POLYMER FIBRE REINFORCED THERMOMECHANICAL PULP (TMP) BASED PAPERS

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Forestry
University of Toronto

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Gregory Richard Williams, Doctor of Philosophy, 1999
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ABSTRACT

This study looks at a new type of material, a TMP/polymer composite sheet. No separate binders were used. Since there is heat available in the papermaking process, heat was used to create an adhesive bond between components. The polymer fibres used were polypropylene (PP), polyamide 6/polyamide 12 copolymer (CoPA), polyamide 6 (PA6), poly(ethylene terephthalate) (PET) and regenerated cellulose (Rayon). The properties of unheated sheets were characterized, to provide a baseline.

The focus of this study was on the tensile and tear properties of TMP/polymer composite sheets. Simply adding polymer fibres to the sheets resulted in poorly bonded sheets with poor properties. Modelling the behaviour of the composites indicated that the polymers actually had a deleterious effect on sheet properties. They disrupted the bonding in the pulp component of the sheet. Adding polymer fibres was worse than adding nothing, i.e. reducing the mass of the sheet.

The heat treated sheets gave much better results, if the heat supplied was sufficient to soften the polymer. Heat treated polypropylene and polyamide copolymer blends gave sheets that were tougher than 100% TMP sheets and which had comparable strength and only slightly lower stiffness. These effects were attributed to thermal bonding: the polymer fibres softened,
became tacky and adhered to the wood pulp.

Tear energy was the exception. Adding polymer fibres dramatically increased the energy required to tear unheated sheets, with the degree of improvement closely correlated to the length of the polymer fibre. Heat treating the composite sheets resulted in decreased tear.

In terms of tensile properties, the most important properties of a polymer fibre reinforcement are strength, stiffness and melting point. For tear energy fibre length is the dominant property. Long, low melting point fibres will give the best balance of tensile and tear properties. The polymer fibres should have the highest strength and modulus possible in a low melting point material.
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GLOSSARY OF SYMBOLS

\( T = \) tensile strength of the sheet

\( Z = \) zero span tensile strength of the fibres

\( A = \) average cross-sectional area of fibres

\( \rho = \) density of the fibrous material

\( g = \) acceleration due to gravity (not needed with metric units)

\( b = \) shear bond strength per unit bonded area

\( P = \) perimeter of the fibre cross section

\( L = \) fibre length

\( RBA = \) relative bonded area of the sheet

\( \alpha = \) bonded area/gram of fibrous material

\( x_c = \) the critical length of the fibres, the length at which they pull out instead of breaking.

\( N = \) number of fibres per unit cross section of the crack

\( l = \) fibre length

\( \tau = \) bond shear strength

\( \sigma = \) tensile strength of the fibres

\( r = \) fibre radius.

\( \omega = \) fibre width

\( n_k = \) the number of kinks or curls in the fibre that will not transmit axial load

\( L = \) fibre length

\( G_f = \) shear modulus of the fibres

xi
\[ E_f^* = \text{the average elastic modulus of the fibres, accounting for} \]
\[ \text{microcompressions and out of plane curl} \]
\[ v = \text{Poisson's ratio} = \text{-tensile strain/lateral strain} \]
\[ \sigma_c = \text{the tensile strength of the composite} \]
\[ \sigma_{tu} = \text{the ultimate tensile strength of the component which fails} \]
\[ v_1 \& v_2 = \text{the volume fractions of component 1 \& 2, respectively} \]
\[ E_1 = \text{the elastic modulus of the component which fails} \]
\[ E_2 = \text{the elastic modulus of the component which does not fail} \]
\[ W = \text{work per unit area to open a crack in tear} \]
\[ F = \text{an index that describes the resistance of fibres to breakage} \]
\[ B = \text{an index that describes the resistance of bonds to breakage} \]
\[ BI = \text{Bonding Index, developed in this paper} \]
\[ \text{CSF} = \text{Canadian Standard Freeness} \]
\[ \text{PE} = \text{polyethylene} \]
\[ \text{PP} = \text{polypropylene} \]
\[ \text{PA 6} = \text{polyamide (nylon) 6} \]
\[ \text{CoPA} = \text{polyamide 6/polyamide 12 copolymer} \]
\[ \text{PET} = \text{poly(ethylene terephthalate)} \]
\[ T_m = \text{the melting temperature of a crystalline polymer} \]
\[ T_g = \text{the glass transition temperature of a polymer} \]
\[ \text{TMP} = \text{thermomechanical pulp} \]
\[ \text{USDA} = \text{United States Department of Agriculture} \]
\[ \text{PID} = \text{proportional integral derivative, a type of control algorithm} \]
ISO = International Standards Organization
TAPPI = Technical Association of the Pulp and Paper Industry
SEM = scanning electron microscope
FESEM = field emission scanning electron microscope
TIF = tagged image file format
JPEG = joint photographic experts group file format
U of T = University of Toronto
TEA = tensile energy absorption

\[ n = \text{an exponent} \quad \begin{cases} \text{2.5 for moderately bonded sheets} & (T = 4/9Z) \\ \text{3.0 for highly bonded sheets} & (T = 8/9Z) \end{cases} \]

\[ s = \text{scattering coefficient} \]
\[ r = \text{reflectivity, a material property} \]
\[ A_0 = \text{‘optically visible’ unbonded surface area} \]
CHAPTER 1 - INTRODUCTION

1.1 Background

There are many types of paper and paper-like products and it can be difficult to distinguish between them. Wood pulps also come in a large number of forms and different pulps can have very different properties. In order to discuss these materials it is important to define them carefully.

In the Collins Dictionary of the English Language paper is defined as, "1. A substance made from cellulose fibres derived from rags, wood, etc., often with other additives, and formed into flat thin sheets suitable for writing on, decorating walls, etc.....". Smook [1982] defines paper as "a felted sheet formed on a fine screen from a water suspension of fibres." These two definitions together give a good description of what is traditionally thought of as paper.

Of particular interest to this project are papers made from bleached kraft pulps, a type of chemical pulp, and thermomechanical pulp (TMP), a type of mechanical pulp. TMP based paper is of interest because Canadian paper companies, including Abitibi-Consolidated, a sponsor of this work, are major producers of TMP. Kraft based paper is of interest as a benchmark. Paper containing mechanical pulp is often referred to as "groundwood" paper while paper that contains no mechanical pulp is called "woodfree".

Papers made from bleached kraft pulp tend to be strong, bright and smooth and are used for high quality printing and writing papers. Mechanical pulps yield papers with good opacity and ink absorption but the papers are weak and will yellow with time. This fact limits their use to certain applications such as newsprint and directory paper. While these markets consume very...
large volumes, the value of each ton of paper is relatively low. It would be desirable for the producers of TMP and groundwood papers to expand into higher value markets. In order to use these papers in new markets their properties need to be changed and improved. One way to accomplish these changes is to blend TMP with other materials and blending TMP with kraft pulp is common practice today. Addition of polymer fibres to papers, such as currency papers, is also industrially practised. However, previous work on paper/polymer composites has focussed on woodfree papers. Adhesion of the two components has been promoted by the addition of binding agents, usually a water soluble polymer, or by treatment of the polymer fibres to make them more hydrophilic.

It was a desire to produce a better groundwood paper, one that could compete with woodfree printing papers, that led to the undertaking of this project. Separate binders were not used in order to keep the cost of the paper down.

The other motives for this work were environmental and patriotic. Replacing chemical pulps with mechanical pulps would save fibre since mechanical pulps are much higher yield than chemical. Mechanical pulps typically retain 90-95% of the starting wood fibre while chemical pulps only retain 40-50%, Smook [1982]. It would also particularly benefit the Canadian industry which is a major producer of mechanical pulp and groundwood papers such as newsprint.
1.2 Literature review

1.2.1 Properties of Wood Fibres and Pulps

Panshin & de Zeeuw [1980] give a thorough overview of the types and structures of cells found in trees. The structure of wood and chemistry of its components have been the subject of many books. This section will highlight just a few of these issues.

For the purposes of papermaking it is convenient to classify the cells of trees in two categories, structural and non-structural. The structural cells: tracheids in softwoods, tracheids and fibres in hardwoods, are the long, strong cells that form good pulp. From a papermaking point of view the other types of cells are impurities.

Tracheids and fibres are shaped like long, narrow, hollow cylinders with tapered ends. The cell wall is composed of a number of layers: the middle lamella, the primary wall, the secondary wall and sometimes a tertiary wall or warty layer. The secondary wall is the thickest layer and it largely controls the structural properties of the cell. The most important chemical components of the cell walls are lignin, hemicellulose and cellulose.

Lignin is an aromatic polymer made up of phenylpropane units, Browning [1963]. It is an amorphous, network polymer that probably exists in two forms. The lignin in the middle lamella is a random, three dimensional network while the lignin in the secondary wall is a more ordered two dimensional network, Goring [1989]. Lignin acts as the plastic matrix that attaches wood fibres to each other and provides support for the cellulose.

Lignin, an amorphous polymer, does not have a melting point. It does have a softening point at which it becomes tacky and capable of mechanical bonding. Goring [1966] studied the
softening of the components of wood including lignin. He found that the softening temperature of lignin ranged from 127-193 °C and that it was highly influenced by the moisture content of the sheet. Water uptake in the range of 10 g/100 g lowered the softening point by as much as 54 °C. The same paper, Goring [1966], reports that the adhesive properties of lignin become noticeable once the softening point is exceeded. The softening temperature is taken to be the glass transition temperature, $T_g$, of lignin.

Hemicellulose describes a large number of compounds, primarily polymers of five and six carbon sugars, Browning [1963]. Some of the most important of these sugars are xylose, arabinose, glucose, mannose and galactose. Hemicelluloses form highly branched chains and are thus amorphous. The molecular weight of these polymers is relatively low, in the range of 20,000-40,000 g/mol. Hemicelluloses are thought to have a structural function, Browning [1963], but their exact role is unknown.

As with lignin, hemicellulose has a moisture dependent $T_g$. Goring [1966] reports the two particular hemicelluloses, birch xylan and pine glucomannan, soften at 167 °C and 181 °C respectively. Once $T_g$ is exceeded, hemicellulose also exhibit adhesive properties.

Cellulose is the largest and most important fraction of the woody cell wall, particularly from a structural point of view, Panshin & de Zeeuw [1983]. It is a linear polymer of $\alpha$-D-glucose and is highly crystalline. The molecular weight of natural cellulose is very high, on the order of 2-3,000,000 g/mol. The cellulose chains in wood bundle together to form fibrils which act as very stiff, strong structural units.

Because cellulose is a crystalline polymer, the melting point, $T_m$, is more significant than $T_g$. For crystalline polymers the softening temperature is near $T_m$, well above $T_g$. The softening temperature of cellulose was found by Goring [1966] to be greater than 230 °C. The softening
temperature was not significantly affected by water content. Subjecting a sheet to a temperature this high would start to degrade the other components. It is also much higher than the temperatures typically found in a paper machine. So, adhesion of cellulose is not going to be of practical significance.

The middle lamella is entirely composed of a three dimensional network of lignin and the primary wall is mostly lignin with some hemicellulose. The secondary wall contains a significant amount of lignin, probably in the form of a two dimensional network, and hemicellulose but it is dominated by cellulose. The secondary wall can actually be thought of as a composite made up of reinforcing fibres (cellulose fibrils) in a plastic matrix (lignin and hemicellulose). The tertiary wall or warty layer results from the deposition of proteins on the inside of the cell after the cell dies.

The object of pulping is to separate wood into fibres. Clark [1985], Smook [1992] and Scott [1995] all contain overviews of pulping methods and paper properties. These references provided the basis for the following discussion.

The two basic forms of pulping are chemical and mechanical. Chemical pulping uses chemical reactions to dissolve the lignin and hemicellulose which bind cellulose fibres together. Mechanical pulping uses mechanical stress to physically separate the fibres. Once the fibres are separated they can then be used to make paper.

Kraft pulping uses chemicals, particularly sodium hydroxide (NaOH) and sodium sulfide (NaS$_2$) to dissolve the lignin and hemicellulose which binds the fibres together. Bleaching kraft pulp results in further lignin removal. The low yield of kraft pulping is do to the fact that the lignin, hemicellulose and some cellulose are removed from the fibres and dissolved into the process water. The final kraft fibres are almost entirely cellulose.
Kraft pulp fibres tend to be the same length as the initial wood fibre and they usually collapse into flat ribbons. After pulping kraft fibres are mechanically beaten to loosen some of the fibrils on the fibre surface. This gives kraft fibres a ‘hairy’ appearance and results in a large surface area available for bonding. These characteristics of kraft pulp result in a sheet of bright, long, well bonded fibres. This gives woodfree sheets high strength and stiffness.

Thermomechanical pulping uses heat to soften the lignin and then mechanical shear to tear the fibres apart. As a result, the fibres retain almost all of their initial lignin and hemicellulose. Because very little mass is lost from the fibres TMP is a high yield pulping process.

TMP fibres are shorter than the initial wood fibres, due to breakage, and they tend to retain their cylindrical shape. TMP fibres will be fibrillated, but not to the same extent as well beaten kraft fibres. TMP also contains a large amount of fines, small fragments of pulp. It is actually the fines which provide most of the surface area needed for bonding. Due to its morphology and the presence of lignin, TMP pulp yields sheets containing dark, short, poorly bonded fibres.

Despite the many technical advantages of kraft pulps, mechanical pulps are better for certain applications. Groundwood sheets have high opacity so that relatively thin sheets can be printed on both sides without the print showing through. They also have very good printing properties, such as low ink absorption. Finally, TMP mills are less expensive to build and groundwood papers are less expensive to produce.
1.2.2 Pulp & Paper Property Relationships

The relationships between pulp properties and sheet properties have been studied by many people including Dorland [1962], Forgacs[1963], Koran [1974] Mutton [1996] and Lee [1992]. The general consensus is that a relatively small number of fibre properties, especially morphological properties, can be used to explain practically all of the physical properties of a sheet. Forgacs [1963] suggested that the number of fundamental properties is two: one related to fibre length and one to fibre shape.

Lee [1992] was particularly thorough. He studied a total of 19 pulp-fibre properties and 29 paper properties using advanced statistical techniques. Because many of these properties are highly correlated he was able to reduce the lists to 11 pulp-fibre properties for pulp and 12 paper properties. He then produced 12 regression models, one for each paper property, and found that these models could account for 83% ± 10% of the variance in paper properties. Thus his models do a good job of predicting paper properties from pulp-fibre properties.

Lee [1992] concluded that "there are no universally optimum fibre properties which allow attainment of all maximum paper properties at the same time. Instead a compromise must be made to achieve an acceptable balance of properties." Thus a change in pulp properties which improves one sheet property may degenerate another sheet property. For example, consider fibre coarseness, which is a measure of fibre stiffness. High coarseness leads to higher tear strength but lower tensile strength. Other authors [Smook, 1992; Dorland, 1962; Forgacs, 1963] have observed the same general phenomenon and have reached the same conclusion.

The advantages of mechanical pulp, high bulk and opacity and good ink absorption, make it very well suited for newsprint. However, the limitations of mechanical pulp, particularly low
strength and stiffness, mean it is not well suited for many other paper grades. Due to the nature of the relationship between pulp and paper properties, as described briefly in the previous paragraph, attempts to overcome the strength limitations of mechanical pulps have required unacceptable trade-offs. Thus companies which make paper from mechanical pulp are generally confined to a limited range of products.

From a material science point of view, one obvious way to try to avoid property compromises is to make a composite. The addition of another type of material that does not have the same property trade-offs might make it possible to improve a property such as tensile strength without sacrificing tear, or vice versa. It is also well known that combining materials in composites can produce a synergistic effect. In other words, the composite can be stronger than the weighted sum of its components.

1.2.2.1 Tensile Properties of Pulp and Paper

In addition to the general pulp/property relationship studies mentioned in the previous paragraphs, considerable work has been done on just the relationship between pulp properties and the tensile properties of paper such as strength and modulus. Dr. Derek Page was particularly active in this field and he looked at both paper properties and single pulp fibre properties.

Page [1960] and Page & Tydeman [1960] examined the subject of fibre-to-fibre bonds. These papers described a way to observe fibre-to-fibre bonds, some factors which control fibre bonding and ways in which the bonds react when under stress. One particularly important point is that fibre-to-fibre bonds were strong enough to prevent fibres from sliding against each other.
This means relative fibre movement can only occur after bonds are ruptured. So paper does not fail in a ductile manner, it fails by fast fracture.

Page [1969] presents the Page Equation for tensile strength. This is an empirical equation based on two premises. The first is that as paper is strained fewer and fewer fibres will bear the load due to failure of fibre bonds. Eventually the load on the remaining fibres will exceed the fibre rupture strength and these fibres will fail. At this point the paper fails. The second premise is that the fibres crossing the rupture line will fail or pull out depending on which is stronger, the fibre or the bonds holding it in the sheet.

From these premises the following equation was derived:

\[
\frac{1}{T} = \frac{9}{8Z} + \frac{12 A}{bPL(RBA)}
\]

1.1

where: 
- \( T \) = tensile strength of the sheet, MPa
- \( Z \) = zero span tensile strength of the fibres, MPa
- \( A \) = average cross-sectional area of fibres, m²
- \( b \) = shear bond strength per unit bonded area, MPa
- \( P \) = perimeter of the fibre cross section, m
- \( L \) = fibre length, m
- \( RBA \) = relative bonded area of the sheet

Equation 1.1 was shown to fit a large amount of experimental data very well, including data generated by the authors and that found in the literature available at the time. These data are described in Page [1969]. A much later paper, Page & Seth [1988], further reinforced the validity of the equation.
The Page Equation (Equation 1.1) has been adopted as an acceptable explanation of sheet strength, despite the lack of a rigorous analytical derivation. For the purpose of this work, the main point to note is that the equation has two parts: the first is a function of fibre strength, the second is a function of the number and strength of fibre bonds. This point will be re-visited in detail in section 3.2.

