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Synthesis, Modification, Characterization and Processing of Molded and Electrospun Thermoplastic Polymer Composites and Nanocomposites

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Synthesis, Modification, Characterization and Processing of Molded and Electrospun Thermoplastic Polymer Composites and Nanocomposites

by

Tamalia Julien

A dissertation submitted in the partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Keywords: Polycarbonate Polyurethane, Nanoparticles, Nanosilica, Nanosilver, Carbon black, Soft Thermoplastic Urethane

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Dedication

This dissertation is dedicated to my father, Nicholas Anthony Lawrence Julien, who has passed before this day could be realized but who firmly believed that I was destined for greatness since I was a child. I love you and miss you every day Dad.
Acknowledgments

Firstly, I would like to give thanks and praise to the Lord for his unwavering love and guidance (Psalm 27). My mom, who has been my rock, and my number one supporter, I would like to thank you for your love and guidance and encouraging words, that has lifted me up through the low times and kept me going. My sister Tanielle, who was always just a facetime call away who has always filled me with laughter and energy. To Lyndon for your unwavering support in helping to raise our son while I was completing my studies, thank you for all your help. To my son Julien who gives me strength and motivation and to the rest of my family and friends, I am truly thankful and appreciative of your love and support.

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Abstract

This dissertation focuses on the versatility and integrity of a novel, ultrasoft polycarbonate polyurethane (PCPU) by the introduction of nanoparticles and lithium salts. Additionally, the research takes into account the use of electrospinning as a technique to create PCPU and polyimide (PI) fibers. These polymers are of interest as they offer a wide range of properties and uses within the medical and industrial fields.

An industrial batch of an ultrasoft thermoplastic polyurethane (TPU) was synthesized using a two-step process. The first was to create an end capped pre-polymer from methylene bis (4-cyclohexylisocyanate), and a polycarbonate polyol made up of 1,6-hexanediol and 3-methyl-1,5-pentanediol. The second step was done by reacting the pre-polymer with an excess of the polycarbonate polyol with a chain extender, 1,4-butanediol. Biocompatibility testing such as USP Class VI, MEM Elution Cytotoxicity and Hemolysis toxicology reported that PCPU showed no toxicity. This novel type of polyurethane material targets growing markets of biocompatible polymers and has been used for peristaltic pump tubing, but also can be utilized as balloon catheters, enteral feeding tubes and medical equipment gaskets and seals. This material is ideal for replacing materials such as soft plastisols containing diethylhexyl phthalate for use in biomedical and industrial applications. After extensive characterization of this polymer system another dimension was added to this research.

The addition of nanoparticles and nanofillers to polyurethane can express enhanced mechanical, thermal and adhesion properties. The incorporation of nanoparticles such as
nanosilica, nanosilver and carbon black into polyurethane materials showed improved tensile strength, thermal performance and adhesion properties of the PCPU. Samples were characterized using contact angle measurements, Fourier transform spectroscopy (FTIR), differential scanning calorimetry (DSC), parallel plate rheology and tensile testing.

The second chapter entails the fabrication and characterization of PCPU nanofibers and nanomembranes through a process known as electrospinning. The resulting PCPU nanomembranes showed a crystalline peak from the WAXS profile which is due to electrospun and solution strain induced crystallinity. The PCPU nanocomposite nanomembranes displayed increased thermal stability and an increase in tensile performance at higher weight percent. The nanomembranes were investigated using contact angle measurements, thermogravimetric analysis (TGA), DSC, WAXS, SAXS and tensile testing.

The final chapter focuses on investigating the rheological properties of PCPU/lithium electrolytes as well as transforming an unprocessable polyimide powder into a nanomembrane. The PCPU/ lithium composite electrolyte showed an increase in the activation energy and conductivity, while the PI/lithium showed increased conductivity over time. Dynamic mechanical analysis and four-point probe was used to investigate the samples.
Chapter 1:
Thermal and Mechanical Analysis of Sustainable Biopolymer Nanocomposites

1.1 Introduction

Polymer nanocomposites are created when nanoparticles are introduced to polymer systems whether post synthetically or in-situ polymerization [1–4]. The formation of nanocomposites by introducing nanoparticles as a reinforcing filler with the goal of enhancing and modifying the performance and characteristics of polymers have been used for a long time in nanotechnology [1,5-7]. Nanocomposite materials cover a wide range material from inorganic glasses to organic polymers [8] and are important materials for many modern and future technologies, primarily due to their wide tunability in properties and light weight [9-11].

Nanoparticles are extremely diverse and can be placed in many sub categories depending on their use. They can be metallic such as Iron oxide (Fe$_3$O$_4$), gold (Au), Silver (Ag), carbon derived such as single walled and multiple walled carbon nanotubes, graphene and carbon black as well as organic nanoparticles such as dendrimers, micelles and ferritin. They can also be
described as zero dimensional such as spheres, one dimensional such as nano wires and nanorods, 2 dimensional such as thin films and plates and three dimensional also known as bulk nanomaterials. Because of these attributes, nanotechnology attained acceptance by industrial sectors due to its applications in electronic storage systems [13-14], biotechnology [15], targeted drug delivery [16,17] and vehicles for gene therapy and drug delivery [14-18].

The polymer utilized in this study can be categorized as a thermoplastic polymer and can be further categorized as a semi crystalline polymer which is made up of not well-defined hard crystalline segments with a low percent crystallinity and soft amorphous region. Polycarbonate polyurethane is an ultrasoft polymer synthesized with methylene bis (4-cyclohexylisocyanate), 1,4- butanediol as a chain extender and a polycarbonate polyol containing 1, 6-hexanediol and 3-methyl-1, 5-pentanediol [19-21]. It displays remarkable mechanical properties together with the proficiency to re-heal after rupture without the need for additives or implanted healing agents. A combination of properties such as high tensile strength, ultimate elongation, toughness, abrasion, tear resistance, low compression and tensile set, low temperature performance and resistance to oil have allowed polyurethanes to be used in many demanding applications [22-24].

Figure 1.2 Synthetic scheme showing the process of synthesizing PCPU [20].
PCPU is a thermoplastic polyurethane (TPU) which is a class of polymers that possess excellent properties including toughness, abrasion resistive, excellent hydrolytic stability, elastomeric and durability, making it versatile for widespread uses [19-21,25–30]. Because of its biocompatibility, non-toxicity, robustness and functionality TPUs can be used in the biomedical industry as implantable devices (vascular grafts, pacemaker leads, blood bags, bladders and artificial heart valves) and medical applications [31–34]. Moreover, it can also be utilized in other industries such as electronics, automotive, sporting goods and foams [35-38].

In addition, PCPU also has properties similar to segmented polyurethanes (PUs), which consists of hard and soft segments. It exhibits microphase separation, due to a high degree of mixing of hard and soft segments because of hydrogen bonding between the hard segment urethane groups and the soft segment carbonate groups [41-42]. Additionally, the mixing can be confirmed by the small percent crystallinity with crystal lamellae d spacing of 0.45Å [20].

1.1.2 Types of Nanocomposites

Three different types of zero dimensional spherical nanoparticles are being investigated herein; fumed nanosilica, nanosilver and carbon black. Each imparting its own unique properties into the PCPU.

Fumed silica is produced by high-temperature hydrolysis of silicon tetrachloride in a flame [39-40]. The use of silica with polyurethanes has been widely studied but nanosilica has not been introduced to our novel polymer. The addition of fumed silicas to polyurethanes in solution conveys viscosity, thixotropy and pseudoplasticity, also there is an improvement in mechanical properties [40]. The surfaces of silica nanoparticles possess an unknown number of surface silanol (Si-OH) groups which may participate in hydrogen bonding with amines within the urethane unit.
Fumed nanosilica is known to be hydrophilic and when added to the polyurethane, the degree of phase separation escalates because of the interaction between hydrogen-bonded silanol groups on the nanosilica surface and soft segments of the polyurethane. This leads to an increase in the segmental incompatibility on the polyurethane with the presence of the hydrophilic nanosilicas. Studies have shown that these specific polymer materials have the ability to form hydrogen bonds which result in higher phase separation due to less direct interactions between phases. Furthermore, silanol and carbonyl group interactions are weaker than those between -NH and ester carbonyl groups, with the addition of silica the polycarbonate chain mobility increases and becomes more ordered relative to the neat polyurethane [43-45].

Carbon black (CB) is abundant, low cost and possesses properties such as heat stability and electrical conductivity [46-50]. It is a versatile nanoparticle which can be incorporated in electrochemistry and mechanical enhancements and other fields. When a conductive filler such as carbon black is introduced into a polymer matrix a conductive polymer nanocomposite is formed with excellent thermal and mechanical properties as well as electrical conductivity which can be applied to sensors, conductors and anti-static materials. In this study the use of low weight percent loading of CB nanoparticles was investigated as it is known that high amounts of CB cause poor mechanical properties and complex loading [50-51]. Also, this particular type of carbon black used is known to be more effective at low loadings to impart maximum enhancement of the material’s properties.

