000

2.140"

2 1/2"

1"

Sliding fit with plug

Sliding fit with retaining screw

1" Drill

All internal corners 1/16" radius.

9/16" - 18

7/16"

60°

3"

45°

3/4"

3 3/4"

5 3/4"

Figure D5. Top closure assembly - section dimensions.
Figure D6. Bottom closure- section dimensions.
Figure D7. Bottom pressure vessel (volume compensator) - section dimensions.
Figure D8. Support structure - overall schematic.
Figure D9. Support structure - machining dimensions.
Figure D10. Shaft collar - section dimensions.
Figure D11. Loading and gripping assembly: front plan, front section, side view.
Figure D12. Load cell - section dimensions.
Appendix E

High Pressure Hydraulics

There are some special considerations that must be given when using high pressure systems. Those that affect this system are mentioned briefly here.

Oil

The selection of oil used when testing polymers at elevated temperatures must consider some additional factors. First, the polymer should not be solved by the oil. Second, the vapour pressure of the oil should be low and the flash point high. Third, the oil should not be too viscous, otherwise cavitation occurs during the draw stroke. And fourth, the oil should not "freeze" at elevated pressures.

 Initially, a fluorocarbon-based synthetic oil was chosen. It was chemically inert to the polypropylene, had high temperature properties, and was non-flammable. Unfortunately, the oil "froze" at 200 MPa, and 25 °C. In the end hydraulic oil was used (Shell hydraulic oil, TELLUS OIL 46, 407-163-30). Tests were carried out to determine if the oil would dissolve into the polypropylene, and they showed it did not. A layer of gold was sputtered onto the surface of the polypropylene to act as a barrier as a precaution.

Connections

The design of hydraulic connections for 400 MPa service uses the cone-on-cone geometry, as shown in Figure E1. The cone angles are different, the male tip having an angle of 57 - 59 °, and the female having an angle of 60°. Line contact is first made at the tip of the male part. Forcing the two together plastically deforms both, and the contact area grows radially outward. Sealing occurs since the force holding the two parts together is greater that the force exerted by the hydraulic fluid pushing them apart.

The sealing principle is the same for feedthrough connections (Figure E2). The tube and collar are replaced by a plug, which is drilled down its middle. A stainless steel sheathed thermocouple wire inserted into the hole and the two silver soldered together. The clearance between the two pieces is .003" to allow silver to flow freely into the joint. The thermocouple wires themselves are insulated form the outer sheath by MgO powder. Since the MgO is deliquescent, the feedthrough connectors were heated to 125 °C to remove all traces of water, and then sealed with epoxy. Electrical connections were high temperature soldered (T_m = 300 °C) to the thermocouple wire.
Figure E 1: Cone-on-cone connections used for 420 MPa service. The male tip has a cone tip angle of 57-59°, and the female cone angle is at 60°.

Figure E 2: High pressure electrical feedthrough connection. The stainless steel sheathed thermocouple wire is silver soldered to the high pressure plug.
Seals

Closures

The seals for closures consist of an "O"-ring and a metal backup ring (Figure E3). The metal ring has a triangular cross-section and fits on a similarly angled shoulder on the closure. It presents a flat surface to the "O"-ring. The metal backup ring is also known as an anti-extrusion ring since the "O"-ring would be extruded into the gap between closure and vessel. As pressure is applied, the "O"-ring pushes on the metal ring, deforming it so that no gap between the metal ring and the closure or vessel remains.

Sliding Seals

Sliding seals are used with the actuation shaft of the machine, the pumps and the valves. Two types of sliding seals were used with the actuation shaft, a "Polypak" seal and a teflon "V"-ring seal. They are illustrated in Figures E4 and E5. The "Polypak" seal is composed of an elastomeric "O"-ring encased in the open end of a hard fluorocarbon. The "O"-ring end faces the pressure. Pressure deforms the elastomeric "O"-ring more easily than the casing, and it in turn pushes the flanges outwards against both the vessel and the sliding shaft. There is an aluminum-bronze packing washer, which has a .001" clearance with the actuation shaft. Its function in this case is only to retain the seals, and not to squeeze them. The gland is seen in the illustration to bottom out without squeezing the seals. Failure of these seals usually occurs with a section of the flanges turning inside out. The resistance to shaft motion is relatively low, due to the fluoro-elastomer used in the casing, and the fact that no squeezing action is used.

For higher temperature service (230 °C), teflon "V"-rings are used. The open part of the "V" faces the pressure. The bottom packing washer forces the first "V"-ring to splay open. Another four or so "V"-rings are then inserted into position. The top packing washer (the same as that used for the "Polypak" seals) squeezes the "V"-rings together to form the seal. The proper torque applied to the gland is not set. Tightening is done until leakage ceases. Tightening should never be done with the system pressurized. Always release the pressure first and then tight the gland before re-pressurizing.
Figure E-2: Closure seal, composed of a metallic anti-extrusion ring and an O-ring.
**Figure E 4:** Sliding seal for 420 MPa service. The polypak seals have a hard outer fluorcarbon casing, with the open end containing an "O"-ring.

**Figure E 5:** Sliding seal composed of Teflon "V"-ring seals. These seals can be used to 230 °C, and 420 MPa service.
Safety

Rupture discs are designed to release the pressure inside the system should the pressure exceed their pressure rating. They are commercially available at a number of pressure ratings. The rating used in this machine is 450 MPa.

The energy stored due to compression alone in a fluid system is two to three orders of magnitude less than that for a gas pressurized system. The energy stored in a system due to compression is given by

$$E_{\text{comp}} = \int_{V_o}^{V_f} P(V) \, dV$$

where $E_{\text{comp}}$ is the energy due the compression alone,

- $P$ is the pressure, and
- $V$ is the volume.

A rough measure of the stored energy of this system can be obtained by measuring the volume of fluid ejected from the system when pressure is released. For this machine, which has a capacity of 650 ml, 85 ml of oil was ejected upon depressurization from 300 MPa. Assuming a linear relationship between $P$ and $V$, the stored energy is given as $1/2 P_h \Delta V$, and is equal to 13,000 joules. (This estimate is over-conservative, since the shape of the $P$-$V$ curve is concave away from the origin rather than linear.) As a comparison, a standard laboratory cylinder of hydrogen at 14 MPa (2000 psi) stores $60 \times 10^6$ joules, or 4600 times more energy than this high pressure tensile testing system.
High Pressure Hydraulic Suppliers

Most of the components were purchased from the following company:

High Pressure Equipment Company
122 Linden Avenue
Erie, Pennsylvania 16505
(814) 838-2028

The industry has, for the most part, adopted a common standard for the connections. Other companies include the following.

AE Autoclave of Canada Ltd
A subsidiary of Autoclave Engineers, Inc of Erie Pennsylvania
Eastern Canada Operations
4129 Harvester Road
Burlington, Ontario
(416) 632-6961

Pressure Products Industries (PPI)
9542 Hardpan Rd
Angola, NY 14006
(216) 338-3107

Flowtron, Inc
30 Industrial Drive
Ivyland, PA 18974
(215)335-9970
APPENDIX F

Load Cell Design

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APPENDIX F

Load Cell Design

Design Requirements

Determining the design requirements for the load cell was an iterative process. Sample dimensions and range of anticipated strengths when testing under conditions of room temperature and 420 MPa pressure (high loads) and elevated temperature and low pressures (low loads) were the first consideration. Next was the design of the mechanical transducing element so that this range was matched, followed by selection of the transducer grade strain gauges matched to the anticipated strain range and heat sink conditions.

The units of measure used in the design of the load cell were British. This is consistent with the units used for the design of the other machine components. The reason for this was that the machine shops fabricating the components were using these units.

The design requirements for the load cell can best be summarized by the following:

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Load</td>
<td>1000 lbs</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Ideally, 1/1000 of maximum load</td>
</tr>
<tr>
<td>Response</td>
<td>Linear</td>
</tr>
<tr>
<td>Environmental Conditions</td>
<td>Temperature Range: 25 °C - 230 °C</td>
</tr>
<tr>
<td></td>
<td>Pressure Range: 0 - 420 MPa</td>
</tr>
<tr>
<td>Dimensional Limitations</td>
<td>4&quot; length x 1.5 &quot; diameter</td>
</tr>
<tr>
<td>Other Considerations</td>
<td>Must be able to rigidly support the bayonet connector</td>
</tr>
</tbody>
</table>

Structural Design

A tube geometry was selected because design was simple and fabrication was straightforward. As well it offered rigid support for the bayonet connector. Designs based on bending beams were considered, and offered the advantage of a greater degree of signal augmentation. They were discarded because they were multi-component assemblies which required more design time and fabrication expense. The one disadvantage of tubular construction is that there is no overload protection. On some commercial load cells, there is a limited load cell range of motion before another, more robust element starts to pick up the load. In this way, the load cell is protected from being damaged due to extension outside its load range.

The final design is shown in Figure F1. The ratio of gauge length to diameter is 4. This aspect ratio was chosen to reduce the effects of the inhomogeneous strain distribution which occurs at the ends of the tube.

In order to maximize the strain signal for a given load, the cross-sectional area must be minimized. Since strain must be entirely within the elastic regime, a high tensile strength is required. As well, the strain signal is also maximized for a given load if the material has a relative low modulus. Ti-6Al-4V, a high strength alloy with a modulus about half that of steel, was selected.
Figure F1: Section and view of the load cell tube.
The design specifications for the loading element of the load cell are:

- **Maximum Load:** 1000 lbs
- **Tube geometry**
  - Thickness: .012 "
  - Diameter: 5/8 "
- **Material:** Ti-6Al-4V
  - **Yield Strength:** 123,000 psi
  - **Modulus:** 16 x 10^6 psi

- **Stress at maximum load:** 42,400 psi
- **Safety factor:** 123,000 psi / 42,400 psi = 2.9
- **Strain at maximum load:** 2,650 μ strain

**Excitation Voltage and Sensitivity**

Once the load has been selected and the strain maximized in the transducing element, the next step is to maximize the output signal. The output voltage signal can be augmented by increasing the excitation voltage and/or the amplification. The relationship between voltage and strain is developed fully in Appendix C.

As shown in Appendix C, the measured voltage, \( \Delta E \), is related to the excitation voltage, \( E_{\text{excitation}} \), and the strain, \( \varepsilon \), for a quarter bridge by the following equation.

\[
\frac{\Delta E}{E_{\text{excitation}}} = \frac{F \varepsilon}{4 - 2F \varepsilon}
\]

Quarter Bridge

where \( F \) is the gauge factor. This is the equation for a Wheatstone bridge circuit with one arm "active" (i.e. with one strain gauge on the transducing element).

The equation for a half bridge is given as

\[
\frac{\Delta E}{E_{\text{excitation}}} = \frac{2F \varepsilon}{4 - 2F \varepsilon}
\]

Half Bridge

This equation is simply twice that of the quarter bridge.

