Dynamic Mechanical Properties of Short Fiber Reinforced Polymers

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science

Mechanical and Industrial Engineering

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Abstract

Recently there has been a drive to replace traditional engineering materials with polymeric solutions. Fiber reinforced polymers offer combine the inherent benefits of polymers such as light weight and anti-corrosion with high strength and stiffness to weight ratios. Polymers are highly viscoelastic meaning they have both elastic, solid, and viscous, fluid like behavior and their mechanical properties are time dependent. Dynamic mechanical analysis is a useful tool in measuring the viscoelastic behavior of materials, and glass transition in response to cyclic loading cycles. Each chapter in this work studies the dynamic mechanical behavior of a different class of polymer, from polyurethane thermosetting rubber, to polyester based thermoplastic elastomer, to high performance polyamide thermoplastic. In each case, novel composite materials have been developed and characterized by reinforcement with selective fibers which was found to significantly enhance the mechanical and thermal properties of the pure polymer.
Acknowledgments

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Chapter 1
Introduction

1.1 Preamble

Recently there has been a growing trend in many industries to replace traditional materials with polymeric material solutions. One only needs to look as far as the next generation Boeing 787 Dreamliner aircraft where over 50% of the primary structure is made of polymer composite materials [1]. Polymeric materials offer many inherent benefits over more traditional industrial solutions, especially metallic structures. The primary benefit of polymer systems is low density and light weight which strives to reduce costs of the materials system [2]. Additionally, environmental restrictions in the automotive industry relating to fuel consumption had driven demand for light weight alternatives to classically metallic structures. Other benefits of polymers include inherent anti-corrosion and relatively simple manufacturing, such as injection and compression molding, and extrusion [3], [4]. The drawback with pure polymeric based systems is their relatively weak mechanical properties which has classically limited their applicability to low stress and temperature applications. In this sense the development of fiber reinforced polymers has recently been very important to industry and research to extend the functional base of polymers [2], [5]. Many polymers also see much use in vibration damping applications due to their highly viscoelastic nature which makes them ideal to reduce mechanical vibrations in an engineering system [6], [7]. Therefore, the study of the time dependent properties of polymer materials, and fiber reinforced polymer materials, in response to a sinusoidal stress or strain profile is of great importance. Dynamic mechanical analysis is a useful tool to study the viscoelastic properties of materials, as well important transitions such as glass transition [8], [9].

Chapter one introduces the objectives and motivation for the thesis followed. The organization of the thesis is then explained with a brief description of each subsequent chapter. The relevant contributions are then detailed.
1.2 Viscoelastic Properties and Behaviour

Polymers exhibit viscoelastic characteristics, meaning they are not perfect elastic solids, therefore, when considering strains one must not only account for stress but also the rate at which stress is applied [8]. In contrast to a perfectly elastic-plastic solid the stress-strain response of a viscoelastic material is non-linear due to the fact that in a constant strain rate experiment time is increasing as well as stress [10]. The main difference between elastic solids, such as metals and ceramics, and polymers which account for this behaviour, is that polymers are made up of long molecular chains [8]. When a mechanical stress is applied to viscoelastic materials it causes time effects in strain as the molecules flow [8]. The viscoelastic nature of polymers give rise to two interesting phenomena: creep, and stress relaxation. Creep behaviour in viscoelastic materials is a response of increasing strain when a constant stress is applied to the material. Conversely, when a constant strain is applied to a viscoelastic material their response is for stress to decrease, called stress relaxation.

If a cyclic loading pattern is applied to a viscoelastic material mechanical hysteresis occurs leading to the dissipation of energy in the material. When a periodic sinusoidal stress is applied to a viscoelastic material the strain response lags behind with a phase angle of delta [11]. The storage modulus (G’, E’) is the modulus associated with the component of stress in phase with the strain. The loss modulus (G”, E”) is associated with the component of stress out of phase with the strain [9].

In terms of materials behaviour the storage modulus is comparable to Young’s elastic modulus and it represents the proportion of energy “stored” or transferred through the material. In contrast, the loss modulus is representative of the material’s viscous nature and serves to represent the amount of applied energy that is “lost” or dissipated in the material through the generation of heat caused by internal friction of the sliding polymer chains. The loss factor, or tan(δ), is the ratio of the loss modulus to the storage modulus and is representative of the portion of the applied energy that is absorbed by the material [9].

The viscoelastic behaviour of materials is fundamental to their performance in structural and engineering applications. For example, creep and stress relaxation may be unwanted material
behaviour for many structural applications, particularly ones involving forces applied over long periods of time. On the other side viscoelastic behaviour in response to dynamic loadings may be taken advantage of in many vibration damping, impact resistance, and sound absorption applications.

1.3 Thesis Objectives and Motivation

The overall goal of this thesis is the development of novel short fiber reinforced polymeric materials for use in emerging applications. Primary focus will be spent on the characterization of the time dependent, viscoelastic, properties of the materials through the use of dynamic mechanical analysis. The understanding of these properties, storage modulus, loss modulus, and loss factor, is very important in determining suitability and performance limits of the developed materials. Specifically, the objectives can be broken down into three main points.

1. Gain a thorough understanding of the viscoelastic properties of a wide variety of materials including thermosets, thermoplastics, and elastomers. Understand the nature of the polymer matrix molecular structure and how it influences the dynamic mechanical properties and important phenomenon such as glass transition. Study the viscoelastic properties as a function of frequency, temperature, and strain where applicable.

2. Investigate other important mechanical and thermal properties associated with manufacturing and end use applications. These include the study of thermal stability by thermogravimetric analysis, and melting and crystallization behaviour, where applicable, by differential scanning calorimetry. Investigate, through the use of thermomechanical analysis, the thermal expansion behaviour of selected polymers, where applicable. Study the constant strain rate mechanical properties and determine the modulus of elasticity, yield strain, and yield stress.

3. Develop novel polymeric composite materials by incorporating a variety of short reinforcing fibers in an effort to improve the mechanical, and dynamic mechanical properties. Understand the influence of adding fibers relating to the mechanical and thermal properties described above.
1.4 Thesis Organization

The chapters of this thesis each represent a different class of polymeric materials, starting in chapter two where the focus of research is directed towards soft thermoset elastomers. Chapter three then follows by encompassing medium hardness thermoplastic elastomers and flexible thermoplastic. In chapter four the topic of research then becomes the development and characterization of fiber reinforced thermoplastic materials for high temperature and demanding applications. A broad range of reinforcing fibers were studied including ceramic based fibers, alumina, in chapter two, and glass, in chapter four, polymeric based fibers, aramid, in chapter one, and poly(p-phenylene-2,6-benzobisoxazole) (PBO), in chapters two and three, and carbon based fibers, in chapter three.

In chapter two composites with a thermoset polyurethane elastomer matrix were developed. Polyurethane based systems offer many inherent benefits such as low temperature flexibility, high abrasion resistance, biocompatibility, and resistance to many chemicals. However, the relatively weak mechanical properties of the base matrix limit its potential range of applications. In an effort to improve the mechanical behaviour composite materials of polyurethane elastomers were reinforced with Kevlar pulp, alumina micro fibers, and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers. Firstly, the thermal stability of the composite materials was analysed through thermogravimetric analysis (TGA), following ASTM E2550, and the degradation onset temperature was used as a quantitative measure of the thermal stability. Next the coefficient of linear thermal expansion was analysed by thermomechanical analysis (TMA) following ASTM E831. Finally, the dynamic mechanical properties, ASTM D5992, were measured as functions of increasing strain, frequency, and temperature in order to gain a thorough understanding of the viscoelastic nature of these composites.

In chapter three carbon and PBO short fibers were used as reinforcement in two grades of a polyester based thermoplastic elastomer. This research focused on two grades of material, first a medium hardness polymer possessing the mechanical properties and behaviour of a typical thermoplastic elastomer. Secondly, a high hardness polyester based elastomer was studies which has mechanical properties more similar to flexible thermoplastics such as polyethylene. Again, the thermal stability of these materials was measured by TGA, ASTM E2550. Since these materials are semi-crystalline thermoplastics, an investigation into the melting a crystallization
behavior was conducted by differential scanning calorimetry (DSC), following ASTM D3418. The mechanical properties, modulus of elasticity, yield strain, and yield stress were determined by standard constant strain rate tensile testing, ASTM D638. A dynamic mechanical analysis (DMA) with the materials response to increasing temperature, and frequency was conducted to study the viscoelastic behaviour of the prepared materials. For all tests an extensive discussion was completed describing and comparing the effect of each reinforcing fiber type, carbon and PBO, when combined with the neat polymer matrix.

Chapter four focused on the study of high temperature and performance polyamide thermoplastic materials. Initially three base polyamide materials were characterised for their thermal, mechanical, and dynamic mechanical performance by conducting the same tests as in chapter three (TGA, DSC, Tenslie, DMA). The three primary polyamides that were studied comprised of a neat material, a highly impact modified material containing carbon black and rubber particles, and finally a glass fiber reinforced polyamide. Next polyamide hybrid composite materials were created by melt blending the impact modified and the glass fiber reinforced material containing composites filled with both rubber particles and stiff glass fibers. The thermal and mechanical properties of these hybrid materials were then compared to the base grades as previously tested.

1.5 Contributions

This work makes several key contributions towards the field of fiber reinforced polymer research, especially the viscoelastic properties of these materials. The key contributions are listed as follows.


b. Reinforcement of thermoplastic elastomeric materials by use of carbon and PBO short fibers creating innovative polymer composite materials.

c. Development of high-temperature performance polyamide rubber particle and glass fiber reinforced hybrid composites
d. Characterization and analytical discussion of the thermal stability, thermal expansion, and dynamic mechanical properties with respect to strain, frequency and temperature of the new composite materials.

e. Study of glass transition phenomena in original semi-crystalline thermoplastic composites as a function of fiber content and frequency by dynamic mechanical analysis.
1.6 References


Chapter 2

2 Novel polyurethane elastomeric composites reinforced with Alumina, Aramid, and poly(p-phenylene-2,6-benzobisoxazole) short fibers, development and characterization of the thermal and dynamic mechanical properties

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2.1 Abstract

Polyurethane is an extremely versatile material having seen use in a variety of applications. However, its relatively weak mechanical properties limit the scope of applicable functions. In this paper, composite elastomers of polyurethane have been reinforced with Kevlar pulp, Alumina micro fibers, and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers. The thermal and dynamic mechanical properties were characterized by thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA). Upon the addition of the reinforcing fibers an improvement in thermal stability as well as a significant reduction of 37% to the coefficient of linear thermal expansion was found. Additionally, an improvement of 97% to the storage modulus (G’) was found with the inclusion of a small amount of PBO fibers, 1wt%, to the polyurethane matrix.
2.2 Introduction

Polyurethane based systems offer many inherent benefits such as low temperature flexibility, abrasion resistance, biocompatibility, and resistance to many chemicals [1], [2]. These characteristics make polyurethane an exceptionally versatile material proven to be suitable for a diverse range of applications from coatings in high performance engineering and aerospace applications to biomedical analogues [3]-[8]. Furthermore, polyurethane materials see extensive use in more traditional consumer grade products including footwear, furniture, insulation materials, and elastomers [7]. Of particular importance to this study are soft polyurethane elastomers with strong damping characteristics. With the intention of expanding the use of polyurethanes to an ever broader range of applications the incorporation of novel fillers, additives, and reinforcing materials to polyurethane matrices has been continuously studied. Much research has been done on the addition of graphene and other conductive nano-particles to introduce electrical conductivity to the overall material system [8]–[11]. Additionally, polyurethane has been adapted to demonstrate self repairing behaviour [12], flame retardants [13]–[16], and mechanochromism for strain sensing applications [17]. Furthermore, the shape memory behavior of polyurethanes has been widely studied [18]–[23].

The reinforcement of the relatively weak polyurethane matrix has garnered significant interest. Significant improvement in various mechanical and thermal properties can be achieved by the incorporation of a variety of appropriate fillers. In this sense polyurethane has been shown to be a suitable matrix for a number of reinforcing fillers including: carbon nano-particles [24]–[29], silicon carbide [30], iron oxide [31], iron particles to fabricate magnetorheological elastomers [32], carbon black, silica, and aluminium oxide [33], micro fibrillated cellulose [34], and banana fiber [35]. Other reinforcing fillers have also included more traditional carbon, and glass fibers [36]–[39].