There are a number of papers on single fibre strength, including Page, et. al. [1972], El-Hosseiny & Page [1975], Kim, et. al. [1975]. These were important because they identified the theoretical maximum strength of fibres and the role of fibril angle and fibre defects in reducing the actual strength to some fraction of the theoretical maximum. When fibres are treated as helically wound, fibre reinforced composite tubes it is possible to calculate their strength based on the strength of their main structural component, cellulose. However, the actual composition and structure of fibres is difficult to know exactly so it is easier to determine the ultimate strength empirically. Kim, et. al. [1975] report the ultimate strength of an unflawed, zero fibril angle fibre as 20 GPa (20 x 10^9 dynes/cm^2). Note that a zero fibril angle fibre has all of the cellulose chains parallel to the fibre length.

While Page treated single fibres as composites, Shallhorn and Karnis [1979] applied composite theory to entire sheets. This required a number of assumptions. First, they assume that the fibres form a continuous network so that, on average, all fibres experience the same forces. Second, it is assumed that all fibres have the same geometry and that strength properties are uniformly distributed. Finally they assumed that all fibres are perpendicular to the fracture line.

With these simplifying assumptions they derived an equation for the tensile strength of paper that was completely analytical. According to their reasoning, the tensile strength of paper
is given by the sum of the tensile strength due to fibre pull out and the tensile strength due to breakage. Tensile strength, $T$, is the sum of equations 1.2 and 1.3:

$$T_{\text{pull}} = \int_0^{x_c} (2N/l)(2\pi r \tau x)dx$$ \hspace{1cm} 1.2

$$T_{\text{break}} = \int_{x_c}^{l/2} (2N/l)\sigma \pi r^2 dx$$ \hspace{1cm} 1.3

where: $x_c =$ the critical length of the fibres, the length at which they pull out instead of breaking.

This length can be found by equating the pull out and breakage forces, so $x_c = \sigma r / 2\tau$.

$\ N =$ number of fibres per unit cross section of the crack

$\ l =$ fibre length

$\ \tau =$ bond shear strength

$\ \sigma =$ tensile strength of the fibres

$\ r =$ fibre radius.

The sum of these equations is identical to the Page equation, Page [1969], except for numerical factors, if the following equivalencies are assumed:

$\ \tau = b*RBA$, shear strength/unit bonded area times relative bonded area

$\ \sigma = Z$, zero span tensile strength

$\ l = L$, mean fibre length

$\ r/2 = \pi r^2/2\pi r = A/P =$ ratio of fibre area to perimeter

Page, et. al. [1979], Page & Seth [1980a] and Page & Seth [1980b] deal with the elastic modulus of paper and the effect of pulp properties on paper properties. The seminal work of Cox
[1952] on the modulus of two dimensional random networks can be applied to paper and it works quite well. This gives a maximum theoretical sheet modulus equal to one third of the cellulose fibre modulus. Since the moduli of softwood pulp fibres tend to fall in the range 45-55 GPa, Page et. al. [1979], paper moduli would be expected to be between 15 and 18 GPa.

Page, et. al. [1979], identifies the controlling mechanisms for paper modulus: the elastic modulus of the fibres, fibre length, the degree of bonding and the presence of imperfections, such as microcompressions, curl, crimps and kinks, in the fibres. The first factor determines the theoretical maximum modulus for the sheet. Fibre length and the degree of bonding determine how well bonded the sheet is and how close to the theoretical maximum the actual modulus will be. Imperfections will reduce the effectiveness of stress transfer and will thus lower the modulus for a given degree of bonding.

While perfect fibres have a very high modulus, actual fibres and actual sheets have much lower moduli. This is the opposite of the case for polymer fibres. Since polymer fibres tend to be very straight and relatively free of imperfections, they can approach their maximum modulus. In fact, the process of drawing fibres causes the molecules to become highly oriented and fibre modulus can greatly exceed the modulus commonly reported for a given polymer. So, while it would not make sense to reinforce cellulose with nylon, it is a much more reasonable proposition to reinforce wood pulp with nylon fibres.

Page & Seth [1980a] and Page & Seth [1980b], present equations for the elastic modulus of paper that account for a number factors that Page, et.al. [1979], identified as being important to sheet modulus. The equations are based on the work of Cox [1952], modified to apply specifically to paper. The final equation for modulus is quite rigorous analytically but it does ignore a term which accounts for the effectiveness of load transfer by assuming that the factor is
equal to unity. As with the Page equation for strength, the equation for modulus works quite well.

The equation in Page & Seth, [1980b], is for handsheets. Handsheets are sheets that prepared in a laboratory. The fibres in handsheets are randomly oriented so the sheets are isotropic. It is possible to modify the equation to apply to the more oriented structure of a machine-made sheet but this was not necessary for this project since it is handsheets that will be studied. The equation for the elastic modulus of a sheet, \( E_p \), is:

\[
E_p = \frac{1}{3} E_f^* \left\{ 1 - \left[ \frac{\omega (n_k + 1)}{L RBA} \right]^{1/2} \right\}
\]

where: \( \omega = \) fibre width

\( n_k = \) the number of kinks or curls in the fibre that will not transmit axial load

\( L = \) fibre length

\( RBA = \) relative bonded area of the sheet

\( G_f = \) shear modulus of the fibres

\( E_f^* = \) the average elastic modulus of the fibres, accounting for microcompressions and out of plane curl

As with tensile strength, the elastic modulus of a sheet is basically controlled by a fibre property, effective modulus in this case, and fibre bonding.

1.2.2.2 Tear Properties of Paper

Tear strength is somewhat difficult to define because it depends to some degree on how
the test is conducted. The most common tear test is the Elmendorf internal tearing resistance test, Scott & Abbott [1995]. This test, which has been used for this project, measures the amount of energy required to continue a tear which has already been started. A standard sample length is used for the test. The tearing force is applied perpendicular to the plane of the sheet. Elmendorf tear strength is an important quantity for papers which are handled on converting equipment which can subject them to out-of-plane stress.

Shallhorn & Karnis [1979] developed an equation for the tear strength of mechanical pulps in addition to their equation for mechanical strength. Once again they made the simplifying assumptions about fibre geometry, properties and orientation and they assumed that two failure modes are occurring, fibre pullout and fibre breakage. However, in tear fibre breakage is considered to consume negligible energy compared to fibre pull out. Because of this assumption, two equations are needed.

The first equation applies to weakly bonded sheets or sheets with short fibres. In these cases all of the fibres pull out. Thus the work integral applies to all fibres with embedded lengths from 0 to \(l/2\). Since \(l/2\) is the maximum possible embedded length, the integral will account for all the fibres in a sheet. The actual equation in this case is, Shallhorn & Karnis [1979]:

\[
W = \int_0^{l/2} (2N/l)(\pi r \tau x^2)dx = N\pi r \tau l^2 / 12 \tag{1.5}
\]

where:

- \(W\) = work per unit area to open the crack
- \(l\) = fibre length
- \(N\) = number of fibres per unit area of the crack line
- \(r\) = fibre radius
- \(\tau\) = bond shear strength
The second equation is used for more strongly bonded sheets or sheets which contain some long fibres. In these cases there will be some fibres which are above the critical length and which will break. These fibres need to be excluded from the integral since fibres which break are assumed to consume a negligible quantity of energy. The critical length can be found by equating the pull out and breakage forces, so \( x_c = \sigma r / 2\tau \). Now the integral only includes thus fibres up to the critical length and the equation becomes, Shallhorn & Karnis [1979]:

\[
W = \int_0^{\sigma r / 2\tau} (2N/l)(\pi r^2 x^2)dx = N\pi r^4 \sigma^3 / 12l\tau^2
\]

where \( W = \) work per unit area to open the crack

\( l = \) fibre length

\( N = \) number of fibres per unit area of the crack line

\( r = \) fibre radius

\( \tau = \) bond shear strength

\( \sigma = \) tensile strength of the fibres

The implication of these two equations is that tear strength increases linearly with degree of bonding or fibre length up to a maximum. Once the critical degree of bonding or fibre length is exceeded fibres will start breaking and tear strength will begin to drop. This prediction is consistent with experimental observations.

Under controlled conditions there is an inverse relationship between the two properties, tensile strength and tear strength, for any given pulp, Page & MacLeod [1992]. When working with handsheets, once a certain critical degree of bonding has been reached any increase in tensile strength will lead to a decrease in tear. This is a logical consequence of the equations of
Shallhorn & Karnis [1979]. Once you reach the point where fibres start breaking instead of pulling out tear strength drops because fibres which break do not contribute significantly to work of rupture. They do, however, continue to contribute to tensile strength.

While Page & MacLeod [1992] looked specifically at softwood kraft pulps the general concepts should also apply to mechanical pulps, since it is the degree of bonding that is most important. The equation derived for Page & MacLeod [1992] is:

$$W = \frac{KZ^n}{T}$$

(1.7)

where: $W =$ work of tear (Elmendorf 4-ply)

$K =$ an arbitrary constant

$Z =$ zero span tensile strength of the pulp

$T =$ tensile strength of the sheet

$n =$ a number between 2.5 and 3.0

The exponent, $n$, was found to be 2.5 for moderately bonded sheets and 3.0 for well bonded sheets. Moderately bonded sheets were defined as those where $T \sim 4/9Z$ while for well bonded sheets $T \sim 8/9Z$. The authors noted that this equation only applies for the Elmendorf 4-ply tear test and that the results may differ for other failure modes. Note that this equation leads to the conclusion that for a constant sheet tensile strength a loss in fibre tensile strength should lead to a loss in sheet tear strength that is 2.5-3 times as great.

Page later amended his theory, Page [1994], and proposed that fibre breakage actually plays a much greater role in tear strength. In fact, he proposes that fibre failure accounts for most of the energy consumed during tear. The decrease in tear for very well bonded sheets is
explained by the fact that increased bonding means smaller fibre spans and rupture zones so the work of failure actually goes down.

This new mechanism could have implications for polymer fibre/TMP composites. Given the fact that the polymer fibres examined here are somewhat hydrophobic and that they have a relatively low surface area, due to lack of fibrillation, good bonding is not expected. Also, the polymer fibres have higher extensibility and tensile strength than wood pulp. The polymer fibres are unlikely to rupture.

Also, the polymer fibres are generally longer than wood pulp fibres. This suggests that the work of pull out may be significant, even at low levels of bonding. Thus, if the earlier pull-out dominated mechanism, Shallhorn & Karnis [1979] holds true the polymer fibres could be expected to increase tear. The increase in tear strength should be linearly proportional to the polymer fibre length.

If Page’s failure dominated mechanism, Page [1994], is true then adding polymers should decrease tear. The polymer fibres, which are not rupturing, will be displacing pulp fibres so there will be fewer fibres breaking. So, the decrease in tear should be roughly proportional to the number of pulp fibres displaced by polymer fibres.

At this time the actual mechanism of paper tearing remains in question. Yan & Kortschot [1997] have proposed a model that can account for either mechanism and they have even adapted it to apply to TMP. Their model accounts for both pull out and breakage and it uses an iterative approach.

A given force is applied to the sheet and then each fibre in the sheet is checked to see how much load is translated to the fibre. This is basically a function of fibre length and the number of bonds formed by the fibre. Bond strengths are assumed to be uniform throughout the sheet. The
force on the fibre is compared to the fibre strength and the bond strength. If one of the strengths is exceeded then the fibre is considered to be broken or pulled out. All the fibres that fail are dropped from the model and the force on the remaining fibres is calculated and again each fibre is checked to see if it fails. If no fibres fail in a given pass the force on the sheet is incremented and the process is started over again. This continues until all the fibres fail.

As each fibre fails the work of failure is recorded. The work of failure is summed for all the fibres and the total is the energy required to tear the sheet. This statistical approach can be applied to sheets with varying fibre orientation and complex fibre strength distributions. Thus it does not require as many simplifying assumptions as the previous analytical approaches.

While the actual equations are quite complicated, they can be simplified by dimensional analysis. Doing this reveals that the most important factors are the ratio of fibre pull-out to fibre breakage and the contribution of pull-out and breakage to the total tear energy. So, as with the previous models there are still two types of fibre: longer ones which break and shorter ones which pull-out. The two main factors affecting tear energy are fibre strength and fibre bonding.

1.2.2.3 Scattering Coefficient

Scallan and Borch, [1972], applied the fundamental theories of optics originally developed by Kubelka-Munk and Stokes to paper. Of particular interest here is the equation they derived which related scattering coefficient to unbonded surface area:

\[ s = \frac{r}{1 - r} A_0 \]  \hspace{1cm} (1.8)

where \( s \) = scattering coefficient

\( r \) = reflectivity
\[ A_0 = \text{‘optically visible’ unbonded surface area}. \]

Since \( r \) is a material property which depends only on the refractive index of the materials in the sheet and the angle of incidence of the incoming light, for a given material changes in \( s \) should be directly related to changes in unbonded area, \( A_0 \). This relationship has been supported by the well known phenomenon that increasing beating, which increases bonding, decreases scattering coefficient.

It has also been established that if a substance is an intimate mixture of components then, with respect to optical properties, it can be treated as a homogeneous material, Scallan [1985]. The scattering and absorption coefficients can be found by simply applying the Rule of Mixtures, which is described in Appendix III.

This equation means it should be possible to detect the occurrence of thermal bonding by measuring scattering coefficient. Heating a blended sheet should not significantly alter the reflectivity of the components, so any change in scattering coefficient should be attributable to a change in unbonded surface area. A decrease in scattering coefficient would suggest less bonded area and thus more bonding.

1.2.3 Paper Composites

The idea of improving groundwood papers by adding some kind of reinforcement is not new, in fact it is standard practice. Mechanical pulps are routinely reinforced with water soluble polymers and/or kraft pulp and these mixtures have been extensively studied. Since this project deals with fibre reinforced composites they will be discussed in more detail below while soluble polymers will be touched on only briefly.
Alava and Niskanen [1997] discuss a number of different aspects of the use of reinforcing fibres, which they call RIFs. While they do discuss RIFs in general terms, their models assume good bonding between the RIF and the pulp fibre and the experimental RIF they use is softwood kraft. Even so, several of their conclusions are relevant to this project.

Alava and Niskanen [1997] state that a good RIF is long, strong and ductile with high conformability and bonding capacity. The mechanical properties, such as strength, elastic modulus and toughness, of these mixtures change in a non-linear fashion and these changes can be synergistic. The synergistic effect is predicted based on models of how RBA changes with RIF content.

It is a natural extension of kraft/TMP blends to consider making composites of TMP and synthetic polymer fibres. Kraft pulps are stronger and stiffer than most polymer fibres but the polymer fibres are tougher and more dimensionally stable in water. TMP fibres are weaker than most polymer fibres so they can be reinforced.

A reinforcement improves the properties of a composite while a filler does not. The difference between a reinforcement and a filler comes down to the fact that a reinforcement is bonded to the matrix while a filler is not. The matrix is the continuous phase in a composite. In the case of paper the wood pulp is the matrix. According to Oliver [1981] there are four key requirements for a strong adhesive joint:

1. There must be no weak boundary layers
2. The adhesive must wet (have a lower surface energy than) the substrate
3. There must be extensive interfacial molecular contact
4. The adhesive must be able to set.

In pulp/polymer systems numbers 1 and 4 are relatively minor problems so studies have focussed
on meeting requirements 2 and 3. One way to meet requirements 2 and 3 is to use chemically pulped fibres and soluble polymers. Chemical pulp fibres, being basically all cellulose, have a reasonably well characterized surface chemistry and soluble polymers can intimately contact the pulp.

A number of studies looked at the addition of soluble polymers in water, or in an organic solvent, to paper. These studies include: Robertson [1968, 1973], Alince, et. al. [1976], Alince [1977], Rígadalh, et.al., [1983] and Engman, et.al., [1976]. Fisa and Marchessault [1974] took a unique approach to ensuring that they obtained well coated fibres. They coated filter paper with a catalyst in an organic solution and then exposed it to ethylene. The result was polyethylene (PE) formed directly on the fibres. This lead to a product with the core properties of cellulose and the surface properties of PE.

The results of the above studies [Robertson, Alince et.al., Alince, Rígadalh et.al., Engman et.al., Fisa & Marchessault] need not be discussed in detail because they all came to the same general conclusion and it is this conclusion that is of interest. These studies showed that adding synthetic polymers to pulp can create a sheet with superior mechanical properties and that a synergistic effect is possible. These soluble polymers are now in common use as retention aids and wet strength agents.

1.2.3.1 Polymer Fibres in Paper

A different method of reinforcement is to use long polymer fibres rather than soluble polymers. The work with kraft fibres, Alva & Niskanene [1997], suggests that this approach can yield good results. Unfortunately, synthetic polymers do not tend to be as compatible with TMP
fibres as kraft fibres are. Fibre geometry also limits bonding potential because non-fibrillated fibres have a relatively small surface area. This makes adhesion a problem. One solution to this problem is addition of a binder to the system.

Battista [1964] provides a good overview of the early work done on adding synthetic fibres to chemical pulps, specifically sulfite pulps. The polymers which receive particular attention are rayon, acrylics, polyamides, polyesters and polyolefins. A number of binders, usually soluble polymers, were used.

Synthetic polymer fibres were found to improve mechanical properties such as wet tensile strength, tear, elongation, toughness and fold resistance. For the most part they caused dry tensile strength to decrease, though not always. Polyesters and polyolefins do not absorb significant amounts of water so they improved dimensional stability. All of the polymers required some kind of binder to be at all effective.

The following three tables are excerpted from tables that appear in Battista [1964] on pages 16, 78 and 94 respectively. They show the behaviour of rayon, nylon and polyester in blends with sulfite pulps and binders. These particular tables were chosen because the fibres used are similar to the fibres that were used in this project.