The equation for a full bridge in tension is not as straightforward an extension from the quarter bridge case. As developed in Appendix C, the last two arms of the Wheatstone bridge have the strain gauges mounted transversely. The transverse compressive strain adds to the tensile strain in the first two gauges. The longitudinal strain and the transverse strain are proportional, as related by Poisson's ratio. The equation for a full bridge is given as

\[
\frac{\Delta E}{E_{\text{excitation}}} = \frac{2(1 + \nu)F \varepsilon}{4 - 2(1 + \nu)F \varepsilon}
\]

Full Bridge in Tension

Both the half bridge and the full bridge in tension were used successfully.

One can see from each of the above equations that the measured voltage, \( \Delta E \), is proportional to the excitation voltage, \( E_{\text{excitation}} \). Increasing the excitation voltage then increases the output voltage.
Increasing the output voltage can also be done by amplifying the signal. There is a limit to this, determined by the range of the input A to D voltages used, in this case 0 to 5V. In other words, the gain selected cannot increase the output voltage to a value over 5V. The A/D system used offered amplification factors of 2, 10, 20, 100, 200, and 1000. What is found by examining the effect of various excitation voltages is that the sensitivity of the measurements at low loads is increased by the increased excitation voltage. Table F1 shows the effects of excitation voltage on the sensitivity of the measurements for two loads, 250 lb and 25 lb.

<table>
<thead>
<tr>
<th>Max Load (lb)</th>
<th>$E_{\text{Excitation}}$ (V)</th>
<th>$\Delta E$ (V)</th>
<th>Gain</th>
<th>Amplified Voltage Output (V)</th>
<th>bits/lb</th>
<th>lb/bit</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>5</td>
<td>.00348</td>
<td>1000</td>
<td>3.480</td>
<td>5.69</td>
<td>.175</td>
</tr>
<tr>
<td>250</td>
<td>25</td>
<td>.0174</td>
<td>200</td>
<td>3.480</td>
<td>5.69</td>
<td>.175</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>.000348</td>
<td>1000</td>
<td>0.348</td>
<td>5.69</td>
<td>.175</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>.00174</td>
<td>1000</td>
<td>1.739</td>
<td>28.49</td>
<td>.035</td>
</tr>
</tbody>
</table>

One can see that at the higher loads, there is no difference in the sensitivity due to changing the excitation voltage. Any increase in the output voltage, $\Delta E$, is made up for by selecting a larger gain. However, at the lower maximum loads of 25 lbs, the difference is notable. The sensitivity increases as the excitation voltage increases. In this case, the available gain is at its limit.

Another point is that the amplification carries its own noise and instabilities. In other words, the amplified signal with a gain of 200 is cleaner than the amplified signal with a gain of 1000.

The excitation voltage selected was 25 V. This offered the cleanest signal, and the best sensitivity when low maximum loads were being measured.
Strain Gauge Selection

The first consideration was the resistance and the gauge area. All strain gauges generate some heat due to $V^2/R$ heat losses. The potential problem is that if the substrate cannot dissipate the heat fast enough, the substrate will heat up and expand, registering a strain. The factors that affect this are the thermal conductivity and mass of the substrate, the area of the strain gauge, and the resistance of the strain gauge. Formulas based upon the factor $V^2/RA$ (where $A$ is the grid area of the strain gauge), and the thermal characteristics of the substrate are given by the strain gauge manufacturer. The formula for transducer use is, of course, more stringent.

In order to use 25 V excitation, without self-heating effects required a sizeable resistance of about 10,000 ohms. In order to achieve this, two 4,500 ohm gauges were used in series on each arm.

Transducer grade strain gauges have thinner backing to more directly transfer the substrate strain to the alloy grid. This was also a concern because of the pressures used, since some compression of the polymer backing could be expected. The other concern was the curvature of the 5/8" diameter load cell.

The strain gauges selected had the following specs:

Type: TK-06-S076K-45C/DP Intertechnology Inc.
Back ing Material: Glass-fiber reinforced phenolic backing, thickness = .0008"
Karma foil alloy (Karma is a nickel-chromium alloy)
Self-Temperature-Compensated to match the titanium substrate
Resistance: 4500 ohms +/- .2%
Duplex Pads of copper for easier soldering
Dimensions: Overall: .180" x .080"
            Grid: .100" x .080"
Temperature: 200 °C
Gauge Factor: 2.05
Strain limits: +/- 1.5%

Supplier: Intertechnology Inc.
1 Scarsdale Road
Don Mills, Ontario M3R 2R2
(416) 445-5500

The strain gauge locations on the tube for the half bridge circuit are shown in Figure F2. The gauges located at the mid-point of the tube are the load sensing gauges, or active gauges. The gauges located on the lower flange are the compensation gauges, or passive gauges. They are mounted on a surface with the same radius as the active gauges. Any apparent strain generated by either the temperature or the pressure on the active gauges should be equal to the apparent strain on the compensation gauges, so that there will be no net effect on output signal. The apparent strain due to changing temperature is caused by the difference in expansion between the gauge and the substrate. The apparent strain due to changing pressure is due the compression (or expansion) of the strain gauge laminate backing. This causes a strain in the transverse direction because of the 5/8" diameter of the load tube. The radius of the grid will change due to the compression (or expansion), and an output signal registered. In this case as well, the compensation gauges will experience the same compression (or expansion), and the net effect on the Wheatstone bridge circuit zero.
Active Gauges

Terminal Pads

Compensation Gauges

Figure F2: Strain gauge locations for the half bridge tension circuit.
**Strain Gauge Application**

The application procedure involves surface preparation, aligning the strain gauge on the substrate surface, and heating the strain gauge and substrate to 175°C and applying a pressure of 45 psi (plus/minus 10 psi). This was quite challenging considering the surface curvature of the 5/8" diameter of the tube. The other challenge was the relatively small dimensions of the strain gauges themselves (.180" x .080"). It is important that thin and even gluelines result. This is critical considering the pressures the gauge will be experiencing.

The method used to apply the pressure during the 175°C heat curing cycle was a vacuum bagging technique used in the aerospace industry to set up composites. A .005" Mylar film, made to withstand the temperature and having good flexibility, is sealed with a high temperature putty. A breather wrap, which is a high loft textile, is first wrapped around the tube. The Mylar film is then wrapped around it and sealed with the putty. A copper tube is inserted through the putty and into the breather pad, and a vacuum is drawn. This assembly will keep sealed to temperatures of 200°C.

This only accounts for 15 psi of the 45 psi required. A magnifier is then required. A rubber pad of 1 mm thickness, and a proper resilience, is placed on the strain gauge. The rubber pad acts to squeeze the excess epoxy to the sides of the gauge during the cure cycle. Above it is placed a metal backup plate. If the backup plate is three times greater than the area of the rubber pad, the resulting pressure on the strain gauge will be 45 psi. What is important here is how the Mylar film drapes the pad/backup plate. If there is not sufficient Mylar film to conform to the profile of the rubber pad/backup plate then bridging will occur and a larger area than that of the backup plate will be pressurizing the rubber pad.

The procedures used closely followed the strain gauge manufacturers' recommendations. The following is a brief synopsis of the method used.

**Surface Preparation**

Surface preparation is important for good adhesion between substrate and epoxy. As well the flatness of the surface will influence glueline thickness which should be minimized. Finally, an even abrasion of the surface provides some mechanical linking between substrate and epoxy.

1. The surface was degreased with isopropyl alcohol.
2. The surface was then abraded with consecutively courser grits, finishing with 400 grit. Rinsing was done between abrasions.
3. The titanium surface was then given a mild acid etch. (4 ml HNO₃ + 2 ml HF + water to 100 ml)
4. A mild alkaline solution was used to neutralize the surface (ammonia/water mixture).
5. A thin layer of M-bond 610 adhesive was applied to the surface within 10 minutes of final abrasion. Only 10 minutes is given because the titanium oxidizes extremely quickly.

M-bond 610 is a two component, solvent thinned epoxy-phenolic adhesive available from Intertechnology. It is a low viscosity system, capable of gluelines < .0002". Long working life (up to 10 hours) are possible before curing.

**Application of Strain Gauge to Surface**

First, epoxy is applied to the back of the strain gauge, and allowed to dry. Drying takes about 15 minutes, depending on the temperature, and amount of epoxy applied.

Some means of aligning the gauge on the surface is employed. This is usually done by burnishing marks on

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1 Strain Gage installation Procedure for Transducers, Measurements Group, 1989  
M-Line Accessories. Instruction Bulletin B-130-13, Measurements Group 1979  
Strain Gages for Transducers, James Dorsey, Vishay Measurements Group 1978
the substrate. In this case a template was made, and the gauge aligned along its side. Alignment is not as critical if the load cell is subsequently calibrated. The difference in signal output will vary as the cosine of the misalignment angle. For example, a 5° misalignment will change the output signal by a factor of 0.9969.

One edge of the gauge is taped to fix the gauge into position. The tape, which is capable of withstanding the thermal cycle, is available from the strain gauge supplier.

**Heat Cycle**

A release layer, usually a strip of Teflon, is placed over the gauge. On top of this is placed a 1 mm rubber pad of the same area as the gauge. During the heat cycle, the epoxy liquifies before setting, and is squeezed out. Therefore placement of the rubber pad is critical. As well, the hardness of the rubber pad throughout the temperature range is important. RTV silicone rubber used for auto gaskets was used effectively (GE Black Auto Seal). The rubber pad was taped in place. On top of the rubber pad is place the metal backup plate, with an area three times that of the strain gauge. This increase the effective pressure of the vacuum from 15 to 45 psi.

The titanium tube was then wrapped with the breather cloth, followed by the Mylar film, and sealed with high temperature putty as described above. A vacuum is drawn and the assembly placed inside a furnace.

The thermal cycle involves a slowly heating to 175°C, at a rate between 3 - 13°C. If heating is too fast, the epoxy will form small bubbles throughout the adhesive layer. If the heat-up rate is too slow, the adhesive sets up before the excess can be squeezed out from under the strain gauge. The temperature is held at 175°C for 1 hour followed by furnace cooling.

A post cure cycle of 205°C - 230°C for two hours is made to relieve any residual stress in the gauge due to the adhesive cycle.

**Electrical Connections**

Electrical connections are made to the solder pads on the strain gauges, and routed to terminal pads. From the terminal pads the wires run to the electrical feedthroughs and exit the pressure vessel. The solder used is a high temperature solder \( T_m = 300 \) °C), which is necessary for the in service temperatures of 200 °C. (93% Pb - 5.2% Sn - 1.8% Ag)

The electrical connections with the electrical feedthrough were also soldered. Initially, attempts at soldering failed and silver soldering was employed. Silver soldering was also difficult but successful. the main problem with the solder is that it would not wet. This was due to two reasons. First, the thermocouple wires were compacted in MgO inside the stainless steel sheathing. Some MgO still remains after scraping the wires clean, and this hinders wetting. The other difficulty is the easy formation of a layer of oxide on the pool of solder which makes wetting impossible. A temperature controlled soldering iron set at just above the melting temperature reduces the rate of oxidation considerably. At the temperature that the solder melts (300°C), the oxide forms almost instantly. The technique used to overcome this was to simultaneously feed fluxed wire into the solder pool on the iron as the solder connection was made.
**Electrical Feedthrough**

Sending and receiving electrical signals to and from high pressure systems has posed a particular challenge in the development of high pressure studies. The main difficulty has been the mechanical properties of the insulation materials. Early efforts by P. W. Bridgman used a conical feedthrough made from lava rock, or pyrophyllite. This approach has changed, and the technique generally used is stainless steel swaged magnesia insulated thermocouple wire.