Amongst the nanoparticles, silver (Ag) nanoparticles are of high interest as silver-based products are continuously being sought after in the biomedical field. Silver nanoparticles allow for enhanced thermal, mechanical and antimicrobial properties that are necessary for biomaterials such as bandages, catheters, surgical instruments and topical ointments [52-54]. However, there
are adverse effects from prolonged exposure of Ag nanoparticles on human health. One way to combat this is to entrench the silver particles into the polymer matrix. PCPU is biocompatible; therefore, it becomes an impeccable candidate for the Ag nanoparticles which can then be used for prosthesis as well as drug delivery devices [52, 55-56].

Herein, a series of PCPU nanosilica, nanosilver and nanoscale carbon black composites were produced via ultrasonication. Our novel PCPU was designed to be highly flexible while keeping its mechanical properties. This introduction of the nanoparticles will allow for increased mobility which is expected to lead to greater thermal and mechanical performance. Also, the literature is quite rare on rheological studies and viscoelastic behavior of PCPU nanocomposites, therefore, the rheological properties of these PCPU nanocomposites were studied to investigate its melt processability.

1.2 Experimental

1.2.1 Materials

Nanosilver (NTX-300ET) was purchased from Nanux Inc (Yungnam,Korea) with an average particle size of 30-50nm. Carbon black nanoparticles (VXC72) were mass produced by Cabot Corporation (Victoria, Australia) with a particle size of 10-30 nm. Fumed silica (nanosilica HDK N20) was mass-produced by Wacker-Chemical Corporation (Michigan, United States). The majority particle size in all nanosilicas used was 7 nm. All particles were used as received without further purification. The certified ACS grade reagent tetrahydrofuran (THF) 99.9% was purchased from Sigma-Aldrich and used without further purification.

1.2.2 Purification of polycarbonate polyurethane

100 g of PCPU chips were mixed with 1000 ml of THF in a 3L reactor for 3 hours until the polymer was fully dissolved. Deionized water was then added to the reactor in a dropwise
fashion to guarantee proper crashing-out of the polymer. The water was then removed, and the process was repeated. The purified polymer was then dried under vacuum at 60°C.

1.2.3 Polymer-nanoparticle composite synthesis

Polycarbonate polyurethane/nanoparticle composites were prepared by dispersing the nanoparticles using a sonicator. 10g of the purified PCPU was dissolved in 100 ml THF (ACS reagent, 99.9% sigma Aldrich) and then the desired amount of nanoparticles (0.1-1.0 w.t.%) were introduced to the solution and then mixed by ultrasonication (Fisher Scientific Sonic Dismembrator 550) at a mixing rate of 10 minutes with 3 second rest intervals for two hours to ensure homogeneity of composites. The composites were then crashed out using deionized water and the resulting materials were dried overnight under vacuum.

1.2.4 Preparation of molded nanocomposites

Before samples were characterized, they were compression molded using a Carver laboratory press (model C) at 250°C and 3 tonnes of pressure.

1.2.5 Surface Energy Measurements

Surface energy or surface tension of solid samples gives an insight into the samples’ wettability. This behavior is of great importance as it plays a significant role in many industrial processes such as lubrication, painting and printing [57]. The surface energy of a solid cannot be directly measured therefore the use of liquid on a solid surface via contact angles is employed. There are many different theories employed in surface energy measurements such as Zisman (one component model), Owens/Wendt (two component), Fowkes (two component) and van Oss (three component) theories.

This study focuses on the two-component model specifically Fowkes theory. Owens/Wendt theory and Fowkes theory are similar in that they both specify that the solid surface
has two components; a dispersive force and a polar (non-dispersive) force. The difference between the two is the method with which the theories are utilized.

Fowkes theory is centered on three essential equations describing the interactions between solid surfaces and liquids [58]. As with all theories, they begin with Young's Equation which describes the contact angle of a liquid drop on an ideal solid surface;

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \]  

(1.1)

where: \( \gamma_{lv} \) = liquid-vapor interfacial tensions, \( \gamma_{sv} \) = solid-vapor interfacial tensions, \( \gamma_{sl} \) = solid-liquid interfacial tension, and \( \theta \) = the contact angle between the liquid and the solid.

Fowkes theory also considers Dupre's Definition of Adhesion Energy

\[ I_{SL} = \sqrt{\gamma_{sv}^d \times \gamma_{sv}^d} + \sqrt{\gamma_{lv}^p \times \gamma_{sv}^p} \]  

(1.2)

where: \( I_{SL} \) = Adhesion energy per unit area between a liquid and a solid surface.

Fowkes stipulated that the adhesive energy between a solid and a liquid can be expanded into interactions between the dispersive components of the solid and liquid as well as the interactions between the polar components of the two components.

\[ I_{SL} = 2 \left[ \sqrt{\gamma_{iv}^d \times \gamma_{sv}^d} + \sqrt{\gamma_{iv}^p \times \gamma_{sv}^p} \right] \]  

(1.3)

where: \( \gamma_{iv}^d \) = dispersive component of the surface tension of the test liquid, \( \gamma_{iv}^p \) = polar component of the surface tension of the test liquid, \( \gamma_{sv}^d \) = dispersive component of the surface energy of the solid surface, and \( \gamma_{sv}^p \) = the solid surface polar component.

The combination of the three equations produces the primary equation of the Fowkes' surface energy theory:

\[ \sqrt{\gamma_{iv}^d \times \gamma_{sv}^d} + \sqrt{\gamma_{iv}^p \times \gamma_{sv}^p} = \frac{\gamma_{SL}(\cos \theta + 1)}{2} \]  

(1.4)
To use the Fowkes' theory on a solid sample to determine solid surface energy, the first liquid must only have a dispersive component for example a liquid must have $\gamma_L^p = 0$, so that $\gamma_L^d = \gamma_{SL}$.

Because of this, the primary equation condenses to:

$$\gamma_{sv}^d = \frac{\gamma_{lv} (\cos \theta + 1)^2}{4} \quad (1.5)$$

and $\gamma_{sv}^d$ can be calculated directly from the contact angle measured from the solid surface.

The next step is to test the solid for contact angle with another liquid which has both a dispersive component and a polar component. The contact angle produced from the liquid on the solid and the calculated $\gamma_{sv}^d$ from the previous step, $\gamma_{sv}^p$ can be calculated as the only unknown in the equation 1.4. The overall surface energy of the solid, $\gamma_{sv}$ is then calculated as

$$\gamma_{sv} = \gamma_{sv}^p + \gamma_{sv}^d \quad (1.6)$$

Uniform drops of deionized water and cyclohexane were displaced on the polymer nanocomposite surface and the contact angles were measure using a KSV CAM-101 video based optical contact angle measuring device equipped with a hamilton syringe in an environmentally controlled chamber (KSV-1TCU). All measurements were performed in air, at room temperature. The samples were tested and then the surface was cut away and the cut surface was retested with the deionized water.

1.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

Perkin Elmer spectrum two furnished with an Attenuated Total Reflection (ATR) accessory was utilized for this study. A scanning range of 400-4000cm$^{-1}$ set at a resolution of 4cm$^{-1}$ and 16 repetitions were done on the nanocomposites. The composites were scanned, then cut along its length and then re-scanned for 24 hours to detect any shifts of functional groups.
1.2.7 Differential Scanning Calorimetry (DSC)

DSC analysis was performed using TA instruments 2920 Differential Analysis Calorimeter to obtain glass transition temperature ($T_g$) and melt temperature ($T_m$) of the polymer and polymer nanocomposites. The heat cool heat method was utilized a starting temperature of -70°C and then heated to 200°C at a ramp rate of 10°C/minute to ensure all samples has the sample thermal history. The sample was the cooled down to -70°C, using a refrigerated accessory, with the similar ramp rate and then reheated to 200°C. The $T_g$ values were taken from the second heating run.

1.2.8 Parallel Plate Rheology

Rheological properties of the polymer nanocomposites were analyzed by TA instruments AR 2000 equipped with parallel plates with a 25mm diameter. The plate gap was kept at 3mm during experimentation. The measurements were done at different temperatures from 100°C to 190°C

The strain sweeps were performed from 0.01% to 100% at a constant frequency of 0.33HZ. This was done to detect the linear viscoelastic region at different temperatures.

Frequency sweeps were carried at strains within the viscoelastic region of 1% and 5% respectively. The frequency sweeps were done from 0.05 to 100 Hz. Specimen discs were of average of 25mm and 3mm thickness.

A temperature ramp was done at different strains of 1% and 5% at a constant frequency of 1Hz to detect the viscoelastic behavior at high temperatures.

1.2.9 Tensile Testing
Tensile strength characterization was done using Shimadzu ASJ tensile tester to measure displacement of samples. All tensile testing was done at a rate of 100mm/min at room temperature according to ASTM D638 IV. Dog bone cut samples were of various thickness 0.8 to 1mm. Five measurements for each sample were done and the average tensile strength was recorded.