Here the dynamic mechanical and thermal properties have been enhanced using novel filler materials, alumina and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers, as well as more traditional aramid fibers. PBO fibers were selected due to their excellent mechanical properties [40]–[43], in addition to other added benefits such as excellent fatigue properties [44], and improved abrasion resistance [45]. Moreover, the influence of PBO fibers to an elastomeric matrix and the impact on the dynamic properties is not widely studied. Alumina fibers are
interesting due to their excellent thermal resistance as well as very good mechanical properties
[46]. The smaller size of the alumina fiber should also make for easier dispersion. Similar to
PBO, aramid fibers have garnered interest due to their excellent mechanical properties and high
strength to weight ratio, as well as their good thermal performance and high degradation
temperature [47]–[49].

The aim of this present study is to characterize the dynamic mechanical properties, thermal
stability, and coefficient of thermal expansion of polyurethane reinforced with alumina, Kevlar,
and PBO short fibers. These composite elastomers were designed to improve upon the relatively
weak mechanical, and thermal properties of the pure polyurethane matrix while retaining
excellent vibration damping characteristics. A simple and easily scalable high-shear mixing
process was used to fabricate the composites. In this study we show that alumina, Kevlar, and
PBO fibers are promising reinforcing materials for polyurethane. We have observed an increase
in thermal stability, coefficient of thermal expansion, and dynamic modulus upon the addition of
the selected fibers.

2.3 Experimental

2.3.1 Materials

Two-part polyurethane casting resin (Shore A 60) was purchased from Fibre Glast. The resin,
Part A, contains an undisclosed proprietary polyol mixture, and the hardener, Part B, contains a
proprietary isocyanate mixture. The specific gravity is 1.06 for the cured compound. Kevlar pulp
specific gravity of 1.44 (pre-processing fiber length of 1.05 mm) was also purchased from Fibre
Glast. Alumina fibers, with a chemical composition of 72% Al₂O₃ and 28% SiO₂ and specific
gravity of 3.1 (pre-processing fiber length 30-50mm), were provided my Mitsubishi Plastics
under the brand name of MAFTEC. Zylon HM, specific gravity of 1.56 (pre-processing fiber
length 3mm), purchased from Toyobo Co. were used as the PBO reinforcing fibers. The weight
fractions of Alumina fibers prepared were 0.5%, 1%, and 3%; referred to as AL 0.5, AL 1, and
AL 3 respectively. Additionally, Kevlar fibers of 0.5% and 1% by weight, referred to as KF 0.5
and KF 1 respectively, were prepared. Finally, PBO (Zylon HM) were prepared with weight
fractions of 0.5% and 1%, referred to as PBO 0.5 and PBO 1 respectively. Table 2.1 provides a
list of prepared materials.
Table of Prepared Composites

<table>
<thead>
<tr>
<th>Reinforcing Filler</th>
<th>Fiber Weight</th>
<th>Fiber Volume</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>0.50%</td>
<td>0.17%</td>
<td>Al 0.5</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>0.34%</td>
<td>Al 1</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>1.05%</td>
<td>Al 3</td>
</tr>
<tr>
<td>Kevlar Pulp</td>
<td>0.50%</td>
<td>0.37%</td>
<td>KF 0.5</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>0.74%</td>
<td>KF 1</td>
</tr>
<tr>
<td>PBO (Zylon HM)</td>
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<td>0.34%</td>
<td>PBO 0.5</td>
</tr>
<tr>
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<td>1%</td>
<td>0.68%</td>
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</tr>
<tr>
<td>Polyurethane Neat</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: Nomenclature, and fiber content of prepared composites

2.3.2 Polyurethane Composites Fabrication

Approximately 35g urethane casting resin Part A was weighed in a beaker, and Part B was then weighed at a ratio of 100:55 A:B by weight, as specified by the manufacturer. The desired amount of reinforcing fiber was then weighed in a separate container. The reinforcing fiber was then mixed and stirred into Part A polyol, by hand for approximately 5 minutes. The fibers were then further dispersed using a high shear mixture, Mixerdirect DP1 Standard Single Shaft Disperser, with the following procedure. An initial rotational speed of 500rpm was first used to break apart the fiber agglomerates. The speed was then increased by 500rpm at three minute intervals until a final speed of 2000rpm was reached. The mixture was then left at 2000rpm for a period of ten minutes. The reinforcing fibers were added and mixed with 0.5wt% increments, so the mixing and dispersing process was repeated until the full fiber loading had been achieved; ie. the mixing procedure, for 1wt% fiber loadings, was performed twice, once at 0.5wt% and again at the full 1wt%. A diagram outlining the major processing steps is shown in Figure 2.1. Due to a limitation in the polyurethane matrix, the reinforcing materials, and the dispersing method, higher PBO and KF fiber concentration could not reasonably be achieved. The polyol, resin part A, when dispersed with more than 1wt% of either the PBO or KF fibers becomes too viscous for the shear mixer. To achieve higher weight fractions of fiber a solvent, such as acetone, or other
dispersing agent would need to be used. However, the use of these types of solvents have been previously shown to negatively impact mechanical properties, Young’s modulus, tensile strength, and others and this was to be avoided here [50]–[52]. The use, and affect, of a dispersing agent or solvent to achieve higher filler loadings in this system is a potential topic for further research. Once the total fiber loading was achieved the polyol with dispersed fibers was degassed in a vacuum chamber for 20 minutes. After removal from the vacuum chamber casting resin Part B was added and manually stirred for one minute and the mixture was poured into a rectangular silicone mould with dimensions approximately 120x50x6mm. The mould was then placed back in the vacuum chamber for an additional 12 minutes and finally left to cure at room temperature for a period of 48 hours before testing.

Figure 2.1: Diagram of composite fabrication process outlining major processing steps
2.3.3 Scanning Electron Microscopy

Scanning electron microscope (SEM) images were taken using a JEOL JSM6600 scanning electron microscope (Jeol Corp., Tokyo, Japan) operated at 10 KV. Samples were cut from the middle of the larger composite piece and then sputter coated with a thin layer of platinum particles. Secondary electron imaging was used to view to surface morphology and wetting between the fibers and matrix.

2.3.4 Thermogravimetric Analysis

An investigation of the decomposition temperature of the prepared polyurethane composites was carried out using thermogravimetric analysis (TGA Q50, TA Instruments). Samples were cut to a weight of approximately 20mg and tested to 500 °C in a nitrogen atmosphere with a heating rate of 20°C/min, in accordance with ASTM E2550-11. Decomposition onset temperatures were measured automatically using TA Instruments Universal Analysis software.

2.3.5 Thermomechanical Analysis

Thermomechanical analysis (TMA Q400, TA Instruments) was performed to measure the coefficient of linear thermal expansion (CTE) for each of the polyurethane composites. The CTE measurements followed ASTM E831-14, samples were cut to size and tested from 30 to 90 °C with a heating rate of 5°C/min using the supplied standard expansion probe.

2.3.6 Dynamic Mechanical Analysis

A dynamic mechanical analysis (DMA Q800, TA Instruments) was performed on the polymer composites, testing procedure followed ASTM D5992. The dynamic mechanical properties were measured by shear deformation using the shear sandwich clamp supplied by TA instruments. For all tests two equal samples with dimensions 7x7x2.5mm were used, as recommended by TA Instruments. Three separate experiments were performed with the composites’ response to increasing shear strain, frequency, and temperature studied.

First the dynamic mechanical properties were measured at increasing displacement amplitudes from 5 to 400 µm. This strain sweep test was performed at a constant 5Hz and 40°C ambient temperature. Next a frequency sweep was performed by testing the composites from 0.5 to 50Hz with a displacement amplitude of 1% shear strain and an ambient temperature of 40°C. Finally,
the dynamic mechanical properties were analysed under increasing temperature from 35 to 80°C, with a heating rate of 3°C/min, a displacement amplitude of 1% shear strain, with a constant frequency of 5Hz.

2.4 Results and Discussion

2.4.1 Thermogravimetric Analysis

The thermal stability of the polyurethane and composite materials were tested using thermogravimetric analysis as reported in Figure 2.2 and Table 2.2. It has been demonstrated previously that the decomposition of polyurethane takes place over two well defined regions [53]–[55], which is the behaviour seen here. In general, the behaviour seen is for the addition of fillers to increase the decomposition temperature, by up to 10°C for both the first and second degradation onset temperature. This is primarily due to the excellent thermal stability of the selected reinforcing fibers [56]. It can also be seen that there is no overall trend in the increase of thermal stability amongst the fiber types and reinforcement amount. Most likely, this is a result of the tested composites having a low fiber volume. A topic of further study would be to observe the effect of a larger amount of fiber content on the thermal stability of polyurethane composites.

Figure 2.2: Thermogravimetric thermograms of prepared composites
<table>
<thead>
<tr>
<th>Composite</th>
<th>1st Onset (°C)</th>
<th>2nd Onset (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>212.83</td>
<td>410.08</td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>211.91</td>
<td>418.89</td>
</tr>
<tr>
<td>AL 1%</td>
<td>212.54</td>
<td>416.47</td>
</tr>
<tr>
<td>AL 3%</td>
<td>216.19</td>
<td>415.95</td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>217.59</td>
<td>420.52</td>
</tr>
<tr>
<td>KF 1%</td>
<td>217.23</td>
<td><strong>420.8</strong></td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td><strong>222.59</strong></td>
<td>419.62</td>
</tr>
<tr>
<td>PBO 1%</td>
<td>222.07</td>
<td>419.74</td>
</tr>
</tbody>
</table>

Table 2.2: First and Second onset degradation temperatures of prepared materials

2.4.2 Thermomechanical Analysis, Coefficient of Linear Thermal Expansion

The coefficient of linear thermal expansion was measured using the TA Instruments TMA Q400. The specific coefficient values for the composites was determined using TA Universal Analysis by taking the slope of the linear section, 40°C to 90°C, of the dimension change (µm/m) versus temperature (°C) curve. Selected curves, and thermal expansion coefficients for each prepared material are shown in Figure 2.3.
It is well known that there is typically a decrease in thermal expansion coefficient with the inclusion of reinforcing fibers due to the stiffening of the overall composite material, and the low expansion coefficients of the reinforcing fibers [57]–[60]. This is the general trend seen in the data here. For the alumina and Kevlar fiber types an increase in fiber content corresponds to a decrease in thermal expansion coefficient. However, for PBO reinforcement, while there is improvement over the pure polyurethane, it is seen that an increase in fiber content from 0.5wt% to 1wt% does not significantly decrease the thermal expansion. A t-test, assuming unequal variances, comparing each filled composite material with the neat polyurethane was conducted using Microsoft Excel. The goal of this statistical test was to measure whether the inclusion of fibers had a significant impact on the thermal expansion coefficient. A summary of these test can

Figure 2.3: Top: Selected thermal expansion curves for prepared polyurethane materials and composites. Bottom: Coefficient of linear thermal expansion for polyurethane and prepared composites
be seen in Table 2.3, showing the expansion coefficients for each of the materials, the change in coefficients, as a percentage, for the fiber reinforced composites with respect to the neat sample, and whether this change was statistically significant based on the results of the t-test.

<table>
<thead>
<tr>
<th>Composite</th>
<th>CTE (µm/m°C)</th>
<th>% Change</th>
<th>Significant (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>221.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>223.5</td>
<td>0.77%</td>
<td>N</td>
</tr>
<tr>
<td>AL 1%</td>
<td>186.4</td>
<td>-15.96%</td>
<td>Y</td>
</tr>
<tr>
<td>AL 3%</td>
<td>140.4</td>
<td>-36.70%</td>
<td>Y</td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>216.2</td>
<td>-2.52%</td>
<td>N</td>
</tr>
<tr>
<td>KF 1%</td>
<td>204.7</td>
<td>-7.71%</td>
<td>Y</td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td>182.9</td>
<td>-17.54%</td>
<td>Y</td>
</tr>
<tr>
<td>PBO 1%</td>
<td>180.8</td>
<td>-18.49%</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table 2.3: Summary of coefficient of linear thermal expansion of composites with comparison to neat polyurethane

It can be seen from this analysis that the addition of 0.5% alumina or Kevlar fibers to the polyurethane has no significant impact on the thermal expansion coefficient due to the small amount of fiber added in this case.