Joining the thermocouple wire to a component, usually a high pressure fitting, such as a plug, is the critical step. Any joint must be able to withstand the high pressures as well as the temperatures. An analysis of the forces shows that the yield strength of the joint is given by

\[ \tau = \frac{P}{4} \frac{D}{L} \]

where \( \tau \) is the shear strength of the joining material

- \( P \) is the pressure
- \( D \) is the diameter of the feedthrough

and \( L \) is the length of the joint

One can see that a low shear strength of the joining material can be overcome by either having a low diameter, a long joint length, or a combination of these.

Joining is done by silver brazing, soldering, or using epoxy. For elevated service temperatures, silver brazing must be used. However, one must be aware of the effect of silver brazing on the heat treated properties of the high pressure component one is brazing to. A review of electrical feedthroughs approaches is given in Table F2. A schematic of the feedthrough in position is shown in Figure F3.

The following lists the materials and technique used in this work.

**Thermocouple wire**

- Stainless steel swaged, MgO insulated
- 063-JJ-316
- Diameter: .0625"
- Type J thermocouple (Iron-Constantan (copper nickel alloy)
- 4 - wires
- Cladding: 316 stainless steel

**High pressure fitting**

- Standard high pressure (60,000 psi) plug
- Stainless steel 304

**Joint**

- Silver brazing
- Hole diameter: .067" (No. 51 drill)
- Hole clearance: .0045"
- Length of joint: 1"

Care must be exercised when making the connections. The excitation wires must be connected to the same type of thermocouple wire. The same is true for the measurement wires. If they are not, there is a chance that a voltage may be generated if the connections themselves are at different temperatures (Seebeck effect). By connecting the excitation wires to the same type of thermocouple wire, any Seebeck voltage generated on the input wire is cancelled by the opposite effect on the output wire. The same argument holds true for the measurement wires.
<table>
<thead>
<tr>
<th>Pressure</th>
<th>Temperature</th>
<th>Medium</th>
<th>Dia x length</th>
<th>Feedthrough Connector</th>
<th>Function</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>60,000 psi</td>
<td>300 °C</td>
<td>Oil</td>
<td>.062&quot; x 1.5&quot;</td>
<td>Threaded steel plug</td>
<td>Swaged magnesia insulated thermocouple wires</td>
<td>Ivan Simon (The Review of Scientific Instruments 28,963 (1957))</td>
</tr>
<tr>
<td>400,000 psi</td>
<td></td>
<td>liquid</td>
<td>.062&quot;</td>
<td>Piston, silver soldered</td>
<td>Special tool to strip TC wires</td>
<td>R H Cornish &amp; Arthur L Ruoff (The Review of Scientific Instruments 32, 639 (1969))</td>
</tr>
<tr>
<td>40,000 psi</td>
<td></td>
<td></td>
<td></td>
<td>Hole in wall</td>
<td>Silver soldering may weaken heat-treated high pressure fitting.</td>
<td>J L Downs and R T Payne (The Review of Scientific Instruments 40, 1278 (1968))</td>
</tr>
<tr>
<td>140,000 psi</td>
<td>120 °C</td>
<td>gas</td>
<td>.062&quot; x .5&quot;</td>
<td>Plug &amp; shrink fitted cylindrical piece with ( R_e = 53 )</td>
<td>Soft solder applied to boundary between shrink fit pieces</td>
<td>Duk Yoon (Rev Sci Instruments 37, 1611 (1966))</td>
</tr>
<tr>
<td>45,000 psi</td>
<td></td>
<td>fluid</td>
<td>.125&quot; x 2&quot;</td>
<td>Plug</td>
<td>Drying of MgO: 150 °C x 3 days</td>
<td>M Whitfield (Rev Sci Instruments 39, 1053 (1968))</td>
</tr>
<tr>
<td>60,000 psi</td>
<td>0-300°C</td>
<td>He</td>
<td>.040&quot;</td>
<td>Plug (O-ring seal)</td>
<td>Silver Solder (600°C)</td>
<td>J E Schirber &amp; D W Shafeldt (Rev Sci Instruments 39, 270 (1968))</td>
</tr>
<tr>
<td>105,000 psi</td>
<td></td>
<td>HP tube connection</td>
<td>.040 -.125 x 1&quot;</td>
<td>High frequency</td>
<td>Heat to 150°C</td>
<td>Heydemann (Rev Sci Instruments 38, 558 (1967))</td>
</tr>
<tr>
<td>300,000 psi</td>
<td></td>
<td>Bridgeman connector</td>
<td>.0625&quot; x 1.25&quot;</td>
<td>Radio Freq.</td>
<td>Silver soldered AlO(_3)</td>
<td>Peter L M Heydemann (Rev Sci Instruments 41, 1896 (1970))</td>
</tr>
<tr>
<td>600,000 psi</td>
<td>naphtha</td>
<td>.0625&quot; x .5&quot;</td>
<td>Steel spool on top of plug</td>
<td>Manganin wire pressure sensor</td>
<td>Sealed with epoxy</td>
<td>A. Lavergne &amp; E. Whalley (Rev Sci Instruments 49, 923 (Jul. 1978))</td>
</tr>
<tr>
<td>27 kbar</td>
<td>hydraul. fluid</td>
<td>.0625&quot; x .25&quot;</td>
<td>Collar soft soldered to upper surface of lower steel plug</td>
<td>Conductance cell</td>
<td>A. Lavergne &amp; E. Whalley (Rev Sci Instruments 57, 2791 (Nov 1986))</td>
<td></td>
</tr>
</tbody>
</table>
Figure F3: Section of the high pressure electrical feedthrough.
Balancing Circuit

The Wheatstone bridge circuit initially not balanced. The resistivities of the strain gauges rarely balance exactly. As well, the circuit becomes unbalanced during heating, pressurization or loading of the sample. Two solutions can be considered. First, the test can be run from a non-zero starting point and the data corrected later during conversion to stress and strain. There are obvious drawbacks to this approach. The second option is to balance the bridge prior to each test. This was the route taken.

The adjustment circuit that was developed is basically just an extension of the Wheatstone bridge principle. The design had to meet the following considerations.

1. The addition to the Wheatstone bridge circuit should draw only an insignificant amount of current.
2. Rebalancing should be able to adjust the voltage in either direction.
3. Any adjustment should ideally be sensitive and linear.

The basic circuit is shown in Figure F4. The balancing arm consists of a potentiometer set between two resistors. The third arm of the pot is connected to the midpoint of one of the bridge arms at point "a". The pot is adjustable, with the pot setting, x, varying between 0 and 1. An analysis was carried out to see how the magnitudes of the various resistances affected the circuit. The key here is to derive an equation which can separate the effect of the zeroing circuit from the Wheatstone bridge circuit.

Summing the currents at point A and point B we obtain:

\[ i_1 = -i_4 - i_4 \]
\[ \frac{E - E_A}{R_1} = -i_4 + \frac{E_A}{R_2} \]
\[ i_2 = i_1 + i_4 \]
\[ \frac{E - E_A}{R_Z - (1 - x) R_{POT}} = \frac{E_A}{x R_{POT} + R_Z} \]

Summing, we obtain

\[ (E - E_A) \left[ \frac{1}{R_1} + \frac{1}{R_Z - (1 - x) R_{POT}} \right] = E_A \left[ \frac{1}{R_2} - \frac{1}{R_Z + x R_{POT}} \right] \]

Rearranging, we obtain

\[ E \left[ \frac{1}{R_1} \right] \left[ 1 + \frac{R_1}{R_Z - (1 - x) R_{POT}} \right] = E_A \left[ \frac{R_1 R_2}{R_1 R_2} \right] \left[ 1 + \frac{2 R_Z - R_{POT}}{(R_Z - (1 - x) R_{POT}) (R_Z + x R_{POT})} \right] \frac{R_1 R_2}{R_1 - R_2} \]

A final rearrangement gives

\[ \frac{E_A}{E} = \frac{R_1}{R_1 + R_2} \left[ \frac{1 + \frac{R_1}{R_Z + (1 - x) R_{POT}}}{1 + \frac{R_1}{R_Z - (1 - x) R_{POT}} \frac{2 R_Z - R_{POT}}{(2 R_Z - R_{POT}) \frac{R_2}{R_1 + R_2} \frac{R_2}{R_1 + R_2}} \right] \]
Figure F4: Balancing circuit for Wheatstone bridge.
The form of this equation is

\[
\frac{E_A}{E} = \frac{R_1}{R_1 + R_2} \left[ \frac{1 + A}{1 + AB} \right]
\]

One can see that the equation is the same as that for the Wheatstone bridge with the adjustment factor \((1+A)/(1+AB)\).

The effect of adjusting the potentiometer setting for various value of \(R_Z\) and \(R_{POT}\), keeping in mind that the adjustment circuit should draw very little current. Figure F5 shows the effect of pot setting on the adjustment factor for the following cases.

1. \(R_Z = 222 \, R_1\), \(R_{POT} = 555 \, R_1\)
2. \(R_Z = 222 \, R_1\), \(R_{POT} = 11 \, R_1\)

The values of \(R_Z\) and \(R_{POT}\) selected are much higher than the strain gauge resistances, \(R_1\), in order to minimize the current draw from the Wheatstone bridge circuit. As can be seen, when \(R_Z = R_{POT}\), the response is close to linear over the whole range of pot settings. Greater values of \(R_Z\) and \(R_{POT}\) decrease the slope.

The actual balancing circuit utilizes two balancing arms, one for coarse adjustment and one for fine adjustment. The actual resistivities used are the same as those used in Figure 5.
Figure F5: The effect of pot position on the adjustment factor for a Wheatstone bridge circuit.

\[ R_Z = 222 \, R_1 \]
\[ R_{POT} = 555 \, R_1 \]
Figure F6. Load cell circuit incorporating two balancing arms with the Wheatstone bridge circuit.
Noise

The measured signal from the load cell is in the millivolt range. The external environment of electrical and/or magnetic fields can superimpose their own signatures on the measured signal. These signatures, or noise, can be reduced to tolerable levels by suitable practices. The specific noise pickup points in the load cell circuitry are:

1. Excitation voltage generator
2. Leadwires, both excitation and measurement
3. Strain gauges
4. Instrumentation (balancing arm, signal amplification, and A/D conversion)

There are two types of noise sources: electrostatic and magnetic fields. Electrostatic fields are generated in the presence of voltage without current flow, as well as with current flow. In both cases, the voltage induces a build-up of charge on elements surrounding the strain gauge circuitry, which in turn may cause a build-up of charge of opposite sign in the strain gauge components (capacitative coupling). This build-up of charge is associated with a voltage bias which is superimposed on the measurement signal. Common examples of high voltage sources which create electrostatic fields include CRT’s and fluorescent lights. As well, static build-up can occur in the instrumentation housings if they are non-conductive or not properly grounded.