**Table 1.1 Physical Properties of Papers Made from Sulfite Pulp and Regular Rayon Staple and Vinyon (18-lb. handsheet)**

<table>
<thead>
<tr>
<th>Sulfite Pulp, %</th>
<th>Rayon1 (%)</th>
<th>Vinyon2 (%)</th>
<th>Tensile Str. (lb/in)</th>
<th>Elmendorf Tear (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>4.4</td>
<td>28</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>5</td>
<td>9.6</td>
<td>24</td>
</tr>
<tr>
<td>75</td>
<td>25</td>
<td>5</td>
<td>7.7</td>
<td>29</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>5</td>
<td>6.0</td>
<td>61</td>
</tr>
</tbody>
</table>
1- The rayon fibres were 1.5 denier in diameter and 0.25" long
2- Vinyon is a fibrous binder, not a soluble one.

Table 1.2 Properties of Resin-Saturated Nylon /Pulp Blend Papers

<table>
<thead>
<tr>
<th>Sulfite Pulp, %</th>
<th>Nylon %</th>
<th>Rhoplex %</th>
<th>Basis Wt. (gsm)</th>
<th>Tensile Str. (lb/in)</th>
<th>Toughness (in*lb/in²)</th>
<th>Elmendorf Tear (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>55</td>
<td>16</td>
<td>0.21</td>
<td>110</td>
</tr>
<tr>
<td>77</td>
<td>0</td>
<td>23</td>
<td>71</td>
<td>23</td>
<td>0.72</td>
<td>59</td>
</tr>
<tr>
<td>55</td>
<td>22&lt;sup&gt;a&lt;/sup&gt;</td>
<td>23</td>
<td>69</td>
<td>13</td>
<td>0.55</td>
<td>601</td>
</tr>
<tr>
<td>55</td>
<td>22&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23</td>
<td>69</td>
<td>13</td>
<td>0.25</td>
<td>NA</td>
</tr>
</tbody>
</table>

a- this Nylon was 15 denier per fibre, 0.75" long
b- this Nylon was 3 dpf and 0.25".
The binder was Rhoplex B-15, a polyacrylate dispersion from Rohm & Haas.

Table 1.3 Properties of Resin-Saturated Polyester-Cellulosic Pulp Blend Papers

<table>
<thead>
<tr>
<th>Sulfite Pulp, %</th>
<th>Dacron %</th>
<th>Everflex A %</th>
<th>Basis Wt. (gsm)</th>
<th>Tensile Str. (lb/in)</th>
<th>Toughness (in*lb/in²)</th>
<th>Elmendorf Tear (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>17</td>
<td>0.285</td>
<td>104</td>
</tr>
<tr>
<td>91</td>
<td>0</td>
<td>9</td>
<td>53</td>
<td>24</td>
<td>0.500</td>
<td>91</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>0</td>
<td>55</td>
<td>10</td>
<td>0.120</td>
<td>231</td>
</tr>
<tr>
<td>64</td>
<td>27</td>
<td>9</td>
<td>56</td>
<td>17</td>
<td>0.368</td>
<td>326</td>
</tr>
</tbody>
</table>

Note: Everflex A is a trademark of Dewey & Almy.

The above tables show that adding binder increases strength and decreases tear while adding fibres does the opposite. The combination produces a good balance. There are a number of other tables and graphs in Battista [1964]. Taken all together they lead to the following general conclusions. It should be noted that the list is only a general guideline. Because polymer fibres can vary widely, specific results will vary widely.
1. Tensile strength decreases monotonically with increasing polymer concentration but there are some exceptions, particularly with nylon.

2. Tear increases to a maximum and then decreases as polymer fibre content increases.

3. MIT fold endurance increases with polymer fibre content.

1.2.3.2 Modified Polymer Fibres in Paper

Chtourou, et. al. [1993a, 1993b, 1994, 1997] worked with synthetic pulp, particularly polyethylene (PE) pulp, without binders. Synthetic pulps differ from synthetic fibres in that they tend to be much shorter and they have been fibrillated by a mechanical beating action. Synthetic pulps have significantly more specific surface area than a typical cylindrical fibre but they are much shorter and finer. They are also weaker than fibres.

Because the pulps used were hydrophobic they were treated with poly(vinyl alcohol) to improve dispersion in water. This coating was not anchored and is assumed to wash off during sheets making. Thus it does not lead to compatibility with wood fibres, Rave [1978]. Surface treatment was used to improve compatibility.

Chtourou et. al. [1993a, 1993b, 1994] dealt with characterization of the synthetic pulp after it had been treated with ozone and/or fluorinated gases and corona discharge. They found that the polymer would oxidize and carbonyl groups would form on the surface. After sufficient time, approximately 2.5 h, the oxidation would even penetrate into the bulk fibre. Degradation of the fibres occurred due to treatment and the effects were most pronounced after 2.5 h of treatment. The conclusion is that ozonation can be used to make polyolefin pulps more hydrophilic but care must be taken not to carry the reaction too far. On the other hand, the
fluorine gas and corona discharge treatment only affected the fibre surface and not the bulk.

Chtourou et. al., [1997], treated the synthetic pulp, blended it with wood pulp and characterized the resulting composite sheets. The treatments used were ozonation and oxyfluorination (treatment with O\textsubscript{2} and F\textsubscript{2} gas). The wood pulps used were an explosion pulp and a kraft pulp. The properties measured were breaking length, burst index and tear index.

They found the following trends:
- oxyfluorination gave better results than ozonation
- increasing oxyfluorination increased bonding in the sheet and increased all properties, with tear and burst showing the biggest increases
- increasing synthetic pulp content decreased properties
- the best composite sheet had a breaking length equal to that of the pure wood pulp sheets.
- the best composite sheet had a burst index equal to that of the explosion pulp but all of the blends had better burst than the kraft pulp.
- the best composite sheet had a tear index equal to that of the kraft pulp but all of the blends had better tear than the explosion pulp.

They concluded that oxidation clearly improved the properties of the composite sheets and this was due to improved adhesion. However, the PE pulp was so weak that even well bonded sheets were not very strong. The authors suggested that if stronger PE pulp could be oxyfluorinated then it could lead to "extra-strength PE pulp paper" [Chtourou et. al. 1997].

1.2.3.3 Bonding Polymer Fibres in Sheets

Adhesion between fibres is necessary to make a sheet. It is especially important in the
case of polymer/wood pulp composites because without bonding the sheet will not take advantage of the properties of both components. Unbonded polymer fibres would simply weaken the sheet by displacing wood pulp fibres.

Bonding between fibres in a sheet of paper is a drying phenomenon. As the sheet dries surface tension pulls the fibres together. The work done to pull the fibres together is described by the following equation, described by Zismer in Fowkes [1964]:

\[ W_{ad} = \gamma_{LV} (1 + \cos \theta) \]

where \( W_{ad} \) = work of adhesion

\( \gamma_{LV} \) = free energy of the liquid at the liquid/saturated vapour interface

\( \theta \) = Contact angle of liquid on solid

In the case of fully wet fibres \( \theta = 0^\circ \) so \( \cos \theta = 1 \) and the driving force is simply twice the surface tension of the liquid, which in the case of paper is water. Note that this equation is for a smooth surface, a rough surface has a larger actual area so \( W_{ad} \) will increase with surface roughness.

Because individual fibres are so small, and they are brought in close proximity to each other, the surface tension forces can create tremendous pressures. Clark [1985] gives an example that two surfaces which are 10 Å apart will experience a liquid tension force of 1470 kg/(cm² of contact area) drawing them together. This brings the fibres in close enough contact that hydrogen bonds can form.

While the polymers are somewhat hydrophobic and thus will not wet completely, the \((1 + \cos \theta)\) term will stay in the range of approximately 1.0 to 1.5 so the attractive force will still be considerable. Also, this lower attractive force applies to two adjacent polymer fibres. The much more common situation of a polymer fibre next to a wood pulp fibre should have a greater
attraction than that between polymer fibres. Thus, the lack of attractive force should not be a barrier to sheet bonding.

Once the fibres are drawn into contact they form bonds, primarily hydrogen bonds. In the case of wood pulp fibres there is also interweaving of the fibrils, Clark [1985]. So fibrils provide frictional binding in addition to increasing surface area and thus allowing for more hydrogen bonding. The relatively smooth polymer surfaces do not provide these benefits so even though there is sufficient force to draw the fibres together they may not form strong bonds.

Since it is difficult to estimate the effect of fibrils on bonding, it is not possible to compare the unfibrillated polymer fibres directly to the wood pulp fibres. However, since the chemical composition of the polymers is reasonably well defined, it should be possible to compare their relative hydrogen bonding potential. This is done in Section 3.1 when the strength models for these materials are developed.

1.3 Scope and Approach

Despite all of the work that has been done and described above, the area of synthetic RIFs in mechanical pulps has been largely overlooked. There are a number of possible reasons that this area has not been explored. From an academic point of view, TMP pulps are more chemically and physically heterogeneous than kraft pulps so they are difficult to describe. This makes model development more challenging and it means that more assumptions will be needed.

From a practical point of view, groundwood papers are not valuable enough to justify the use of expensive polymer fibres and binders. Kraft pulp has the largest market share and thus receives the most attention. Also, the use of kraft fibres to reinforce TMP has been reasonably
successful so there has been no real driving force to find substitutes.

However, in spite of these hurdles there are considerations which make this project worth pursuing. Synthetic polymer fibres have more in common with TMP than with kraft. They tend to be cylindrical, hydrophobic and unfibrillated. So, like TMP fibres they will not tend to form well bonded sheets. However, the fines which account for much of the bonding in TMP may act on the polymer fibres and improve bonding. Also, the lignin left in TMP may be able to assist bonding with synthetic fibres by acting as a binder. Eliminating the addition of a binder significantly improves the economic potential of these composites. Finally, while the polymer fibres are not stronger than kraft they are stronger than TMP and may prove beneficial even with weak bonding.

Lignin is more hydrophobic than cellulose and thus might be able to physio-chemically bond with a hydrophobic polymer. Failing that, it may be possible to use heat to melt the lignin so that it could act as a thermal bonding agent. Goring [1966] showed that heating lignin significantly increased its bond strength. Also, Battista [1964] and Tao, et. al. [1997], have shown that thermal bonding improves polymer/pulp composite sheet mechanical properties.

In terms of economics, it is true that even the least expensive polymer fibres cost more per pound than kraft. However, most synthetic fibres are less dense than kraft so on a volumetric basis they can be competitive. Even so, it is not likely that polymer fibres will replace kraft fibres in existing applications such as newsprint and directory paper.

The potential for polymer/TMP composites lies in opening new markets. Groundwood papers tend to be less expensive than woodfree papers so they could compete very effectively, except that they do not have sufficient properties. In some cases only minor improvements would be needed to make groundwood papers competitive. This would open up entirely new
markets to groundwood paper producers. Also, polymers have entirely different properties than wood pulp so there may be opportunities that have not even been thought of yet.

The scope of this project is to examine the tensile properties of handsheets made from blends of TMP with synthetic polymers. The polymers chosen are commercially available products that are already used by the paper industry. The primary variables are polymer type, polymer concentration and heat treatment conditions. Within the heat treatment conditions the variables are time, temperature and pressure.

The approach is to make and test handsheets according to standard TAPPI methods. In order to control for the inherent variability of the pulp, all of the blends, treated and untreated, are compared to an untreated 100% TMP sheet made at the same time as the blends. Qualitative analysis of the structure of the blends is combined with the property data to build simple mathematical models. The models combine elements of models from the area of paper physics with models taken from basic composite theory. It is assumed that the composites can be treated as two phase materials; the voids are treated as lack of mass and not as air.

1.4 Hypothesis

Some of the ideas discussed in previous sections, specifically those listed below, are central to the hypothesis of this study.

1. Papers made from only mechanical wood pulp are limited to certain products, in part because their tensile properties are inferior to those of kraft pulp based papers.
2. Pulp/polymer fibre blends can lead to a sheet with superior mechanical physical
properties but a binding agent, or some type of fibre treatment, is needed in order to
promote adhesion between the components.

3. Studies have looked at the effect of adding synthetic polymer fibres to kraft fibres but
TMP/polymer fibre blends have largely been overlooked.

4. Thermal energy may be used to melt the lignin and/or the polymer fibres in TMP based
sheets and this could lead to adhesion without binders.

Combining the above ideas with some practical considerations leads directly to the
wording of the hypothesis of this work:

The relationship between mechanical pulp properties and final paper properties can be
controlled through the addition of thermoplastic polymer fibres to the pulp, such that the
resulting composite sheet has superior physical properties to a sheet made from pulp alone.

1.5 Objectives

Since TMP/polymer fibre composites have not been previously studied, this project was
divided into two parts. The first phase was called the Exploratory Study. During this phase the
properties of the components were studied. Then a number of different polymers were used and
blends were made at many different concentrations. In addition to looking at the general effect of
adding polymer fibres to TMP sheets, two specific areas were studied in this phase.

It was decided to look particularly closely at the effect of low polymer concentrations,
<1.0%, because previous, unpublished, work done at Abitibi-Price showed that some synergy did
occur. An optimum concentration between 0.5 and 1.5% polymer was reported. These addition
levels are attractive from an economic point of view.
It was also decided to examine the effect of heat on these composite handsheets. It was mentioned at the outset that adhesion is crucial to composite performance. Since the polymers, and the lignin in the TMP, are thermoplastic it may be possible to induce thermal bonding between the two components. A variety of conditions were used for heat treating the blends.

The objectives of the Exploratory Study were:

i. to develop a data set which described what sort of properties could be expected from these composites,

ii. to illustrate the effect of polymer concentration and polymer fibre properties on the properties of the resulting blends,

iii. to combine existing models and the known structural information to produce mathematical models which describe the behaviour of these composites,

iv. to identify a composite with superior properties that would be worth examining in more detail.

The output from the exploratory study became the input for Phase 2 - Detailed Study.

The purpose of the detailed study was to look at the effect of heat treatment. This knowledge could then be put to use to produce blends with commercially useful properties.

The objectives of the Detailed Study were:

i. to gain an understanding of the effects of heat treatment on the composites

ii. to produce a blend with generally superior tensile properties, when compared to an untreated 100% TMP hand sheet,

iii. to provide recommendations for further study of these new materials.
1.6 Industrial Significance

The driving force behind this project is the ongoing effort of groundwood paper producers to diversify their product line. It was mentioned in the Introduction that the properties of groundwood papers have a number of limitations, such as low strength, that confine their use to certain paper grades. It was also pointed out that the mechanical pulps which make up groundwood papers have been well studied and that the limitations of groundwood paper are a result of the property of these pulps.

Efforts to improve mechanical pulp seem to have gone about as far as they can go. Reinforcing these pulps with kraft fibres is common, but kraft is significantly more expensive than TMP. Also, kraft suffers from the property compromise and variability problems inherent in wood pulps. The key to improving TMP papers may be another type of reinforcing material.

Polymer fibres potentially offer a number of useful properties such low density, dimensional stability, relatively well defined size and shape, and excellent toughness. They are not as strong and stiff as kraft pulp fibres but they are stronger than and equally as stiff as TMP pulp fibres. Polymer fibres have higher extensibility and toughness than either kraft or TMP. It may be possible to combine them with mechanical pulps to create sheets that do not suffer from the limitations of traditional groundwood paper. For example, the addition of polymer fibres may be used to produce toughened groundwood paper for products such as envelopes.

This would allow mechanical pulp producers to get into new markets with their product. Given the low growth in their primary existing market, newsprint, this diversification is desirable. The industrial relevance of this project is that it may provide groundwood paper producers with a way to get groundwood papers into new product markets.
CHAPTER 2 - METHODOLOGY

2.1 Experimental

2.1.1 Materials

The basic materials used in this project were thermomechanical pulp and polymer fibres. Each of these are described in more detail in the following paragraphs. No binders or special additives were added to the sheets and all the polymer fibres used are available 'off the shelf'. All of the supplies used in the making of handsheets were generously supplied by Abitibi-Consolidated. They would be found in any pulp and paper wet lab and will not be described here.

All of the pulps used in this project were supplied by Abitibi-Consolidated’s Beaupré mill. This mill is located in Quebec, near Chicoutimi. The pulps are mechanical printing paper pulps and they were taken from the paper making process just after the bleach tower. At this point the pulp is approximately 4% consistency and it contains some fillers. The materials most likely to be present in trace amounts are: sodium silicate, DTPA and synthetic clay or sodium aluminosilicate.

Two separate batches of pulp were used for Phase 1 of this project. Experiments 48-n, 69-n, 96-n and 108-n were made with the first batch. All other experiments were done with the second batch. The pulps were peroxide bleached TMP, around 70% ISO brightness, consisting of roughly 95% black spruce and 5% balsam fir. The consistency of the pulps, as received, was 3-5%.
A total of five types of synthetic polymer fibres were used. They were: polypropylene (PP), copolyamide 6/12 (CoPA), polyamide 6 (PA6), poly(ethylene terephthalate) (PET) and regenerated cellulose (Rayon). Note that nylon is the common name for polyamide. The PP fibres were actually a synthetic pulp, they were mechanically beaten to flatten them and generate fibrils. The CoPA, PA6 and PET are smooth cylinders with flat ends. The Rayon fibres are cylinders with ridges along their length. Figure 3.7.2 is an optical microscope photo of CoPA fibres and Figure 3.7.8 is an SEM photograph of PA6 fibres.

The PP, CoPA, PA6 and PET were obtained directly from the manufacturer while the Rayon was obtained from a flocking company which cut the fibres to length and applied a ‘paper maker’s coating’. This coating is intended to improve dispersion and its exact composition is proprietary. The coating is based on phosphoric acid esters and fatty acid esters. The coating is water soluble. It should wash off during blending and thus not affect the compatibility of the polymer, Rave [1978].

The four types of fibre obtained from directly the manufacturer were supplied in a large enough quantity that the same sample was used for all the experiments. The rayon, however, was supplied in two batches. There was a long time in which no Rayon was available so a series was made without Rayon. This explains the missing points for 5% Rayon in Figures 3.2.A-3.2.D.