1.3 Results and Discussion

1.3.1 Surface Free Energy Measurement

The surface free energy was determined from contact angle measurements using deionized water and cyclohexane, and is presented in Figures 1.3, 1.4 & 1.5. The total surface energy of a polymer’s surface is equal to the sum of the dispersion component and the polar component. The polar water creates a noticeable semicircular shape while the non-polar cyclohexane spreads across the surface of the composite. Fowkes theory which is explained in the experimental section was then used to calculate the dispersive component of the surfaces as well as the polar component. Table 1.1 gives the contact angles of the PCPU nanocomposites together with the resulting surface energies. The contact angles for the nanocomposites when the water was used had varying trends. For the silver nanocomposites there was a decrease in the contact angle from 102° for the neat PCPU to 96°, 85°, 100° and 88° for the 0.1%, 0.25%, 0.375% as well as the 0.5% w/w. Then the 0.75% and 1.0% w/w increased to 107°. The silica nanocomposites showed a slight decrease in contact angle to 96° and the carbon black composite as seen displayed a slight decrease in the angle from the neat PCPU. However, when the cyclohexane was used the contact angle for the neat PCPU was 12.8°. The contact angle increased slightly for the Ag nanocomposites to as high as 19°; it doubled for the silica composites with 24° and a slight increase to 20° for the carbon black nanocomposites. There was a trend demonstrated on the
calculation of the dispersive component for the nanocomposites. The silver nanocomposites trended downward with a constant decrease in the dispersive energy from 24.4 mJ/m to 24.0 mJ/m as well as the silica component from 24.4 to 23.1 mJ/m. The carbon black nanocomposites however, trended upwards showing that the increase in the % w/w of carbon black nanoparticles added, increased the dispersive component of the polymer matrix.

When the PCPU nanocomposite surface was cut away the use of the cyclohexane as a testing parameter was futile. Figures 1.6, 1.7 & 1.8, show the contact angle of the pristine surface against the ruptured surface of the nanocomposites using deionized water only. When the surface is cut away there is a decrease in the contact angle below that of 90° compared to the pristine surface >100°. Moreover, the general trend downward for the silver nanoparticle composite is noted with an increase in the Ag content resulting in increased hydrophilicity. This is evidence of available hydrogen bonding sites, which will be explained further in the FTIR section.
Figure 1.3 Contact Angle data for PCPU/Ag nanocomposites using water and cyclohexane.
Figure 1.4 Contact angle data for PCPU/SiO2 nanocomposites using water and cyclohexane.

Figure 1.5 Contact angle data for PCPU/CB nanocomposites using water and cyclohexane.
Table 1.1 Contact angle data: Contact angle measurements and surface tension for PCPU and PCPU nanocomposites

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>AVG CA (H20)</th>
<th>AVG CA (C6H6)</th>
<th>$\gamma_{sv}$</th>
<th>$\gamma_{sv}^{D}$</th>
<th>$\gamma_{sv}^{P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEAT PCPU</td>
<td>102 ± 2</td>
<td>12.5 ± 1.2</td>
<td>25.3</td>
<td>24.7</td>
<td>0.6</td>
</tr>
<tr>
<td>0.1WT% AG</td>
<td>96 ± 5</td>
<td>18.9 ± 5.5</td>
<td>26.2</td>
<td>24.5</td>
<td>1.7</td>
</tr>
<tr>
<td>0.25WT% AG</td>
<td>85 ± 3</td>
<td>11.6 ± 2.7</td>
<td>30.0</td>
<td>24.5</td>
<td>5.5</td>
</tr>
<tr>
<td>0.375WT% AG</td>
<td>100 ± 4</td>
<td>16.9 ± 0.8</td>
<td>25.3</td>
<td>24.4</td>
<td>0.9</td>
</tr>
<tr>
<td>0.5WT% AG</td>
<td>88 ± 5</td>
<td>17.2 ± 2.7</td>
<td>28.4</td>
<td>24.2</td>
<td>4.2</td>
</tr>
<tr>
<td>0.75WT% AG</td>
<td>107 ± 5</td>
<td>17.5 ± 3.4</td>
<td>24.3</td>
<td>24.2</td>
<td>0.1</td>
</tr>
<tr>
<td>1.0WT% AG</td>
<td>107 ± 2</td>
<td>18.5 ± 5</td>
<td>24.2</td>
<td>24.02</td>
<td>0.2</td>
</tr>
<tr>
<td>0.1WT% SIO2</td>
<td>102 ± 3</td>
<td>12.6 ± 2.3</td>
<td>25.0</td>
<td>24.4</td>
<td>0.6</td>
</tr>
<tr>
<td>0.25WT% SIO2</td>
<td>100 ± 2</td>
<td>18.2 ± 1.8</td>
<td>25.5</td>
<td>24.4</td>
<td>1.1</td>
</tr>
<tr>
<td>0.375WT% SIO2</td>
<td>97 ± 3</td>
<td>17.4 ± 2.5</td>
<td>25.9</td>
<td>24.2</td>
<td>1.7</td>
</tr>
<tr>
<td>0.5WT% SIO2</td>
<td>96 ± 8</td>
<td>17.5 ± 2.1</td>
<td>26.0</td>
<td>24.2</td>
<td>1.8</td>
</tr>
<tr>
<td>0.75WT% SIO2</td>
<td>103 ± 1</td>
<td>19.6 ± 3.5</td>
<td>24.5</td>
<td>23.9</td>
<td>0.6</td>
</tr>
<tr>
<td>1.0WT% SIO2</td>
<td>96 ± 2</td>
<td>24.3 ± 0.7</td>
<td>25.1</td>
<td>23.1</td>
<td>2.0</td>
</tr>
<tr>
<td>0.1 WT % CB</td>
<td>94 ± 4</td>
<td>19.9 ± 4.8</td>
<td>25.6</td>
<td>23.2</td>
<td>2.4</td>
</tr>
<tr>
<td>0.25WT% CB</td>
<td>99 ± 5</td>
<td>20.0 ± 3.3</td>
<td>25.0</td>
<td>23.8</td>
<td>1.2</td>
</tr>
<tr>
<td>0.375WT% CB</td>
<td>104 ± 4</td>
<td>17.9 ± 3.9</td>
<td>24.5</td>
<td>24.1</td>
<td>0.4</td>
</tr>
<tr>
<td>0.5WT% CB</td>
<td>102 ± 2</td>
<td>20.3 ± 3.9</td>
<td>24.6</td>
<td>23.9</td>
<td>0.7</td>
</tr>
<tr>
<td>0.75WT% CB</td>
<td>92 ± 8</td>
<td>17.2 ± 5.5</td>
<td>27.1</td>
<td>24.2</td>
<td>2.9</td>
</tr>
<tr>
<td>1WT% CB</td>
<td>102 ± 3</td>
<td>18.4 ± 2.4</td>
<td>24.6</td>
<td>24.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 1.6 Water contact angle of pristine and ruptures PCPU/ Ag nanocomposite surfaces.

Figure 1.7 Water contact angle of pristine and ruptures PCPU/ SiO2 nanocomposite surfaces.
1.3.2 Fourier-Transform Infrared Spectroscopy (FTIR)

Figure 1.9 shows the IR spectra for cut and uncut surfaces of the PCPU and its nanocomposites. The expected absorbance for associated N-H groups is 3318-3338 cm\(^{-1}\) and associated C=O 1718 cm\(^{-1}\) and unassociated C=O is 1740 cm\(^{-1}\). Yokoyama et al. 1968 [59]; Seymour et al. 1970 [60]; Boerio and Wirasate 2006 [61]; Na, Lv et al. 2009 [62] all have done studies to demonstrate associated and unassociated hydrogen bonding using FTIR. The characteristic peaks for nanoparticles; SiO2 (1626, 1103, 809 cm\(^{-1}\)), CB (1630, 1114, 1118 cm\(^{-1}\)) and silver nanoparticles (3420 and 1638 cm\(^{-1}\)) did not show up on any of the FTIR spectra. This can be as a result of the low concentrations together with the nanometer size of the particles used.

Figure 1.10 and 1.11 show a magnified view of the –NH region and –C=O of the spectra. There is a shift in the wave number of the associated -NH region from 3305 cm\(^{-1}\) to 3307 cm\(^{-1}\) on
the addition of the nanoparticles. This suggests interactions between the particles and the NH
groups within the polymer matrix. When the surface is cut away there is a decrease in the %
transmittance for the H-bonded region at 3305 cm\(^{-1}\) which tells us that when the surface is cut
away hydrogen bonds become available and the H-bonded regions are reduced. This correlates
with the decrease in the contact angle when the surface is cut away. Available H-bonds allow for
lower contact angle which makes the surface hydrophilic. Figure 1.12 shows what happens to
these bonds if they are left over time. After 1 hour you see the transmittance decrease and after 24
hours the scan gets closer to the original scan. This is evidence of the hydrogen bonds folding
onto themselves when left alone [21].

![Figure 1.9 FTIR spectra for cut and uncut PCPU and PCPU/1% w/w nanocomposites.](image)

**Figure 1.9** FTIR spectra for cut and uncut PCPU and PCPU/1% w/w nanocomposites.
Figure 1.10 FTIR of –NH group showing the change in transmittance from cut and uncut PCPU nanocomposites.