2.4.3 Dynamic Mechanical Properties – Effect of Strain

The strain sweep was performed and the generated curves for storage modulus (G’), loss modulus (G’’), and loss factor (tan delta) are shown in Figure 2.4. From the testing, it is found that the stiffest material, highest storage modulus, is the PBO 1% reinforced composite, followed by AL 3% at low strains and KF 1% at high strains (> 9.5%). Further decreasing storage modulus is PBO 0.5% followed by KF 0.5%, AL 1%, AL 0.5% and finally neat polyurethane. It is well known that typical behaviour for fiber reinforced composites is for the storage modulus to decrease with increasing strain, for temperatures above glass transition, which is the behaviour seen here [61]–[63]. Table 2.4 quantifies the change in storage modulus and tan delta, from 1% to 15% shear strain, for the tested materials. It can be seen that the inclusion of fibers affects the
materials resistance to increasing strains. The storage modulus for the neat polyurethane decreases 12.4%, from 1% to 15% shear strain, in comparison to AL 3% where the storage modulus drops 28.9% over the same period. From this analysis, it is also shown that the PBO filled composites show the least resistance to increasing strains. PBO 0.5 and PBO 1 display a larger drop in storage modulus than the Kevlar and alumina filled composites of the same weight fractions. When fiber volume fractions are considered instead of weight fractions the PBO filled compounds still show the least resistance to strain as evidenced by a larger decrease in storage modulus for PBO 0.5 than AL 1, which have the same volume fraction (0.34%). The Kevlar reinforced composites show the best resistance to increasing strain compared to the other filled compounds, suggesting that the fiber-matrix bonding between the Kevlar pulp and the polyurethane is superior to that of the PBO or the alumina fibers. This idea is confirmed by observation of SEM images shown in Figure 2.5. Here it is established that there is superior wetting between the fiber and the matrix for Kevlar filled composites and that the PBO reinforced composites show reduced wetting between the fiber and the matrix. The influence of wetting between fiber and matrix, seen by SEM images, on the mechanical properties of fiber filled composites has been done previously by others [45], [62]–[64]. For all three types of fiber reinforced composites the reduction in storage modulus, from 1% to 15% shear strain, increases with the amount of reinforcement. As the strain is increased bonds between the fiber and the matrix break and the load transferred to, and carried by the fiber is reduced thus lowering the effective modulus, and as the fiber content is increased the effect becomes greater. In terms of damping it is also seen that the loss modulus remains relatively constant throughout the strain sweep and therefore, the loss factor must increase. In the neat polyurethane material, the increase in loss factor with strain is due to the increased molecular sliding at higher strains which results in greater internal friction and heat generation in the material causing increased energy dissipated in the material. The inclusion of fibers to polymer matrices introduces new methods of energy dissipation, primarily due to the nature of the matrix-fiber interface [65]. As the bonds between the matrix and fiber are broken with increasing strain it allows the polymer chains to slide over and around the fiber generating increased internal friction leading to increased energy dissipation. Furthermore, the breaking of the fiber-matrix bonds due to increasing strain requires additional energy which is dissipated in the material. From these experiments, it was found that there was an increase in loss factor, for the fiber reinforced composites, from 1% to 15% shear
strain, when compared to the neat polyurethane. Furthermore, for the alumina and PBO filled compounds this increase in loss factor becomes greater as the fiber content is increased.

Figure 2.4: Storage modulus (top), loss modulus (middle), tan delta (bottom) for composites with respect to increasing strain
<table>
<thead>
<tr>
<th>Composite</th>
<th>$G'$ (MPa) at 1%</th>
<th>$G'$ (MPa) at 15%</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>1.278</td>
<td>1.119</td>
<td><strong>-12.4%</strong></td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>1.462</td>
<td>1.205</td>
<td><strong>-17.6%</strong></td>
</tr>
<tr>
<td>AL 1%</td>
<td>1.774</td>
<td>1.409</td>
<td><strong>-20.6%</strong></td>
</tr>
<tr>
<td>AL 3%</td>
<td>2.53</td>
<td>1.798</td>
<td><strong>-28.9%</strong></td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>1.793</td>
<td>1.493</td>
<td><strong>-16.7%</strong></td>
</tr>
<tr>
<td>KF 1%</td>
<td>2.331</td>
<td>1.908</td>
<td><strong>-18.1%</strong></td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td>2.166</td>
<td>1.698</td>
<td><strong>-21.6%</strong></td>
</tr>
<tr>
<td>PBO 1%</td>
<td>2.645</td>
<td>1.949</td>
<td><strong>-26.3%</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composite</th>
<th>Tan Delta at 1%</th>
<th>Tan Delta at 15%</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>0.1474</td>
<td>0.1633</td>
<td><strong>10.8%</strong></td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>0.1394</td>
<td>0.1691</td>
<td><strong>21.3%</strong></td>
</tr>
<tr>
<td>AL 1%</td>
<td>0.1277</td>
<td>0.1583</td>
<td><strong>24.0%</strong></td>
</tr>
<tr>
<td>AL 3%</td>
<td>0.1215</td>
<td>0.1627</td>
<td><strong>33.9%</strong></td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>0.1268</td>
<td>0.1518</td>
<td><strong>19.7%</strong></td>
</tr>
<tr>
<td>KF 1%</td>
<td>0.1171</td>
<td>0.1384</td>
<td><strong>18.2%</strong></td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td>0.1205</td>
<td>0.1486</td>
<td><strong>23.3%</strong></td>
</tr>
<tr>
<td>PBO 1%</td>
<td>0.1146</td>
<td>0.146</td>
<td><strong>27.4%</strong></td>
</tr>
</tbody>
</table>

Table 2.4: Top: Comparison in storage modulus ($G'$) for composites at 1% shear strain and 15% shear strain. Bottom: Comparison in loss factor (Tan Delta) for composites at 1% shear strain and 15% shear strain.
2.4.4 Dynamic Mechanical Properties – Effect of Frequency

The storage modulus, loss modulus, and loss factor curves for the polyurethane and polyurethane composites subjected to dynamic mechanical testing under increasing frequency are seen in Figure 2.6. The trend is for the storage and loss moduli as well as the loss factor to increase with frequency, this is consistent with previous studies done for short fiber reinforced composites above the glass transition temperature [66]–[68]. Due to the highly viscoelastic, time dependent, nature of the material in question a drop in elastic modulus, over time, is seen when a constant strain is applied [66]. This is a result of the molecular rearrangement of the matrix material to reduce internal stress concentrations. Thus the observed modulus will be higher if measured over a short period, high frequency, than if measured over a long period, low frequency [69]. It also follows that the energy dissipation, and subsequently loss factor, will increase with frequency due to the amplified internal friction and heat generation seen at high frequencies. Upon the
addition of reinforcing fibers, it is expected, and demonstrated, that the storage modulus will increase due to the transfer of load to the stiffer fiber. The amount of reinforcement provided by the fiber primarily depends on the mechanical behaviour and properties of the fiber itself, and secondly, the nature and strength of the fiber-matrix bond. Additionally, the inclusion of reinforcing fillers will tend to act to decrease the loss factor of the material by preventing the molecular rearrangement of the matrix material, causing more elastic like behaviour. It is evident that the fiber type has a dramatic effect on the amount of reinforcement in terms of the storage modulus in addition to the subsequent reduction in the loss factor. Table 2.5 quantifies the change, from neat polyurethane, in the storage modulus and loss factor, at 10Hz, due to the addition of fibers. The polyurethane with 1\% PBO fiber reinforcement shows the highest level of reinforcement with a 97\% increase in storage modulus over the neat polyurethane. In terms of both weight and volume fraction the PBO fibers offer the most reinforcement due to the exceptionally high stiffness and mechanical properties of these fibers. The storage modulus of the 0.5wt\% and 1wt\% PBO filled composites is higher than the comparative alumina and Kevlar filled composites. While it has been established that the interfacial strength between the PBO fibers and polyurethane is weaker than, most noticeably, the Kevlar fibers, it is not a critical factor in the low strain condition in this test. When fiber weight fraction is considered the Kevlar filled composites show superior dynamic stiffness than alumina fiber composites. However, when volume fraction is considered the reinforcement between Kevlar and alumina fibers is comparable. The Al 1 and KF 0.5 composites have volume fractions of 0.34\% and 0.37\% respectively and the corresponding storage modulus, at 10Hz, for these composites is 1.864MPa and 1.899MPa. Furthermore, as a qualitative comparison the storage modulus curves for these materials is almost indistinguishable. In all cases the addition of fibers to the matrix results in a reduction in the damping capabilities of the overall system. However, this loss of damping capabilities is outweighed by the increase in the mechanical properties of the system with the stiffest material, 1\% PBO and polyurethane, showing only a 20\% drop in loss factor. The alumina filler offers the best compromise between stiffness and damping. From the storage modulus and loss factor curves in Figure 2.5 the AL 3 composite provides both a higher storage modulus and loss factor than the PBO 0.5 and KF 1 composites.
Figure 2.6: Storage modulus (top), loss modulus (middle), tan delta (bottom) for composites with respect to increasing frequency
<table>
<thead>
<tr>
<th>Composite</th>
<th>G' (MPa) at 10Hz</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>1.369</td>
<td></td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>1.561</td>
<td>14.0%</td>
</tr>
<tr>
<td>AL 1%</td>
<td>1.864</td>
<td>36.2%</td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>1.899</td>
<td>38.7%</td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td>2.16</td>
<td>57.8%</td>
</tr>
<tr>
<td>KF 1%</td>
<td>2.404</td>
<td>75.6%</td>
</tr>
<tr>
<td>AL 3%</td>
<td>2.597</td>
<td>89.7%</td>
</tr>
<tr>
<td>PBO 1%</td>
<td>2.696</td>
<td>96.9%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composite</th>
<th>Tan Delta at 10Hz</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>0.1442</td>
<td></td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>0.1388</td>
<td>-3.7%</td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>0.1302</td>
<td>-9.7%</td>
</tr>
<tr>
<td>AL 1%</td>
<td>0.128</td>
<td>-11.2%</td>
</tr>
<tr>
<td>AL 3%</td>
<td>0.1217</td>
<td>-15.6%</td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td>0.1205</td>
<td>-16.4%</td>
</tr>
<tr>
<td>KF 1%</td>
<td>0.1167</td>
<td>-19.1%</td>
</tr>
<tr>
<td>PBO 1%</td>
<td>0.1151</td>
<td>-20.2%</td>
</tr>
</tbody>
</table>

Table 2.5: Top: Storage modulus values for prepared materials at 10Hz with composite materials compared to neat polyurethane. Bottom: Loss factor values for prepared materials at 10Hz with composite materials compared to neat polyurethane.
2.4.5 Dynamic Mechanical Properties – Effect of Temperature

In addition to strain, displacement, and frequency, time, dependence the dynamic properties of the polyurethane and composites also show dependence on temperature. The effect of increasing temperature on the dynamic properties, storage and loss modulus, and loss factor is shown in Figure 2.7. All prepared materials show similar behaviour with respect to increasing temperature with a slight decrease in dynamic moduli and loss factor. Aside from adjusting the magnitude of the values in question the addition of fibers does not change the behaviour of the material over the tested temperature range. The storage modulus is compared at 35 °C and 75 °C for the prepared materials in Table 2.6. The corresponding drop in storage modulus ranges from 13.5% for the PBO 0.5 composite to 19.6% for the AL 0.5 composite, however, there does not exist any real trend between the samples with the performance of the neat polyurethane falling in the middle, showing a storage modulus decrease of 17.5%. In general, the decrease in storage modulus throughout the temperature range is due to the increased molecular motion of the matrix molecules. As the temperature is increased the matrix polymer chains are able to move more freely thereby reducing the overall stress in the system leading to a reduction in the modulus.