2.1.2 Equipment

All of the work for Phase 1 of this study was conducted at the Sheridan Park labs of Abitibi-Consolidated. Handsheets were made on a standard British handsheet maker. The
pulp/water slurry was not re-circulated. Polymers were dispersed in water with a British Disintegrator. The calendering experiments were done on a Beloit-Wheeler lab scale calender with two chrome plated steel rolls.

For the heating experiments a Carver press with 6" electrically heated platens was hooked up to a CAL 3200 PID temperature controller. The platen temperature was monitored with a K type thermocouple inserted into the top platen. The platen temperature was maintained at a set temperature by turning the electrical supply to the platens on and off. The platens were closed, so that both sides of the sheet were heated, but no pressure was applied.

The tensile data was obtained from a Lorenz & Wettre horizontal tensile tester. For the tear data an L&W tear tester was used for all of the series up to and including 2-36. For 2-37 the TMI Monitor/Tear Model 83-11-00 at the University of Toronto was used.

The experimental work for Phase 2 was carried out at the University of Toronto. The 2-89 series was actually made at Sheridan Park, in the last days before it was shut down, but it was tested at the University of Toronto. The 2-96 series was made and tested at University of Toronto as were all the 100% polymer sheets used to measure surface tension.

The University of Toronto handsheet maker and disintegrator are basically the same as those that were at Sheridan Park. The tensile tester is a Sintech vertical tensile tester hooked up to a PC running Testworks II. As previously mentioned, the tear tester is a TMI Monitor/tear Model 83-11-00. The Zero Span tester is a Pulmac TS-100. Calipers were measured with a TMI Precision Micrometer Model 49-61 and most weights were taken on a Mettler AE 200.

The micro-tensile tester was constructed at the University of Toronto. Specimens were tested horizontally. The moving stage was attached to an ST20 stepper motor and the fixed stage was attached to a 5 lb load cell. The grips were aluminum bars with holes at each end. The
clamping force required to hold the specimens was provided by screwing the bars into the stages. The motor turned 1.8°/step and had a maximum speed of 1000 steps/s.

Scattering coefficient was measured by a Technidyne Color Touch Model ISO. Permission to use the Technidyne was generously granted by the National Silicates research lab in Etobicoke.

The optical microscope used is a Reichert research microscope, number 316 563, which can be found in the Faculty of Forestry. Polarizing filters were used but they were not crossed. The polymers and wood pulp appear to have similar degrees of crystallinity because crossed polarizing filters did not distinguish them any more than regular light did. Since crossed polars made it difficult to get enough light to take pictures they were not used.

The electron microscopes used can be found in the electron microscope lab in the Materials Engineering Department at the University of Toronto. Some preliminary work was done on the S-2500, a standard scanning electron microscope (SEM). More detailed work was done on the S-4500, a field emission scanning electron microscope (FESEM). The same samples that were examined by SEM were used.

Contact angle was measured using the goniometer in Dr. Neumann’s lab in the Mining Building at the University of Toronto. The liquid used was water. The polymer sheets were made by melting 100% polymer handsheets between two sheets of Teflon® in the Craver press.

2.1.3 Methods

All handsheets were prepared according to TAPPI standard method T 205 sp-95. This method calls for 1.2 g handsheets to be made from 400 mL of 0.3% consistency pulp suspension.
Since the pulp, as received had a consistency in the range of 3.0% it was necessary to dilute it before making handsheets.

Polymer was added as a suspension just before final dilution. Polymer suspensions were made by weighing out the required amount, adding it to 1 L of water and beating in a British disintegrator for 5 minutes to disperse the fibres. The weight of polymer needed was calculated based on the weight of the handsheets to be made. For example, if five 1.2 g handsheets were needed and the blend was going to be 10 wt% polymer a total of 0.6 g of polymer was added to a pulp suspension containing 5.4 g of pulp. The polymer was assumed to have a 100% consistency.

The pulp freeness and fibre length were measured according to TAPPI methods T 227 om-94 and T 233 cm-95. The sheets were stored in a controlled atmosphere, as described by TAPPI method T 402 om-93. Basic sheet properties such as grammage, thickness and moisture content were measured according to TAPPI methods T 410 om-93, T 411 om-89 and T 412 om 94, respectively.

All of the paper tests were conducted on standard instruments according to accepted TAPPI methods, in particular T 220 sp-96, T 231 cm-96, T 414 om-88, T 425 om-91 and T 494 om-88. The only noteworthy variation was that a grip speed of 10 mm/s was used for the tensile tests, instead of the more common 25 mm/s. A lower speed was used in order to keep the time to break in the range of 15 s, as prescribed by the TAPPI method. A clamping pressure of 80 psi was used for the zero span tensile strength measurements.

The individual polymer fibres were tensile tested on a specially designed microtensile tester at the USDA Pineville lab. This machine is a horizontal tensile tester specially adapted to test single fibres. The grips of the machine are actually drops of glue which attach the fibre to
The motor speed used was 25 pulses/s, which corresponds to 2.25 mm/min. The distance travelled by the grips was 2,500 steps or 3.75 mm.

Heat treatment of the sheets was done in a Carver press heated to the required temperature and closed but not pressurized. The platens were closed in order to ensure that the sheets were heated from both sides. A maximum time of 90 s was used because it was found that longer times led to noticeable darkening of the sheets.

Calendering of the sheets was done on a Beloit-Wheeler laboratory calendar with two chrome plated steel rolls. The lowest speed, 10 rpm, was used. Since the roll diameter was 47.9
cm this gave a linear speed of 4.8 m/min. The samples used were 10.2 cm square so the time taken for a sheet to pass through the rollers was approximately 1 s.

The temperatures used were 150, 200 and 250 °F (66, 93 & 121 °C). 250 °F was the maximum temperature the rolls could reach. In order to maintain an even pressure profile the handsheets were cut into squares. The largest square a handsheet will yield is 10 cm by 10 cm. This meant there was only enough material to do tensile tests so there is no tear data for these experiments.

Polymer contact angle was measured on 100% polymer sheets, except in the case of rayon. The sheets were made as standard handsheets, with polymer fibres instead of wood pulp, and then dried and melted in the heated Carver press. The polymer mats were placed between two sheets of Teflon® in order to prevent sticking to the platens. The melted mats were allowed to cool before they were removed from between the Teflon® sheets. This minimized contact between the hot polymer and air.

Contact angle was measured at one spot on each of three different sheets. The angle on both sides of the drop was measured, for a total of 6 measurements per polymer. The actual measurement involved putting a drop on a sheet and then lining up and focussing the goniometer. Then some more water was added to the drop and the contact angle was recorded immediately. The resulting measurement is referred to as the advancing contact angle. All the contact angles reported in this paper are advancing contact angles.

The single fibre heating experiments used CoPA fibres that were separated by hand using tweezers. The fibres are difficult to see even though they are relatively long, because they are very thin, so the work was done on a black background. The fibres were heated on glass slides in the Carver press. The slides were then covered with cover slips and observed with the Reichert
optical microscope.

The SEM samples were taken from the fracture edge of a tear specimen and gold coated. A 20 kV accelerating voltage was used for the SEM while 10 kV was used for the FESEM.

Sample preparation for optical microscopy involved soaking a small piece of hand sheet in water overnight. The soaked pieces were torn again and a small amount transferred to a glass slide with 2-3 drops of water. The fibres on the slide were manually separated using tweezers. Once the water evaporated a slip cover was placed on the slide and the slides were photographed through the Reichert microscope using Kodak Max 400 black and white film.

The optical photographs were used to calculate fibre lengths. The fibres were measured by laying a piece of string over the picture. A mm scale was also photographed and piece of string equivalent to 1 mm was measured. The length of the fibre was then calculated as the length of the fibre string divided by the length of the 1 mm string.

All of the scanning electron microscope (SEM) photos were digitally captured directly from the SEM using the PCI software package. They were saved as JPEG files and imported directly into this document using WordPerfect. The optical microscope photos were digitized by scanning them with a Hewlett-Packard ScanJet IIcx scanner. They were converted from TIF files to JPEG files using Microsoft Photo Editor and then imported into this document.

2.2 Analytical

2.2.1 Design of Experiments

The experiments were designed so that one or two factors were varied while all the others
were held constant. Because wood pulp is so variable it is impossible to control its properties from batch to batch. In order to minimize the effect of variations in sheet properties due to variations in the pulp, a number of 100% TMP control sheets were made. In fact, separate TMP control sheets were made for all but one or two experiments.

Property values for all of the blends are reported as a percentage (%) change from the control results. The formula used for % change is simply:

\[
% \text{ change} = \frac{(\text{blend value} - \text{control value})}{\text{control value}}.
\]

The underlying assumption is that for a given set of experiments the pulp properties are more or less constant so any variation is primarily to the presence of the second component and or the treatment used. Of course there will be normal experimental variation so all reported results are averages of five, eight or ten readings taken from four or five different handsheets.

In several cases the same blend was used in more than one experiment. For example, 90/10 TMP/CoPA, untreated, hand sheets were made and tested as part of the 46-n, 118-n and 140-n series. The results for all three sets of sheets were graphed together so there would be up to 30 points used to calculate the mean value which appears on the graph. When this is the case, the data is combined after the % change is calculated and not before. So, all the points for a given series are compared to the baseline for the same series.

2.2.2 Statistical Analysis

Statistical analysis was done using SAS version 6.12. Standard TAPPI methods call for at least five handsheets to be made for each sample to be tested. These handsheets are then cut in
such a way as to yield ten tensile strips and five tear specimens. The tear specimens are then put together in groups of two or four and torn up to four times. The result of all this is ten readings for tensile strength, stiffness and TEA and eight readings for tear. This can vary due to circumstances and any significant variations are noted. The multiple readings were then treated as independent for the purpose of statistical analysis.
CHAPTER 3 - RESULTS AND DISCUSSION

The first group of experiments done determined the properties of the raw materials being used. The experiments in the Exploratory Study, as outlined in Section 1.5, can be conveniently fitted into three groups. The Detailed Study focussed on the effect of heat treatment. The goal of the detailed study was to describe the structure of, and to derive an explanation for the behaviour of, these materials. The groups of experiments are listed below and then described in more detail in the following sections.

3.1 Properties of Wood Pulp and Polymer Fibres
3.2 Effect of Varying Polymer Concentration
3.3 Effect of Low, <1%, Polymer Concentrations
3.4 Effect of Calendering
3.5 Effect of Heat Treatment
3.6 Scattering Coefficient Data
3.7 Microscopy Results.
3.1 Properties of Wood Pulp and Polymer Fibres

3.1.1. Thermomechanical Pulp (TMP) Properties

All of the pulp used in this project was provided by the Abitibi-Consolidated Beaupre mill. The pulp was supplied at ~5% consistency in 5 gallon pails. In an experimental oversight the first batch of pulp was made into handsheets before the pulp properties were measured. Thus information on the pulp properties for this batch is not available. However, the pulp in the second batch, which was used for the bulk of the experiments was characterized as follows:

Bauer-McNett length fraction = 13.2% R-14
28.2% R-28
18.9% R-48
10.0% R-100
6.0% R-200
23.7% P-200.

When the Abitibi-Consolidated Research Centre at Sheridan Park was closed down in April of 1998 the second batch of pulp was thrown out and the Bauer-McNett classifier was moved. Thus the Phase 2 experiments were done on a third batch of pulp. The length of this pulp was analysed using a Fibre Quality Analyser (FQA). Pulp number three can be characterized as follows:

Length weighted length = 1.19 mm
Length weighted % fines = 13.75%

The tensile properties of the TMP fibres which appear in Table 3.1 were obtained experimentally while the other values are from the literature. Note that the density is actually the density of the cellulose component of the fibre so it represents the density of the dry fibres.
Fibres in a slurry will often contain air trapped in the lumen so their apparent density will be lower, from 880-1,080 kg/m³, Clark [1985]. The fibre surface free energy data is that for mature black spruce TMP.

**Table 3.1 Properties of Wood Fibres**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elongation, %</td>
<td>2.3</td>
</tr>
<tr>
<td>Tensile Strength (Zero Span), MPa</td>
<td>32.6</td>
</tr>
<tr>
<td>Tensile Modulus, GPa</td>
<td>4.7</td>
</tr>
<tr>
<td>Specific Surface Area, (m²/kg)</td>
<td>~1000</td>
</tr>
<tr>
<td>Density, dry fibres, (kg/m³)</td>
<td>1,570</td>
</tr>
<tr>
<td>Surface Free Energy, mN/m</td>
<td>44</td>
</tr>
</tbody>
</table>

The values in Table 3.1 are well short of the values of 45-55 GPa, Page *et al.* [1979], for modulus and 20 GPa, Kim, *et al.* [1975], for tensile strength that are mentioned in Section 1.0. This is due to the fact that mechanical pulping produces very damaged fibres with large amounts of non-cellulose materials. The result is that TMP fibres have properties that are far below the theoretical maximum.

3.1.2 Synthetic Polymer Properties

All of the polymer fibres are described in the following tables. Table 3.2 describes the physical properties of the fibres and these data were taken from the suppliers specification sheets. Where the supplier's data was not available, values were estimated from the literature, Saechtling [1995]. The length and width of the PP fibres are given as approximates because the process of
making the fibres into pulp gives them a very irregular morphology and makes it practically impossible to know the length and diameter exactly.

The supplier's data for tensile properties was not complete so the fibres were tested by an independent lab. The tensile data for the polymers, which appears in Table 3.3, are all based on the results of the independent tests. The exception to this was the PP pulp because these fibres were too short to test. Fortunately, the supplier did have tensile data for this particular material so this was used in the table.

The testing lab was the USDA Pineville Lab in Louisiana, which was working in cooperation with the Biocomposites Centre at the University of Wales, Bangor. Both labs have a tensile testing machine designed to test single fibres. However, their apparatus is designed primarily for plant fibres, such as wood, and they ran into considerable difficulty with the polymer samples. In particular, the very long extensions of the polymers and their tendency to neck caused problems. There was also some difficulty with adhesion between the epoxy and the polymer fibres.

As a result, while 20 fibres were tested for each of the CoPA, PA6, PET and Rayon fibres, several results that had to be estimated because the fibres slipped through the grips before failing. When a fibre slipped the maximum displacement could not be found. It was also necessary to estimate the maximum force and the slope.

The rayon was the extreme case. Due to fibre slipping 17 of the 20 data points were estimated. Except for the rayon results, all of the estimated data were dropped from the data set before the averages and standard errors were calculated. The rayon results are considered close estimates because the fibre slipped through the grips after the proportional limit. In conclusion, the data in Table 3.3 is the best available but they are only a good approximation.
Table 3.2 Physical Properties of Polymer Fibres

<table>
<thead>
<tr>
<th>Property</th>
<th>PP</th>
<th>CoPA</th>
<th>PA6</th>
<th>PET</th>
<th>Rayon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Mini-Fibers Inc.</td>
<td>EMS-American Grilon</td>
<td>EMS-American Grilon</td>
<td>DuPont</td>
<td>Claremont Flock</td>
</tr>
<tr>
<td>Name</td>
<td>Fybrel</td>
<td>Grilon K140 NV</td>
<td>Grilon NV</td>
<td>Dacron</td>
<td>RC8B0-05</td>
</tr>
<tr>
<td>Grade</td>
<td>Y-600</td>
<td>K-140 NV</td>
<td>NV</td>
<td>112A74</td>
<td>RC8B0-05</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>0.91</td>
<td>1.07</td>
<td>1.14</td>
<td>1.50¹</td>
<td>1.51</td>
</tr>
<tr>
<td>Melting temp, °C</td>
<td>165</td>
<td>125-145</td>
<td>223</td>
<td>310¹</td>
<td>NA</td>
</tr>
<tr>
<td>Fibre length, mm</td>
<td>~1</td>
<td>6</td>
<td>6</td>
<td>12.7</td>
<td>5.08</td>
</tr>
<tr>
<td>Fibre diameter, μm</td>
<td>~1</td>
<td>22</td>
<td>19</td>
<td>17.6</td>
<td>30.3</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>~1000</td>
<td>273</td>
<td>316</td>
<td>722</td>
<td>168</td>
</tr>
<tr>
<td>Specific Surface Area</td>
<td>~1000</td>
<td>170</td>
<td>185</td>
<td>152</td>
<td>88</td>
</tr>
</tbody>
</table>

¹ - these values are actually for fully stretched crystalline film so they should be close to the fibre values. They are taken from Saechtling [1995].

Table 3.3 Tensile Properties of Polymer Fibres

<table>
<thead>
<tr>
<th>Property</th>
<th>PP</th>
<th>CoPA</th>
<th>PA6</th>
<th>PET</th>
<th>Rayon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. load, g</td>
<td>-</td>
<td>11</td>
<td>9</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Elongation, μm</td>
<td>-</td>
<td>171</td>
<td>164</td>
<td>125</td>
<td>6.3</td>
</tr>
<tr>
<td>Slope, mg/micron</td>
<td>-</td>
<td>80</td>
<td>76</td>
<td>132</td>
<td>481</td>
</tr>
<tr>
<td>Strain, %</td>
<td>500¹</td>
<td>20</td>
<td>15</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>Tensile Strength, MPa</td>
<td>37.2¹</td>
<td>283</td>
<td>327</td>
<td>485</td>
<td>197</td>
</tr>
<tr>
<td>Tensile Modulus, GPa</td>
<td>1.6²</td>
<td>1.7</td>
<td>5.1</td>
<td>5.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

¹ - from supplier’s data
² - from Saechtling [1995]

Note that in Table 3.2 the fibre length and diameter data is given by the suppliers
technical specification sheets while aspect ratio, the ratio of length to width, and specific surface area were calculated. Similarly, in Table 3.3 load, extension and slope are the measured values while strain, tensile stress, and modulus are all calculated from the tensile data and the dimensions of the fibres.

Finally, Table 3.4 contains values for the surface properties of the polymers. Contact angles for PP, PET, PA6 and CoPA were determined experimentally. Rayon could not be measured because a melted sheet could not be made. Literature values for contact angle have been provided for comparison. The literature values for PP, CoPA, PA6 and PET are from Neumann & Spelt [47]. Note that no value was found for PA 6/12 so the CoPA value is actually for PA 6/10. The Rayon value is actually a value for cellulose acetate. It and the value for PP are taken from Gupta & Whang [1998]. The experimental values are higher than those found in the literature, probably due to surface roughness.