Figure 1.11 FTIR of –C=O group showing the change in transmittance from cut and uncut PCPU nanocomposites.
1.3.3 Differential Scanning Calorimetry (DSC)

The glass transition, $T_g$ and melting temperatures were recorded as seen in Figure 1.13, 1.14 and 1.15. Stevens et al demonstrated that the addition of nanoparticles would induce plasticization of the polymer composites leading to lower $T_g$. The PCPU/Ag composites’ $T_g$ ranged from $-23.5^\circ C$ to $-25.4^\circ C$ as the % w/w of silver nanoparticles were added. The PCPU silica composites’ $T_g$ ranged from $-24.1^\circ C$ to $-22^\circ C$ and the PCPU/CB composites were from $-24^\circ C$ to $-22.5^\circ C$.

The trends of the nanoparticles are shown in figure 1.16. The silica nanocomposites and the carbon black nanocomposites responded similarly. There was an initial decrease in the glass transition temperature at the lower %w/w which is due to the increase in free volume space of the polymer chains, then at 0.5 %w/w nanoparticles, the glass transition temperature increased. This can be due to the reduction in the motion of the polymer backbone from the additional nanoparticles which would reduce the plasticization effect and therefore allowed a rise in the $T_g$. 

Figure 1.12 FTIR of –NH group showing the change in transmittance over a 24-hour period.
Because the silica and carbon black have the ability to aggregate and agglomerate this may cause a reduction in the free volume of the polymer backbone which leads to the increase in the glass transition temperature. Contrastingly, nanosilver particles do not aggregate so the increase in the amount of nanosilver added increases the ability to plasticize and which leads to a continuous decrease in the glass transition temperature.

Figure 1.13 DSC Data: DSC thermogram of neat PCPU and PCPU/SiO2 nanocomposites.
Figure 1.14. DSC thermogram of neat PCPU and PCPU/carbon black nanocomposites.
Figure 1.15. DSC thermogram of neat PCPU and PCPU/Ag nanocomposites.

Figure 1.16. DSC glass transition (Tg) trends for PCPU and PCPU nanocomposites.
1.3.4 Parallel Plate Rheology

Parallel plate rheology tells about the deformation of flow for viscoelastic polymer composites at elevated temperatures above their T_g. This is essential for the processability for the polymers. Figure 1.17 shows the melt rheology profile of the neat PCPU at different temperatures. The PCPU nanocomposites all showed that the viscosities of the polymer composites are temperature dependent as well as frequency dependent and that our material is in fact viscoelastic. This can be seen when the frequencies are lower the viscosity is proportional to the change in frequency but as the frequencies increase the viscosity is directly proportional to the frequency. Additionally, an increase in the temperature allowed for a decrease in the viscosity. Hence, the polymer demonstrates pseudo plastic behavior by the decrease in viscosity with increase in frequency and shear thinning occurs. Erdmann et al [63] also experienced lower viscosities and modulus as the temperature is increased which is typical thermoplastic behavior. The intersection point between the G’ and G” shifts to a higher frequency with increasing temperature because of mobility and flexibility of the PCPU chains so that disentanglement is easier [63].

Figures 1.18-1.20 show the complex viscosities vs shear rate for the neat PCPU vs PCPU/silver, silica and CB nanocomposites. The silver nanocomposites’ complex viscosity decreased with increasing silver nanoparticle concentration, but this is expected as stated by Ghosh and Maiti that at high shear rates, the viscous stresses predominate over the silver particle-particle interactions, leading to particle alignment and, therefore, lower melt viscosity [64-66]. The silica PCPU nanocomposites showed an initial decrease in the viscosity but the 1%w/w PCPU/silica showed a higher complex viscosity at low shear rates, but it decreased as the shear rate increased. What is also noted is that all the composites joined at the higher shear rate at a viscosity of 630 Pa which is not evident in the other nanocomposites. The carbon black
nanocomposites showed very little variation in complex viscosity compared to the neat PCPU but as the % w/w increased the viscosity decreased.

The log of complex viscosities (n), of the nanocomposites was plot against the inverse temperature; the result was a straight line which represents Arrhenius behavior. The Arrhenius expression for viscosity

\[ n = A e^{\Delta \text{Ea} / RT} \]  \hspace{1cm} (1.7)

Where n is the complex melt viscosity, A is the Arrhenius constant, \( \Delta \text{Ea} \) is the activation energy of viscous flow and R is the universal gas constant. The slope of the line generated from the plot can be used to calculate the activation energy of viscous flow. The \( \Delta \text{Ea} \) of viscous flow for neat PCPU came to be 70.1kJ/mol. With the addition of the Ag nanoparticles the \( \Delta \text{Ea} \) decreased but as the %w/w increased the Activation energy remained unchanged giving the aspect that the activation energy is independent of the silver content. The silica’s activation energy was close to that of the neat polymer which suggests homogeneity of the composite. Contrastingly the \( \Delta \text{Ea} \) for the carbon black PCPU composites almost doubled at higher %w/w of carbon black nanoparticles. This suggests that the carbon black nanocomposites are less temperature sensitive as the nanoparticles have the packing ability, so it provides less change in free volume space as the temperature changes as experienced by Ghosh and Plochcki [66-67].
Figure 1.17 Complex viscosity ($\eta$), Storage Modulus ($G'$) and Loss Modulus ($G''$) vs angular frequency ($\omega$) at 100, 120, 150 & 175°C.
Figure 1.18 Complex viscosity vs shear rate for neat PCPU and PCPU/Ag nanocomposites at 150°C.
Figure 1.19 Complex viscosity vs shear rate for neat PCPU and PCPU/ SiO2 nanocomposites at 150°C.
Figure 1.20 Complex viscosity vs shear rate for neat PCPU and PCPU/CB nanocomposites at 150°C.

Figure 1.21 Melt Rheology Data: Arrhenius plot of melt viscosity for neat PCPU.
Table 1.2 Activation energies of viscous flow for neat PCPU and PCPU nanocomposites.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>EA OF VISCIOUS FLOW (KJ/MOL)</th>
<th>EA OF VISCIOUS FLOW (KCAL/MOL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEAT PCPU</td>
<td>70.1</td>
<td>16.7</td>
</tr>
<tr>
<td>0.1WT% AG</td>
<td>62.5</td>
<td>14.9</td>
</tr>
<tr>
<td>0.25WT% AG</td>
<td>62.5</td>
<td>14.9</td>
</tr>
<tr>
<td>0.375WT% AG</td>
<td>63.7</td>
<td>15.2</td>
</tr>
<tr>
<td>0.5WT% AG</td>
<td>64.4</td>
<td>15.4</td>
</tr>
<tr>
<td>0.75WT% AG</td>
<td>62.2</td>
<td>14.9</td>
</tr>
<tr>
<td>1.0WT% AG</td>
<td>62.3</td>
<td>14.9</td>
</tr>
<tr>
<td>0.1WT% SIO2</td>
<td>69.8</td>
<td>16.7</td>
</tr>
<tr>
<td>0.25WT% SIO2</td>
<td>72.6</td>
<td>17.3</td>
</tr>
<tr>
<td>0.375WT% SIO2</td>
<td>70.2</td>
<td>16.8</td>
</tr>
<tr>
<td>0.5WT% SIO2</td>
<td>69.4</td>
<td>16.6</td>
</tr>
<tr>
<td>0.75WT% SIO2</td>
<td>55.8</td>
<td>13.3</td>
</tr>
<tr>
<td>1.0WT% SIO2</td>
<td>60.9</td>
<td>14.6</td>
</tr>
<tr>
<td>0.1WT% CB</td>
<td>69.8</td>
<td>16.7</td>
</tr>
<tr>
<td>0.25WT% CB</td>
<td>67</td>
<td>16</td>
</tr>
<tr>
<td>0.375WT% CB</td>
<td>63.8</td>
<td>16.4</td>
</tr>
<tr>
<td>0.5WT% CB</td>
<td>124.5</td>
<td>29.7</td>
</tr>
<tr>
<td>0.75WT% CB</td>
<td>110.8</td>
<td>26.4</td>
</tr>
<tr>
<td>1WT% CB</td>
<td>116.9</td>
<td>27.9</td>
</tr>
</tbody>
</table>
1.3.5 Tensile Testing

PCPU can be described as a viscoelastic material, which means they are positioned between viscous liquids and elastic solids as mentioned above. Melt rheology gives us an idea of the mechanical behavior of the polymer at elevated temperatures and frequencies. There are two laws associated with the elasticity and viscosity of materials. Hooke’s Law demonstrates that for an ideal linear elastic solid, the stress is directly proportional to the strain; and Newton’s law for an ideal viscous liquid which states that the stress should be proportional to the rate of change of the strain [66]. Tensile testing allows us to take into consideration the mechanical behavior at room temperature. An ideal linear elastic solid obeys Hooke’s law, i.e. stress is proportional to strain. An ideal viscous liquid obeys Newton’s law, i.e. stress is proportional to the rate of change of strain.