<table>
<thead>
<tr>
<th>Composite</th>
<th>G' (MPa) at 35°C</th>
<th>G' (MPa) at 75°C</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>1.432</td>
<td>1.182</td>
<td>-17.5%</td>
</tr>
<tr>
<td>AL 0.5%</td>
<td>1.66</td>
<td>1.335</td>
<td><strong>-19.6%</strong></td>
</tr>
<tr>
<td>AL 1%</td>
<td>1.987</td>
<td>1.6</td>
<td>-19.5%</td>
</tr>
<tr>
<td>AL 3%</td>
<td>2.673</td>
<td>2.262</td>
<td>-15.4%</td>
</tr>
<tr>
<td>KF 0.5%</td>
<td>1.971</td>
<td>1.623</td>
<td>-17.7%</td>
</tr>
<tr>
<td>KF 1%</td>
<td>2.512</td>
<td>2.112</td>
<td>-15.9%</td>
</tr>
<tr>
<td>PBO 0.5%</td>
<td>2.21</td>
<td>1.912</td>
<td>-13.5%</td>
</tr>
<tr>
<td>PBO 1%</td>
<td>2.82</td>
<td>2.416</td>
<td>-14.3%</td>
</tr>
</tbody>
</table>

Table 2.6: Comparison of storage modulus values from 35°C to 75°C
Figure 2.7: Storage modulus (top), loss modulus (middle), tan delta (bottom) for composites with respect to increasing temperature
2.5 Conclusions

Polyurethane composites with alumina (Al₂O₃:SiO₂), Kevlar pulp, and poly(p-phenylene-2,6-benzobisoxazole) (PBO) reinforcing fibers have been prepared by a simple manufacturing process utilizing a high shear mixer for fiber dispersion followed by degassing of the two-part resin and casting into a mould. The composites were then tested for their thermal and dynamic mechanical properties by TGA, TMA and DMA. An increase in the thermal stability of the composites was found with the addition of reinforcing fibers as well as up to a 36.7% decrease in the coefficient of linear thermal expansion. The addition of the reinforcing fibers also contributed to an increase in the storage modulus over the neat polyurethane matrix. For 1wt% PBO fiber reinforcement a 97% increase in storage modulus was observed while the loss factor was only reduced by 20%, thus achieving the goal of producing a stiffer polyurethane compound without sacrificing the excellent damping characteristics of the pure matrix material.

2.6 Acknowledgements

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2.7 References


2012.


Chapter 3

3 Polyester based thermoplastic elastomer composites reinforced with carbon and poly(p-phenylene-2,6-benzobisoxazole) short fibers
3.1 Abstract

Thermoplastic elastomers combine the excellent toughness and resilience of traditional thermosetting rubbers with the ease of fabrication and ability to be remolded inherent to thermoplastics. The reinforcement, with the addition of fibers, of the relatively weak matrix can serve to extend the functionality of the pure matrix material. Here, a medium hardness and high hardness grade of polyester based thermoplastic elastomers have been reinforced with short carbon and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers. The thermal stability, melting and crystallization behaviour, mechanical, and viscoelastic properties of these new materials have been characterized. A remarkable increase in strength was found with the addition of the reinforcing fibers. With 10wt% carbon fiber a 628% and 188% increase in tensile modulus was found for the medium and high hardness material respectively. Additionally, dynamic mechanical analysis found significant improvement of the performance of the materials at high temperatures.
3.2 Introduction

Thermoplastic elastomers are an interesting class of materials which offer the many inherent benefits such as quick fabrication, and the ability to be remolded and recycled of traditional thermoplastics [1]. This behaviour is combined with the flexibility and extremely tough behaviour of traditional thermosetting rubbers [2]. Their wide range of properties have made them applicable in many research fields as well as industrial applications [3]. The smart material applications of thermoplastic elastomers have also been of interest. Research has been done to investigate the shape memory potential and applications of thermoplastic elastomer materials [4]. Magneto-rheological elastomers have been created by incorporating magnetically active fillers to a thermoplastic elastomer matrix [5], [6], and conductive, usually carbon based, particles have been added to create thermoplastic elastomeric strain sensors [7]–[10]. Thermoplastic elastomers are also commonly blended with hard thermoplastics usually with the goal of improving impact strength and toughness [11], [12]. The reinforcement of the relatively weak thermoplastic elastomer matrix by the inclusion of stiff composite fibers has also garnered significant interest. Fibers which have been studied include natural fibers [13]–[17], PTFE nanofibers [18], glass fiber [19], nano-clay [20], and others.

In this study two grades of thermoplastic elastomers have been reinforced with poly(p-phenylene-2,6-benzobisoxazole) (PBO) as well as carbon fibers in an effort to improve the mechanical and dynamic mechanical properties of the pure material. The matrix materials studied are polyester based thermoplastic elastomers, one having a medium hardness, Shore D 55, and medium modulus, while the other grade has a high hardness, Shore D 82 and relatively high stiffness. PBO is a liquid crystal polymeric material, comparable to aramid based fibers, with excellent mechanical properties [21]–[24]. Previously we have demonstrated successful reinforcement of a thermoset elastomeric polyurethane material with PBO fiber which showed excellent dynamic mechanical and thermal performance [25]. Other benefits of PBO fibers include improved abrasion resistance in thermoplastic elastomeric materials [26], and excellent fatigue resistance [27]. Polymers containing PBO fibers are also have potential space applications owing to their combination of high strength and light weight [28]. Additionally, while carbon fiber reinforced polymers have been shown to display poor impact performance the liquid crystalline polymer based fibers, aramid and PBO, have proven to be superior in this regard [29]–[31]. In this sense the comparison of PBO and carbon fiber reinforced polymers is
interesting as while they have similar mechanical performance each system offers different inherent benefits making them suitable for differing applications.

The goal of this study is to improve the mechanical and dynamic mechanical performance of polyester based thermoplastic elastomer materials by the inclusion of short carbon and PBO fibers to serve as reinforcement of the relatively weak mechanical properties of the base material. Additionally, the impact of including the reinforcing fibers and their impact on the thermal stability and melting a crystallization behaviour was also analysed. The mechanical properties of these composites were characterized by a constant strain rate tensile test while dynamic mechanical analysis was used to characterize the viscoelastic properties of the composites. Upon completion of these studies it was found that the addition of stiff fibers to the thermoplastic elastomer matrix significantly improved the tensile properties, modulus, and yield stress as well as the dynamic stiffness of the material especially with respect to increasing temperatures.

3.3 Materials and Methods

3.3.1 Materials

Thermoplastic polyester elastomer (TPC-ET) materials, brand name Hytrel, were provided by DuPont. Specific grades used in this study were Hytrel 5556 with a nominal Shore D hardness of 55, and Hytrel 8238 with a nominal Shore D hardness of 82. Hytrel 5556 has a specific gravity of 1.19, and the specific gravity of Hytrel 8238 is 1.28. Zylon HM, provided by Toyobo, were used as the PBO fibers, and carbon fibers, Panex 35, were provided by Zoltek. The specific gravity of the fibers is 1.56 and 1.81 for PBO and carbon fiber respectively, and both fibers have pre-processing lengths of 3mm. Tensile modulus of the PBO fibers is reported to be 270GPa and for the carbon fiber the modulus is 242GPa. The reported tensile strength is 5.8GPa and 4.1GPa for PBO and carbon fibers respectively.

3.3.2 Composites Fabrication Process

The two grades of thermoplastic polyester elastomer materials were reinforced with 5wt% and 10wt% carbon fiber and PBO fiber, Table 3.1 is a table of prepared composites providing nomenclature fiber weight fraction, and fiber volume fraction for all prepared materials. Composite materials were prepared by compounding on a lab scale twin screw compounder (DSM Xplore 15, DSM Netherlands). The co-rotating screws were kept at a constant speed of
50rpm for all fabrication runs, and the compounding time was also constant at 10 minutes. The compounding temperature was set to 230°C for the Hytrel 5556 composites and 250°C for the Hytrel 8238 composites. Tensile, and standard test bar samples, used for dynamic mechanical analysis were fabricated by injection molding using a mini injection moulding system (DSM IM5.5, DSM Netherlands). For the Hytrel 5556 and its composites the barrel temperature was set to 230°C and the mold temperature was kept constant at 45°C. Temperatures of 250°C and 50°C for the barrel and mold were used for the neat Hytrel 8238 and reinforced composites. Injection molding temperatures and process parameters were set according to the material manufacturers’ specification.

<table>
<thead>
<tr>
<th>Matrix Material</th>
<th>Reinforcing Filler</th>
<th>Fiber Weight %</th>
<th>Fiber Volume %</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>5556</td>
<td>PBO</td>
<td>5</td>
<td>3.9</td>
<td>5556 5PBO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>7.8</td>
<td>5556 10PBO</td>
</tr>
<tr>
<td></td>
<td>Carbon Fiber</td>
<td>5</td>
<td>3.3</td>
<td>5556 5CF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>6.8</td>
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</tr>
<tr>
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<td>8238 5PBO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>8.3</td>
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</tr>
<tr>
<td></td>
<td>Carbon Fiber</td>
<td>5</td>
<td>3.6</td>
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<td></td>
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<td>7.3</td>
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<tr>
<td></td>
<td>Neat</td>
<td></td>
<td></td>
<td>5556</td>
</tr>
<tr>
<td></td>
<td>Neat</td>
<td></td>
<td></td>
<td>8238</td>
</tr>
</tbody>
</table>

Table 3.1: Fiber content and nomenclature of prepared composites

### 3.3.3 Thermogravimetric Analysis

An investigation into the thermal stability of the TPC-ET composites was conducted by thermogravimetric analysis (TGA Q50, TA Instruments), in accordance with ASTM E2550. Samples were cut to a weight of approximately 20mg and heated to 600°C at a rate of 20°C/min in a nitrogen atmosphere. The degradation onset temperature was measured by taking the temperatures corresponding to 5%, 10% and 50% mass loss.
3.3.4 Differential Scanning Calorimetry

Melting and crystallization temperatures were measured through the use of differential scanning calorimetry (DSC Q2000, TA instruments). Samples were prepared to a weight of approximately 10mg and subjected to heat-cool-heat temperature profile from -80°C and 260°C. the heating rate was set to 10°C/min and the cooling rate was 5°C/min, in accordance with ASTM D3418.

3.3.5 Tensile Properties

The tensile properties, modulus, yield strain, yield stress, and stress strain behaviour of the TPC-ET materials and composites were tested on an Instron 5848 universal testing machine. The injection molded samples were subjected to a constant strain rate of 5mm/min and tested in accordance with ASTM D638. The tests were conducted at room temperature and humidity.

3.3.6 Dynamic Mechanical Analysis

The dynamic mechanical properties, storage modulus and tan delta, of the thermoplastic polyester elastomer materials and composites were measured by dynamic mechanical analysis (DMA Q800, TA Instruments). Testing procedure followed ASTM D4065 and the dynamic mechanical properties of the injection molded samples, approximate dimensions of 60x12x2mm, were measured in dual cantilever mode using the 35mm dual cantilever clamp provided by TA Instruments. The materials’ response to both increasing temperature and frequency was tested. The DMA testing was performed with a constant strain of 0.01% while the temperature was increased from 35-110°C with a rate of 3°C/min. The viscoelastic properties were measured at two frequencies 1Hz, and 10Hz.