It is difficult to convert contact angle data into more useful surface energy data so the decision was made to use literature data. The references used were Gupta & Whang [1998] for PP, Gupta [1998] for Rayon, and Neumann & Spelt [1996] for PA6, CoPA and PET. Again, a value for PA6/12 was not available so a value for PA6/10 was used.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Contact Angle, Measured</th>
<th>Contact Angle, Literature</th>
<th>Surface Energy (mN/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>104</td>
<td>96</td>
<td>23.0</td>
</tr>
<tr>
<td>CoPA</td>
<td>76</td>
<td>71¹</td>
<td>40.5¹</td>
</tr>
<tr>
<td>PA6</td>
<td>74</td>
<td>60.5</td>
<td>46.6</td>
</tr>
<tr>
<td>PET</td>
<td>86</td>
<td>79</td>
<td>36.0</td>
</tr>
<tr>
<td>Rayon</td>
<td>--</td>
<td>56²</td>
<td>46.1</td>
</tr>
</tbody>
</table>
1. These values are for PA 6/10 not PA 6/12. The surface energy of PA 6/12 is probably 1 or 2 mN/m² lower.

2. This value is actually for cellulose acetate but it should be similar to the value for rayon.

3.2 Effect of Varying Polymer Concentration

3.2.1 Effect of Concentration on Properties/Grammage

The first set of graphs, 3.2.A-3.2.D, show property/grammage versus polymer concentration for five different blends. The range of concentration in these graphs is 0-20%. All of the points, except 5%, represent at least two different sets of sheets so each point of tensile data is an average of at least 20 measurements while the tear data points are an average of at least 16 measurements. The data for 5% blends comes from only one set of sheets.

Standard errors for each of the points are all approximately ±1-2% for strength, stiffness and TEA and ±5-10% for tear. The standard errors do not vary significantly between the different polymers so in order to improve the clarity of the graphs, only the error bars for PP have been included on the tensile graphs. On the tear graph the error bars are on the CoPA points, the PP has very low tear values so the standard error is low and not representative.

Both tensile strength and stiffness decrease with increased polymer concentration, in a nearly linear way. There is no obvious correlation between polymer strength and blend strength, and this will receive more attention in section 3.2.1.1 when the strength models are developed. Similarly, there is no obvious explanation for the stiffness results but they will be dealt with in more detail in section 3.2.1.2.
Figure 3.2.A

Tensile Str./Grammage vs. Polymer Conc.
All polymers. 46, 118, 141, 181 & 187/88 series

Figure 3.2.B

Stiffness/Grammage vs. Polymer Conc.
All polymers. 46, 118, 141, 181 & 187/88 series
Figure 3.2.C

TEA/Grammage vs. Polymer Conc.

All polymers: 46, 118, 141, 181 & 187/88 series

Figure 3.2.D

Tear/Grammage vs. Polymer Conc.

All polymers: 46, 118, 141, 181 & 187/88 series
The toughness indicator, tensile energy absorption (TEA) gives better results than the strength and stiffness. TEA stays more or less unchanged up to 5% polymer and then starts to decrease. The TEA results are discussed in more detail in section 3.2.1.3.

Finally, the tear results are very different from the tensile results. Tear increases dramatically for the PET and polyamides but only slightly for the rayon and not at all for the PP. Note that the scale on this graph is much larger than the others, the range is 200% instead of 35 or 40%. This time there is a correlation, between polymer fibre length and blend tear strength. The tear results are discussed further in section 3.2.1.4.

Despite the lack of extraordinary properties for these composites, except for tear, there are a number of interesting general observations to be made. Looking first at the tensile strength and stiffness graphs, the polymers do not have a significantly different effect at concentrations below 10%. This is surprising given the large difference in hydrophobicity and in physical properties among the fibres.

It was shown in the literature review that relationship between fibre strength and stiffness and sheet strength and stiffness have been thoroughly studied. In the next section, some of this work will be adapted to the current polymer wood pulp blends and the expected results will be compared to the results observed in 3.2.A-3.2.D.

3.2.1.1 Strength Models for Composite Sheets

The first step in modelling these composite sheets is to assume that the Page equation, Page [1969], adequately describes paper-like networks of fibres. The Page equation in units stress instead of breaking length is:
\[
\frac{1}{T} = \frac{9}{8Z} + \frac{12A}{bPL(R.B.A)} \tag{3.1}
\]

where: \( T = \) tensile strength of the sheet, MPa

\( Z = \) zero span tensile strength of fibres, MPa

\( A = \) fibre cross section area, m²

\( b = \) shear bond strength per unit area

\( P = \) perimeter of fibre cross section, m

\( L = \) fibre length, m

\( R.B.A. = \) relative bonded area, dimensionless

According to the various theories of strength and modulus, Page [1969], Shallhorn & Karnis [1979] and Page & Seth [1908b], there are two critical factors which control these properties in paper. The first is the properties of the fibres themselves and the second is the degree of bonding in the sheet. The degree of bonding can be further broken down into two main components: number of bonds, or bonded area, and strength per bond. So, the Page equation could be re-written as:

\[
\frac{1}{T} = \frac{1}{F} + \frac{1}{B} \tag{3.2}
\]

where \( T = \) the strength of the sheet, N

\( F = \) the force required to break the fibres, N

\( B = \) the force required to break the bonds between fibres, N

Page [1969] used equation 3.1 to describe two component sheets made from sulfite pulp and Rayon with a guar gum binder. The equation fit the experimental data so it seems to be valid.
for two component sheets. However, a modification will be needed in order to use this equation to describe the separate effect of each component.

The simplest way to model these composite sheets would be to use a Rule of Mixtures approach, as described in detail in Appendix III. However, while the simple rule of mixtures works for modulus calculations it does not work for strength calculations, because one component will fail before reaching its ultimate strength. So, the tensile strength of a composite is the sum of the volume fraction times the strength of the component which fails first and the volume fraction times the stress in the other component, Piggott [1980]. This can be written as:

$$\sigma_c = v_1 \sigma_{1u} + v_2 E_2 \sigma_{1u} / E_1$$  \hspace{1cm} 3.3

where: $\sigma_c =$ the tensile strength of the composite, MPa

$\sigma_{1u} =$ the ultimate tensile strength of the component which fails, MPa

$v_1 \& v_2 =$ the volume fractions of component 1 & 2, respectively

$E_1 =$ the elastic modulus of the component which fails, MPa

$E_2 =$ the elastic modulus of the component which does not fail, MPa

Note that this equation is derived from the simple rule of mixtures equation using the equation for elastic modulus, $E = \sigma/\epsilon$, and assuming that the fibres do not slip, so that the strain, $\epsilon$, is the same for both components.

In the TMP/polymer systems studied it is the TMP which fails first, so it would be component 1 in the equation 3.3. Unbroken polymer fibres can clearly be seen extended from the fracture surface of the tensile test specimens. The fact that the polymer fibres have greater extensibility explains why the TMP fibres fail first. Lack of sufficient bonding between the two components would explain why the polymer fibres do not fail at all.

Combining the concepts embodied in the paper by Page [1969] and the modified rule of
mixtures equation (Piggott [1980]) gives a useful model. The fibre breakage term, $F$, for a composite sheet can be given by the equation:

$$ F = \frac{8(v_1 Z + v_2 E_2 \varepsilon)}{9} \quad 3.4 $$

where $Z =$ the zero span tensile strength of the fibres, MPa

$E_2 =$ the modulus of the polymer fibres, MPa

$v_1 \& v_2 =$ the volume fraction of components 1 & 2 respectively, dimensionless

$\varepsilon =$ the strain in the sheet, dimensionless

The fibre bonding term, $B$, can be determined from the simple rule of mixtures. This gives the equation:

$$ B = v_1 B_1 + v_2 B_2. \quad 3.5 $$

Of all the variables, $Z$ and $\varepsilon$ can be determined directly from experiments while $v_1$, $v_2$ and $E_2$ are given. $B_1$ can be determined by using the Page equation with tensile data for 100% TMP sheets. $B$ can be found for the composite sheets using the Page equation again and thus $B_2$ can be calculated as an unknown. From the Page equation it is known that:

$$ B_2 = \frac{12 A_2}{b_2 P_2 L_2 (RBA)_2} \quad 3.6 $$

All of the variables are known except for the bonding terms $b_2$ and $(RBA)_2$. So, the available data can be used to derive a value for $b_2(RBA)_2$. Equations 3.1 to 3.5 are used to calculate $F$, $B$, $B_1$ and $B_2$ in Appendix II.

One way to validate the model is to determine if the values of $b_2$ and $(RBA)_2$ which are
generated are reasonable. Since neither quantity can be measured the derived values cannot be compared to experimental results. However, a theoretical estimate of the bonding terms can be developed if a number of reasonable assumptions are made. The theoretical and empirical values can then be compared.

The primary problem in developing an expression for the bonding of pulp fibres is estimating what fraction of the surface area of the polymer component will be in contact with the pulp. There is no theoretical basis for this estimate. Thus bond strength per unit area, \( b \), and relative bonded area, \( RBA \), cannot be used.

It is possible to make a reasonable estimate of the bond strength for a single polymer wood pulp bond. This term can be designated \( b^* \). It is also possible to estimate the tendency of a given surface area of polymer to form bonds. This term can be designated the Bonding Index, \( BI \). Now the denominator of equation 3.6 becomes \( b^*P_2L_2(BI) \). The result is that \( B_2 \), the bonding term for the polymer component, has the same units as and is directly analogous to \( B_1 \), the bonding term for wood pulp. The expression cannot be used to generate absolute values because \( BI \) is the number of bonds per unit surface area and the total surface area in contact with pulp is unknown. However, it is reasonable to assume that ratio of contact area to available area is the same for all the polymers so that the equations 3.4 to 3.6 can be used to compare the polymers.

In developing a theoretical expression for the bonding of polymer fibres in a composite sheet the first assumption is that the polymers only form hydrogen and van der Waals bonds with the pulp. This implies that there is no interweaving of fibrils but this is reasonable since the polymers have no fibrils. The polypropylene is an exception, it is fibrillated, but given the hydrophobicity of polypropylene it is not a bad assumption that the fibrils do not interweave.

For this model the average value of 25 kJ/mol will be used for all of the polar groups. Van der Waals bonds are much weaker than hydrogen bonds, with dissociation energies on the order of 1 kJ/mol, Israelachvili [1992]. Converting bond energies into forces requires an estimate of the bond length. For hydrogen bonds in water Israelachvili [1992] gives a length of 0.176 nm. The length of the van der Waals bonds can be estimated by summing the van der Waals radii of oxygen and hydrogen. The result is 0.26 nm, Israelachvili [1992].

Work is given by the area under a force versus distance graph. If we assume that the bonds behave as linear springs the force versus distance graph is a straight line. The equation for work is then simply:

\[ W = 0.5Fd \]  \hspace{1cm} 3.7

where:  
- \( W \) = work, J 
- \( F \) = force, N 
- \( d \) = distance, m

Both bond energy, or work, and bond distance are given in the above paragraph so the bond forces can be calculated by division. The force required to break a hydrogen bond is \( 2.84 \times 10^{14} \) N/mol and the force required to break a van der Waals bond is \( 7.70 \times 10^{12} \) N/mol. The force required to break a single bond found by dividing by Avogadro's number, \( 6.02 \times 10^{23} \). So, the force required to break a single hydrogen bond is \( 4.72 \times 10^{-10} \) N and the force required to break a single van der Waals bond is \( 1.28 \times 10^{-11} \) N. Note that the ratio of force required to break the two types of bonds is 36.9:1.

So, the bond strength of the polymer bonds, \( b^* \), will be either \( 4.72 \times 10^{-10} \) N or \( 1.28 \times 10^{-11} \) N, depending on the type of bond formed. Whether a bond is a hydrogen or van der Waals bond depends on the functional groups involved in the bond. The number and type of functional
groups on the polymers, and thus the number of each type of bond formed, will be accounted for in the bonding Index, \( BI \). The bonding index is derived in the following paragraphs.

The next assumption is that the number of bonds formed by the polymers, or their tendency to bond, is based on the number and type of functional groups on the polymer chain and whether or not a given group forms hydrogen or van der Waals bonds. Highly polar functional groups are able to hydrogen bond. The highly polar functional groups on the polymers used in this project are hydroxyls (O-H), carbonyls (C=O) and amides (N-H). The non-polar functional groups form very weak van der Waals bonds, Solomons [1984]. The aliphatic hydrogen group, C-H, is non-polar.

The first step in determining bonding tendency is to count the number of functional groups on a monomer, as given by the chemical structure of the monomer. Dividing this number by the monomer's molecular weight gives the number of functional groups per gram. However, while the polymers are added to the sheet on a mass basis, only the surface can participate in bonding. So, the number of groups needs to be converted from a mass basis to an area basis. This can be done by dividing by the specific surface area of the polymer. The final number has units of functional groups/surface area and this makes the last term of the Page equation dimensionally correct.

However, the number of functional groups/surface area does not account for the fact that the groups are very different. Not only will some groups form hydrogen bonds while others will form van der Waals bonds, the groups will have differing reactivity. It is reasonable to assume that the more reactive groups are more likely to form bonds.

So, in order to convert the number of functional groups into a number of bonds the number of each type of group must be multiplied by its reactivity. The relative reactivity of the
groups is not known but since both hydrogen and van der Waals bonding are due to dipole-dipole interactions it is possible to compare the reactive groups based on their different polarity.

One measure of the polarity of a bond is the difference in the electronegativity between the atoms in the bond, Lide [1997]. This does not allow for a distinction between the amide carbonyls on the CoPA and PA6 and the ester carbonyl on the PET but this difference is negligible. All the electronegativity data in Table 3.5 is from Lide [1997] and is based on the Pauling scale. The values are dimensionless.

Table 3.5 Polarity of Active Groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Polarity,</th>
<th>X₁ - X₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>O-H</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>N-H</td>
<td>0.84</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6 shows the number of functional groups on each type of monomer present in the different polymers. The chemical structures of the monomers can be found in Appendix II. The ratio of PA6 to PA12 used in the CoPA is unknown, the information is proprietary. A conservative estimate is a 1:1 so that is the ratio that was used was used.
Table 3.6 Number of Functional Groups/ Monomer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight</th>
<th># of C-H groups</th>
<th># of O-H groups</th>
<th># of amide C=O groups</th>
<th># of amide N-H groups</th>
<th># of ester C=O groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>42</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA6</td>
<td>113</td>
<td>10</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>CoPA (PA 6/12)</td>
<td>310</td>
<td>32</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>PET</td>
<td>192</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Rayon</td>
<td>340</td>
<td>12</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The data in Tables 3.4 and 3.5 can be used to calculate the reactivity term. Finally, if the number of groups per unit area is further multiplied by a factor to account for the type of bond formed by the group, the result is a Bonding Index, $BI$. If groups which hydrogen bond are given a weight of 1, the groups which van der Waals bond are given a weight of $1/36.9 = 0.0271$. All of the calculations for $BI$ appear in Appendix II.

Even though model developed can only describe the relative tendency of the polymers to bond and not the actual value of the bonding term, the model can still be compared to the empirical data. The use of the weighting factor to account for the different bond strength in $BI$ means that the equations 3.3 to 3.6 should yield a value of $b^*$ that is the same for all polymers.

So, equations 3.3 and 3.4 can be used to calculate $B_1$ by applying them to the 100% TMP data. They can then be applied to the blend data to get $F$ and $B_2$ for all of the blends. Then equation 3.6 can be used with the polymer property data in section 3.1 and the values of $BI$ calculated in Appendix II to calculate $b^*_2$ for all of the blends. If the resulting values are all close to equal it validates the model that was developed.
Examination of the calculations in Appendix III show that a problem arises during the empirical calculations that prevents them from being compared to the theoretical values. Specifically, the values of $B_2$ that are derived are negative. Any attempt to then derive $b^*_2$ would result in a negative bond strength. This has no physical meaning. However, there is a reasonable interpretation of the negative values of $B_2$: adding the polymer fibres disrupts the wood pulp bonding in the sheet.

This derivation has assumed that the pulp bonding term $B_i=b_i(RBA)_i$ is the same for 100% TMP and for all of the blends. If this assumption were changed and $B_i$ were allowed to decrease as polymer fibres were added positive values for $B_2$ could result. However, if $B_i$ varies the equation 3.5 cannot be solved. In short, this model cannot be used to calculate the actual degree of bonding in the sheet using the data available. It does provide a useful framework for future modelling work.

3.2.1.2 Stiffness Models for Composite Sheets

The law of mixtures is commonly used to describe the behaviour of composites which have a solid matrix and a well bonded fibre, Piggott [1980], Ashby & Jones [1980]. While paper is not a solid matrix the pulp fibres in paper are considered to be well bonded. If the polymer fibres are also well bonded then the law of mixtures should apply because the fundamental assumption, that the pulp and polymer will have equal strain when the sheet is stressed should hold. Since the sheets studied are handsheets, both types of fibres are randomly oriented so the distribution of angles with respect to the direction of stress will be the same for both components.

So, the law of mixtures should provide the upper limit for the modulus of the blends since
it assumes essentially perfect bonding. The law of mixtures is expressed in terms of volume fractions, because stress is transmitted through the area of the fibres and for a given cross section the area fraction and volume fraction are equal, Piggott [1980]. Since the sheets were made on a mass fraction basis a conversion is required. However, due to the large void fraction in the sheet, it is not possible to use sheet density directly to determine volume fraction.

The required calculation is grammage times sheet area, to get a mass per sheet. This number is then multiplied by the mass fraction of each component to get the mass of each component per sheet. Dividing the mass of each component by its respective density will then yield a volume for each component in the sheet. Volume fraction is then the component volume divided by the sum of the two components' volumes. A sample volume fraction calculation appears in Appendix III.