Tensile testing was conducted to evaluate mechanical properties of the resulting composites for the reasons discussed in the introduction. Stress-strain curves are given for the averages of 5 specimens of each sample: Neat vs Silica nanocomposites (figure 1.23), neat vs carbon black composites (figure 1.24), neat vs silver nanocomposites (figure 1.21). The results of the tensile test including averages and statistical data are summarized in table 2.3. The tensile curve of the neat PCPU is similar to that of other polyurethanes [67], consisting of three distinct regions of deformation. The first region is known as the elastic region where Young’s modulus is calculated and the resistance to deformation of the polymer is noted. Just after the curve or yield point, there is a plateau region associated with the plastic region where the amorphous soft segments of the polymer deform, and the last region is known as the strain hardening region associated with strain induced crystallinity and hard segment disassociation as demonstrated by the steep slope right before fracture [68].
**Figure 1.22** Tensile Data: Stress vs Strain curve neat PCPU and PCPU/Ag nanocomposites.

**Figure 1.23** Tensile Data: Stress vs Strain curve neat PCPU and PCPU/SiO2 nanocomposites.
Table 1.3 Tensile Data: Tensile test results for PCPU and PCPU/CB, PCPU/SiO2 & PCPU/Ag nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Youngs Modulus Mpa</th>
<th>Ultimate Tensile strength Mpa</th>
<th>Elongation%</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat pcpu</td>
<td>2.3 ± 0.1</td>
<td>10.2 ± 0.2</td>
<td>1071 ± 18</td>
</tr>
<tr>
<td>0.1 wt % cb</td>
<td>2.9 ± 0.03</td>
<td>12.1 ± 0.6</td>
<td>777 ± 11</td>
</tr>
<tr>
<td>0.25 wt% cb</td>
<td>2.8 ± 0.02</td>
<td>13.1 ± 0.2</td>
<td>783 ± 18</td>
</tr>
<tr>
<td>0.375 wt% cb</td>
<td>3.3 ± 0.02</td>
<td>10.2 ± 0.4</td>
<td>720 ± 14</td>
</tr>
<tr>
<td>0.5 wt% cb</td>
<td>3.3 ± 0.07</td>
<td>10.2 ± 0.8</td>
<td>708 ± 20</td>
</tr>
<tr>
<td>0.75 wt% cb</td>
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<td>737 ± 12</td>
</tr>
<tr>
<td>1 wt% cb</td>
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<td>12.4 ± 0.5</td>
<td>708 ± 15</td>
</tr>
<tr>
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<td>864 ± 13</td>
</tr>
<tr>
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<td>661 ± 23</td>
</tr>
<tr>
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<td>4.4 ± 0.1</td>
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<td>873 ± 15</td>
</tr>
<tr>
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<td>11.4 ± 0.1</td>
<td>847 ± 12</td>
</tr>
<tr>
<td>0.75 wt% SiO2</td>
<td>2.2 ± 0.1</td>
<td>12.2 ± 0.5</td>
<td>922 ± 25</td>
</tr>
</tbody>
</table>

Figure 1.24 Tensile Data: Stress Strain Curve neat PCPU and PCPU/ carbon black nanocomposites.
The tensile curves indicate that the addition of nanoparticles displays an increased mechanical behavior. This is confirmed by an increase in the elastic modulus and yield strength as well as, ultimate tensile strength but a slight reduction in the ductility as seen in the elongation %. The increase in mechanical properties is drastic in the silica composites such as the 0.25% w/w silica, where the Young’s modulus rose to 5.4 MPa from 2.3 MPa of the neat PCPU and the ultimate tensile strength moved from 10.1 to 19.1 MPa. The show of superior mechanical strength illustrates successful interfacial adhesion as well as good homogeneity and compatibility between the silica nanoparticles and the polymer matrix. What is also demonstrated in the silica composites is that there is an effected load amount needed. As the %w/w increased to 0.75 and 1.0% the tensile properties decreased which suggests that the interfacial adhesion is no longer effective leading to a mechanically inferior nanocomposite. The most surprising results come from the carbon black nanocomposites which showed less free volume space in the melt rheology results, which should have allowed for a stronger and tougher material. The nanocomposites showed only a small increase in tensile properties as well as ultimate tensile strength at room temperature which could mean that higher tensile strength may be seen at higher temperatures. On the other hand, the silver nanocomposites showed promising results as the tensile strength doubled from 2.3 MPa to 4.8MPa and 4.9 MPa for the majority of the silver nanocomposites. The

<table>
<thead>
<tr>
<th></th>
<th>1.0wt% SiO2</th>
<th>0.1wt% Ag</th>
<th>0.25wt% Ag</th>
<th>0.375wt% Ag</th>
<th>0.5wt% Ag</th>
<th>0.75wt% Ag</th>
<th>1.0wt% Ag</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.1 ± 0.2</td>
<td>12.4 ± 0.1</td>
<td>656 ± 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1wt% Ag</td>
<td>2.2 ± 0.1</td>
<td>12.3 ± 1.2</td>
<td>936.6 ± 24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25wt% Ag</td>
<td>4.8 ± 0.6</td>
<td>13 ± 0.4</td>
<td>874 ± 14</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.375wt% Ag</td>
<td>4.8 ± 0.2</td>
<td>14.9 ± 1.0</td>
<td>542 ± 26</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.5wt% Ag</td>
<td>3.0 ± 0.1</td>
<td>10.1 ± 0.7</td>
<td>602 ± 36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75wt% Ag</td>
<td>4.9 ± 0.5</td>
<td>15.3 ± 0.2</td>
<td>838 ± 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0wt% Ag</td>
<td>3.6 ± 0.1</td>
<td>9.2 ± 1.2</td>
<td>787 ± 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
tensile data showed good interfacial adhesion of the nanoparticles to the polymer matrix to create a mechanically enhanced polymer nanocomposite.

1.4 Conclusion

This study herein proves that enhancement of the thermal and mechanical properties of PCPU can be successfully done by the dispersion of spherical silica, silver and carbon black nanoparticles. The spherical nature of the nanoparticles showed ease of movement of the polymer matrix by the reduction of the glass transition temperature showing that these nanoparticles move in association with the polymer backbone. This allows for a higher thermal performance of PCPU. Additionally, hydrogen bonding played a key role in the properties of the PCPU nanocomposites as evidenced by the change in the contact angle and the change in the FTIR spectra. Characterization of the polymer nanocomposites via parallel plate rheology supports previously stated literature that the activation energy of viscous flow is independent of the addition of silver nanoparticles. The silica nanoparticles showed homogeneity of mixing and the carbon black nanoparticles showed that it can increase the activation energy by its packing ability to decrease free volume space. The rheology also showed no drastic changes in complex viscosity on the addition of the nanoparticles. The tensile properties of the ultrasoft polymer increased on the addition of the nanoparticles especially at the low concentrations where the Young’s modulus was double that of the neat PCPU.

The implications of the formation and characterization of the polymer nanocomposites suggests that polymeric materials for industrial use can be enhanced by the addition of nanoparticles to create superior polymers with high thermal and mechanical performance.
1.5 References

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Chapter 2

Fabrication of Polycarbonate Polyurethane Nanofibers and Nanomembranes

2.1 Introduction

In 1900 John Francis Cooley was the first to file a patent for electrospinning. But, the first presence of electrostatic attraction of a liquid, dates back to 1600 which was observed by William Gilbert. By 1745, Bose used the electrical potentials on the surface of droplets in order to develop aerosols. Christian Friedrich Schönbein was able to produce highly nitrated cellulose in 1846 and then in 1887 Charles Vernon Boys described the process in a paper on nano-fiber manufacture. After the filing of the first patent occurred published work on the behavior of fluid droplets began by John Zeleny in 1914 and since then patent and publications about electrospinning have increased each year [1].

Electrospinning is a well-established versatile technique that produces fibers with diameter sizes in the micro and nanometer range [3-4]. This methodology employs an electrostatic potential to create nanofibers from viscoelastic polymer solutions or polymer melts [5-7]. Electrospinning ensues when a polymer solution or melt emits a charged fluid jet in the presence of an electric field. When the electric field force reaches a certain threshold, the charged polymer overcomes the surface tension and the jet undergoes a series of vigorous stretching and splaying until it reaches a grounded target, thereby completing the circuit [5,9]. Material properties, such as viscosity, conductivity, molecular weight and surface tension, as well as
processing parameters, such as applied electric field, the distance between the tip and the collector feeding rate, air temperature and humidity, all influence spinnability and tuning properties of the fabricated products [10-11].

The electrospinning process has the ability to produce highly porous membranes with structural integrity. The nanofiber scaffolds possess extremely high surface to volume ratio, tunable porosity and malleability and can be produced in a wide variety of sizes and shapes [13]. Due to these advantages, nanofiber membranes are being used in various fields like bio-medical, pharmaceutical, nanotechnology-based industries, optical electronics, environmental engineering and the defense industry [2, 11]. Electrospun materials have been proven to be an excellent candidate for tissue engineering, drug delivery, vascular grafts, protective clothing systems, and
wound dressing as well as filtration systems for sub atomic particles [12-24].