3.3.7 Scanning Electron Microscopy

Scanning electron microscopy images were taken using a JEOL JSM-IT100 using secondary electron imaging. Samples were cut in a way that the imaged surfaced was normal to the preferred fiber direction and sputter coated with a thin layer of gold particles prior to imaging.
3.4 Results and Discussion

3.4.1 Scanning Electron Microscopy

Scanning electron microscopy images for all 5556 and 8238 materials and composites are shown in Figure 3.1. The mechanical properties of fiber reinforced polymer not only depend on the individual properties of the matrix and fiber but the fiber dispersion and strength of the fiber matrix bond as well. Here we can see that there is good wetting between the carbon fibers and both 5556 and 8238 matrices, this provides evidence of good fiber matrix-bond strength which will allow for more efficient transfer of load to the fiber. In comparison, the PBO fiber reinforced samples had much more evidence of fiber pullout caused by the cutting force of the blade and there was less fiber wetting from the matrix material as well. This was more noticeable for the 8238 material than the 5556 material where the PBO fiber generally showed comparatively better wetting and less pullout. Additionally, the relative brittleness and ductility of the fibers can be seen. The carbon fiber seemed to fracture under the cutting force while the PBO showed much more ductile behaviour and seemed to be pulled across the matrix material. All of the fiber reinforced samples showed good dispersion and there were no noticeable sites of fiber agglomeration within the samples. This suggests that the compounding procedure was sufficient to allow for adequate dispersion of the reinforcing fibers.
Figure 3.1: Left column top to bottom: 5556x100, 5556 5CFx350, 5556 10CFx750, 5556
5PBOx750, 5556 10PBOx350. Right column top to bottom: 8238 x100, 8238 5CFx750, 8238
10CFx350, 8238 5PBOx350, 8238 10PBOx750
3.4.2 Thermogravimetric Analysis

Thermal stability of polymer materials and composites is commonly measured by thermogravimetric analysis. The thermogravimetric thermograms, showing the percentage of remaining mass with increasing temperature, for Hytrel 5556 and 8238 and their composites with carbon and PBO fibers are shown in Figure 3.2 and Figure 3.3. The thermal stability, degradation onset temperatures, of these materials was measured by recording the temperature corresponding to 5% mass loss. This temperature, along with temperature values associated with 10%, and 50% mass loss are shown in Table 3.2. The pure materials, 5556, and 8238, show near identical decomposition behaviour with equal 5%, and 10% mass loss temperatures. Additionally, the 50% mass loss temperature for the neat materials is very similar, 448, and 447°C, for 5556 and 8238 respectively, signifying that the rate of decomposition is also similar for both grades of materials. The thermal decomposition of the fiber reinforced composites show two different stories with the carbon fiber reinforced materials displaying lower decomposition temperature and the PBO reinforced composites demonstrating superior thermal stability relative to the neat materials. In both the 5556 and 8238 PBO reinforced composites there is an increase in degradation onset temperature as the content of PBO fiber increases from 5wt% to 10wt%.

![Thermogravimetric thermograms for 5556 and composites](image)

Figure 3.2: Thermogravimetric thermograms for 5556 and composites
Figure 3: Thermogravimetric thermograms for 8238 and composites

<table>
<thead>
<tr>
<th>Material</th>
<th>5% Mass Loss (°C)</th>
<th>10% Mass Loss (°C)</th>
<th>50% Mass Loss (°C)</th>
</tr>
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<tr>
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<td>412</td>
<td>422</td>
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<td>411</td>
<td>420</td>
<td>446</td>
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<tr>
<td>5556 10CF</td>
<td>409</td>
<td>419</td>
<td>446</td>
</tr>
<tr>
<td>5556 5PBO</td>
<td>417</td>
<td>427</td>
<td>453</td>
</tr>
<tr>
<td>5556 10PBO</td>
<td>418</td>
<td>428</td>
<td>455</td>
</tr>
<tr>
<td>8238</td>
<td>412</td>
<td>422</td>
<td>447</td>
</tr>
<tr>
<td>8238 5CF</td>
<td>409</td>
<td>418</td>
<td>443</td>
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<tr>
<td>8238 10CF</td>
<td>409</td>
<td>418</td>
<td>444</td>
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<td>8238 5PBO</td>
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<td>454</td>
</tr>
<tr>
<td>8238 10PBO</td>
<td>427</td>
<td>437</td>
<td>464</td>
</tr>
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</table>

Table 3.2: Temperatures corresponding to 5%, 10%, and 50% mass loss of prepared composites
3.4.3 Differential Scanning Calorimetry

The melting and crystallization temperatures as found by differential scanning calorimetry for the 5556 material and composites are seen in Table 3.3, and for the 8238 material and composites in Table 3.4. The cooling and secondary heating curves for these materials are shown in Figure 3.4. It is immediately noticeable that the inclusion of both carbon and PBO fibers to the 5556 and 8238 matrices dramatically increases the crystallization temperature by around 20-30°C depending on the fiber type and concentration. In this sense, it is seen that the PBO fibers leads to a greater increase in crystallization temperatures than the carbon fiber. This provides evidence that both fibers act as efficient nucleating agents for the Hytrel materials. Previous studies on reinforced Hytrel materials have concluded similar results [32]. For the 8238 material with 5wt% and 10wt% carbon fiber and 5wt% PBO dual melting peaks are observed. This behaviour occurs when two distinct crystal structures are formed in the material, the melting of secondary or imperfect crystal structures occurs at a lower temperature and the melting of primary crystal structures subsequently takes place at higher temperatures [33]–[35]. However, also of note, is that as the content of PBO fibers is increase to 10wt% the evidence of dual melting endotherms disappears. While the inclusion of fibers increases the nucleation sites, the polymer chain mobility is restricted which leads to the formation of more smaller crystals. Therefore, it can be said that the 10wt% PBO filled 8238 material prevents the formation of secondary crystal structures in the matrix due to the restriction on the mobility of the polymer chain. On the melting curve of the 5556 materials there also exists a smaller endothermic peak occurring around 215°C for the pure 5556 material and a very small peak for the fiber filled compounds. Previously, it has been demonstrated that there is sufficient mobility to allow for recrystallization during the heating process for Hytrel 5556 [32]. This leads to a re-melting of crystal structures formed during the heating cycle at a higher temperature.
Figure 3.4: Differential scanning calorimetry thermograms of 5556 materials (Left) and 8238 materials (Right)

<table>
<thead>
<tr>
<th>Material</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5556</td>
<td>202.6</td>
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</tr>
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</tr>
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<td>5556 5PBO</td>
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</tr>
<tr>
<td>5556 10PBO</td>
<td>204.3</td>
<td>180.4</td>
</tr>
</tbody>
</table>

Table 3.3: Melting and crystallization temperatures of 5556 materials and composites

<table>
<thead>
<tr>
<th>Material</th>
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<th>Tm2 (°C)</th>
<th>Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>8238 5CF</td>
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<td>222.1</td>
<td>193.6</td>
</tr>
<tr>
<td>8238 10CF</td>
<td>214.3</td>
<td>222.1</td>
<td>194.1</td>
</tr>
<tr>
<td>8238 5PBO</td>
<td>216.8</td>
<td>222.0</td>
<td>198.0</td>
</tr>
<tr>
<td>8238 10PBO</td>
<td>221.5</td>
<td>N/A</td>
<td>202.5</td>
</tr>
</tbody>
</table>

Table 3.4: Melting and crystallization temperatures of 8238 materials and composites
3.4.4 Tensile Properties

The stress-strain curves for both grades of the TPC-ET materials and composites are shown in Figure 3.5. It can be seen from these curves that the softer 5556 material behaves similar to more traditional elastomeric materials where the neat grade of 8238 has tensile properties and a stress response more similar to flexible thermoplastics such as polyethylene. The elastomeric 5556 material composites experienced ductile failure with very high maximum elongation (>150%) until failure with the exception of the 5556 10PBO compound which exhibited very little to no plastic deformation before failure. The failure in the 8238 composites was much more brittle, even for the 5wt% filled compounds, where no necking behaviour was observed as in the pure 8238 material. This more brittle behaviour is not unexpected and has been observed many times before for plastics reinforced with stiff fibers. The tensile modulus values for all prepared samples are shown in Figure 3.6 while the values for yield strain, and yield stress are shown in Figure 3.7 and Figure 3.8 respectively. For both grades of TPC-ET, the carbon fiber reinforced composites have a higher elastic modulus when compared to PBO reinforced materials, however, the benefit of the addition of PBO fibers in clearly seen in the significant increase in yield stress, or tensile strength. At just 10wt% carbon fiber added to 5556 material the modulus is increased by 628%, for 10wt% PBO fiber the increase in modulus is 593%. For the stiffer 8238 material, the addition of 10% carbon fiber leads to an increase of 187% to the elastic modulus and for 10wt%PBO this increase is 84.0%. When the fiber volume fraction is considered, instead of weight fraction, the improvement to modulus for the carbon fiber filled samples becomes even greater owing to its lower volume fraction compared to the relatively loaded PBO samples. When yield stress is concerned the addition of 10wt% carbon, and 10wt% PBO fiber results in improvements of 162% and 280% respectively to the 5556 elastomeric material. For the 8238 material, these improvements to yield stress are 95.1% and 180% for 10wt% carbon fiber and 10wt% PBO fiber respectively. The cost of improving the modulus and yield stress with the addition of stiff reinforcing fibers is the reduction is yield strain of over 40% in the best-case scenario for the 8238 materials and a reduction of over 50% for the 5556 composites. The effectiveness of reinforcement for a stiff fiber filled polymer depends on the mechanical properties of the fiber, the homogeneity of the fiber dispersion and the nature of the fiber matrix interface. In terms of the 5556 and 8238 composites it is suggested that the effectiveness of load transfer to the fibers at high strains is better for PBO reinforced materials as evidenced by the
significantly higher yield stress for the PBO composites. This suggests that at higher strains and stresses the good bonding between the matrices and the carbon fiber begin to break leading to premature yielding of the material in comparison to the PBO reinforced composites. An explanation for this behaviour is that the compounding process of mixing the fibers and the matrix causes breakage of the fibers. Some breakage of the stiff fibers is expected under these extremely high shear conditions and it is theorized that the more brittle carbon fibers experience more breakage. The PBO fibers, being polymeric in nature, are inherently more tough than the carbon fibers and their resistance to the compounding process is superior resulting is less fiber breakage. The result of this is that the effective fiber length of the carbon fiber composites is likely shorter than the PBO filled materials. It is well known that a longer fiber length will have more effective reinforcement, which is especially noticeable after initial loading meaning the modulus will not be as affected as the yield strength. We have established, through the use of SEM, that there appears to be superior initial wetting between the carbon fiber and matrix materials, this idea is partially confirmed by the relative tensile modulus of the composites. We see that the modulus for PBO reinforced materials is lower than that of the carbon fiber composites, especially for the 8238 material, despite the PBO fibers themselves having a greater modulus, than carbon fiber, and a relatively higher volume fraction, thus a higher PBO composite modulus would be expected. At the low strain, pre-yield, conditions where the modulus is measured the fiber breakage effect, as previously discussed would not be as relevant; however, there is another explanation which must be considered. The PBO fibers have a much lower compression modulus and strength than the carbon fibers. Therefore, in the injection molding process, where high compressive stresses are involved, it is likely that there is less fiber alignment for PBO fibers. Additionally, as the composites are injected, the PBO fibers may become deformed which would reduce the reinforcement effectiveness of the PBO fibers.
Figure 3.5: Stress-strain curve for 5556 (Left) and 8238 (Right) materials and composites

Figure 3.6: Tensile modulus values for 5556 (Left) and 8238 (Right) materials and composites
Figure 3.7: Yield strain values for 5556 (Left) and 8238 (Right) materials and composites

Figure 3.8: Yield stress values for 5556 (Left) and 8238 (Right) materials and composites
3.4.5 Dynamic Mechanical Analysis

3.4.5.1 Effect of Temperature

*TPC-ET Hytrel 5556*

The storage modulus and tan delta curves, tested with a frequency of 1Hz, for the 5556 material and composites with carbon and PBO fibers are shown in Figure 3.9. The 5556 10CF material shows the highest storage modulus throughout the temperature range, followed by 5556 10PBO, 5556 5CF, 5556 5PBO, and neat 5556 having the lowest storage modulus. The trend is for the storage modulus, which is analogous to the elastic modulus, to decrease with increasing temperature. In general, as the temperature of the system is increased the reduction in storage modulus is due to increased molecular motion of the matrix molecules. At higher temperatures, the polymer chains of the matrix material are able to move more freely allowing them to more effectively reduce the stress in the system thereby leading to reduced modulus. The reduction in modulus is not dramatic, the modulus does not drop sharply at over a small temperature range, as this material does not experience glass transition over the tested temperature range. This is further evidenced by observation of the tan delta curve which does not display a local maximum value and instead steadily increases throughout the whole temperature profile of the test.