For fibres parallel to the applied stress (i.e. equal strains) the Rule of Mixtures gives:

\[ E_c = v_f E_f + v_m E_m \]  \hspace{1cm} 3.8

where: 
\( E_c \) = tensile modulus of the composite \\
\( E_f \) = tensile modulus of the polymer fibres \\
\( E_m \) = tensile modulus of the wood pulp matrix \\
\( v_f \) = volume fraction of the fibres \\
\( v_m \) = volume fraction of the matrix 

Finally, there are the issues of fibre orientation and possible batch to batch variations in the pulp. The fact that the fibres are randomly oriented can be accounted for by multiplying the
modulus obtained in the above equation by 1/3, Cox [1952]. Batch to batch variation in the pulp has been accounted for by making a 100% TMP control for every set and then reporting blend properties as a % change from the control properties. This process of normalizing the modulus will also eliminate any error caused by assuming unidirectional fibres because the 1/3 factor will cancel out. Normalizing gives \( E_m = 1 \) and \( E_f = \text{polymer modulus}/4.6 \). A sample calculation of normalized sheet modulus appears in Appendix III.

Table 3.7 shows the two predicted moduli and the actual moduli for a range of concentrations. The modulus predicted by the model assumes good bonding between components and it is the expected upper limit. The modulus predicted by setting the polymer modulus to zero assumes that there is no bonding between components and is the expected lower limit. The data were taken from the 46-n and 69-n series. A result somewhere between the two lines could shed some light on the degree of bonding in the composite sheets.

However, all of the blends perform well below the value predicted by the law of mixtures and most underperform compared to the lower limit predicted values, with the notable exception of the PP pulp, which behaves slightly better than predicted, and the 20% Rayon which is 4% better than predicted. Overall, adding polymers leads to worse results than adding nothing. This suggests that the polymer fibres are disrupting the network and perhaps acting as stress concentrators. The tensile strength results lead to the same conclusion.

The anomalous results for PP and 20% Rayon can fit into this explanation as follows. The PP fibres are much smaller and more pulp-like than the other polymer fibres, so they would be expected to disrupt the network the least. As for the Rayon, it is has by far the best bonding potential so at high concentrations there may be enough surface to allow for some bonding.

In order to successfully apply the strength and stiffness models, more information on the
bonding in the sheet is needed. Single fibre pull out tests were conducted in order to determine a value for $b_2$. The force required to pull out a single fibre did not register on the equipment used, so it must be $< 0.01$ N. Yan and Kortschot [1996] performed single fibre pull-out test on black spruce kraft fibres and the results were on the order of 0.02-0.04 N. So, the pull-out energy for the polymer fibres could be of the same order of magnitude as for kraft fibres, which should be well bonded.

Table 3.7 Actual vs. Predicted Modulus for a Range of Blend Compositions

<table>
<thead>
<tr>
<th>Blend Polymer Content</th>
<th>Pulp volume fraction</th>
<th>Polymer volume Fraction</th>
<th>Predicted Modulus Model</th>
<th>Predicted Modulus No Polymer</th>
<th>Actual Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% PP</td>
<td>0.983</td>
<td>0.017</td>
<td>-1.11 %</td>
<td>-1.70 %</td>
<td>-1.69 %</td>
</tr>
<tr>
<td>10% PP</td>
<td>0.839</td>
<td>0.161</td>
<td>-10.50 %</td>
<td>-16.10 %</td>
<td>-14.28 %</td>
</tr>
<tr>
<td>20% PP</td>
<td>0.699</td>
<td>0.301</td>
<td>-19.63 %</td>
<td>-30.10 %</td>
<td>-28.35 %</td>
</tr>
<tr>
<td>1% CoPA</td>
<td>0.985</td>
<td>0.015</td>
<td>-0.95 %</td>
<td>-1.50 %</td>
<td>-6.10 %</td>
</tr>
<tr>
<td>10% CoPA</td>
<td>0.860</td>
<td>0.140</td>
<td>-8.83 %</td>
<td>-14.00 %</td>
<td>-15.23 %</td>
</tr>
<tr>
<td>20% CoPA</td>
<td>0.732</td>
<td>0.268</td>
<td>-16.90 %</td>
<td>-26.80 %</td>
<td>-31.69 %</td>
</tr>
<tr>
<td>1% PA6</td>
<td>0.986</td>
<td>0.014</td>
<td>-0.15 %</td>
<td>-1.40 %</td>
<td>-3.55 %</td>
</tr>
<tr>
<td>10% PA6</td>
<td>0.867</td>
<td>0.133</td>
<td>-1.45 %</td>
<td>-13.30 %</td>
<td>-13.27 %</td>
</tr>
<tr>
<td>20% PA6</td>
<td>0.744</td>
<td>0.256</td>
<td>-2.78 %</td>
<td>-25.60 %</td>
<td>-30.16 %</td>
</tr>
<tr>
<td>1% PET</td>
<td>0.990</td>
<td>0.010</td>
<td>-0.09 %</td>
<td>-1.00 %</td>
<td>-0.55 %</td>
</tr>
<tr>
<td>10% PET</td>
<td>0.896</td>
<td>0.104</td>
<td>-0.88 %</td>
<td>-10.40 %</td>
<td>-14.41 %</td>
</tr>
<tr>
<td>20% PET</td>
<td>0.793</td>
<td>0.207</td>
<td>-1.80 %</td>
<td>-20.70 %</td>
<td>-18.46 %</td>
</tr>
<tr>
<td>1% Rayon</td>
<td>0.990</td>
<td>0.010</td>
<td>-0.02 %</td>
<td>-1.00 %</td>
<td>-5.16 %</td>
</tr>
<tr>
<td>10% Rayon</td>
<td>0.896</td>
<td>0.104</td>
<td>-0.23 %</td>
<td>-10.40 %</td>
<td>-12.58 %</td>
</tr>
<tr>
<td>20% Rayon</td>
<td>0.794</td>
<td>0.206</td>
<td>-0.45 %</td>
<td>-20.60 %</td>
<td>-14.33 %</td>
</tr>
</tbody>
</table>
3.2.1.3 Toughness of Composite Sheets

The polymer fibres are stronger than TMP fibres and have similar stiffness. In addition, the polymer fibres tend to fail in a ductile manner, with high extensions. The extensions of the different materials are shown in tables 3.1 and 3.3 and the polymer extensions are generally an order of magnitude higher. The polymer fibres will absorb significantly more energy during failure than TMP pulp. Toughness is defined as the energy absorbed during failure, Ashby & Jones [1980], so the polymer fibres will be tougher than TMP.

Unfortunately, there are no simple models for TEA that lend themselves to adaptation like the strength and stiffness models in the previous sections. However, it is possible to make some general comments about the results shown in Figure 3.2.C. The fact that high polymer concentrations do not lead to a significant increase in TEA suggests that the polymers are not strongly bonding to the pulp or to each other.

Proof that the polymers do not bond well to each other is the fact that the 100% polymer sheets were too weak to handle. They fell apart, so they could not have been bonded. As for the lack of strong bonding between the polymers and the wood pulp, it has not been proven but it is suggested by all of the tensile data shown so far. It is further supported by the heat treatment results in section 3.5.

3.2.1.4 Tear of Composite Sheets

Finally, there are the tear results, as shown in Figure 3.2.D. The polymer blends, except for the PP/TMP blends, all have significantly increased tear energy and the difference between
polymers is greater for tear than any other property. It turns out that the tear strength of the blends at any given concentration is highly correlated to the polymer fibre length. This is illustrated in Table 3.8, which shows the correlation coefficient, $r^2$, for tear strength vs. fibre length at four polymer concentrations.

Table 3.8 Correlation Between Blend Tear Strength and Polymer Fibre Length

<table>
<thead>
<tr>
<th>Blend Concentration (wt% polymer)</th>
<th>Correlation coefficient, $r^2$, between Tear Strength and Fibre Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.81</td>
</tr>
<tr>
<td>5</td>
<td>0.93</td>
</tr>
<tr>
<td>10</td>
<td>0.92</td>
</tr>
<tr>
<td>20</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Going back to the discussion of tear strength mechanisms in section 1.2.1.2, this evidence appears to support the pull-out dominated mechanism adopted by Shallhorn and Karnis [1979] over the fibre failure dominated mechanism proposed by Page, [1994]. The data at very high concentrations further supports this argument. 100% polymer sheets could not be made because the polymer did not stick together, solid evidence that the polymer fibres do not bond to each other. 80% polymer sheets could be made but they were so weak that the tensile strength did not register on the L&W tensile tester. The threshold load for the L&W was 5 N.

However, they did have a measurable tear strength. In the case of the very short PP fibres the tear strength at 80% PP was only 12% of the tear strength of a TMP sheet. However, for the longer CoPA and PA6 fibres the tear strength was approximately half that of TMP (48% and 56% respectively). If the polymer fibres were inert, the 20% TMP blends should all have had 20% of the tear energy of TMP.
The fact that the 80/20 PP/TMP tear strength is lower than expected is consistent with the network disruption and minimal inter-component bonding theory. However, the much better performance of the CoPA and PA6 blends contradicts this theory. If there is minimal bonding, why does tear energy increase with fibre length?

The usual explanation is that longer fibres have more fibre-to-fibre bonds. While the longer fibres should have more bonds, the tensile and single fibre pull out data suggest that these additional bonds will be relatively weak and few in number. So, the additional bonds would lead to increased tear but it is unlikely that they account for all of the increase. The tear strength of the CoPA and PA6 blends were more than double the expected value. Instead a two part explanation is needed.

In the pulp portion of the blend the increased tear can be explained by the difference between the energy absorbed by fibre breakage and fibre pull-out. The tensile data suggests that adding polymers decreases inter-fibre bonding, even between wood pulp fibres. With fewer bonds to transfer stress, fibre breakage will decrease and fibre pull out will increase. Thus the pulp portion of the blends is absorbing an unusually high amount of energy. The fact that tear increases as pull-out increases supports the fibre pull-out dominated mechanism of Shallhorn & Karnis [1979].

In the polymer portion of the blend the explanation is more complicated. Bond breakage is occurring, but it is only a part of the mechanism. Even though the fibres are poorly bonded they are not voids. When the advancing crack reaches a polymer fibre it cannot break the fibre so it is forced around the fibre and this greatly increases crack length. Also, the tear test is an out of plane test so the fibre will be bent. The polymer fibres are solid cylinders while the pulp fibres will be hollow cylinders or flattened ribbons. So the polymer fibres will have a much
higher bending stiffness than the wood fibres, even though the moduli are similar. Finally, the frictional forces involved in fibre pull-out are not insignificant in the case of wood pulp, Yan & Kortschot [1996], so they will be a factor for the long stiff polymer fibres.

Increasing fibre length would increase both crack length, and thus bond breakage, and frictional forces. Thus the explanation is consistent with the direct relationship between fibre length and tear energy.

The effect is more noticeable in tear than in TEA because the mechanisms are very different. Elmendorf tear is a sequential process, each bond added to the path length has to be stressed and broken. TEA is a more simultaneous mechanism, each bond added to the path is already stressed so they do not consume as much extra energy. In addition, the Elmendorf tear test applies a force perpendicular to the sheet so there will be fibre bending. TEA is measured using an in-plane force so there would be no fibre bending.

This theory could be proved by observing failure in tear and tensile specimens using a video camera and a microscope. In unheated specimens the two types of fibres are readily distinguished. The polymer fibres have a much more regular geometry.

So, the effects of concentration on specific properties can be summarized in the following way. The polymer fibres do not bond to the wood pulp fibres to any significant degree. In fact, they are worse than adding nothing so they must disrupt the wood pulp network and perhaps act as stress concentrators. The result is that the composite sheets have lower strength, stiffness and TEA.

However, the polymers have a large positive effect on tear strength. This suggests that fibre pull-out is a more important mechanism than fibre failure. This is worth following up. None of the properties change in a simple additive manner and the probable explanation lies in
the bonding between components. This issue is worth following up.

3.3 Effect of Low, <1%, Polymer Concentration

Two series in particular, 141-n and 187/88-n, focus on the low concentrations range. However, a number of other series include one or two points in the low concentration range, so there are replicates of several points at or below 1%. There were typically 30 points for the tensile data and 18 for the tear data, although this did vary somewhat. The baseline TMP results are based on 40 points for tensile and 28 for tear.

The purpose of these experiments was to determine if there is a synergistic effect at low concentrations. A previous Abitibi-Price study and some of the early work in this study suggested that there might be a useful effect.

Analysis of the results showed that no significant synergy is apparent. The effect of polymer addition at very low concentrations is negligible. This is illustrated in the graphs 3.3.A to 3.3.D. The standard errors were generally in the 2-4% range and they were similar for all the polymers. In order to reduce clutter, error bars were included for PP only.

In many cases the error bars for PP overlap with points from other series and with the 0 % change line. This indicates that many points are not significantly different from each other or from 0. Also, there are no clear trends for any of the polymers. Thus it is safe to conclude that low polymer concentrations do not have any significant effect and there is certainly no worthwhile synergy.

The exception to this conclusion is tear. Tear does seem to increase significantly, even for low polymer concentrations, for all of the polymers except PP. This is consistent with the
findings in the previous section, where higher polymer concentrations led to very high tear values. Again, however, there is no obvious synergy at low concentrations, the increase in tear is a roughly linear function of polymer concentration.
Figure 3.3.A

Tensile/Grammage vs. Polymer Conc.
(Low concentrations series, 141 & 187/88)

% Change
0 0.2 0.4 0.6 0.8 1 1.2
Polymer Concentration (wt%)

Figure 3.3.B

Stiffness/Grammage vs. Polymer Conc.
(Low concentrations series, 141 & 187/88)

% Change
-8 -6 -4 -2 0 2 4 6
Polymer Concentration (wt%)
Figure 3.3.C

TEA/Grammage vs. Polymer Conc.
(Low concentrations series, 141 & 187/88)

% Change

Polymer Concentration (wt%)

Figure 3.3.D

Tear/Grammage vs. Polymer Conc.
(Low concentrations series, 141 & 187/88)

% Change

Polymer Concentration (wt%)
3.4 Effect of Calendering

The original calendering series, 58-n, looks at temperatures of 63, 97 and 121 °C and pressures of 1,339, 17,412 and 37,502 kg/m. The temperatures were chosen because 121 °C was the highest the Beloit-Wheeler calender could achieve and the other two temperatures gave a balanced design. The pressures were chosen because 1,339 kg/m was the lowest that could reliably be obtained while 17,412 and 37,502 kg/m were so high that the caliper of test handsheets made from 100% TMP did not change much from one pressure to the other.

Any difference between the two higher pressures might then be attributed to the presence of polymer in the sheet. In particular, the degree of bonding between the polymer and the wood pulp might be expected to change as the high pressures created more areas of contact in the sheet.

The blends used were 100% TMP, 90/10 TMP/PP and 90/10 TMP/CoPA. PP and CoPA were chosen because they have the lowest melting points and would be most likely to flow under the given conditions. The experiments were designed as a $2^3$ factorial with replicates at 3 points. When the 140-n series was run it included samples heated to 63, 97 and 121 °C with no pressure. The two series were combined to extend the pressure range down to 0 kg/m.

It would have been desirable to look at temperatures above the melting point of the polymers, such as 150 and 175 °C. It was initially thought that the calender could be easily modified to provide the higher temperatures. However, this assumption turned out to be incorrect, so no higher temperature experiments were run.

Figures 3.4.A-3.4.C show the effect of temperature and pressure on the adjusted tensile strength of the three blends. Tensile strength decreases rapidly as the load is increased from 1,339 to 17,412 kg/m and then much more slowly from 17,412 to 37,502 kg/m. The total
reduction is on the order of -60% so high calendering pressures are clearly deleterious. There is no tear data because the tensile tests consumed all the material in the calendered samples.

It is noteworthy on these graphs that the high pressures are less damaging at higher temperatures. Also, the polymer blends do not show any improvement as the load is increased from 17,412 to 37,502 kg/m, so there is no evidence to support the hypothesis that higher pressures lead to increased bonding. A reason for this might be that the high pressures collapse the wood fibres but do not have a significant effect on the polymer fibres, and it is the lack of surface area of the polymer fibres that limits bonding.

Graphs of stiffness/grammage show exactly the same trends and very similar values so they have been omitted here. TEA does not behave in the same way as strength and stiffness, as shown in Figures 3.4.D-3.4.F. TEA/grammage actually increase at the lowest pressure used. This phenomenon has been documented before, especially by M.F. Gratton at Paprican, and is attributed to an increase in stretch.
Figure 3.4.A

Tensile Str./Grammage vs. Calender Load
100% TMP

Figure 3.4.B

Tensile Str./Grammage vs. Calender Load
10% PP
Figure 3.4.C

Tensile Str./Grammage vs. Calender Load
10% CoPA

Figure 3.4.D

TEA/Grammage vs. Calender Load
100% TMP
Figure 3.4.E

TEA/Grammage vs. Calender Load
10% PP

Figure 3.4.F

TEA/Grammage vs. Calender Load
10% CoPA
Figures 3.4.G-3.4.I show the effect of pressure on the different blend types at 121 °C. The data has been redisplayed this way to show that the blends behave in a very similar manner. The exact same trend appears at the other two temperatures studied so the additional graphs were omitted.

The fact that higher temperatures decrease the damage caused by pressure, coupled with the results in Section 3.5 which show that temperatures above the softening point of the polymer result in superior sheets, suggests that calendering composite sheets could lead to superior properties. It would be worthwhile to investigate higher temperatures and lower pressures than were available on the equipment used here.