Over the years a wide variety of polymer fibers including polyethylene (PE), polystyrene (PS), polylactides, polyurethanes, poly(vinylidene fluoride), and polyamides have been generated by electrospinning for various research findings [20,25]. Gazzano et. al., used semicrystalline polymers such as, polyacrylonitrile (PAN), Nylon 6,6 (NYL) and poly(ethylene oxide) (PEO) to investigate the structural and morphological properties of the fibers [26]. Song et al modified a polyurethane using polyhedral oligomeric silsesquioxane (POSS) to look at improved blood compatibility [27]. Most recently Li et. al, researched tensile properties in silica/polydimethysiloxane (PDMS) and polymethyl methacrylate(PMMA) fibrous mats [5]. These examples show the broad range in which such a simple technique can create different research outcomes.

The ability to electrospin our novel polycarbonate polyurethane to fabricate nanofibers and nanomembranes, has broadened its applications in the medical and industrial fields for sensor fabrications, drug delivery systems and scaffolds for tissue engineering where lightweight material with larger surface area is needed. Moreover, the addition of nanoparticles to the polymer can aid in improved catalytic activity and selectivity by silica nanoparticles [28-30], silver nanoparticles can decrease surface inflammation and promote zinc utilization in wound healing, [13] and carbon black nanoparticles added to a polymer matrix can create an electroactive polymer nanomembrane [31]. These factors are in addition to its enhanced thermal and mechanical properties already imposed on the PCPU material.

Our previous research [31-33] on the novel PCPU has shown that our polymer is ultrasoft with a shore A hardness of 70, has high tensile strength and shows partial self-healing, which can be enhanced with the addition of carbon nanotubes [31,33]. Now it is imperative to investigate
the effect of transforming the PCPU to fiber membranes to investigate whether the thermal and mechanical properties are affected as well as how the addition of the nanoparticles affects the overall properties of the polymer. In these studies, the utilization of thermal and mechanical testing were completed to compare the characteristics of electrospun polymers with the bulk PCPU and the electrospun neat PCPU with PCPU nanocomposite fibers. This research looks at the thermomechanical and structural properties of electrospun PCPU and PCPU nanocomposite nanofibers. Thermal properties were examined by differential scanning calorimetry (DSC). Structural analysis was performed by Wide Angle X-ray scattering (WAXS) and Small Angle X-ray scattering (SAXS), at room temperatures. Mechanical characterization was done by tensile testing and morphological studies on the fiber membranes were done using Scanning Electron Microscopy (SEM).

2.2 Experimental

2.2.1 Materials

The certified ACS grade reagent dimethylformamide (DMF) 99.9%, chloroform, tetrahydrofuran (THF) with 250 ppm BHT inhibitor 99.9% and Ethyl Acetate (EtOAc) was purchased from Sigma-Aldrich and used without further purification. The Polycarbonate polyurethane was synthesized as described earlier [32-34] and the bulk sample was produced by hot pressing in a carver press to create a film. PCPU was dissolved in the following solvent mixtures: ChCl3: EtOAc, 90:10, THF: EtOAC, 90:10 and Dimethylformamide-ethylacetate (DMF:EtOAc) solution in a 90:10 ratio. Polymer concentrations varied from 8-18% w/v. For the polymer nanocomposites, the 16%w/v solution was used as the control. 0.25%, 0.5%, 0.75% 1.0% w/w of silver, silica and carbon black nanoparticles were then added to the solution by ultrasonication for 2 hours to produce a composite polymer solution.
2.2.2 Electrospinning process

For the electrospinning process, each of the solutions was filled up in a 3ml syringe. A 20-gauge needle with a flat tip was used as a spinneret. A collection distance of 20cm was done and a fixed voltage of 20kV was applied at a feeding rate of 50μl/min.

2.2.3 Solution Viscosity Measurement

A Fungilab alpha series rotational viscometer equipped with a TR8 spindle was used to measure the viscosity of the polymer solutions. 10ml of each solution was placed in the cylindrical chamber and the spindle is immersed in the solution. The rotational speed was varied, and viscosity readings were recorded. All measurements were performed at 21°C.

2.2.4 Scanning Electron Microscopy (SEM).

Scanning Electron Microscopy (SEM) is typically used to study surface topology such as, the shapes and sizes of nanoparticles, the dispersion of nanoparticles within materials as well as phase boundaries in polymer blends [35]. Research in polymer nanocomposite fiber membranes has utilized SEM to investigate the shape and fiber diameter of electrospun polymers. In SEM there is an electron beam and a beam in a cathode ray tube which is simultaneously scanned across the surface of the sample. A signal is then produced by scattered electrons resulting in an image with a three-dimensional appearance [35].

A Hitachi S-800 SEM was used in my work which has a magnification power of 300,000 times the actual sample size. SEM gives us information about fiber diameter, bead formation, quality of the fibers or fiber membranes. The SEM is located in the Nanomaterials and Nanomanufacturing Research Center in the Department of Engineering at the University of South Florida.
2.2.5 Contact Angle Measurement

Uniform drops of the deionized water were deposited on the bulk PCPU and PCPU electrospun membrane surface and the contact angles were measured using KSV CAM-101 video-based optical contact angle measuring device equipped with a Hamilton syringe in an environmentally controlled chamber (KSV-1 TCU). All measurements were performed in air, at a temperature of 25°C. Five right angles and five left angle measurements were recorded for each sample.

2.2.6 Thermogravimetric Analysis (TGA)

A TA instruments Q500/50 TGA equipped with a standard furnace was used to detect the degradation temperature of the polymer and polymer composite membranes. A sample weight between 15-20mg was placed on a tared 100 ml platinum pan. Measurements were carried out under nitrogen atmosphere as the samples were heated to 600°C at a heating ramp rate of 10°C per minute.

2.2.7 Differential Scanning Calorimetry (DSC)

DSC analysis was performed using a TA instruments 2920 Differential Analysis Calorimeter to obtain glass transition temperature (Tg) and melt temperature (Tm) of the polymer and polymer membranes. The heat cool heat method was utilized a starting temperature of -70°C and then heated to 200°C at a ramp rate of 10°C/ minute to ensure all samples had their thermal history erased. The sample was then cooled down to -70°C, using a refrigerated accessory, with the similar ramp rate and then reheated to 200°C. The Tg values were taken from second heating run.
2.2.8 Wide Angle X-ray Scattering (WAXS)

WAXS powder X-ray diffraction was used to investigate the degree of crystallization of the PCPU polymer segments. In our earlier paper [32] the degree of crystallinity was measured for the bulk PCPU there was no visible crystal peak until the polymer was stressed for 12 hours and a peak at 12.8°. X-ray diffraction patterns were collected with a Bruker D8 Focus x-ray diffractometer. The data collection was recorded in the range of 5–80° with a step of 0.010° at 25°C. Pre-electrospun polymer film was cast from the solvent and measured. These scans were compared to scans on electrospun mats.

![XRD showing detection of ordered structure](image)

**Figure 2.2.** XRD showing detection of ordered structure in a. pre-stressed neat PCPU and b. stressed undeformed bulk PCPU [32].
2.2.9 Small Angle X-Ray Scattering (SAXS)

SAXS data was collected on a Rigaku with a MicroMax-002+ generator, a Cu anode tube and a 120mmDET detector and a wavelength of 1.45Å. The bulk PCPU film and the fiber membranes were tested.

2.2.10 Tensile Testing

Tensile strength characterization was done using Shimadzu AGS-J tensile tester equipped with a 50N load cell to measure displacement of samples. All tensile testing was done at a crosshead speed of 100mm/min at room temperature according to ASTM D638. Dog bone cut samples from compression molded and fiber membrane samples had thicknesses 0.15mm; triplicate samples were tested, and average was reported.

2.3. Results and Discussion

Preliminary electrospinning tests were run on the polymer solutions with varying solvents. The results here within are based on the polymer solutions using DMF: EtOAc in a 90:10 ratio. The CHCl₃:EtOAc as well as the THF:EtOAc combinations caused sputtering of the fibers during the electrospinning process.

2.3.1 Solution Viscosity

Solution viscosity is important in electrospinning of polymer solutions in order to create quality fibers. The solution viscosities at varying shear rates of the pre-spun polymers are shown in figure 2. As the concentration of the polymer increased the viscosity overall increases. For the 8%w/v solution at the lowest shear rate of 9 s⁻¹, the viscosity was 126mPa, and for the 18%w/v at the same shear rate, the viscosity was found to be more than 5 times the viscosity at 729 mPa.
Overall it shows that the viscosity of the polymer solution decreased with increasing shear rate. Even the 8% w/v solution had a small but consistent decrease from 126 mPa to 122 mPa with increasing shear rate. This demonstrates the pseudo plasticity of the PCPU in solution meaning a change in the shear rate changes its viscosity.

![Graph showing solution viscosities](image)

**Figure 2.3.** Solution Viscosities of 8% w/v, 10% w/v, 12% w/v, 14% w/v, 16% w/v & 18% w/v neat PCPU solution concentrations.

2.3.2 Scanning Electron Microscopy (SEM)

When fibers were spun with concentrations varying from 8% w/v to 18%, lower concentrations (8, 10 & 12 % w/v) exhibited beading and the materials were too frail to be tensile tested. This is partially attributed to low viscosities (<400 mPa). Samples spun from 14, 16, and 18% w/v for the DMF:EtOAc easily released from the collecting plate and were fully characterized and discussed below.