Electrostatic noise is reduced by surrounding the electrical component, e.g. leadwires or instrument housing, with a conductive shield which is grounded. The shield acts to remove the charge buildup to ground before it can build-up. If the shield is not grounded, the charge builds up in the shield, which in turn induces a charge in the leadwires.

Magnetic fields are caused by either current flow or permanent magnets. If a conductor moves through a magnetic field, either by physically moving itself or in the presence of a changing magnetic field, then a voltage develops in the conductor (as well as a current). AC motors, generators and transformers are examples of magnetic fields. Also important is an AC power line which the signal wire may pass by.

Magnetically-induced noise is very difficult to shield. Instead, the approach taken is to minimize the effect of the induced voltage by

1. Removing the current carrying source as far away as possible.
2. Inducing the same voltage in both the input and output signal wire. This is done by twisting the signal wires together so that both wires are close to equal distances from the noise source. Another way of stating this is to minimize the amount of area between the two signal conductors. As well, the signal wires should be twisted separately from any other wiring (excitation wire or another signal wire pair).
3. If the signal is amplified, a linear differential amplifier with good common-mode rejection will amplify only the difference between the two wires. The noise should largely cancel out.

Line noise (115 V) can affect the A/D and amplification functions. As well, the instrumentation itself can contribute significantly to the noise, and its rejection, depending on its quality.

Checks can be made for the contributions to noise from the various components.
1. Instrumentation can be checked by removing strain gauge and leadwires, inserting an equivalent resistance, and measuring the resulting signal.
2. Noise pick-up in the leadwires and gauge can be checked by turning the excitation voltage off, and measuring the resulting signal. Differences between this and the measurement of the instrumentation alone will indicate this noise contribution.
3. Turn surrounding machinery and lights on and off and watch for any effect on measuring signal.
Specifically, the following practices were used with each of the components in the load cell circuit:

1. Excitation Voltage Generator: An AC driven DC voltage source always contains some AC component after rectification. A sol-gel battery was used, which eliminated these problems.
2. Leadwires: The leadwires were twisted (reducing the effect of magnetically-induced voltages), and shielded with aluminum foil wrap (reducing electrostatic field effects). The shielding was grounded.
3. Strain Gauges: Capacitive coupling can occur if the substrate develops charge. The pressure vessel and the Instron frame were grounded to the same ground as the leadwire shielding to avoid ground loops. (Grounds are not necessarily at the same potential. Grounding at the same source eliminates this problem).
4. Instrumentation: Housings are conductive and grounded.

**Calibration**

The load cell was calibrated in two steps; first at ambient temperature and pressure, and the second at elevated pressures.

Calibration at ambient temperature and pressure was done by suspending calibration weights from the load cell. Load cell response was linear, showed no hysteresis, and was reproducible from test to test.

Calibration at elevated pressures posed a challenge. Suspension of weights was complicated for two reasons. The internal diameter of the pressure vessel is only 1.5", and only light weights could be introduced into the vessel. More importantly, the density effects from the hydraulic oil would have to be accounted for. Since oil density changes with pressure, a density calibration for various pressures would first have to be carried out. Calibration under these circumstances would not have given the accuracy desired.

The technique used to calibrate the load cell at elevated pressure used a helical steel spring. The effect of pressure on the modulus of the steel was assumed to be negligible since the modulus is 500 times greater than the maximum pressure. The spring was given a precise displacement of 1" and the load measured. This procedure was repeated from ambient pressure to 55,000 psi at 5,000 psi intervals. The load difference in all cases was the same.

What was also noticed was that the pressure itself changed the 'no load' starting point of the test. This was determined to be due to the compression of the laminate backing on the gauge. Grid sections which are oriented transversely to the tube axis are susceptible, since they are at a radius of curvature of 5/16". Under pressure, as the backing compresses, the radius of curvature of the grid section becomes smaller, and the gauge registers a compressive strain. Calculations showed that the amount of compression necessary to make this strain contribution at 55,000 psi was only 60 microns.

The opportunity to determine if this was true came when overheating of the pressure vessel destroyed the load cell. Instead of using transversely mounted strain gauges mounted on the arms opposite the longitudinal gauges, another set of longitudinal gauges were mounted on a 5/8" diameter flange added to the load cell (the same diameter as the active gauges). This flange carried no load, and so these gauges functioned as compensation gauges. There was a penalty of a factor of \( v \), the Poisson's ratio, in the output. The load cell was calibrated in the same manner as before and showed very little pressure effect on the 'no load' signal.

The response of the polymer backing to the pressure is viscoelastic in nature. The change is rapid at first, and approaches a stable value after 10 minutes. To accommodate this effect, the load cell and sample were "conditioned" for 45 minutes prior to initiation of the tensile test.
Appendix G

Computer Programs

Data Acquisition

The following data acquisition program was written to not only record the data, but to graph it in real-time. Since the tensile test is inside the vessel, there is no visual indication of what is happening to the sample, such as fracture or slippage in the grips. The real-time graphing gives an indication of these events and others.

The equipment used for data acquisition was an IBM compatible PC, a data acquisition board, and a multiplexer/amplifier board. Both the data acquisition board and the multiplexer/amplifier boards were manufactured by Metabyte, with the following general descriptions.

DAS-8 An 8 channel, high speed A/D converter and timer counter interface

The DAS-8 takes an analogue voltage input between -5V to +5V, and assigns it an integer between 0 and 4095 (0 being -5V and 4095 being +5V), and saves it. There are also timers which allow the time of each data acquisition to also be recorded.

EXP-16 Expansion multiplexer/amplifier system

The expansion board allows 16 separate inputs to be made to each of the 8 channels on the DAS-8. It does this by multiplexing the signal sent to the DAS-8 board. As well, all of the inputs can be amplified by a user selectable dip switch on the EXP board. Amplifying factors between 0.5 to 1000 are available. Finally, the EXP board also had a cold junction to allow thermocouple measurements to be referenced.

The DAS-8 board plugs into one of the expansion slots in an IBM compatible. The EXP-16 has a cable connection between it and the DAS-8 board. The DAS-8 and EXP-16 come with driver programs written in assembler. The drivers can be accessed by BASIC programming commands through CALL functions.

The program is documented and explains itself for the most part. Most importantly, it works.

The raw data collected (force and time) from this program is then converted to stress and strain. The conversion program is listed, starting on page G16.
This program performs scanning and measurement of input signal voltages connected to one EXP-16.

Steps are:
1. Dimension other arrays and provide set up information
2. Initialize DAS-8
3. Measure temperature of connector block from CJC channel
   (CJC = cold junction compensation)
4. Set up graph
5. Set up loop to
   1) measure input voltages on EXP-16
   2) average (user determined)
   3) save data point
   4) convert to deg C, lbs, MPa, mV etc.
   5) display output in real time on graph
6. Option to SAVE DATA in a sequential (ASCII) file.

CONNECTIONS
----------
Thermocouple/transducers: 1) should be attached to the HI & LO's of selected channel on the EXP-16 board.
2) LO should also be connected to L.L. GND. on each channel

Set the EXP-16 OUTPUT CHANNEL jumper block to channel 0 (Pin Connector J4).
Set the EXP-16 CJC CHANNEL jumper block to channel 7 (Pin Connector J3).

PRELIMINARY SOFTWARE SET-UP
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Before this program can run the driver must first be loaded.
(The driver is the program DAS8.) This is done by loading the driver library as the QuickBASIC program is called.
Specifically, type the following (when in the QB directory):
...
QB> "qb/1 das8 nameofprogram".
DOS may then ask location of the DAS8.QLB.
Respond by inputing pathname: e.g. \PROGRAMS\DATAQ\DAS8\DAS8.QLB

When using a HERCULES Hi-Res Monographic display, BASIC graphics commands are enabled by:
1. Using the DOS level command "MSHERC" BEFORE!!! entering the QB environment.
2. Declaring "SCREEN 3" in QuickBASIC.
'DIMENSION ARRAYS, DECLARE SUBPROGRAMS

DIM SHARED ChSignalType$(15)
DIM t(15), k(15), j(15)
DIM d%(15), LT%(15), ylast(15), ymax(15), plot$(15), label$(15), ChLast(15), Ch(15)
COMMON SHARED d%((), LT%(()) 'Initialize an integer array D%(15) to receive data
DECLARE SUB DAS8 (MODE%, ByVal dummy%, flag%)
DECLARE SUB GRAPHSETUP ()
DECLARE SUB DATACONVERSION ()
DECLARE SUB LOADTABLE ()

KEY OFF
SCREEN 3: cls

'LOAD THERMOCOUPLE LOOKUP TABLES

The interpolation method of determining temperatures is used instead of
a fifth order polynomial because it is over 3 times faster.

PRINT "Loading lookup tables."
GOTO LOOKUPTABLE

LOOKUPTABLEREAD:
CLS

'INITIALIZE VARIABLES

SIGNALTYPE:

CLS
LOCATE 1, 1: INPUT "Low Channel selected ", LoCh
LOCATE 2, 1: INPUT "High Channel selected ", HiCh
NumCh = HiCh - LoCh + 1
LOCATE 3, 1: PRINT "Indicate type of signal on each Channel"
LOCATE 4, 1: PRINT " For millivolts, type 'mV'"
LOCATE 5, 1: PRINT " For lbs, type 'lbs'"
LOCATE 6, 1: PRINT " For Newtons, type 'N'"
LOCATE 7, 1: PRINT " For j-type thermocouple, type 'j'"
LOCATE 8, 1: PRINT " For t-type thermocouple, type 't'"
LOCATE 9, 1: PRINT " For k-type thermocouple, type 'k'"

FOR i = LoCh TO HiCh
  LOCATE i - LoCh + 11, 1: PRINT USING "Channel ## - "; i:
  LOCATE i - LoCh + 11, 15: INPUT ", ChSignalType$(i)
  LOCATE i - LoCh + 11, 25: INPUT ; "Plot this channel? ", plot$(i)
  SELECT CASE ChSignalType$(i)
    CASE "k": label$(i) = "deg C"
    CASE "j": label$(i) = "deg C"
    CASE "t": label$(i) = "deg C"
    CASE ELSE: label$(i) = ChSignalType$(i)
END SELECT
NEXT i

LOCATE 12 + NumCh, 1: INPUT "Gain? ", gain
LOCATE 13 + NumCh, 1: INPUT "Ave? ", ave
LOCATE 14 + NumCh, 1: INPUT "Excitation voltage? ", Vexcitation

LOCATE 24, 1: INPUT "Are the settings correct? ", ans$
IF LCASE$(ans$) = "n" THEN GOTO SIGNALTYPE

'************************************************************
'INITIALIZE THE das8 - MODE 0

md% = 0: BASADR% = &H300: flag% = 0
CALL DAS8(md%, VARPTR(BASADR%), flag%)
IF flag% <> 0 THEN PRINT "INSTALLATION ERROR"

'************************************************************
'GET COLD JUNCTION COMPENSATION TEMPERATURE

' Ch #7 must be selected (jumped) on Pin Connector J3 on EXP board.
' Mode 1 locks the das8 (via LT%(0) & LT%(1)) to the same Channel #7.
' Output of CJC channel is scaled at 24.4mV/deg.C. (also 10V/2^12 = 2.44 mV)
' This corresponds to 0.1 deg.C./bit. Dividing output in bits by 10 = deg C.