To conclude this section, pressure is clearly the dominant variable with higher pressures leading to lower properties. The exception is TEA, which actually increases after light calendering before decreasing at higher calendering pressures. Temperature has a weak effect. Higher temperatures result in slightly better properties. Also, all three furnishes give nearly identical results. This is true for all the properties at all the temperatures. So, calendering does not increase the degree of bonding, at least not at these temperatures.
Figure 3.4.G

Tensile Str./Grammage vs. Blend Type @121 C

Figure 3.4.H

Modulus/Grammage vs. Blend Type @ 121 C
Figure 3.4.1

TEA/Grammage vs. Blend Type @ 121 C

Blend type

% Change

100% TMP  10% PP  10% CoPA

-100 -80 -60 -40 -20 0 20 40

0 kg/m
1339 kg/m
17412 kg/m
37502 kg/m
3.5 Effect of Heat

The first four graphs in this section, Figure 3.5.A-3.5.D, present the effect of temperature on TMP and two blends, 90/10 TMP/PP and 90/10 TMP CoPA. Sets of five sheets were made for each blend at each temperature, so a total of thirty sheets per blend were needed. The sheets were placed in the pre-heated press, at zero pressure, for ten seconds. Once a set for each of the blends had been treated at a given temperature the temperature on the press was changed and the next set of sheets were treated.

As in the calendering experiments, PP and CoPA were chosen for heat treatment because of their relatively low melting points. The lower temperatures were chosen to be the same as the temperatures used in the calendering experiments so that the data might be combined.

The upper two temperatures, 149 °C and 177°C, were chosen because the melting points of the polymers are \(-140 °C\) for the CoPA and \(-165 °C\) for the PP. Thus the first temperature should be enough to melt one polymer but not the other and the second temperature is high enough to melt both polymers. All sheets were heated for 10 seconds. Note that the point at 149 °C was done in two separate experiments so it is an average of 20 values.

The tensile strength, tensile stiffness and TEA graphs, Figures 3.5.A-3.5.C, are all quite similar. Temperature has little effect up to about 100 °C, after which the properties of the sheets improve. Also, the TMP and the blends show very similar trends, up until the highest temperature. It is well known that drying can strengthen and stiffen a sheet so drying probably accounts for most of the changes seen on these graphs. However, at the highest temperature the blends are still improving while the TMP has levelled off.

This temperature is above the melting point of the polymers and this suggests that the
polymers may be starting to thermally bond. Given the relatively short time, 10 s, and the limits of heat transfer through a non-conducting network, the amount of melting is probably quite small. This would explain the small improvement in the blends. It is also possible that the highest temperature is enough to cause some degradation in the wood pulp, which would serve to hide some of the improvement made by the polymer.

The most interesting observation from these graphs is that at the highest temperature the tensile strength and TEA of the blends approach that of the 100% TMP. In contrast, the results shown in section 3.2, the effect of adding polymer without heat, and the lower temperature results in these graphs all indicate that the blends are clearly weaker. So, heat treatment may be the key to making blends that are better than pure TMP. Also, since the TMP values are levelling off, or declining, while the blend values are increasing more may be better in terms of heating. Of course, there will be an upper limit at which the wood pulp will start to degrade significantly and the sheets will start to discolour.
Figure 3.5.A

Tensile Strength/Grammage vs. Temperature
(Blends are 10% polymer, time = 10 s)

Figure 3.5.B

Stiffness/Grammage vs. Temperature
(Blends are 10% polymer, time = 10 s)
Figure 3.5.C

**TEA/Grammage vs. Temperature**
(Blends are 10% polymer, time = 10 s)

![Graph showing the relationship between TEA/Grammage and temperature. The graph compares different blends, showing their % change at various temperatures.](image)

Figure 3.5.D

**Tear/Grammage vs. Temperature**
(Blends are 10% polymer, time = 10 s)

![Graph showing the relationship between Tear/Grammage and temperature. The graph compares different blends, showing their % change at various temperatures.](image)
The tear graph, Figure 3.5.D, is very different from the tensile graphs. In the case of tear, heat has minimal effect on the TMP and the PP/TMP blend, both of which start out with relatively low tear values. However, the CoPA, which starts out with a high tear, shows a steady decrease with temperature. Also, the tear starts to decrease at less than 100 °C, which is well below the melting point of the polymer. This is at odds with the previous results which show that polymer melting is required to achieve significant property changes.

However, the trend shown in Figure 3.5.D may well be an artifact of the way that the software draws lines. Given that the first three points are 45%, 50% and 44% and the standard errors are +/- 2.6, 3.8 & 4.0% they are not actually statistically significantly different. Thus the first three points could actually be a flat line. Next, there is no point between 93°C and 121 °C so the software drew in a downward sloping line. However, given that 121 °C is approaching the melting range of the CoPA (125-145 °C) it is possible that a step change associated with melting is more accurate.

These two suppositions are represented by the dotted line labelled 'Hyp. CoPA', the Hyp. being short for hypothetical. This graph is more consistent with the tensile results because it shows that melting is indeed the reason for the significant change in properties. However, the effect of melting in Figures 3.5.A-3.5.C is not apparent until temperatures well above 121 °C, and the effect is not as dramatic in the previous graphs. This suggests that there are different mechanisms affecting the tensile and tear.

The logical conclusion to be drawn from the tensile graphs is that 10 s is not sufficient time to cause softening and bonding at temperatures much below 177 °C. So, the explanation that the CoPA fibres are bonding to the wood pulp and thus breaking rather than pulling out, with a resulting reduction in tear energy, cannot be used. It is possible that the lignin is softening and
creating increased bonding.

If the lignin is responsible for increased bonding in the sheet, there should be increased bonding and fibre breakage in the TMP as well as in the blend. So the tear energy of the TMP should also drop, but it does not. It could also be a drying effect, but then the TMP and TMP/PP blend would behave in the same way as the TMP/CoPA. This is not the case.

A more likely explanation lies in the fact that tear does not depend on the same factors as the tensile properties. The results in Section 3.2 clearly indicate that tear is primarily a function of fibre length and not of bonding. The drop in tear strength for CoPA observed in graph 3.5.D may be due to the fibres shrinking axially as they heat up. Since the fibres are cold drawn there will be considerable frozen in stress in the axial direction at the molecular level. As the polymer chains gain thermal energy they will tend to relax and curl up.

This explanation is supported by visual evidence. When three 6.0 mm long CoPA fibres were placed on a glass slide heated to 120 °C they rapidly shrank but they did not stick to the slide. When the fibres were removed after just a few seconds of exposure their lengths were 1.7, 1.8 and 1.6 mm. When the fibres were placed on a slide and then heated at 177 °C they melted into droplet with diameters less than 0.5 mm. Upon cooling the droplets were stuck to the slide.

Heat transfer in a sheet will not be as good as it is on a slide but it is still significant. Optical micrographs of CoPA fibres from actual heat treated sheets in the 2-96-n series show that there are no 6 mm fibres left in the sheet. Four polymer fibres were identified and measured and their average length was 2.5 mm. The actual pictures can be seen in Section 3.7.1.

The conclusion to be drawn is that heat treating increases bonding but decreases fibre length. Fibre shrinkage occurs at a lower temperature than bonding. So, the blends improve significantly upon heating, except in the case of tear. The right conditions could lead to blends
that are stronger and tougher than a 100% TMP sheet. The loss of tear could be compensated for by using longer fibres. Lengths of 25 mm or more are commercially available.

The next series of graphs explores the possibility of making better blends by heat treating. The amount of heat supplied was varied by changing the heating temperature and time. Only the highest two temperatures, 149 °C and 177°C, were used because they are above the polymer melting point and some melting will be needed for thermal bonding. A minimum time of 10s was selected so that the data could be combined with the earlier temperature series results thus giving some replicates. A maximum time of 90 s was selected because experiments showed that 90 s at 177 °C is the point at which the sheets started to turn brown.

The graphs, Figures 3.5.E - 3.5.H, show the change in property/grammage for the sheets compared to a baseline of unheated TMP. The blends start out with negative values as expected, from the effect of concentration results, Figures 3.2.A-3.2.D. As the heat treatment becomes more severe, the blends show positive values so heat treatment is clearly beneficial. In some cases the blends even outperform the TMP.
Figure 3.5.E

Tensile Str/Grammage vs. Heating Time

Unheated 100% TMP baseline

Figure 3.5.F

Stiffness/Grammage vs. Heating Time

Unheated 100% TMP baseline
Figure 3.5.G

TEA/Grammage vs. Heating Time
Unheated 100% TMP baseline

Figure 3.5.H

Tear/Grammage vs. Heating Time
Unheated 100% TMP baseline
There are a number of interesting phenomena apparent in these graphs. The 100% TMP shows improved properties at the lowest level of heat treatment, 10 s at 149 °C and further treatment has little effect. Since the temperatures used are above the boiling point of water it is likely that what is being seen is a drying effect. This is consistent with the temperature graphs, Figures 3.5.A-3.5.D.

However, the improvement in properties for the blends at the highest level of heat addition cannot be due to drying. There are two reason that drying cannot explain the strength improvement in the blends. The first reason is the fact that the moisture loss for the pulp in the TMP and in the blends is almost the same. The second reason is the change in the relative strength of the blends.

Figure 3.5.1 shows the moisture loss for the sheets. Note that the moisture loss is expressed as a percentage of the pulp weight. It is assumed that the polymer fibres hold a negligible amount of water. What the data in Figure 3.6.1 shows is that moisture loss from the pulp does not vary much between the TMP and the blends. Moisture loss was measured only once for each set of sheets so a standard error cannot be determined. It should be on the order of 10-20% of the reported value, i.e. ± 0.1-0.2% for 1% moisture loss.

The fact that drying is not responsible for the changes in strength of the blends is most clearly illustrated by comparing the relative strength of the unheated samples to the relative strength of the heated samples. This data is given in Table 3.9.
Moisture Loss as a % of Pulp Wt.
(2-36-n series, 3 baselines)
Table 3.9 Tensile Strength/Grammage of Selected Heat Treated Samples

<table>
<thead>
<tr>
<th>Furnish</th>
<th>Specific Tensile Strength</th>
<th>Specific Tensile Strength</th>
<th>Relative Strength</th>
<th>Relative Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unheated</td>
<td>Heated 90 s @ 177 C</td>
<td>Unheated</td>
<td>Heated</td>
</tr>
<tr>
<td>TMP</td>
<td>0.038</td>
<td>0.043</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>90/10 TMP/PP</td>
<td>0.034</td>
<td>0.042</td>
<td>0.89</td>
<td>0.99</td>
</tr>
<tr>
<td>90/10 TMP/CoPA</td>
<td>0.034</td>
<td>0.041</td>
<td>0.88</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Clearly heating improves the strength for all the samples, as indicated on the graph 3.5.E. However, it is interesting to note that the unheated blends have only about 90% of the strength of the unheated TMP. This is what would be expected if the polymer was contributing nothing to strength: the blends have 90% as much pulp and therefore should have 90% of the strength.

In the heated samples the relative strength goes up to nearly 99% for the PP blend and nearly 97% for the CoPA blend, but there is still only 90% as much pulp. Therefore, either drying has a much larger effect on the pulp in the blends or the polymers have started contributing to the strength. Since Figure 3.5.I shows that, if anything, the pulp in the blends loses less moisture and not more it makes no sense to attribute the strength gain to increased drying. This leads to the conclusion that the polymers are starting to contribute to sheet strength and thus they must be bonding. Since the bonding only becomes evident at temperatures high enough to melt the polymers, it is probably adhesion due to the polymer fibres melting and sticking to the pulp. A convenient term for this process is thermal bonding.

More evidence for the theory of thermal bonding can be seen in Figures 3.5.J to 3.5.M. These graphs show how PA6 blends react to heat treatment. The melting point of PA6, 223 °C, is well above the temperatures used so there will be no softening and thermal bonding. Heat treatment has no effect on the strength and stiffness of the PA6 blends, Figures 3.5.J & 3.5.K.
There are no points for 10 s treatment time because no bonding was expected, even at 90 s exposure, so the short exposure time experiments were not done.

Figure 3.5.L shows that at 149 °C TEA drops as heating time is increased from 50 to 90 s but then does not change once the temperature is increased. This would be consistent with a drying effect. Drying decreased TEA by making the pulp in the sheet more brittle. TEA does not change at the higher temperatures because the sheet is already fully dried. The increase in TEA observed for the PP and CoPA blends does not occur because the PA6 does not soften and bond.

Figure 3.5.M, which shows the effect of heat treatment on tear. Increasing temperature causes tear to decrease slightly, but increasing time has no noticeable effect. The large drop in tear that is observed for the CoPA blend is not seen for the PA6 blend, even though the unheated blends have similar tear values. This result fits with the fibre shrinkage observed in Section 3.7.1. It is also consistent with the hypothesis that thermal bonding is occurring and resulting in increased fibre breakage and decreased fibre pull-out.
Figure 3.5.J

Tensile Str/Grammage vs. Heating Time

Unheated 100% TMP baseline

% Change

Time (s)

Figure 3.5.K

Stiffness/Grammage vs. Heating Time

Unheated 100% TMP baseline

% Change

Time (s)
Figure 3.5.L

TEA/Grammage vs. Heating Time
Unheated 100% TMP baseline

Figure 3.5.M

Tear/Grammage vs. Heating Time
Unheated 100% TMP baseline
Lastly, there are the graphs for the 2-96 series, which show the effect of heat on blends with a range of CoPA concentrations. These graphs, Figures 3.5.N -3.5.O, serve two purposes. First, they compare the performance of unheated blends to heated blends of the same composition on the same graph. As seen in previous results, the heated blends have better properties in every case except tear. This suggests that thermal bonding is occurring and that when it does the polymers contribute to sheet strength and stiffness.

The fact that the strength and stiffness drop steadily with polymer concentration, Figures 3.5.N & 3.5.O, even for heated blends, shows that bonding the polymer is not enough to overcome the disruption of the network caused by the polymer fibres. The models suggest that it would be possible to reverse this effect by using very strong, stiff polymer fibres.

In the case of TEA, Figure 3.5.P, the heated blends actually outperform unheated TMP while the unheated blends do not. The unheated 2% CoPA blend does show a positive change in TEA, but this result is not statistically significantly greater than zero. The error bars for the heated samples are quite large, in part because only 10 points are used for this graph. Because the data for the 2-96 series were measured on a horizontal tensile tester and not a vertical tensile tester it was not combined with any of the data from the 2-37 series.

In comparison, the value of % change in TEA for the equivalent point in the 2-36 series is +28.6%, which is well above the point shown on the graph. It is quite likely, therefore that the upward trend indicated by the data is real. So, the graphs show downward trends for strength and modulus, an upward trend for TEA and a more or less flat line for tear. This suggests that there is some optimum concentration at which TEA is increased without a significant loss in strength, stiffness or tear.

This optimum appears to be somewhere in the 5-10% polymer range. If more detailed
Figure 3.5.N

Tensile Str./Grammage vs. CoPA Conc.
(2-96 series. Heat treatment: 90 s @ 177 C)

Figure 3.5.O

Modulus/Grammage vs. CoPA Conc.
(2-96 series. Heat treatment: 90 s @ 177 C)
Figure 3.5.P

TEA/Grammage vs. CoPA Conc.
(2-96 series. Heat treatment: 90 s @ 177 C)

Figure 3.5.Q

Tear/Grammage vs. CoPA Conc.
(2-96 series. Heat treatment: 90 s @ 177 C)
bonding information were available it may be possible to use the models developed in this paper to predict the optimum.

Finally, there are other factors which could be optimized in order to provide better results. These include the heating conditions such as temperature and time. There are also fibre shape factors to consider. It would be possible to get longer fibres of a low melting point polymer and this could improve tear. While higher strength and modulus usually imply higher melting point, it may be possible to get stronger fibres with a sufficiently low melting point. The models suggest that this would lead to stronger, stiffer paper. In summary, heat treated polymer/TMP blends have the potential to make significantly stronger, tougher paper.

3.6 Scattering Coefficient Data

Scattering coefficient data was collected for the heat treated series because if two sheets are made with the same pulp but are treated differently, any difference in unbonded area should show up as a difference in scattering coefficient. Sheets that are made up of two components can be treated as homogeneous for the purpose of determining their scattering coefficient, Scallan [1985]. The relationship between scattering coefficient and unbonded area is described in section 1.2.2.3.

In this project there are several sets of sheets which should be identical except for heat treatment. If heating does produce bonding it is possible that this fact would be reflected by a change in scattering coefficient. The most suitable series for this comparison is 2-96, which consists of heated and unheated sheets of TMP/CoPA in varying ratios. The heating conditions, 90 seconds at 177 °C, should be enough to cause melting of the CoPA and the tensile and tear
data support this supposition.

Figure 3.6.A shows the scattering coefficient data for the 2-96 series. At higher concentration the heated sheets have a lower scattering coefficient. This suggests a decrease in unbonded area. This could be due to thermal bonding, but it could also be due to the fibre shrinkage mentioned in Section 3.5.

The volume of a cylinder is given by the formula \( \pi r^2 l \) while the surface area is \( 2 \pi rl \) so the surface to volume ratio is given by \( 2/r \). Assuming that volume is conserved as the fibre shrinks, \( l \) will decrease and \( r \) will increase. Thus the total surface area will decrease. So, the scattering coefficient results are not conclusive. A method of measuring the unbonded area of each component separately is needed.
Scattering Coefficient vs. CoPA Conc.
(2-96-n series. Heat treatment: 90 s @ 177 C)
3.7 Microscopy Results

Tear specimens of various blends were examined by optical and electron microscopy. The optical microscope was used to determine that the samples studied at very high magnification with an electron microscope were indeed representative. It was necessary to use electron microscopy because at lower magnification it was very difficult to differentiate between the wood and polymer fibres in the heated samples.

3.7.1 Optical Microscopy

The purpose of the optical microscopy was to determine if there were any visual changes in the structure of the sheet due to heat treatment. Visual evidence of polymer wood pulp bonding was also sought. Finally, optical microscopy was also used to confirm the fact that the polymer fibres shrank when heated close to their melting point.

All of the samples that were studied were taken from the 2-96 series tear specimens. They were 100% TMP, heated and unheated and 90/10 TMP CoPA, heated and unheated. The heated samples were heated at 177 °C for 90 seconds. The focus was on the fracture edge of tear samples and on single fibres isolated from the sheet by re-slushing.