Figure 3A-C shows SEM images of 14, 16 and 18% w/v PCPU fibers. Figure 3D-F shows the PCPU fiber material as a film with different thickness. The 14% w/v material was lightweight and had a thickness of 0.09 mm, the 16% w/v had a thickness of 0.12 mm and 18% w/v material
felt tough has a thickness of 0.17mm. The SEM images show the material’s porosity and the randomness of the fibers. An increase in the concentration of the solution resulted in less beading and thinner fiber formation. For the 14% w/v, the SEM image showed some beading which may arise from the presence of solvent during fiber formation resulting in large flat fibers with higher fiber diameters in the 900-2.8\(\mu\)m range. When the concentration was increased to 16% w/v the fiber diameter range was between 900nm-1\(\mu\)m. At 18% w/v, the fiber diameter ranged from 600-950 nm, resulting in a tighter diameter range across fibers.

![SEM images a-c, 14, 16, 18 % w/v fiber membranes; d-f. Film-like membrane composites.](image)

*Figure 2.4. SEM images a.-c., 14, 16, 18 % w/v fiber membranes; d.-f. Film-like membrane composites.*

### 2.3.3 Contact Angle Measurement

A contact angle below 90° indicates the material is easily wetted by the test liquid. When water is used as the test liquid, the indication is that the material is hydrophilic. Contact angles greater than 90° indicate a resistance to wetting by the water and a hydrophobic surface. This is depicted in Figure 4.
Figure 2.5. Illustration of contact angle at $\theta>90^\circ$, $\theta<90^\circ$ and $\theta=90^\circ$ [2].

Pictoral and numeric measurements for contact angles are shown in figure 5. An increase in the contact angle occurred from the change of bulk PCPU film to PCPU fiber membrane. In addition, an increase in contact angle also occurred as the concentration of the polymer solution increased. The contact angles for 14% w/v, 16% w/v and 18% w/v are $103^\circ$, $105^\circ$ and $110^\circ$ respectively. The contact angle for the molded PCPU film was $102^\circ$. The slight increase in contact angle with % w/v of polymer in the electrospun samples may indicate trace amounts of solvent trapper in the fibers; However, TGA studies did not reveal significant weight changes. The use of electrospinning to create fiber membranes has allowed for interesting results for future investigations of PCPU tunable surface wettability of the polymer.
2.3.4 TGA (Thermogravimetric Analysis)

The thermal stability and residual solvent dryness of the PCPU fibers were evaluated by TGA measurements under nitrogen atmosphere. The thermograms of the molded and electrospun PCPU at different % w/v are shown in Figure 5. The corresponding temperature at 5% weight loss and the onset temperature are reported in Table 1. Moving from molded PCPU to the fiber membranes we see a decrease in the onset temperature as well as the temperature at 95% mass. This can be due to the porosity of the fibers and trapping of solvent.

Figure 2.6. Contact Angle Images and graph for the bulk PCPU film and 14, 16 & 18% w/v fiber membranes.
The TGA graph shows that the thermal stability is reduced due to remnant DMF:EtoAc solutions remaining on the fibers but as the concentration of polymer solution increases the thermal stability also increases. The trend shows that the 18% w/v closely mimics the shape of the neat PCPU mold and the 14% w/v and 16% w/v closely mirror each other. This suggests that the removal of solvent leads to a more thermally stable polymer fiber mat.

![TGA graph showing the degradation of PCPU film and PCPU fiber membranes.](image)

**Figure 2.7.** TGA graph showing the degradation of PCPU film and PCPU fiber membranes.

### 2.3.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry gives us an insight into the movement of the polymer backbone. Results are summarized in table 1. The Glass transition temperature tells us how the soft amorphous segments move and the melt temperature (Tm) gives us an idea of when the hard segments melt. The glass transition temperature for the 14, 16 & 18% w/v polyurethane fibers as well as the molded PCPU remained at -22.9°C. This lets us know that the soft segment
interactions have not changed during the electrospinning process. Wong et al mentioned that Tg values of fiber membranes do not show a significant difference due to intermolecular coupling of the polymer chains. DSC indicates that there is not an appreciable amount of solvent in the fibers. The melt temperature, Tm, for the neat PCPU was at 70.5°C, the 14% w/v increased to 78.9°C, 16% to 74.4 and 18% showed two melting temperatures at 78.4 and 145°C. The shift to a higher temperature means the presence of purer or more ordered crystals within the polymer matrix. The 18% w/v PCPU fiber showed a second melting which may be due to hard segment melting. There was also an increase in the enthalpy of melt from 1.3 in the neat PCPU to 1.6 in the PCPU fibers which can lend itself to a higher percent crystallinity not present in the bulk polymer mold.

Figure 2.8. DSC thermogram for the second heating cycle of neat PCPU, 14% w/v PCPU fiber, 16% w/v PCPU fiber & 18% w/v PCPU fiber.
Table 2.1: Glass transition temperature, melt temperature and TGA temperatures of molded and electrospun PCPU fibers.

<table>
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<th>Sample name</th>
<th>First Tg (°C)</th>
<th>Second Tg (°C)</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>TGA onset (°C)</th>
<th>Temp at 99% mass (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat PCPU</td>
<td>-24.8</td>
<td>-22.9</td>
<td>70.5</td>
<td>1.3</td>
<td>292</td>
<td>297</td>
</tr>
<tr>
<td>14% w/v Neat TPU fiber</td>
<td>-25.9</td>
<td>-22.9</td>
<td>78.9</td>
<td>2.7</td>
<td>279.0</td>
<td>287</td>
</tr>
<tr>
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<td>-25.3</td>
<td>-22.8</td>
<td>74.4</td>
<td>1.5</td>
<td>280.0</td>
<td>288</td>
</tr>
<tr>
<td>18% w/v Neat TPU fiber</td>
<td>-24.8</td>
<td>-21.9</td>
<td>76.4/145.6</td>
<td>1.6/0.8</td>
<td>284.0</td>
<td>293</td>
</tr>
</tbody>
</table>

2.3.6 Wide-angle X-ray scattering (WAXS)

The DSC runs indicate that the PCPU is not highly crystalline. Indeed, this polymer is ultrasoft and we expect and have known it to have limited crystallinity [33]. Wide-angle X-ray scattering was used to determine the effect of electrospinning on the crystallization of PCPU. Figure 8 Shows the WAXS intensity profile of the PCPU films cast from solution; Figure 9 is data on the electrospun fiber. These scans exhibit more order than that found earlier in melt processed samples [33]. In the solvent cast films, the scans showed a small peak associated with crystallization at around 12 ° on the 2 theta scale in the 14w/v % and the 16% w/v but it disappears in the 18% w/v PCPU film. This suggests that the DMF:EtOAc solvents influences crystallinity in the polymer chains and as the concentration was increased (reduce the amount of
solvent used) the ability to create the ordered segments is reduced. Sharper reflections were noted in the 40-50 ° regions. The electrospun polymers intensity profile shown in Figure 9, illustrates distinct crystal peaks for all the samples. This suggests that the solvent used as well as the electrospinning process allows for ordering of the crystal segments. Melt processed PCPU exhibits no peak which indicates mixing of the hard crystal lamellae and the soft amorphous regions. This is divergent to the concept that electrospinning reduces the crystallinity of the fibers [36]. Lee et al [37] reported that the crystalline structure in fibers can be developed in ductile polymers. Polymers that have low Tg values such as our novel PCPU (Tg~ -22.9°C) takes a longer time to crystallize [36]. Overall, the sharper reflections in electrospun samples indicate crystallization occurs during the electrospinning process when the polymer fibers are elongating and possibly after the fibers have dried and solidified.

**Figure 2.9.** XRD showing detection of ordered structure for the 14% w/v and 16% w/v solution cast film.
Figure 2.10. XRD showing detection of ordered structure of the 14%, 16% and 18% w/v fiber membranes.

2.3.7 Small-angle X-ray (SAXS)

Small angle x-ray data was recorded to understand structural features that are larger than unit cell dimensions. Specifically, Fig [10]. There exhibits a peak at 0.14 Å indicating an interlamellae spacing of 45 Å. This was reported in our earlier paper on melt processed polymer [33]. We expected more distinct peaks in the electrospun samples, however, amplitude of the 0.14 Å peaks decreased as the concentration of the polymer solution used in spinning increased. It appears as though alignment during the spinning process does not result thicker more well-developed lamellae. The 45 Å structure are less plentiful in spun samples as well.
3.8 Tensile Testing

Representative stress-strain curves are depicted in Fig. 2. Note that samples were run in triplicate. Tensile strength, elastic modulus and strain to break are average values. We see that the formation of electrospun PCPU fibers caused the modulus to initially decrease from 2.5 MPa for the bulk PCPU mold to 0.6 MPa in the 14% w/v neat fiber and 1.6 MPa in the 16% w/v neat fiber then it increased to a modulus of 3.3 MPa in the 18% w/v neat PCPU fiber. This shows that an increase in the concentration of the pre-spun polymer cast solution drastically increases the tensile strength of the polymer membrane. The elastic modulus data exhibits the same trend. The increase in Tm noted in spun samples points to better developed crystals which may enhance tensile moduli and strength. WAXS data did show sharper reflections in spun samples as well. Baji et al tells us that the formation of crystals in the polymer matrix lends itself to increase
tensile strength [36]. The authors proposed that the strength and elastic modulus of the fibers are influenced by the crystal lamellar and amorphous fractions of the chains within the polymer fibers. Additionally, they proposed that structural formation changes taking place in the fibers during electrospinning, specifically crystallinity and molecular orientation impart physical uniqueness to the material and play an important role in the deformation behavior of the fibers [36]. Strain to break values in spun samples are somewhat lower that of neat PCPU. Our future studies will focus on the effect of spinning variables on tensile properties.