*TPC-ET Hytrel 8238*

The storage modulus and loss modulus curves of a temperature ramp experiment with a frequency of 1Hz for carbon fiber reinforced 8238 is shown in Figure 3.10, and for PBO fiber 8238 composites in Figure 3.11. Amorphous polymers, or the amorphous regions in semi-crystalline polymers experience a phenomenon called glass transition. When polymers are cooled below their glass transition they exhibit glassy and brittle behaviour due to a restriction to the mobility of the polymer chains [36], [37]. This is caused by a reduction in free volume in the polymeric material [38]. Upon heating through the glass transition larger segments of the polymer chains are able to reorient leading to more ductile and soft behaviour and the polymer enters its “rubbery” state [37]. Heating a polymer through the glass transition corresponds to a dramatic decrease in mechanical stiffness, and for a semi-crystalline polymer an increase in toughness is also observed [39]. Dynamic mechanical analysis is a useful tool to determine the glass transition temperature (Tg) of the material which is typically taken as the peak of the tan
delta curve generated through a temperature ramp experiment. While the 5556 materials do not experience glass transition through the selected temperature test range the 8238 materials do as evidenced by the local maxima of tan delta. Again, similarly to the 5556 composites, the addition of the reinforcing fibers leads to an increase in storage modulus but also leads to a reduction to the loss factor. Likewise, to the elastic tensile modulus, the 8238 10CF material exhibits the highest storage modulus followed by the 8238 5CF, 8238 10PBO, and 8238 5PBO displaying the lowest storage modulus for the fiber reinforced materials. The inclusion of stiff fibers to a polymeric matrix will tend to decrease the loss factor of the material system. The fibers act to restrict to movement and rearrangement of the polymer chains leading to more elastic like behaviour. In addition to the tan delta peak having a lower magnitude, the temperature corresponding to this maximum is higher for the fiber reinforced materials. In these systems of 8238 with carbon fiber and PBO fiber reinforcement the increase to the glass transition is evidence of good fiber wetting and a strong fiber matrix bond [40]. Previously, it has been reported that if there is sufficient wetting between the fiber and the matrix and there exists a perfect fiber matrix interface then there will be fewer voids in the system. The result of this is that it leads to a restriction to the mobility of the polymer chains in the matrix. Therefore, more energy, temperature in this case, is required to promote the segmental motion of the polymer chains which leads to the glass transition behaviour [40].
Figure 3.9: Storage modulus (Left) and Tan Delta (Right) of 5556 composites with a frequency of 1Hz

Figure 3.10: Storage modulus and tan delta of 8238 reinforced with carbon fiber at a frequency of 1Hz
3.4.5.2 Effect of Frequency

The storage modulus for the 5556 materials and composites tested at 10Hz are compared to the curves generated at 1Hz are shown in Figure 3.12. Figure 3.13 shows the storage modulus of the 8238 materials compared at 1Hz and 10Hz and the tan delta, for these materials and frequencies, are shown in Figure 3.14. For both 5556 and 8238 based composites, there is an increase in observed storage modulus as the frequency is changed from 1Hz to 10Hz. This change is due to the viscoelastic, hence time dependent nature of polymer materials. Stress relaxation phenomenon describes a condition in which a reduction in stress is observed when a constant strain is applied to the material. This is due to the polymer chains naturally reorienting to a lower stress equilibrium state. It then follows that if the modulus is measured over a short period, high frequency, it will be higher than if measured over a long period, low frequency, due to this reduction in stress [25]. At high temperatures, we see that the effect of frequency in terms of storage modulus become less effective for both the 5556 and stiffer 8238 materials. In this case, it is likely that the shorter period, 0.1s, corresponding to 10Hz frequency is sufficient time for the reorientation, and stress reduction, of the polymer chains to take place. The polymer chains at higher temperature gain increased mobility allowing for the reorientation to take place more easily and quickly. The glass transition temperature, corresponding to peak tan delta temperature, for each of the 8238 materials at 1Hz and 10Hz are shown in Table 3.5. From these values, it is demonstrated that the higher frequency scenario leads to an increase in effective glass transition...
temperature for all materials. The observed increase in glass transition temperature is again due to the time dependent nature of the polymeric materials as previously discussed. Taking the definition of glass transition as the point where a large enough group of polymer chain segments are able to undergo rearrangement it is logical that at high frequencies there is not sufficient time to allow for this polymer chain segment movement. Consequently, this movement can only occur when the temperature becomes sufficiently high. Also of note is that while the glass transition increases from 5wt% to 10wt% carbon fiber reinforcement this is not true for the PBO reinforced composites which show a decrease in Tg from 5wt% to 10wt% reinforcement. Previously it has been demonstrated that if there is not sufficient fiber wetting or if the fiber content becomes too high then a decrease in glass transition temperature can be observed [41]. If poor fiber wetting or adhesion is observed, then there will be an increase in segmental mobility and leading to a reduction in glass transition. In this case of PBO reinforced composites it is possible that the 8.3vol%, 10wt%, represents a high enough fiber fraction where there is the beginning of worse fiber wetting or fiber-matrix adhesion when compared to the 4.1vol%, 5wt%, PBO reinforced material.

Figure 3.12: Storage modulus of 5556 reinforced with carbon fiber (Left) and PBO fiber (Right) at 1Hz and 10Hz
Figure 3.13: Storage modulus of 8238 reinforced with 5wt% carbon and PBO fiber (Left) and 10wt% carbon and PBO fiber (Right) at 1Hz and 10Hz.

Figure 3.14: Tan delta of 8238 reinforced with 5wt% carbon and PBO fiber (Left) ad 10wt% carbon and PBO fiber (Right) at 1Hz and 10Hz.
<table>
<thead>
<tr>
<th>Material</th>
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</thead>
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<tr>
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</tr>
<tr>
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<td>8238 10CF</td>
<td>51.00</td>
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<td>52.12</td>
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<tr>
<td>8238 10PBO</td>
<td>48.51</td>
<td>50.60</td>
</tr>
</tbody>
</table>

Table 3.5: Glass transition temperatures of 8238 materials at a frequency of 1Hz and 10Hz

3.5 Conclusions

Two grades of polyester based thermoplastic elastomer materials, brand name Hytrel, have been reinforced by melt blending with carbon fiber and poly(p-phenylene-2,6-benzobisoxazole) fibers. The first grade tested had a medium hardness and stiffness with properties akin to elastomeric materials, this was followed by a high hardness grade with mechanical properties more similar to flexible thermoplastics such as polyethylene. The composites were tested for their thermal, mechanical, and dynamic mechanical properties. Thermogravimetric analysis was done to measure the thermal stability, and differential scanning calorimetry was conducted to analyse the melting and crystallization behaviour. Next, the tensile mechanical properties, modulus of elasticity, yield strain, and yield stress, was measured followed by dynamic mechanical analysis to measure the storage modulus and loss factor, and the effect of temperature and frequency on the composite materials. Significant improvements to the thermal stability, mechanical and viscoelastic properties were found with the addition of the fibers. With 10wt% carbon fiber reinforcement there was an improvement to the tensile modulus of 628% and 187% for the medium and high hardness materials respectively. In terms of yield stress there were improvements of 280% and 180% for the medium hardness and high hardness materials when 10wt% PBO fibers were added. Overall the PBO fibers provide the best reinforcement to the 5556 matrix where the 8238 matrix is better reinforced by the carbon fibers. In the 5556 samples the yield stress gained by the PBO fibers far outweighs the lower modulus compared to the carbon reinforced compounds, where in the 8238 materials there is too much of a difference in modulus between the PBO and carbon reinforced samples.
3.6 Acknowledgements

The authors would like to acknowledge the following agencies for financial support: Natural Sciences and Engineering Research Council of Canada (NSERC), and the Ontario Centres of Excellence (OCE).
3.7 References


Chapter 4

4 Polyamide 6,6 hybrid composites with rubber particles and glass fiber for high temperature applications
4.1 Abstract

Recently, in many industrial fields, there has been a drive to replace traditional metallic components with high strength polymer composites in the interest of reducing weight. Polyamide 6,6 (PA66) is a high strength thermoplastic displaying excellent performance at high temperatures, this behaviour can be further enhanced by the addition of reinforcing fillers. Here, PA66 matrix has been reinforced with chopped glass fiber as well as hybrid composites containing both glass fiber and rubber particles to enhance impact performance and toughness. The composite materials were then tested for their thermal, mechanical, and dynamic mechanical properties. Significant improvement to mechanical performance was found with the inclusion of glass fibers with an increase in modulus of 154%, and a 124% improvement to yield stress for a 30wt% glass reinforced PA66 over a pure material grade.
4.2 Introduction

In many industries, there has recently been a drive to replace heavy metallic components with lightweight composite structures. A prime example of this trend is seen in the automotive and aerospace industries where rising fuel costs, combined with rising pressure due to ever stricter fuel efficiency regulations, have prompted companies to pursue lightweight composite options [1]. In addition to having high mechanical strength the composites must also be resistant to adverse conditions within their typical operating environments, such as high temperatures and chemical attacks.

Polyamides are a class of thermoplastic materials with excellent mechanical strength with many types displaying resistance to high temperatures [2]–[4]. Commercially, there are many types of polyamides available, with the most common being polyamide 6 (PA6), and polyamide 6,6 (PA66). Others include polyamide 11, polyamide 12, polyamide 4,6, and polyamide 6,12 with each of the different types offering varying degrees of performance in terms of mechanical stiffness and toughness, performance at high temperatures, chemical resistance, and moisture absorption [2], [5]–[7]. Polyamides are versatile materials which can be produced into fibers, used in fabrics and textiles, as well as bulk plastics which see use in mechanical components requiring high strength. Polyamide 6,6 is an excellent candidate material for high strength and temperature applications. Currently it is being used in the automotive industry for numerous under the hood applications such as the air intake manifold, and the radiator end tank [8].

The addition of fillers to the PA66 matrix can serve to further extend its range of appropriate applications. Glass fibers have proven to be a suitable reinforcement for polyamide materials owing to their relatively low cost and good mechanical stiffness, which serves to strengthen the polyamide matrix [3], [9]–[13]. Aside from providing additional stiffness to the matrix material, fillers can also be selected to help overcome weaknesses of the base material. Below their glass transition polyamides show poor impact strength [14][Yang], this can be overcome by incorporating a high molecular weight matrix with impact resistant modifiers such as rubber particles [13], [15].

The interest of this study was the development and characterization of thermoplastic materials for high temperature and demanding applications able to replace many heavy and high cost metallic structures. In this study hybrid composites of polyamide 6,6 containing rubber particles
and chopped glass fibers have been analyzed for their thermal behaviour, melting and crystallization temperatures, thermal stability and mechanical properties. Of great interest in the field of polymer research is not only constant strain rate behaviour but time sensitive performance of composite materials, thus emphasis has been placed on the dynamic mechanical properties of the polyamide materials. The performance of the hybrid composites has been compared to a pure glass fiber reinforced polyamide composite, a highly impact modified polyamide containing rubber particles, and a pure PA66 material.

4.3 Materials and Methods

4.3.1 Materials

Three grades of Polyamide 6,6 (PA66) polymer pellets, Vydyne 22HSP, Vydyne 41H, and Vydyne R530HT, were provided by Ascend Performance Materials. Vydyne 22HSP is pure PA66 polymer, Vydyne 41H is a high impact grade containing a proprietary mixture of carbon black and rubber particles, and Vydyne R530HT contains 30wt% chopped glass fiber.

4.3.2 Sample Fabrication

In addition to the three supplied grades, blends of the 41H and R530HT material were prepared at volumetric ratios of 70% 41H and 30% R530HT, and 30% 41H and 70% R530HT. These specific ratios were selected as they roughly correlate to glass fiber content of 10wt% for the 70:30 41H:R530HT material and 20wt% glass fiber for the 30:70 41H:R530HT blend. The blends were prepared by compounding on a lab scale twin screw compounder (DSM Xplore 15, DSM Netherlands). The co-rotating twin screws were set at a speed of 50rpm and the temperature was kept constant at 290°C for each run. The compounding, or mixing, time was ten minutes to ensure thorough mixing of the two materials and the glass fibers. Before molding, all materials were dried in an oven at 80°C for three hours to a level of no more than 0.2% H2O by weight.