Picture 3.7.1 shows the fracture edge for unheated TMP. The body of the sample is to the right of the picture. This photo shows fibres protruding away from the edge, so they must have pulled out to some extent, and it shows a loosening of the matrix at the edge. Photos of unheated TMP and heated TMP cannot be distinguished from each other so heat treatment had no visible effect. This is consistent with the result that heating has very little effect on the tear properties of
TMP, as seen in Figure 3.5.H.

Figure 3.7.2 is a photo of the fracture edge of an unheated 90/10 TMP/CoPA blend. It shows two CoPA fibres extending well past the crack line. The two types of fibre are easily distinguished in the unheated samples. In fact, the CoPA fibres in this sample are visible to the naked eye, giving the fracture surface a hairy appearance.

Figure 3.7.3 shows the fracture edge of 90/10 TMP/CoPA blend which was heated at 177 °C for 90 s. This picture is difficult to distinguish from Figure 3.7.1, unheated TMP. The fibre running down the centre of the photograph is a polymer fibre, it was identified at higher magnification, but it is no longer smooth and cylindrical. The exposure to heat has distorted the fibre and there appears to be significantly more debris bonded to the polymer. This is consistent with the proposal in section 3.5 that suggests that thermal bonding is occurring.

Positive identification of heated fibres by optical microscopy has its limitations but, with practice, it can be done reliably. At higher magnification wood fibres can be identified by such surface features as pits and by the lumen. Even though the heated polymer fibres are distorted they remain smooth and they do not have a hollow centre. Given a slide full of fibre it would be very difficult to positively identify all of the fibres. However, it is possible to positively identify some fibres as wood and some as polymers.
Figure 3.7.1 Torn edge of unheated TMP sample. 100x

Figure 3.7.2 Torn edge of unheated 90/10 TMP CoPA sample. 100x
The photographic evidence clearly shows that the polymer fibres have shrunk upon heat treating. Several polymer fibres were identified and then measured using a millimetre scale in the eyepiece of the microscope. The more highly curved fibres were photographed and then measured with a piece of string. The length of the string was compared to a millimetre scale photographed at the same magnification.

These methods were used to measure six fibres and the average fibre length was approximately 2.5 mm. The string method was used to measure three unheated CoPA fibres and the average length was 5.4 mm. Also, there were no long cylindrical fibres, visible in the heated sample 3.7.3, visible in the unheated sample, 3.7.2, even though the entire fracture surface of the heated sample was examined. This supports the fibre shrinkage hypothesis that was used to explain the tear results in Section 3.5 and the scattering coefficient results in section 3.6.
3.7.2 Electron Microscopy

Several samples were gold coated and examined with a scanning electron microscope (SEM). The first figure, 3.7.4, shows the fracture surface of a tear specimen from heat treated 90/10 TMP/PA6 blend. The PA6 fibres are clearly distinguishable, the temperature used was not high enough to cause fibre distortion. This is visual evidence of the lack of distortion used in Section 3.5 to explain the fact that the properties of the TMP/PA6 blends did not change upon heat treatment.

The last series of pictures show a CoPA and a wood fibre at high magnification. The polymer fibre is the top fibre in Figure 3.7.5 and the wood fibre is the bottom fibre. A close up of the polymer fibre, Figure 3.7.6, shows the distortion of the fibre and a significant number of fibrils attached to the fibre. The CoPA fibres do not have fibrils and are not likely to form fibrils. The fibrils in this picture must be wood fibrils that have bonded after heat treatment.

A close up of the wood fibre, Figure 3.7.7, shows that it has much more surface structure. So, even though the fibres may look very similar in the optical microscope photographs in this section they have been correctly identified.
Figure 3.7.4 Heated 90/10 TMP/PA6 (2-89-2 B90). 50x

Figure 3.7.5 CoPA fibre (top) and wood fibre from sheet heated at 177°C for 90 s. 300x
Figure 3.7.6 Close up of CoPA fibre in 3.7.5. 1,300x

Figure 3.7.7 Close up of bottom, wood, fibre in 3.7.5. 1,300x
To summarize the photographic results, the visual evidence supports the theories proposed in section 3.5 to explain the effect of heat treatment on the tensile properties of the blends. Heat treatment at temperatures above the melting point of the polymer is sufficient to cause fibre distortion and thermal bonding. Softening the lignin alone is not sufficient to cause thermal bonding, if the polymer does not soften the properties do not improve.

Bonding the polymer leads to improved tensile properties, as predicted by the strength and modulus models. The drop in tear upon heat treating is predicted by the fact that the polymer fibres shrink and tear is highly dependent on fibre length. While this evidence does not prove the proposed explanations it does support them.
4.1 Conclusions

A. It is possible to produce polymer fibre/TMP composite sheets with better strength and toughness than 100% TMP sheets by heat treating the composite sheet.

B. The heat treatment conditions must be sufficient to soften the polymer fibre. Blends containing CoPA fibres, $T_m \approx 140 ^\circ C$, improved when heat treated at $177 ^\circ C$ but blends containing PA6, $T_m \approx 220 ^\circ C$, were unaffected by heat.

C. Adding 10% CoPA and heat treating for 90 s at $177 ^\circ C$ resulted in a 7% increase in tensile strength and a 27% increase in TEA, compared to unheated 100% TMP. Tensile modulus was 10% lower than unheated TMP. Using CoPA fibres gave better results than PP pulp.

D. Increased heating time or temperature gives better results. However, there is an upper limit to the amount of heat which can be used because the sheet will start to brown and the components will begin to thermally degrade.

E. The tensile properties of unheated composite sheets were inferior to the properties of unheated 100% TMP sheets. The tensile properties deteriorated as the polymer concentration increased.

F. Modelling this behaviour indicated that the polymers actually disrupted the bonding in the pulp component. Adding polymers was worse than adding nothing.

G. The Elmendorf tear behaviour of the composite sheets was opposite to the tensile
behaviour. Unheated composite sheets had much higher tear strength than 100% TMP, 120% higher when the PET fibres were used. However, heating the composites dropped the tear down to the value for 100% TMP, or below.

H. Tear was highly correlated with polymer fibre length. $R^2 = 0.81$ for 1% polymer sheets and $r^2 > 0.90$ for sheets with 5% or more polymer.

I. The tear behaviour of the composite sheets suggests that fibre pull-out is a more important factor in tear than fibre breakage is. Longer fibres interrupted crack propagation and increased crack length, thus increasing the energy consumed. The polymer fibres are also very stiff and will require more frictional force to pull-out. The effect of length was not noticeable for the tensile properties because the mechanism is very different. In tear the bonds are stressed sequentially, out of plane, while in TEA they are stressed simultaneously, in plane.

J. The decrease in tear for the heated composite sheets can be explained by fibre shrinkage and distortion. These effects occur at temperatures below the softening temperature. Above the softening temperature the increased bonding will also decrease tear because it will favour fibre breakage over fibre pull-out.

K. The fact that the heat treatment conditions used were enough shrink the polymer fibres was confirmed by microscopic examination of a composite sheet containing CoPA fibres (melting point ~145 °C) heated at 177 °C for 90 s. The CoPA fibres to shrank from ~6 mm to ~2.5 mm in length.

L. The fact that fibre shrinkage occurs before becoming tacky was confirmed by heating CoPA fibres on a glass slide. They began to shrink at 120 °C but they did not adhere to
the slide. Heating the fibres to 177 °C on a slide caused them to melt into droplets that stuck to the slide.

M. Use of very long, > 12 mm, low melting point polymer fibres could result in heat treated composite sheets with increased tensile strength, TEA and tear.

N. At higher CoPA concentrations the tensile properties of the heat treated samples started to decrease while the TEA first increased and then decreased. Comparing the property vs. concentration curves for the different properties shows that there is a concentration which will yield an optimum balance of properties. This concentration is in the region of 5 wt%.

O. Polymer fibre length and melting point were found to be the most important material factors for producing a composite sheet with superior properties. Polymer concentration and heating temperature were the most important process factors.

P. In calendering, higher pressures lead to weaker sheets at a given temperature so increased pressure does not lead to increased bonding at temperatures below the polymer melting point.

Q. Scattering coefficient data is not a good indicator of the degree of bonding in heat treated composite sheets. The change in scattering coefficient, and thus unbonded area, could be due to fibre shrinkage with or without increased bonding.
4.2 Recommendations

This work represents a first attempt to characterize a new type of composite, a polymer fibre reinforced groundwood paper. Since the project had to be completed within a relatively short time frame, many unanswered questions remain. If this research were to be pursued, the following points might be considered.

From an academic point of view, it would be interesting to know more about the bonding between components. In particular it would be interesting to compare the bonding before and after heat treatment. This data could prove what has already been suggested by the results to date, that thermal bonding can take the place of chemical binders. It would also make the models useable.

One way to obtain this data would be to perform single fibre pull out tests with a very sensitive load cell. The polymer fibres would have to be very long so that after heat treatment they remained significantly longer than the wood pulp fibres.

An effective way to distinguish between the polymer fibres and pulp fibres after heat treating would also be useful. It could provide insights into polymer distribution and might allow for more accurate measurement of polymer morphology. It would also simplify the single fibre pull out test by making the polymer fibres more identifiable.

From an applications point of view, a number of issues bear further study. First, very long fibres with low melting points need to be studied to determine if it is possible to have heat treated sheets with improved tensile strength and higher tear. Also, the polymer fibre concentration and heating conditions which yield the optimum balance of properties needs to be
discovered. Low pressure, high temperature calendering might also be a useful treatment for
these composites.

Finally, it would be worth looking into polymer fibres with very low melting points. The
perfect fibre would require only the heat available in a dryer section to produce a superior sheet.
The ideal fibre should also have the highest strength and modulus possible for a low melting
point polymer. Polypropylene fibres could fit these criteria and thus would make a very good
candidate.
REFERENCES


Koran, Z. 1974. "Surface structure of thermomechanical pulp fibers studied by electron microscopy".


properties in paper sheets", *paper technology*, 1(5), p. 519-530


Personal correspondence from Dr. Bhupender Gupta, Professor, North Carolina State University, College of Textiles, Raleigh, NC. 1998


APPENDIX I - Index of Series Used

- 'All' indicates that sheets were made with all five polymers, PP, CoPA, PA6, PET and Rayon.
- A '0%' indicates that a 100% TMP baseline sheet was made for this series. Some series share baselines.

46-n: 0, 1, 10 & 20% - PP, CoPA, PA6*
58-n: 0, 10% - PP, CoPA, PA6 (these sheets were calendered, 75-2100 pli, 66-121 °C)
69-n: 1, 10 & 20% - PET and rayon*
96-n: 0.5 & 0.75% - all
108-n: 0, 0.5, 0.75, 10% - all (only tested for Taber)
118-n: 0, 0.5, 1, 5 & 10% - PP, CoPA, PA6, PET
140-n: 10% - PP, CoPA (these sheets, + a TMP control, were heat treated @ 66, 93 & 121 °C for 10 s)
141-n: 0, 0.1, 0.2, 0.3, 0.4% - all
181-n: 0, 10% - PP, CoPA (these sheets were heat treated @ 149 °C for 10 s)
187/88-n: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0% - all**
2-36-n: 10% - PP, CoPA (these sheets, + a TMP control, were heat treated at 149 & 177 °C for 10 - 90 s)
2-37-n: 0, 20, 40, 60, 80 & 100% - all. Note: could not make 100% polymer sheets and most of the 80% sheets were too weak to test.
2-89-n: 0, 10% - PA6 (heat treated at 149 & 177 °C for 50 & 90 s. Meant to fit in with the
results from 2-36-n)

2-96-n: 0, 2, 6, 10, 15 & 20% - CoPA. Half the sheets were heated to 177 °C for 90 s, the other half were untreated.

*These series were made close together, share a baseline and form a complete set when combined so they are treated as one set, 46/69-n.

**These sheets are all part of one series. They have two numbers because the list ran onto two pages in the lab book.
## APPENDIX II - Strength Model & Bonding Index Calculations

<table>
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<tr>
<th>Blend</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$\epsilon$</th>
<th>$T$ (MPa)</th>
<th>$Z$ (MPa)</th>
<th>$E_2$ (GPa)</th>
<th>$F$ (MPa)</th>
<th>$B$ (MPa)</th>
<th>$B_1$ (MPa)</th>
<th>$B_2$ (MPa)</th>
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**Bonding Index, BI, Calculations**

The weighting factors used in these calculations are the polarity of the active groups. This data appears in Table 3.5. The number of C-H groups is further weighted by the ratio of the strength of van der Waals bonds to hydrogen bonds, 0.0271.

**PP**

Monomer: \(-\text{CH(CH}_3\text{-CH}_2\text{-}\)

molecular weight of monomer = 42 g/mole

specific surface area of fibres: 4.389 m\(^2\)/g

# of C-H groups per monomer = 6

Polarity of C-H groups = 0.35

Bonding potential of active groups = (0.0271)(6)(0.35) = 0.0569 bonds/mole

\[
BI = \frac{0.0569}{(42 \times 4.389)} = 0.0003 \text{ bonds/m}^2
\]

**CoPA**

Monomer: \(-\text{NH-(CH}_2\text{)\_10-NH-C=O-(CH}_2\text{)\_10-C=O-}\)

molecular weight of monomer = 310 g/mole

specific surface area of fibres: 0.170 m\(^2\)/g

# of C-H groups in monomer = 32

# of C=O groups in monomer = 2

# of N-H groups in monomer = 2

Bonding potential of active groups = (0.271)(32)(0.35) + (2)(0.89) + (2)(0.84) = 3.76 bonds/mole

\[
BI = \frac{3.76}{(310 \times 0.071)} = 0.071 \text{ bonds/m}^2
\]
**PA6**

Monomer: -NH-(CH₂)₅-C=O-

- molecular weight of monomer = 113 g/mole
- specific surface area of fibres: 0.185 m²/g
- # of C-H groups in monomer = 10
- # of C=O groups in monomer = 1
- # of N-H groups in monomer = 1
- Bonding potential of active groups = (0.271)(10)(0.35) + (1)(0.89) + (1)(0.84) = 1.82 bonds/mole

\[ BI = \frac{1.82}{113 \times 0.185} = 0.087 \text{ bonds/m}^2 \]

**PET**

Monomer: -CH₂-O-C=O-ϕ-C=O-O- \( ϕ = \text{an aromatic ring, } C₆H₄ \)

- molecular weight of monomer = 192 g/mole
- specific surface area of fibres: 0.152 m²/g
- # of C-H groups in monomer = 8
- # of C=O groups in monomer = 2
- Bonding potential of active groups = (0.0271)(8)(0.35) + (2)(0.89) = 1.86 bonds/mole

\[ BI = \frac{1.86}{192 \times 0.152} = 0.064 \text{ bonds/m}^2 \]
Rayon

Monomer: The monomer for rayon consists of two six member rings, -C₆O, attached through an oxygen bridge -O-. Each ring has four side groups, one -CH₂OH and three -OH.

molecular weight of monomer = 340 g/mole

specific surface area of fibres: 0.088 m²/g

# of C-H groups in monomer = 12

# of O-H groups in monomer = 8

Bonding potential of active groups = (0.0271)(12)(0.35) + (8)(1.24) = 10.03 bonds/mole

\[ BI = \frac{10.03}{(340 \times 0.088)} = 0.335 \text{ bonds/m}^2 \]
Rule of Mixtures

The Rule of Mixtures is simply a weighted average sum. In its most general form it is written as:

\[ P_{12} = x_1 P_1 + x_2 P_2 \]

where: \( P_{12} = \) a property of the composite
\( x_1, x_2 = \) the fraction of components 1 & 2 that are present
\( P_1, P_2 = \) the property of each individual component

In the case of the elastic modulus of fibre reinforced composites it is written:

\[ E_c = v_f E_f + v_m E_m \]

where: \( E_c = \) the elastic modulus of the composite
\( E_f = \) the elastic modulus of the fibre
\( E_m = \) the elastic modulus of the matrix
\( v_f = \) the volume fraction of fibres
\( v_m = \) the volume fraction of the matrix

Since it is actually the area of the fibres that receives the transferred stress it is actually the area fraction that is important. However, in a given random cross section the volume fraction and area fraction will be the same.
Calculating volume fraction:

These calculations are illustrated below for a 20% PP sheet. The raw data for grammage is taken from the set 46-n set. The area used is that for a standard 15.24 cm diameter hand sheet. Note that PET and rayon have very similar density to TMP so the volume and mass fraction are effectively the same.

Sheet grammage = 63.42 g/m²
Sheet area = \( \pi(0.1524/2)^2 = 0.018241 \) m²
Sheet mass = 1.15687 g
Pulp mass = \((0.8)(1.15687) = 0.925499 \) g
Polymer mass = \((0.2)(1.15687) = 0.231374 \) g
Pulp volume = \((0.925499/1.57 \times 10^6) = 5.89490 \times 10^{-7} \) m³
Polymer volume = \((0.231374/0.91 \times 10^6) = 2.54258 \times 10^{-7} \) m³
Pulp volume fraction = \(5.89490 \times 10^{-7}/(5.89490 \times 10^{-7} + 2.54258 \times 10^{-7}) = 0.699\)
Polymer volume fraction = \(2.54258 \times 10^{-7}/(5.89490 \times 10^{-7} + 2.54258 \times 10^{-7}) = 0.301\)

Sample sheet modulus calculations

Returning to the case of a 20% PP blend, and adding the case of a 20% PET blend, in which volume fraction = mass fraction gives the following final calculations:

for 20% PP \[ \bar{E}_c = (0.29)(1.6/55) + (0.71)(1) = 0.7111, \text{ which = -28.9\% change} \]
for 20% PET \[ \bar{E}_c = (0.2)(5/55) + (0.8)(1) = 0.8181, \text{ which = -18.2\% change} \]
the actual values are: -24.4\% for PP and -18.5\% for PET. (These values are taken from the 45 & 69 series, the same series used to calculate mass fraction.)