md% = 1: LT%(0) = 7: LT%(1) = 7
CALL DAS8(md%, VARPTR(LT%(0)), flag%)
IF flag% <> 0 THEN PRINT "ERROR IN SETTING CJC CHANNEL" END

md% = 4: CJ% = 0
SumRmTemp = 0
FOR i = 1 TO 10
   CALL DAS8(md%, VARPTR(CJ%), flag%)
   Transfer data to D%(Chan%) 
   SumRmTemp = SumRmTemp + CJ% / 10 'Change output in bits to real temp
NEXT i
RmTemp = SumRmTemp / 10

'************************************************************
'SETUP GRAPH

PRINT
INPUT "Input minimum y-value to be plotted": miny
INPUT "Input maximum y-value to be plotted": maxy
maxx = 1000: minx = 0
xlabel$ = "points": ylabel$ = label$(0)

'************************************************************
'REAL-TIME GRAPHING
'PRE-LOOP STEPS
' 1. Open a file to accept data ("datadump.dat")
' 2. Set up graph (via a subroutine)
' 3. Lock DAS8 to Ch 0 (EXP board connected (via jumpers) to Ch 0 of DAS8)
' 4. Take time reading, and compensate for time to redraw graph

OPEN "datadump.dat" FOR RANDOM AS #1 LEN = 4

SLEEP 1
NumIter = 0 'NumIter counts total number of iterations
NumPts = 0 'NumPts is the total number of data points

REPEATGRAPHSETUP:
    timeingraphsetup = TIMER
    CALL GRAPHS

    md% = 1: LT%(0) = 0: LT%(1) = 0
    CALL DAS8(md%, VARPTR(LT%(0)), flag%)

    j% = 0 'j% is the incremental counter for x axis
    IF NumPts = 0 THEN timein = TIMER
    timegraphsetup = TIMER - timeingraphsetup

'**********************************************
'MAIN LOOP STEPS
' 1. Set EXP channel (mode 14)
' 2. Take a predetermined # of readings, average, and put in datafile
' 3. Convert averaged bit reading to a value, and add to graph
' 4. Check for: i) end of x-axis; ii) end of test
' 5. Repeat steps 1-4, incrementing EXP channel

REPEATSCAN:
    j% = j% + 1
    IF j% >= maxx THEN CLS 1: GOTO REPEATGRAPHSETUP
    NumIter = NumIter + 1

    FOR Chan% = LoCh TO HiCh
        NumPts = NumPts + 1
        md% = 14: CALL DAS8(md%, VARPTR(Chan%), flag%)
        md% = 4

        SELECT CASE plot$(Chan%)
            CASE "y":
                sumd = 0:
                FOR i = 1 TO ave:
                    CALL DAS8(md%, VARPTR(d%(Chan%)), flag%):
                    sumd = d%(Chan%) + sumd:
                NEXT i:
                x = sumd / ave!
                CALL DATAconversion: 'takes x, returns y
                IF NumIter = 1 THEN ylast(Chan%) = y
                LINE (j% - 1, ylast(Chan%)) - (j%, y):
                ylast(Chan%) = y:
CASE "n": CALL DAS8(md%, VARPTR(d%(Chan%)), flag%): 'Do 1 A-D
  x = d%(Chan%):
  CALL DATACONVERSION:

END SELECT

PUT #1, NumPts, x                  'Save in "datadump.dat
IF Chan% - LoCh < 6 THEN LOCATE 20 + Chan% - LoCh, 8 ELSE LOCATE 20 +
Chan% - LoCh, 6, 31
PRINT USING "#####.##"; y;
IF INKEYS <> "" THEN timeout = TIMER: GOTO FINISHED

NEXT Chan%

LOCATE 21, 64: PRINT USING "#####.##"; (TIMER - timein)

md% = 1; LT%(0) = 7: LT%(1) = 7 'Lock DAS8 board to channel 7
CALL DAS8(md%, VARPTR(LT%(0)), flag%)
IF flag% <> 0 THEN PRINT "ERROR IN SETTING CJC CHANNEL": END

md% = 4: CJ% = 0                  'Perform 1 A/D conversion
SumRmTemp = 0
FOR i = 1 TO 10
  CALL DAS8(md%, VARPTR(CJ%), flag%): 'Transfer data to D%(Chan%)
  SumRmTemp = SumRmTemp + CJ% / 10 'Change output in bits to real temp
NEXT i
RmTemp = SumRmTemp / 10
LOCATE 20, 46: PRINT USING "Cold junction temp = ##.## deg C"; RmTemp

md% = 1: LT%(0) = 0: LT%(1) = 0
CALL DAS8(md%, VARPTR(LT%(0)), flag%)

GOTO REPEATSCAN

FINISHED:
  CLOSE #1
  VIEW
  duration = timeout - timein

LOCATE 21, 46: PRINT USING "Time to execute is = ####.## sec "; duration
LOCATE 22, 46: PRINT USING "Averaging = ### "; ave;
LOCATE 23, 46:
PRINT USING "Acquisition Rate = ###.## iter./sec"; NumIter / duration;

***************************************************************************
***************************************************************************
'DATA DISPLAY

LOCATE 25, 46: INPUT "Display data? ", ans$
CLS
SELECT CASE LCASE$(ans$)
      CASE "y"
        LOCATE 25, 1: PRINT "Press any key to stop"
        OPEN "datadump.dat" FOR RANDOM AS #1 LEN = 4

        FOR i = LoCh TO HiCh
            IF i - LoCh < 7 THEN LOCATE 2, 27 + 8 * (i - LoCh): PRINT USING "Ch ": i
            IF i = LoCh THEN LOCATE 3, 1: PRINT "seconds bits mV"
            IF i - LoCh < 7 THEN LOCATE 3, 27 + 8 * (i - LoCh): PRINT

        NEXT i

        PRINT : VIEW PRINT 4 TO 23
        j% = 0
        FOR i = 1 TO (NumIter - 1)
            PRINT
            PRINT USING "####.## "; (duration / NumIter) * i;

            FOR Chan% = LoCh TO HiCh
                j% = j% + 1
                GET #1, j%, x
                IF Chan% = LoCh THEN PRINT USING "####.## "; x; x *
                (5 / 2048) * 1000 / gain;
                CALL DATACONVERSION
                IF Chan% - LoCh < 7 THEN PRINT USING "####.## "; y;

            NEXT Chan%

            IF INKEY$ <> "" THEN GOTO OUTAHERE 'Check for exit key
        NEXT i

      CASE "n"
      END SELECT

OUTAHERE:
      CLOSE #1
      VIEW PRINT 'Clear scrolling text viewport

'SAVE DATA
      LOCATE 25, 1: PRINT SPACES$(40)
      LOCATE 25, 1: INPUT "Save data? ", ans$
      VIEW: CLS

      SELECT CASE LCASE$(ans$)
      CASE "y"
        INPUT "Name of datafile [filename.DAT]; ", filename$

        OPEN filename$ FOR OUTPUT AS #1
        OPEN "datadump.dat" FOR RANDOM AS #2 LEN = 4

        FOR i = LoCh TO HiCh
IF i - LoCh < 9 THEN LOCATE 2, 12 + 8 * (i - LoCh): PRINT USING "Ch "; i

IF i = LoCh THEN LOCATE 3, 1: PRINT "seconds 
IF i - LoCh < 9 THEN LOCATE 3, 12 + 8 * (i - LoCh): PRINT label$(i)

NEXT i

PRINT: VIEW PRINT 4 TO 23
j% = 0
timeperiter = (duration - INT(NumIter / maxx) * timegraphsetup) / NumIter

FOR i = 1 TO (NumIter - 1)
time = i * timeperiter + INT(i / maxx) * timegraphsetup
PRINT
PRINT USING "####.##"; time;
PRINT #1, time;
FOR Chan% = LoCh TO HiCh
  j% = j% + 1
  GET #2, j%, x
  CALL DATACONVERSION
  PRINT #1, y;
  IF Chan% - LoCh < 9 THEN PRINT USING "####.##"; y;
NEXT Chan%
PRINT #1,
NEXT i

CASE "n": GOTO DOANOTHER

END SELECT
CLOSE #1: CLOSE #2
VIEW PRINT

'Clear scrolling text viewport

***************************************************************************/

'DISPLAY CONVERTED DATA

LOCATE 25, 1: PRINT SPACE$(40)
LOCATE 25, 1: INPUT "Display converted data? ", ans$
CLS
SELECT CASE LCASES(ans$)
CASE "y"
OPEN filename$ FOR INPUT AS #1

FOR i = LoCh TO HiCh
  IF i - LoCh < 9 THEN LOCATE 2, 12 + 8 * (i - LoCh): PRINT USING "Ch "; i
  IF i = LoCh THEN LOCATE 3, 1: PRINT "seconds 
  IF i - LoCh < 9 THEN LOCATE 3, 12 + 8 * (i - LoCh): PRINT label$(i)

NEXT i
PRINT: VIEW PRINT 4 TO 23

FOR i = 1 TO (NumIter - 1)
  PRINT
  FOR Chan% = LoCh TO HiCh + 1
    INPUT #1, x
    IF Chan% - LoCh < 10 THEN PRINT USING "####.##"; x;
  NEXT Chan%
NEXT i

CASE "n"
END SELECT

CLOSE #1
VIEW PRINT

'Clear scrolling viewport

'GRAPH

LOCATE 25, 1: PRINT SPACES(40)
LOCATE 25, 1: INPUT "Graph data? ", ans$
SELECT CASE LCASE$(ans$)
  CASE "y"
    OPEN filename$ FOR INPUT AS #1
    CLS
    INPUT "Input minimum y-value to be plotted": miny
    INPUT "Input maximum y-value to be plotted": maxy
    maxx = duration: minx = 0
    graphminx = 0: graphmaxx = duration
    xlabel$ = "sec": ylabel$ = labelS(0)
    CALL GRAPHSETUP
    INPUT #1, seclast
    PSET (0, 0)
    FOR Chan% = LoCh TO HiCh
      INPUT #1, ChLast(Chan%)
    NEXT Chan%
    FOR i = 2 TO (NumIter - 1)
      INPUT #1, sec
      FOR Chan% = LoCh TO HiCh
        INPUT #1, Ch(Chan%)
        LINE (seclast, ChLast(Chan%))-(sec, Ch(Chan%))
        ChLast(Chan%) = Ch(Chan%)
      NEXT Chan%
      seclast = sec
    NEXT i
  CASE "n"
END SELECT
CLOSE #1
DO ANOTHER:
   LOCATE 25, 1: PRINT SPACES(40);
   LOCATE 25, 1: INPUT "Do another data acquisition? ", ans$
   VIEW
   IF LCASE$(ans$) = "y" THEN GOTO LOOKUPTABLE READ
GOTO FINITO

********************************************************************

LOOKUPTABLE:
'-------- Table lookup data for K type thermocouple ***************
'Run this subroutine only in the initialization section of your program
'Number of points, voltage step interval (mV), starting voltage (mV)