Tensile, and standard test bar samples, used for dynamic mechanical analysis were fabricated by injection molding (DSM IM5.5, DSM Netherlands). Injection mold processing temperatures along with material types and nomenclature are reported in Table 4.1. The injection molding temperatures for the barrel and the mold were set according to the material supplier recommendations.
<table>
<thead>
<tr>
<th>Material Name</th>
<th>Material Grade</th>
<th>Nomenclature</th>
<th>Barrel Temperature °C</th>
<th>Mold Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vydyne 22HSP</td>
<td>Pure PA66</td>
<td>22HSP</td>
<td>290</td>
<td>85</td>
</tr>
<tr>
<td>Vydyne 41H BK0677</td>
<td>High Impact Modified PA66</td>
<td>41H</td>
<td>290</td>
<td>85</td>
</tr>
<tr>
<td>Vydyne R530HT BK02</td>
<td>PA66 with 30wt% glass Fiber</td>
<td>R530</td>
<td>295</td>
<td>90</td>
</tr>
<tr>
<td>70:30 41H:R530</td>
<td>Blend containing 70% 41H and 30% R530 by volume. Glass fiber content is 10.6wt%</td>
<td>70-41H</td>
<td>290</td>
<td>90</td>
</tr>
<tr>
<td>30:70 41H:R530</td>
<td>Blend containing 30% 41H and 70% R530 by volume. Glass fiber content is 22wt%</td>
<td>30-41H</td>
<td>290</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 4.1: Nomenclature of prepared PA66 materials and injection molding temperatures

4.3.3 Thermogravimetric Analysis

The decomposition temperature of the polyamide materials was measured by thermogravimetric analysis (TGA Q50, TA Instruments). Thermogravimetric testing was completed in accordance with ASTM E2550. Samples were cut to a weight of approximately 20mg and heated to 600°C at a rate of 20°C/min in a nitrogen atmosphere. The degradation onset temperature was measured by taking the temperatures corresponding to 5%, 10% and 50% mass loss.

4.3.4 Differential Scanning Calorimetry

Melting and crystallization temperatures for the prepared materials were measured by differential scanning calorimetry (DSC Q2000, TA Instruments). A standard heat-cool-heat experiment, from -50°C and 315°C, was conducted for each sample with a heating rate of 10°C/min and a cooling rate of 5°C/min, in accordance with ASTM D3418.
4.3.5 Tensile Testing

The tensile properties, tested on a Instron 5848 universal testing machine, of the materials were measured per ASTM D638. The injection molded samples were subjected to a constant strain rate of 5mm/min. The tests were conducted at room temperature and humidity.

4.3.6 Dynamic Mechanical Analysis

A dynamic mechanical analysis (DMA Q800, TA Instruments) was performed on the PA66 materials, testing procedure followed ASTM D4065. The dynamic mechanical properties of the injection molded samples, approximate dimensions of 60x12x2mm, were measured in dual cantilever mode using the 35mm dual cantilever clamp provided by TA Instruments. The materials’ response to both increasing temperature and frequency was tested. The DMA testing was performed with a constant strain of 0.05% while the temperature was increased from 35-100°C with a rate of 3°C/min. The viscoelastic properties were measured at three frequencies, 0.1Hz, 1Hz, and 5Hz.

4.3.7 Scanning Electron Microscopy

Scanning electron microscopy images were taken using a JEOL JSM-IT100, Samples were cut so that the imaged surface was normal to the preferred direction of the fibers and then sputter coated with a thin layer of platinum particles. Backscatter detection was used for all images to highlight the contrast between the polyamide matrix and the reinforcing glass fibers.
Figure 4.1: SEM images of prepared materials. Top row right to left (R-L), 22HSP 100x, 300x, 650x. Second row R-L, 41H 100x, 300x, 650x. Third row R-L, 70-41H 100x, 300x, 650x. Fourth row R-L 30-41H 150x, 300x, 650x. Bottom row R-L, R530 150x, 300x, 650x.
4.4 Results and Discussion

4.4.1 Scanning Electron Microscopy

Scanning electron microscopy images of the prepared PA66 materials are shown in Figure 4.1. The properties of fiber reinforced plastics depend on the intrinsic properties of the fiber and the matrix as well as the fiber dispersion and wetting, and the nature of the fiber-matrix interface and the strength of this bond. From the SEM images of the glass fiber filled materials we can see that there is good dispersion of the fibers and no non-uniform region of material containing an agglomerate of fiber. This confirms that the compounding time and screw speed were sufficient to properly mix the materials and disperse the fibers uniformly throughout the composite. Additionally, it can be seen from these images that there is good wetting between the fiber and matrix material where the matrix seems to cling to the glass fiber. This good wetting serves as evidence of strong fiber-matrix adhesion and good interfacial properties. Also of note is the visual evidence of the fiber alignment created during the injection molding process. It is expected that the alignment of the fibers will serve to increase the observed mechanical stiffness of the material. This will be especially noticeable in the tensile results where the applied force is parallel to the direction of the fibers.

4.4.2 Thermogravimetric Analysis

The thermal stability of the prepared PA66 materials was tested by thermogravimetric analysis, the TGA thermograms are shown in Figure 4.2, and the temperatures corresponding to 5%, 10% and 50% mass loss in Figure 4.3. In general, the polyamide materials demonstrate excellent resistance to high temperatures with 41H having the highest degradation onset temperature, corresponding to 5% mass loss, at 450°C, and the lowest is the pure PA66 22HSP having a degradation onset temperature of 441°C. The 5% mass loss temperature for the R530 material is 443°C. The material blends of 41H and R530 demonstrate decomposition onset temperatures between the two parent materials with the 70-41H material showing slightly higher thermal resistance compared to the 30-41H material, 449°C versus 446°C respectively. Both blends show a singular well defined onset temperature which gives evidence to their homogeneous nature. In this case the addition of the glass fibers slightly improves the initial thermal stability over the pure material. The impact of the glass fibers is more noticeable at high temperatures corresponding to 50% mass loss. At these temperatures, the glass filled compound show
improvements over the non-reinforced polymers meaning that the decomposition rate is lower for the glass reinforced materials. It is also important to consider the effect of the R530, 41H, and 22HSP being composed of slightly different polymer backbones. The differences seen in the thermal stability of the PA66 compounds is also due to the variances in the polymer chains and not only due to the addition of the various filler materials. The PA66 41H has a higher molecular weight relative to the other tested compounds and demonstrated by the higher initial decomposition temperature corresponding to 5% mass loss, and also greater thermal stability when 10% mass loss is considered [16]. This would also conform with the highly impact modified nature of this material. Additionally, the blends of 41H and R530 show higher decomposition temperatures than the pure R530 material confirming the idea that the decomposition onset temperature is dependent on the molecular weight and differences in the polyamide chain more than the glass fiber content.

Figure 4.2: Thermogravimetric thermograms of PA66 materials
Figure 4.3: Temperatures corresponding to 5%, 10% and 50% mass loss of PA66 materials

4.4.3 Differential Scanning Calorimetry

The differential scanning calorimetry curves generated from the heat-cool-heat experiment are shown in Figure 4.4. Each of the PA66 materials display dual melting peaks between 247°C and 262°C depending on the material grade. On the cooling curves, crystallization temperatures are observed between 221°C and 230°C again depending on the grade. The specific melting and crystallization temperatures for each of the tested materials are displayed in Table 4.2. The existence of the crystallization peaks on the cooling curve confirms the semi crystalline nature of polyamide 6,6. The degree of crystallinity was determined by measuring the heat of fusion, using TA Universal Analysis software, and comparing the measured value to the heat of fusion for a 100% crystallised polyamide 66 material, 226 J/g, which was found in literature [17]. It was found that the pure polymer, 22HSP, exhibited the highest degree of crystallinity at 25.9% while the crystallinity of the filled compounds, 41H and R530 was 19.7% and 22.3% respectively. Expectedly, the crystallinity of the 41H and R530 blend materials exhibited crystallinity fraction between the base materials at 21.6% for 70-41H and 21.3% for 30-41H. The differences seen in crystallinity is in some part be due to the variations in molecular weight and formulations of the base matrix material. It has been demonstrated previously that the degree of crystallinity in polymer materials decreases with increasing molecular weight [18], [19]. This argument explains
the behaviour of the Vydyne 41H material quite well as it exhibits both a higher initial decomposition temperature and lower degree of crystallinity compared to the pure material. The glass filled R530HT material exhibits similar initial decomposition kinetics to the pure material but has a lower degree of crystallinity. This suggests that the glass fibers serve to negatively impact the crystalline fraction of the material. The dual melting peaks seen in the PA66 materials is likely a result of the melting of two different crystal morphologies as well as possible melting-recrystallization. It has been theorised previously for semi-crystalline materials that secondary and primary crystal structures will be formed provided the crystallization time is long enough. Upon heating, the secondary crystal structures show a lower melting temperature with the primary structures melting at a higher temperature [20]. The melting-recrystallization phenomena describes a procedure where the lower temperature melting peak describes the melting of initial crystal structures which are subsequently recrystallized upon further heating. This then leads to the higher melting peak corresponding to the melting of more perfectly formed crystal structures [21]. The 70-41H and 30-41H blended materials show well defined crystallization and melting peaks occurring at a set temperature. This confirms that these blends are behaving as a specific homogeneous material rather than a heterogeneous mixture.

Figure 4.4: DSC thermograms of prepared materials
<table>
<thead>
<tr>
<th>Material</th>
<th>Tc (°C)</th>
<th>Tm1 (°C)</th>
<th>Tm2 (°C)</th>
<th>Crystallinity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>22Hsp</td>
<td>227.7</td>
<td>251.7</td>
<td>262.1</td>
<td>25.9</td>
</tr>
<tr>
<td>41H</td>
<td>230.4</td>
<td>252.1</td>
<td>260.2</td>
<td>19.7</td>
</tr>
<tr>
<td>R530</td>
<td>221.6</td>
<td>247.3</td>
<td>257.1</td>
<td>22.3</td>
</tr>
<tr>
<td>30-41H</td>
<td>226.3</td>
<td>248.6</td>
<td>257.32</td>
<td>21.3</td>
</tr>
<tr>
<td>70-41H</td>
<td>230.4</td>
<td>251.1</td>
<td>259.8</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table: 4.2: Crystallization and melting temperatures, and degree of crystallinity of PA66 materials

4.4.4 Tensile Properties

The tensile stress-strain curves for the PA66 materials are shown in Figure 4.5, and tensile modulus and yield stress values are shown in Figure 4.6. The highly impact modified 41H material exhibited the most ductile behaviour owing to its very high total plastic deformation before failure (>150%). This maximum elongation is impressive when compared to the neat 22Hsp which experiences around 50% strain before failure. While not as high in terms of total elongation before failure and plastic deformation this still represents quite tough behaviour especially considering this testing was conducted at room temperature below the glass transition of the material. The 70-41H material, corresponding to an approximately 10wt% glass fiber reinforced material, experienced some plastic deformation before failure around 11% maximum elongation. As would be predicted as the glass fiber content increases to 20wt%, 30-41H, and 30wt%, R530, the maximum elongation and overall ductility of the material decreases until the point where the R530 material experiences brittle fracture. When compared to the neat 22HSP material the addition of the rubber particles in the 41H material results in a decrease in overall mechanical stiffness and strength. For this material, there is a reduction of 30.0% to the tensile modulus and a 39.4% reduction to yield stress. For the glass fiber reinforced materials, there is expectedly a significant increase in stiffness and mechanical strength as a portion of the applied load is transferred to the stiff glass fibers. Additionally, the injection molding process tends to align the fibers in the direction of flow which in this case is along the direction of applied load.
This makes the effectiveness of the fiber reinforcement greater than if the fibers were randomly oriented in the matrix. The tensile modulus for the R530 material is 154\% greater in comparison to the pure 22Hsp and a 261\% improvement over the impact modified 41H material. Furthermore, there is a 124\%, and 269\% increase in yield stress for the R530 material in comparison to 22Hsp and 41H respectively. The blends of 41H and R530, 30-41H and 70-41H, predictably demonstrate mechanical behaviour and possess mechanical properties in between the two parent materials. The tensile modulus for 70-41H, and 30-41H are 84.7\% and 160\% greater than the 41H material respectively. In terms of yield stress these improvements, relative to 41H are 72.7\% and 127\% for 70-41H and 30-41H respectively. In an effort to predict the properties of the 41H ad R530 blend materials the rule of mixture (E_{41H,R530} = E_{41H}V_{41H} + E_{R530}V_{R530}) provides a reasonable approximation to the observed values. When taking the tensile modulus values for 41H and R530 the rule of mixture for a 70:30 and 30:70 ratio of 41H to R530 predicts a modulus of 2102MPa and 3332MPa. This prediction is only 3.5\% off of the reported value for 70-41H and 8.8\% different from the experimental modulus of 30-41H.
Figure 4.5: Stress-strain curves of PA66 materials
4.4.5 Dynamic Mechanical Analysis

The dynamic mechanical properties were investigated under the effect of increasing temperature and frequency. In Figure 4.7 and Figure 4.8 the storage modulus and tan delta for the three PA66 compounds are compared and a frequency of 1Hz. As expected the 30wt% glass fiber filled R530 compound displays the highest storage modulus followed by the 30-41H material, while the 41H displays the lowest storage modulus. Where in the standard tensile test the 30-41H material had a higher modulus than the 22Hsp pure material, here, at low temperatures, the reverse is true when considering storage modulus in the dual cantilever deformation mode. It is theorized that the rubber particles, and reinforcing glass fibers, involved with the high impact modification of the 41H, and stiffening of the R530 material alters the effective stiffness of the composite differently in bending than in pure tension. While the storage modulus and Young’s modulus are analogous they are not directly comparable due to the time dependent nature of the storage modulus. Therefore, it is further suggested that the rubber particles, and glass fibers, in the 41H material, the R530 material, and the blends drastically effect the time dependent nature of the material. Additionally, the reinforcing effects of the chopped glass fiber are likely more noticeable in tension due to their aligned nature in this mode than in bending. There is an inverse relationship between storage modulus and tan delta for these materials with the glass fiber reinforced materials having a lower loss factor compared to the other PA66 compounds. When an external stress is applied to a viscoelastic polymer the polymer chains will tend to rearrange to
reduce the internal stress in the material. This rearrangement gives rise to the excellent damping characteristics of polymer materials as evidenced by their relatively high tan delta values in comparison to metals which are nearly purely elastic. The inclusion of the glass fibers serve to prevent this molecular rearrangement thus causing the material to behave more elastically and leading to the lower loss factor in this material. The behaviour, as expected, is for increasing amounts of glass fiber reinforcement to inversely correlate with the loss factor of the composite material with the R530 material displaying the lowest tan delta followed by the 30-41H and the 70-41H blends. Also of importance is that the inclusion of the glass fibers greatly improves the materials resistance to increasing temperatures. When the storage modulus of each material is considered at 45°C and 85°C it is seen that the stiffness of the non-glass reinforced compounds decreases significantly more than the glass filled composites. Over this temperature range the storage modulus of the 22Hsp and 41H materials decreases by 3.8x and 4.3x respectively. For the glass filled compounds R530, 70-41H, and 30-41H the decrease in storage modulus is only 1.5x, 1.8x, and 2x respectively. This suggests that the stiffness of the glass fiber is dominant at high temperatures and as the glass fiber content increases, the more resistant to high temperatures the material becomes. This phenomenon of resistance to high temperatures is also dependent on the crystallinity of the material. At temperatures above the glass transition a more crystalline material will exhibit better mechanical performance at high temperatures. When the 22Hsp and 41H materials are compared, this behaviour holds true, however, its effects are dominated by the inclusion of glass fibers. This is evidenced by the R530 material which despite having the second lowest degree of crystallinity exhibits the best resistance to temperature when mechanical stiffness is concerned.
Figures 4.9, 4.10, 4.11, 4.12, 4.13 compare the storage and tan delta curves with increasing frequency, 0.1, 1, and 5Hz for each PA66 material (22Hsp, 41H, R530, 30-41H, and 70-41H respectively). With increasing frequency, the trend is for the storage modulus to increase as well. Due to the viscoelastic, time dependent, properties of these materials when a constant strain is applied the stress in the materials will decrease over time. It then follows that if the modulus is measured over a longer period of time, or a low frequency, it will be lower than if measured over...
a short period, or high frequency, due to this decrease in stress [22]. The glass transition temperature (Tg) is a phenomenon associated with the amorphous regions of polymers [23], [24]. When cooled below their glass transition polymers behave as glassy and brittle structures due by a restriction to the mobility of the polymer chains caused by a reduction in free volume [25], [26]. Upon heating through the transition larger segments of the polymer chain are able to reorient leading to more ductile and soft behaviour. Heating a polymer through the glass transition corresponds to a dramatic decrease in mechanical stiffness, for dynamic mechanical behaviour the Tg of the material is typically taken as the peak of the tan delta curve. For the three PA66 materials the trend is for the Tg, or the tan delta peak temperature, to increase with frequency. This is again due to the time dependent mature of the material as previously discussed. At high frequencies, the molecular chains do not have sufficient time to reorient before the next deformation cycle, therefore, a higher temperature, and more energy, is required to initiate this reorientation. It has been reported that the inclusion of reinforcing fibers to a polymeric matrix can both increase or decrease the glass transition temperature in the material depending on the fiber type, and the strength of the fiber matrix bond [27]–[29]. It has been theorized that if the fiber content is sufficiently high poor fiber wetting and adhesion can cause an increase of segmental mobility in the polymer chain thus leading to a lower observed glass transition in the material [28]. On the other hand, it has been demonstrated that when there sufficiently good fiber wetting the glass transition will increase [29]. If the interface between the fiber and the matrix is perfect, then there will be no voids in these sites which will in turn reduce the mobility of the polymer chain thus increasing the glass transition temperature [29]. Another consideration is the relative molecular weight of the matrix materials in question. The 41H material has a higher molecular weight compared to the R530 material which accounts for discrepancies to the thermal stability and crystallization of these materials. Based on the Flory-Fox equation [30], it has been shown that an increase in molecular weight will subsequently lead to higher observed glass transition temperatures. When the materials in this study are considered both effects, of fiber reinforcement and molecular weight, must be taken into account and the changes to the glass transition of the different materials is due to changes in molecular weight of the polymer backbone as well as the addition of fillers.
Figure 4.9: Storage modulus and Tan Delta for 22Hsp material at 0.1, 1 and 5Hz

Figure 4.10: Storage modulus and Tan Delta for 41H material at 0.1, 1 and 5Hz
Figure 4.11: Storage modulus and Tan Delta for R530 material at 0.1, 1 and 5Hz

Figure 4.12: Storage modulus and Tan Delta for 30-41H material at 0.1, 1 and 5Hz
4.5 Conclusions

High performance polyamide 6,6 composites filled with reinforcing glass fibers and rubber particles to promote high stiffness, strength, and toughness have been prepared by melt blending. The hybrid composites were tested for their thermal stability by TGA, melting and crystallization behaviour by DSC, mechanical properties in tension, and their dynamic mechanical properties, storage modulus and loss factor by DMA. The results of the hybrid composites were then compared to a pure PA66, a highly impact modified material containing rubber particles, and a glass fiber reinforced grade of PA66. It was found that the addition of glass fibers to the matrix resulted in a significant increase in mechanical properties, for the 30wt% glass filled grade a 154% improvement in tensile modulus and a 124% increase in yield stress was found over the pure PA66. Additionally, through DMA it was determined that the reinforced materials showed a much better resistance to high temperatures. The mechanical properties of the hybrid materials are dominated by the influence of the glass fibers. While the rubber particles in the 41H material clearly act as plasticizing agents for the fiber reinforced compounds their effect are less noticeable in these experiments. In the tests performed in this study the properties are dominated by the glass fibers even at 10wt% loading.
4.6 Acknowledgements

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4.7 References


[20] C. L. Wei, M. Chen, and F. E. Yu, “Temperature modulated DSC and DSC studies on the


Chapter 5

5 Conclusions and Future Work

5.1 Concluding Remarks

In summary, this work aimed at expanding the functionality of polymers by the development of novel fiber reinforced composites. Furthermore, the focus was primarily on the effect of the various reinforcing fibers on the viscoelastic properties of these materials and further analysis considered the thermal performance of the new composites. Where applicable, the constant strain rate mechanical properties and thermal expansion of the composites was studied. In an effort to gain insight into many types of polymeric materials a wide variety of matrices were used from thermosetting rubbers to strong and stiff thermoplastics. Additionally, a diverse range of reinforcing fibers were analyzed from carbon fiber to liquid crystal aramid and poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibers to ceramic glass and alumina fibers.

Firstly, a polyurethane thermosetting rubber matrix was reinforced with Kevlar, PBO, and alumina reinforcing fibers. Here, a simple process was used to incorporate the fibers into the matrix through use of a high shear mixing process which should be easily scalable to an industrial scale. Secondly, polyester based thermoplastic elastomer and flexible thermoplastic (TPC-ET) was studied in chapter three, increasing the material stiffness over the first study. Original composites consisting of these matrices reinforced with carbon and PBO fibers were developed and analysed. Thirdly, high performance polyamides and polyamide composites were studied. Hybrid polyamide 6,6 composites were created with glass fiber and rubber particles to promote high strength, stiffness, and toughness.

When considering the viscoelastic properties, an increase in storage modulus was found with the inclusion of reinforcing fibers and this was also coupled with a decrease in damping capacity, tan delta, for the materials. Additionally, the frequency effects revealed that the observed storage modulus of the composite materials increases with frequency. The study of glass transition behavior under a temperature ramp experiment was also key in chapters three and four. While an increase in glass transition temperature (Tg) was found for the carbon and PBO reinforced TPC-ET materials, for the glass reinforced polyamide, in chapter four, the reverse was found.
Furthermore, all composite materials demonstrated better performance throughout the temperature ranges tested signifying the suitability of fiber reinforced plastics for more demanding applications.

The properties of the composite materials not only depended on the base properties of the matrix and fiber but also the nature of the fiber-matrix interface. In chapter two, with the polyurethane composites, it was found that Kevlar fibers had much better interfacial properties with the polyurethane matrix than the PBO fibers. In turn this was found to dramatically affect the materials resistance to increasing strain with the Kevlar composites performing much better. Similar conclusions were made when the matrix changed to TPC-ET materials. Here, the carbon fibers performed better than PBO at low strain conditions, but at high stress/strains the carbon fiber was outperformed due to the manufacturing process which cause more breakage resulting in a shorter length of the carbon fibers.

5.2 Future Work

There are multiple aspects of future work which can be undertaken to expand the scope of this work.

First would be the investigation into the interfacial properties of the fiber and matrix and research into additives which promote better fiber matrix coupling. It has been shown in this work that the strength of the fiber-matrix bond is extremely important to not just the mechanical stiffness, but also the materials performance at high stress and temperature. The nature of this interface also impacts other behaviour such as crystallinity and glass transition. While in this work the interface behaviour was studied with SEM imaging, this only provides a qualitative description of the nature of the fiber-matrix bond. It would be beneficial to research, and also industrial applications, to quantitatively characterize the nature of the fiber-matrix bond.

Secondly is the study of the crystallinity of the thermoplastic composites. A brief study into the crystallinity of these materials was done in the work of this thesis, however a full parametric study into the crystallization and melting kinetics would be beneficial. The crystallization of thermoplastic materials greatly affects the mechanical properties of the materials, from stiffness to toughness and also their performance at high temperatures. The crystallinity of a material is greatly affected by the thermal history and the manufacturing process. Therefore, a study of the
isothermal and non-isothermal crystallization kinetics by use of X-ray diffraction would be beneficial.

Thirdly is to develop a multi-scale material model for these composites. Modelling of these materials is important to enable engineers to adapt them to industrial applications. Particularly of importance would be the modelling of the viscoelastic behaviour of these materials which have traditionally been tough to model. This is especially true when considering their long-term creep behaviour.