DATA 309 , .2 , -6.6
READ nk, sik, svk
'Temperature at -6.6mV, -6.4mV, -6.2mV etc.
DATA -353.5,-249.3,-224.0,-207.6,-194.3,-182.8,-172.3,-162.8,-153.8,-145.4
DATA -373.3,-329.6,-286.0,-242.4,-208.8,-175.3,-143.9,-114.6,-95.3,-76.0
DATA -70.4,-64.6,-58.8,-53.1,-47.5,-42.0,-36.6,-31.2,-25.9,-20.6
DATA -15.4,-10.2,-5.1,  0.0,  5.0, 10.1, 15.1, 20.0, 25.0, 29.9
DATA  34.8,  39.7,  44.6,  49.5,  54.3,  59.1,  64.0,  68.8,  73.6,  78.4
DATA  83.2,  88.0,  92.9,  97.7, 102.5, 107.4, 112.2, 117.1, 122.0, 126.9
DATA 131.8, 136.7, 141.7, 146.6, 151.6, 156.5, 161.5, 166.5, 171.5, 176.5
DATA 181.6, 186.6, 191.6, 196.6, 201.6, 206.6, 211.6, 216.6, 221.5, 226.5
DATA 231.5, 236.4, 241.4, 246.3, 251.2, 256.1, 261.0, 265.9, 270.8, 275.6
DATA 280.5, 285.3, 290.2, 295.0, 299.8, 304.6, 309.4, 314.3, 319.1, 323.9
DATA 328.7, 333.4, 338.2, 343.0, 347.8, 352.6, 357.3, 362.1, 366.9, 371.6
DATA 376.4, 381.1, 385.9, 390.6, 395.4, 400.1, 404.8, 409.6, 414.3, 419.0
DATA 423.8, 428.5, 433.2, 437.9, 442.6, 447.3, 452.0, 456.8, 461.5, 466.2
DATA 470.9, 475.6, 480.3, 485.0, 489.7, 494.4, 499.1, 503.8, 508.5, 513.1
DATA 517.8, 522.5, 527.2, 531.9, 536.6, 541.3, 546.0, 550.7, 555.4, 560.0
DATA 564.7, 569.4, 574.1, 578.8, 583.5, 588.2, 592.9, 597.6, 602.3, 607.0
DATA 611.7, 616.4, 621.2, 625.9, 630.6, 635.3, 640.0, 644.8, 649.5, 654.2
DATA 658.9, 663.6, 668.4, 673.2, 677.9, 682.7, 687.4, 692.2, 696.9, 701.7
DATA 706.5, 711.3, 716.1, 720.8, 725.6, 730.4, 735.2, 740.0, 744.8, 749.7
DATA 754.5, 759.3, 764.1, 769.0, 773.8, 778.7, 783.5, 788.4, 793.3, 798.1
DATA 803.0, 807.9, 812.8, 817.7, 822.6, 827.5, 832.4, 837.3, 842.2, 847.2
DATA 852.1, 857.1, 862.0, 867.0, 872.0, 876.9, 881.9, 886.9, 891.9, 896.9
DATA 901.9, 906.9, 911.9, 916.9, 922.0, 927.0, 932.0, 937.1, 942.2, 947.2
DATA 952.3, 957.4, 962.5, 967.6, 972.7, 977.8, 982.9, 988.0, 993.1, 998.2
DATA 1003.4,1008.5,1013.7,1018.9,1024.0,1029.2,1034.4,1039.6,1044.8,1050.0
DATA 1055.2,1060.4,1065.6,1070.8,1076.1,1081.3,1086.6,1091.9,1097.2,1102.4
DATA 1107.7,1113.0,1118.3,1123.7,1129.0,1134.3,1139.7,1145.0,1150.4,1155.8
DATA 1161.2,1166.6,1172.0,1177.4,1182.9,1188.3,1193.8,1199.2,1204.7,1210.2
DATA 1215.7,1221.2,1226.8,1232.3,1237.9,1243.5,1249.1,1254.7,1260.3,1265.9
DATA 1271.6,1277.3,1282.9,1288.6,1294.3,1300.1,1305.8,1311.5,1317.3,1323.1
DATA 1328.9,1334.7,1340.5,1346.4,1352.2,1358.1,1363.9,1369.8,1375.7

DIM tk(nk - 1)
FOR i = 0 TO nk - 1
   READ tk(i)
NEXT i
Run this subroutine only in the initialization section of your program.

Number of points, voltage step interval (mV), starting voltage (mV)

```plaintext
DATA 257, .2, -8.2
READ nj, si, svj
```

Temperature at -8.2mV, -8.0mV, -7.8mV etc.

```plaintext
DATA -215.0, -205.3, -196.1, -187.7, -179.9, -172.8, -165.9, -159.3, -153.1, -147.1
DATA -141.2, -135.6, -130.0, -124.6, -119.3, -114.2, -109.1, -104.2, -99.2, -94.4
DATA -89.7, -85.0, -80.3, -75.8, -71.3, -66.8, -62.4, -58.0, -53.7, -49.3
DATA -4.0, -0.0, 3.9, 7.9, 11.8, 15.7, 19.6, 23.5, 27.4, 31.2
DATA 35.1, 38.9, 42.7, 46.5, 50.3, 54.1, 57.8, 61.6, 65.3, 69.1
DATA 72.8, 76.5, 80.3, 84.0, 87.7, 91.4, 95.1, 98.7, 102.4, 106.1
DATA 109.8, 113.4, 117.1, 120.7, 124.4, 128.0, 131.7, 135.3, 139.0, 142.6
DATA 146.2, 149.9, 153.5, 157.1, 160.7, 164.3, 168.0, 171.6, 175.2, 178.8
DATA 182.4, 186.0, 189.6, 193.2, 196.8, 200.4, 204.0, 207.6, 211.2, 214.8
DATA 218.4, 222.0, 225.6, 229.2, 232.8, 236.4, 240.0, 243.6, 247.2, 250.8
DATA 254.5, 258.1, 261.7, 265.3, 268.9, 272.5, 276.1, 279.7, 283.3, 286.9
DATA 290.5, 294.1, 297.7, 301.4, 305.0, 308.6, 312.2, 315.8, 319.4, 323.0
DATA 326.7, 330.3, 333.9, 337.5, 341.1, 344.8, 348.4, 352.0, 355.6, 359.3
DATA 362.9, 366.5, 370.1, 373.8, 377.4, 381.0, 384.7, 388.3, 391.9, 395.5
DATA 399.2, 402.8, 406.4, 410.1, 413.7, 417.3, 420.9, 424.5, 428.2, 431.8
DATA 435.4, 439.0, 442.6, 446.3, 449.9, 453.5, 457.1, 460.7, 464.3, 467.9
DATA 471.5, 475.1, 478.7, 482.3, 485.9, 489.5, 493.1, 496.6, 500.2, 503.8
DATA 507.3, 510.9, 514.5, 518.0, 521.6, 525.2, 528.7, 532.2, 535.7, 539.3
DATA 542.8, 546.3, 549.8, 553.3, 556.8, 560.3, 563.8, 567.3, 570.8, 574.2
DATA 577.7, 581.2, 584.6, 588.1, 591.5, 594.9, 598.4, 601.8, 605.2, 608.6
DATA 612.0, 615.4, 618.8, 622.1, 625.5, 628.9, 632.2, 635.6, 638.9, 642.3
DATA 645.6, 648.9, 652.2, 655.5, 658.8, 662.1, 665.4, 668.7, 672.0, 675.2
DATA 678.5, 681.7, 685.0, 688.2, 691.5, 694.7, 697.9, 701.1, 704.3, 707.5
DATA 710.7, 713.9, 717.1, 720.3, 723.5, 726.6, 729.8, 733.0, 736.1, 739.3
DATA 742.4, 745.6, 748.7, 751.8, 755.0, 758.1, 761.2
```

```plaintext
DIM tj(nj - 1)
FOR i = 0 TO nj - 1
    READ tj(i)
NEXT i
```

Run this subroutine only in the initialization section of your program.

Number of points, voltage step interval (mV), starting voltage (mV)

```plaintext
DATA 138, .2, -6.4
READ nt, sit, svj
```

Temperature at -6.4mV, -6.2mV, -6.0mV etc.

```plaintext
DATA -324.6, -253.7, -229.4, -213.5, -199.8, -187.8, -176.8, -166.6, -157.0, -147.9
DATA -139.2, -131.0, -123.0, -115.4, -108.0, -100.8, -93.8, -87.0, -80.4, -74.0
DATA -67.7, -61.5, -55.4, -49.4, -43.6, -37.9, -32.2, -26.7, -21.2, -15.8
DATA -10.5, -5.2, -0.0, 5.1, 10.2, 15.3, 20.3, 25.2, 30.1, 34.9
DATA 39.7, 44.5, 49.2, 53.8, 58.4, 63.0, 67.6, 72.0, 76.5, 80.9
DATA 85.3, 89.7, 94.0, 98.3, 102.6, 106.8, 111.1, 115.3, 119.4, 123.6
DATA 127.7, 131.8, 135.9, 139.9, 143.9, 148.0, 151.9, 155.9, 159.9, 163.8
```
DATA 167.7, 171.6, 175.5, 179.3, 183.2, 187.0, 190.8, 194.6, 198.4, 202.1
DATA 205.9, 209.6, 213.3, 217.0, 219.5, 223.2, 226.9, 230.6, 234.3, 238.1
DATA 241.8, 245.5, 249.2, 252.9, 256.6, 260.3, 264.0, 267.7, 271.4, 275.1
DATA 278.1, 281.6, 285.1, 288.6, 292.1, 295.5, 299.0, 302.4, 305.8, 309.3
DATA 312.7, 316.1, 319.5, 322.9, 326.3, 329.6, 333.0, 336.4, 339.7, 343.1
DATA 346.4, 349.7, 353.0, 356.4, 359.7, 363.0, 366.3, 369.6, 372.8, 376.1
DATA 379.4, 382.6, 385.9, 389.2, 392.4, 395.6, 398.9, 402.1

DIM tt(nt - 1)
FOR i = 0 TO nt - 1: READ tt(i): NEXT i
GOTO LOOKUPTABLEREAD

FINITO:
END

******************************************************************************

SUB DATACONVERSION
******************************************************************************
'This routine takes in a value of x and returns a value for y

SELECT CASE ChSignalType$(Chan%)
CASE "bits": y = x
CASE "mV": y = mV
CASE "lbs": y = (mV / Vexcitation) * (1 / .00287) '.00287 is calibration constant in mV/(V.lbs)
CASE "N": y = (mV / Vexcitation) * (1 / .002997) * 4.448 'N/lb
CASE "j" 'Normalize mV output to 0 deg C
' 1.277 mV @ 25 C (0 C = 0 mV) t-type
' .05155=slope in mV/deg C @ 25 C
vj = mV + 1.277 + (RmTemp - 25) * .05155
'Convert mV output (0 C ref) to temperature using tables
ej = INT((vj - svj) / si)
IF ej < 0 THEN y = -999: GOTO SKIPREST 'Round to lower limit
IF ej > nj - 2 THEN y = 999: GOTO SKIPREST 'Round to upper limit
y = tj(ej) + (tj(ej + 1) - tj(ej)) * (vj - ej * sij - svj) / sij
CASE "t" 'Normalize mV output to 0 deg C
'.992 mV @ 25 C (0 C = 0 mV) t-type
'.040667=slope in mV/deg C @ 25 C
vt = mV + .992 + (RmTemp - 25) * .040667
'Convert mV output (0 C ref) to temperature using tables
et = INT((vt - svt) / sit)
IF et < 0 THEN y = -999: GOTO SKIPREST 'Round to lower limit
IF et > nt - 2 THEN y = 999: GOTO SKIPREST 'Round to upper limit
y = tt(et) + (tt(et + 1) - tt(et)) * (vt - et * sit - svt) / sit

CASE "k" 'Normalize mV output to 0 deg C
 '! mV @ 25 C (0 C = 0 mV) K-type
 '.040667=slope in mV/deg C @ 25 C
vk = mV + 1! + (RmTemp - 25) * .0405
ek = INT((vk - svk) / sik)
IF ek < 0 THEN y = -999: GOTO SKIPREST 'Round to lower limit
IF ek > nk - 2 THEN y = 999: GOTO SKIPREST 'Round to upper limit
y = tk(ek) + (tk(ek + 1) - tk(ek)) * (vk - ek * sik - svk) / sik

SKIPREST:
END SELECT
END SUB

*******************************************************************************
SUB GRAPHSETUP
*******************************************************************************

SHARED maxy, miny, maxx, minx, Yf, Xf, NumCh, LoCh, HiCh, RmTemp
SHARED graphminx, graphmaxx, graphminy, graphmaxy
SHARED ylabel$, xlabel$, ChSignalType$, ymax()
Style1$ = &H5000 'Type of dotted line graphed
CLS

FOR i = 0 TO (NumCh - 1)
    IF ymax(i) > maxy THEN maxy = ymax(i)
NEXT i

DIMENSION X AND Y AXES

log10ofy = LOG(maxy - miny) / LOG(10#)
xpony = INT(log10ofy)
YEXP10 = (EXP(xpony * (LOG(10))))

SELECT CASE ((maxy - miny) / YEXP10)
CASE 1: Yf = .2 * YEXP10
CASE 1 TO 1.25: Yf = .25 * YEXP10:
    IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .4 * YEXP10
CASE 1.25 TO 2: Yf = .4 * YEXP10:
    IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .5 * YEXP10
CASE 2 TO 2.5: Yf = .5 * YEXP10:
    IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .8 * YEXP10
CASE 2.5 TO 4: Yf = .8 * YEXP10:
IF \( \text{ABS} (\text{INT} (\text{miny} / Yf) \times Yf) + 5 \times Yf < \text{maxy} \) THEN \( Yf = 1 \times \text{YEXP10} \)
CASE 4 TO 5: \( Yf = 1 \times \text{YEXP10} \):
IF \( \text{ABS} (\text{INT} (\text{miny} / Yf) \times Yf) + 5 \times Yf < \text{maxy} \) THEN \( Yf = 2 \times \text{YEXP10} \)
CASE 5 TO 10: \( Yf = 2 \times \text{YEXP10} \):
IF \( \text{ABS} (\text{INT} (\text{miny} / Yf) \times Yf) + 5 \times Yf < \text{maxy} \) THEN \( Yf = 2.5 \times \text{YEXP10} \)
CASE ELSE: PRINT "Y-axis out of range"
END SELECT

\[
\log_{10}\text{of} x = \frac{\log_{10}\text{maxx} - \log_{10}\text{minx}}{\log_{10}(10)}
\]
\[
x_{\text{ponx}} = \text{INT}(\log_{10}\text{of} x)
\]
\[
x_{\text{EXP10}} = (\exp(x_{\text{ponx}} \times \log(10)))
\]

SELECT CASE ((\text{maxx} - \text{minx}) / \text{XEXP10})
CASE 1: \( Xf = .2 \times \text{XEXP10} \)
CASE 1 TO 1.25: \( Xf = .25 \times \text{XEXP10} \):
IF \( 5 \times Xf < \text{maxx} \) THEN \( Xf = .4 \times \text{XEXP10} \)
CASE 1.25 TO 2: \( Xf = .4 \times \text{XEXP10} \):
IF \( 5 \times Xf < \text{maxx} \) THEN \( Xf = .5 \times \text{XEXP10} \)
CASE 2 TO 2.5: \( Xf = .5 \times \text{XEXP10} \):
IF \( 5 \times Xf < \text{maxx} \) THEN \( Xf = .8 \times \text{XEXP10} \)
CASE 2.5 TO 4: \( Xf = .8 \times \text{XEXP10} \):
IF \( 5 \times Xf < \text{maxx} \) THEN \( Xf = 1 \times \text{XEXP10} \)
CASE 4 TO 5: \( Xf = 1 \times \text{XEXP10} \):
IF \( 5 \times Xf < \text{maxx} \) THEN \( Xf = 2 \times \text{XEXP10} \)
CASE 5 TO 10: \( Xf = 2 \times \text{XEXP10} \):
IF \( 5 \times Xf < \text{maxx} \) THEN \( Xf = 2.5 \times \text{XEXP10} \)
CASE ELSE: PRINT "X-axis out of range"
END SELECT

'--------------------------------------------------------------------------------------------------------
' DIMENSION GRAPHING WINDOW AND PLACE GRID ON GRAPH
'--------------------------------------------------------------------------------------------------------

\[
\text{graphminy} = \text{INT}(\text{miny} / Yf) \times Yf, \quad \text{graphmaxy} = \text{graphminy} + 5 \times Yf
\]
\[
\text{graphminx} = 0, \quad \text{graphmaxx} = \text{graphminx} + 5 \times Xf
\]
SCREEN 3: CLS
VIEW (50, 20)-(649, 229), 1
WINDOW (graphminx, graphminy)-(graphmaxx, graphmaxy)

LOCATE 1, 1: PRINT ylabel$
FOR i = 0 TO 5
LOCATE 2 + i * 3, 1: PRINT (graphminy + (5 - i) * Yf)
LOCATE 18, 6 + i * 13: PRINT (graphminx + i * Xf)
NEXT i
LOCATE 17, 75: PRINT xlabel$

FOR i = 1 TO 4
LINE (graphminx, Yf * i + graphminy)-(graphmaxx, Yf * i + graphminy), , Style1$
LINE ((graphmaxx - graphminx) * i / 5, graphminy)-((graphmaxx - graphminx) * i / 5, graphmaxy), , Style1$
NEXT i

'--------------------------------------------------------------------------------------------------------
'TABULAR HEADINGS UNDER GRAPH
LOCATE 20, 46: PRINT USING "Cold junction temp = ##.## deg C"; RmTemp;
LOCATE 21, 46: PRINT "Time from start = sec"
LOCATE 25, 46: PRINT "Press any key to stop"

FOR i = LoCh TO HiCh
  SELECT CASE ChSignalType$(i)
    CASE "lbs": ch1$ = " force"; ch2$ = "lbs"
    CASE "p": ch1$ = " pressure"; ch2$ = "MPa"
    CASE "mV": ch1$ = "milliVolts"; ch2$ = "mV"
    CASE "j": ch1$ = " j-type TC"; ch2$ = "deg C"
    CASE "k": ch1$ = " k-type TC"; ch2$ = "deg C"
    CASE "t": ch1$ = " t-type TC"; ch2$ = "deg C"
  END SELECT
  IF i - LoCh < 6 THEN LOCATE 20 + i - LoCh, 1 ELSE LOCATE 20 + i - LoCh - 6, 24
  PRINT USING "Ch # = \"; i; ch2$;
NEXT i

END SUB
Conversion to Stress and Strain

The raw data (force, time) is converted to stress and strain as well as modulus and strain in the following program.

The raw data filename contains the pressure, temperature, crosshead speed and sample number. For example, the filename P100T75B.500 indicates that the sample was tested at a pressure of 100 MPa, a temperature of 75 °C, is the second sample tested (sample "B"), and was tested at a crosshead speed of .500 cm/min.

To convert to stress and strain, the width and thickness of the sample have to be input to the program. This is prompted. The strain is determined from the filename, which gives the crosshead speed (cm/min), and from the gauge length, which for these samples is 2.54 cm.

Two new files are created, which are identical in name as the raw data filename, except for the first letter. The filename for the stress and strain is then named S100T75B.500. The filename for the modulus and strain is named M100T75B.500.
'ConvToSI.BAS  Graphing from a sequential file  Last Revision: Jan 20, 1994
'Convert to SI
'***************************************************************************
'DECLARE SUBPROGRAMS

COMMON SHARED filename$
DECLARE SUB GRAPHSETUP()
KEY OFF
SCREEN 12: CLS

'***************************************************************************
'FIND MIN AND MAX

graphagain:
CLS
LOCATE 1, 1
PRINT "Select 1) New File"
 INPUT " 2) Same file ", say$
SELECT CASE LCASE$(say$)
CASE "1"
    INPUT "path and filename: ", pathfilename$
CASE "2"
END SELECT

filename$ = RIGHT$(pathfilename$, 12)

'***************************************************************************
'Find max and min for each type of graph

OPEN pathfilename$ FOR INPUT AS #1
xmax = 0
xmin = 0
ymax = 0
ymin = 0
xstart = 0
INPUT #1, xlast
INPUT #1, ylast

DO WHILE NOT EOF(1)
    INPUT #1, x
    INPUT #1, y
    IF xstart <> 0 THEN GOTO aa
    IF y > 2 THEN xstart = x
aa:
    IF x > xmax THEN xmax = x
    IF x < xmin THEN xmin = x
    IF y > ymax THEN ymax = y
    IF y < ymin THEN ymin = y
LOOP
CLOSE #1

'*****************************************************************************
OPEN pathfilename$ FOR INPUT AS #1

PRINT "xmin = ", xmin
PRINT "xmax = ", xmax
PRINT "ymin = ", ymin
PRINT "ymax = ", ymax
PRINT

INPUT "Do you wish to select axes? ", ans$
SELECT CASE LCASE$(ans$)
    CASE "y":
        INPUT "Input minimum x-value to be plotted"; minx
        INPUT "Input maximum x-value to be plotted"; maxx
        INPUT "Input minimum y-value to be plotted"; miny
        INPUT "Input maximum y-value to be plotted"; maxy
    CASE "n"
        minx = xmin: maxx = xmax: miny = ymin: maxy = ymax
END SELECT

'*****************************************************************************

GRAPH

'*****************************************************************************
'INPUT "Input label for x axis "; xlabel$
'INPUT "Input label for y axis "; ylabel$
CALL GRAPHSETUP

INPUT #1, seclast
INPUT #1, lblast
PSET (0, 0)

LINE (0, 0)-(seclast, lblast)

DO WHILE NOT EOF(1)
    INPUT #1, sec
    INPUT #1, lb

    LINE (seclast, lblast)-(sec, lb)
    seclast = sec
    lblast = lb
LOOP

CLOSE #1

'*****************************************************************************

'*****************************************************************************

G18
INPUT "Select: a) Raw Data?  b) Convert to Stress & Strain   ", ans$
SELECT CASE LCASES(ans$)
   CASE "a": GOTO graphagain
   CASE "b":
END SELECT

filename$ = RIGHT$(pathfilename$, 12)
sename$ = "s" + RIGHT$(filename$, 11)
mdname$ = "m" + RIGHT$(filename$, 11)
strainrate = VAL(RIGHT$(filename$, 4))

CLS
LOCATE 2, 1: INPUT "Sample width (inches) ? ", w
LOCATE 3, 1: INPUT "Sample thickness (inches)? ", t
gaugelen = 2.54

slast = 0
elast = 0
secstart = xstart
modmax = 0
smax = 0
emax = 0
seclast = 0

OPEN pathfilename$ FOR INPUT AS #1
OPEN sename$ FOR OUTPUT AS #2
OPEN mdname$ FOR OUTPUT AS #3

DO WHILE NOT EOF(1)

    INPUT #1, sec
    INPUT #1, lb

    IF sec < secstart THEN GOTO skip

    s = (lb / (w * t)) * .006895
    slast = (lblast / (w * t)) * .006895

    e = (((sec - secstart) * strainrate) / gaugelen) * (1 / 60)
    elast = (((seclast - secstart) * strainrate) / gaugelen) * (1 / 60)

    eave = (e + elast) / 2
    IF eave < 0 THEN eave = 0

    modulus = ((s - slast) / (e - elast))
IF s > smax THEN smax = s; emax = e

IF lb > (.5 * maxy) THEN
    IF modulus > modmax THEN modmax = modulus
END IF

PRINT #2, e, s
PRINT #3, eave, modulus

skip:
lblast = lb
seclast = sec
elast = e

LOOP
    xmax = e
    CLOSE #1
    CLOSE #2
    CLOSE #3

    PRINT
    PRINT "Modulus (MPa) = ", modmax, " MPa"
    PRINT "Maximum eng stress (MPa) = ", smax
    PRINT "Eng strain at maximum stress = ", emax

'GRAPH.BAS  Graphing from a sequential file
'******************************************************************************

KEY OFF
SCREEN 12

'******************************************************************************

'GRAPH

grafagain:

    LOCATE 15, 1
    PRINT."Select:  a) Graph stress-strain"
    PRINT "  b) Graph modulus-strain"
    PRINT "  c) Quit"

    INPUT ans$

SELECT CASE LCASE$(ans$)
    CASE "a"
        OPEN surname$ FOR INPUT AS #1
        maxy = smax; maxx = e
    CASE "b"
        OPEN mdbname$ FOR INPUT AS #1
        maxy = modmax
        secmax = maxx
maxx = \((\text{secmax} - \text{secstart}) \cdot \text{strainrate} / \text{gaugelen}) \cdot (1 / \text{gaugelen})\)

CASE "c"
    END
END SELECT

INPUT "Do you wish to select axes? ", ans$
SELECT CASE LCASE$(ans$)
    CASE "y":
        INPUT "Input minimum x-value to be plotted"; minx
        INPUT "Input maximum x-value to be plotted"; maxx
        INPUT "Input minimum y-value to be plotted"; miny
        INPUT "Input maximum y-value to be plotted"; maxy
    CASE "n"
        minx = 0
        miny = 0
END SELECT

INPUT "Input label for x axis "; xlabel$
INPUT "Input label for y axis "; ylabel$
CALL GRAPHSETUP

seclast = 0
ylast = 0

DO WHILE NOT EOF(1)
    INPUT #1, sec
    INPUT #1, y
    LINE (seclast, ylast) -(sec, y)
    seclast = sec
    ylast = y
LOOP

CLOSE #1
VIEW

LOCATE 29, 1
INPUT "Select: a) Raw Data? b) Convert to Stress & Strain ", ans$
SELECT CASE LCASE$(ans$)
    CASE "a": GOTO graphagain
    CASE "b": GOTO grafagain
END SELECT

END

******************************************************************************

******************************************************************************
SUB GRAPHSETUP

SHARED maxy, miny, maxx, minx, Yf, Xf
SHARED graphminx, graphmaxx, graphminy, graphmaxy
SHARED ylabel$, xlabel$

STYLE1% = &H5000
' Type of dotted line graphed
CLS

DIMENSION X AND Y AXES

log10ofy = LOG(maxy - miny) / LOG(10#)
xpony = INT(log10ofy)
YEXP10 = (EXP(xpony * (LOG(10))))

SELECT CASE ((maxy - miny) / YEXP10)
CASE 1: Yf = .2 * YEXP10
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .25 * YEXP10
CASE 1 TO 1.25: Yf = .25 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .3 * YEXP10
CASE 1.25 TO 1.5: Yf = .3 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .4 * YEXP10
CASE 1.5 TO 2: Yf = .4 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .5 * YEXP10
CASE 2 TO 2.5: Yf = .5 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .6 * YEXP10
CASE 2.5 TO 3: Yf = .6 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = .8 * YEXP10
CASE 3 TO 4: Yf = .8 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = 1! * YEXP10
CASE 4 TO 5: Yf = 1! * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = 1.2 * YEXP10
CASE 5 TO 6: Yf = 1.2 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = 1.6 * YEXP10
CASE 6 TO 8: Yf = 1.6 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = 2 * YEXP10
CASE 8 TO 10: Yf = 2 * YEXP10:
  IF ABS(INT(miny / Yf) * Yf) + 5 * Yf < maxy THEN Yf = 2.5 * YEXP10
CASE ELSE: PRINT "Y-axis out of range"
END SELECT

log10ofx = LOG(maxx - minx) / LOG(10#)
xponx = INT(log10ofx)
XEXP10 = (EXP(xponx * (LOG(10))))

SELECT CASE ((maxx - minx) / XEXP10)
CASE 1: Xf = .2 * XEXP10
  IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = .25 * XEXP10
CASE 1 TO 1.25: Xf = .25 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = .3 * XEXP10
CASE 1.25 TO 1.5: Xf = .3 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = .4 * XEXP10
CASE 1.5 TO 2: Xf = .4 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = .5 * XEXP10
CASE 2 TO 2.5: Xf = .6 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = .8 * XEXP10
CASE 3 TO 4: Xf = 1! * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = 1.2 * XEXP10
CASE 4 TO 5: Xf = 1.2 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = 1.6 * XEXP10
CASE 5 TO 6: Xf = 1.6 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = 2 * XEXP10
CASE 6 TO 8: Xf = 2 * XEXP10:
    IF ABS(INT(minx / Xf) * Xf) + 5 * Xf < maxx THEN Xf = 2.5 * XEXP10
CASE ELSE: PRINT "X-axis out of range"
END SELECT

' DIMENSION GRAPHING WINDOW AND PLACE GRID ON GRAPH

graphminy = INT(miny / Yf) * Yf: graphmaxy = graphminy + 5 * Yf
graphminx = INT(minx / Xf) * Xf: graphmaxx = graphminx + 5 * Xf

SCREEN 12: CLS
VIEW (50, 20)-(500, 425), , 1
WINDOW (graphminx, graphminy)-(graphmaxx, graphmaxy)

LOCATE 1, 1: PRINT ylabel$
LOCATE 1, 65: PRINT filename$
FOR i = 0 TO 5
    LOCATE 2 + i * 5, 1: PRINT (graphminy + (5 - i) * Yf)
    LOCATE 28, 6 + i * 11: PRINT (graphminx + i * Xf)
NEXT i
LOCATE 27, 67: PRINT xlabel$

FOR i = 1 TO 4
    LINE (graphminx, Yf * i + graphminy)-(graphmaxx, Yf * i + graphminy), , Style1$
    LINE ((graphmaxx - graphminx) * i / 5, graphminy)-(graphmaxx - graphminx) * i / 5, graphmaxy), , Style1$
NEXT i

END SUB
Appendix H
Group I Test Results

The first group of tests were carried out at room temperature, in 69 MPa pressure intervals, at strain rates of 0.002, 0.008, 0.020, 0.080 and 0.200 min⁻¹. The engineering stress-engineering strain curves are shown in Figures H.01 - H.05. The corresponding tangent modulus-strain curves are shown in Figures H.06 - H.10. The y-axis on these latter curves uses the term “Instantaneous Modulus” instead of the “Tangent Modulus”. The two terms are synonymous.

In these figures, the stress definition used was the engineering stress, \( \sigma = F/A_0 \), where \( A_0 \) is the initial cross-sectional area at room temperature and pressure. The strain was determined from crosshead displacement and the initial gauge length at room temperature and pressure. No adjustment was made for dimensional changes in gauge length due to temperature or pressure.

The pressures are rounded values to the nearest MPa. Atmospheric pressure is thus rounded to 0 MPa.

The tangent modulus was determined from the slope of the tangent to the stress-strain curve. Since the strains are determined from the crosshead displacement, values for the tangent modulus cannot be considered accurate at low strains. Contributions to the overall displacement include alignment of the mechanical linkages and the seating of the serrated grips into the polymer besides the elongation of the polymer sample itself. The non-polymer strain contributions quickly saturate by 2-3% strain, and values at strains greater that this will give reasonably accurate values.

Group II test results are reported in the Results section in the main body of the thesis.
Figure H.01: Tensile engineering stress-engineering strain curves for polypropylene at T=25 °C and strain rate of 0.002 min⁻¹ for various pressures.
Figure H.02: Tensile engineering stress-engineering strain curves for polypropylene at $T=25^\circ C$ and strain rate of 0.008 min$^{-1}$ for various pressures.
Figure H.03: Tensile engineering stress-engineering strain curves for polypropylene at $T=25^\circ C$ and strain rate of $0.020\,\text{min}^{-1}$ for various pressures.
Figure H.04: Tensile engineering stress-engineering strain curves for polypropylene at \( T=25 \, ^\circ\text{C} \) and strain rate of 0.080 \( \text{min}^{-1} \) for various pressures.
Figure H.05: Tensile engineering stress-engineering strain curves for polypropylene at \(T=25 \, ^\circ\text{C}\) and strain rate of 0.200 \(\text{min}^{-1}\) for various pressures.
Figure H.06: Tangent modulus-engineering strain curves for polypropylene at $T=25 \, ^\circ C$ and strain rate of $0.002 \, \text{min}^{-1}$ for various pressures.
Figure H.07: Tangent modulus-engineering strain curves for polypropylene at $T=25^\circ C$ and strain rate of 0.008 min$^{-1}$ for various pressures.
Figure H.08: Tangent modulus-engineering strain curves for polypropylene at $T=25^\circ C$ and strain rate of $0.020 \text{ min}^{-1}$ for various pressures.
Figure H.09: Tangent modulus-engineering strain curves for polypropylene at $T=25 \, ^\circ C$ and strain rate of $0.080 \, \text{min}^{-1}$ for various pressures.
Temperature = 25 C
Strain Rate = 0.200 min⁻¹

Figure H.10: Tangent modulus-engineering strain curves for polypropylene at T=25 °C and strain rate of 0.200 min⁻¹ for various pressures.