**Figure 2.12.** a. Stress-Strain behavior, b. Elastic modulus, c. Tensile strength and d. Strain at break of bulk PCPU and PCPU fiber mats.
2.3.9 PCPU/ nanocomposite membranes

2.3.9.1 Solution Viscosity

The solution viscosity for the PCPU and PCPU nanocomposite solutions are given in figure 2.13. The solution viscosities generally increased as the % w/w of nanoparticles were added to the PCPU solutions. For example, the 5% w/v PCPU/silica solution increased to twice that of neat PCPU from 5 at shear rate to 13 mPa. The solutions also displayed pseudoplastic behavior as seen in the neat PCPU which suggests that the addition of the nanoparticles does not change the fluid like behavior of the polymer.

![Graph showing viscosity vs shear rate for different concentrations of nanoparticles in PCPU solutions.](image)

**Figure 2.13** Solution Viscosities of 0.5%w/w Ag, 0.5% w/w SiO2 & 0.5% w/w CB PCPU nanocomposite solutions at 16% w/v concentration.
2.3.9.2 SEM

The SEM images were done to evaluate the fiber diameters for the PCPU nanocomposite fibers. The 16wt% neat PCPU fiber diameter ranged from 900nm to 1μm. The nanocomposite fibers ranged from 469 nm- 855 nm for the carbon black nanoparticles, 277-541nm for the silver nanoparticles and 498nm-1.0μm for the Silica nanoparticles. Overall the nanofiber diameters were drastically reduced when the nanoparticles were introduced to the PCPU solution.

Figure 2.14. SEM images a.-c., 0.5%w/w Ag, 0.5% w/w SiO2 & 0.5% w/w CB PCPU w/v fiber membranes; d.-f. Film-like membrane composites.
2.3.9.3 TGA

The TGA graph for the PCPU and 0.5% w/w nanoparticle membranes are shown in figure 2.15. The graph illustrates that the degradation curve is shifted. The onset temperatures shown in Table 2.2 reveal that the nanoparticles are acting as reinforcements to the PCPU fibers which allow for a higher degradation temperature from 286°C for the neat PCPU fiber to 288°C for the PCPU/SiO$_2$ fiber. Even at 99% mass the composites membranes were at a higher temperature than the neat PCPU increasing from 173°C to as high as 261°C.

![TGA graph of neat PCPU (pink) and 0.5 wt% Ag (blue), 0.5 wt% SiO2 (green) and 0.5wt% CB /PCPU nanocomposite fiber membranes.](image)

**Figure 2.15** TGA graph of neat PCPU (pink) and 0.5 wt% Ag (blue), 0.5 wt% SiO2 (green) and 0.5wt% CB /PCPU nanocomposite fiber membranes.
Table 2.2 TGA data showing onset temperature, temperature at 99% and 50% mass for PCPU/0.5% w/w nanoparticle fiber membranes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Temperature-onset (°C)</th>
<th>Temperature at 99% mass (°C)</th>
<th>Temperature at 50% mass (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat PCPU</td>
<td>289.0</td>
<td>173.6</td>
<td>338.9</td>
</tr>
<tr>
<td>16% w/v neat PCPU fiber</td>
<td>286.0</td>
<td>237.6</td>
<td>329.5</td>
</tr>
<tr>
<td>0.5% w/w Ag fiber</td>
<td>286.5</td>
<td>234.5</td>
<td>332</td>
</tr>
<tr>
<td>0.5% w/w CB fiber</td>
<td>287.0</td>
<td>222.9</td>
<td>337.1</td>
</tr>
<tr>
<td>0.5% w/w SiO2 fiber</td>
<td>288.0</td>
<td>261.8</td>
<td>334.6</td>
</tr>
</tbody>
</table>

2.3.9.4 DSC

The DSC scans for the PCPU composite nanomembranes as shown in figures 2.16. The glass transition temperatures for the nanocomposite fibers have decreased which means that plasticization of the polymer matrix remains even though the polymer was electrospun. The silica nanofiber composite showed a downward trend for the Tg which was opposite to that of the silica molded composite detailed previously. This suggests that the electrospinning process may have broken up any possible aggregation that can occur for the silica composites. The melt temperature of the fibers varied 63°C and 78 °C so there was no apparent melt temperature illustrated. Here the expected crystallization peak is again absent from the thermogram which is similar to that of the neat PCPU fiber composite.
**Figure 2.16** DSC thermos gram of neat PCPU (red) vs 0.5% w/w silver (Blue) and 0.5% w/w carbon black (green) and 0.5% w/w silica (purple) PCPU fiber membranes.

**Table 2.3** DSC data showing glass transition temperature (Tg) and melt temperature (Tm) for PCPU/nanoparticle fiber membranes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Tg (°C)</th>
<th>Tm(°C)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat PCPU</td>
<td>-22.9</td>
<td>83.9</td>
<td>2.9</td>
</tr>
<tr>
<td>16% w/v neat PCPU fiber</td>
<td>-22.8</td>
<td>70.7</td>
<td>3.3</td>
</tr>
<tr>
<td>0.25% w/w Ag fiber</td>
<td>-25.0</td>
<td>73.1</td>
<td>1.1</td>
</tr>
<tr>
<td>0.5% w/w Ag fiber</td>
<td>-25.4</td>
<td>70.1</td>
<td>3.6</td>
</tr>
<tr>
<td>0.75% w/w Ag fiber</td>
<td>-25.3</td>
<td>61.6</td>
<td>0.6</td>
</tr>
<tr>
<td>1.0% w/w Ag fiber</td>
<td>-24.6</td>
<td>74.6</td>
<td>0.3</td>
</tr>
<tr>
<td>0.25% w/w CB fiber</td>
<td>-25.1</td>
<td>61.4</td>
<td>2.8</td>
</tr>
<tr>
<td>0.5% w/w CB fiber</td>
<td>-25.9</td>
<td>63.0</td>
<td>9.9</td>
</tr>
<tr>
<td>0.75 % w/w CB fiber</td>
<td>-22.9</td>
<td>77</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Table 2.3 continued

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 % w/w CB fiber</td>
<td>-25.7</td>
<td>75.0</td>
<td>3.0</td>
</tr>
<tr>
<td>0.25% w/w SiO2 fiber</td>
<td>-23.4</td>
<td>78.1</td>
<td>0.25</td>
</tr>
<tr>
<td>0.5% w/w SiO2 fiber</td>
<td>-25.0</td>
<td>64.5</td>
<td>9.4</td>
</tr>
<tr>
<td>0.75 % w/w SiO2 fiber</td>
<td>-25.1</td>
<td>65.3</td>
<td>0.3</td>
</tr>
<tr>
<td>1.0 % w/w SiO2 fiber</td>
<td>-25.4</td>
<td>77.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### 2.3.9.5 WAXS

The WAXS data for the PCPU nanocomposite membrane are shown in figures 2.17, 2.18 & 2.19. For the silver nanocomposites the indicative intensity peaks at 38.4°, 44.6°, and 64.6° represent the presence of silver nanoparticles. Because of limiting testing standards, the 77.5° peak is not shown. For the 0.25 & 0.5 %w/w, the crystalline nature of the polymer nanomembrane still exists but as we increase the % w/w the crystallinity disappears which means that there can be interactions of the silver nanoparticles interrupting the crystal lamellae. Another peculiar result came from the 1% w/w silver composite. It shows an extra peak which is known as an amorphous peak. This can be from the presence of moisture at the surface of the nanomembrane from the transportation of the fiber for testing. The amorphous nature of the silica nanocomposite became more prevalent at a lower weight percent. There was a small crystal peak present at 12.6° in the 0.25 % w/w nanomembrane but it was absent in the other % w/w nanomembrane samples. The WAXS scans for the PCPU/ carbon black composite nanomembranes showed a crystalline peak at 12.5° and 12.7° for the 0.25 %, 0.5% and 0.75 % w/w. For the 1% w/w carbon black composite fiber, the amorphous nature from the transport of the fibers gave amorphous peaks at 30.1°.
Figure 2.17 WAXS of 0.25% w/w (blue), 0.5% w/w (green), 0.75% w/w (purple) & 1.0% w/w (yellow) PCPU/Ag nanocomposite fiber membranes.
Figure 2.18 WAXS of 0.25% w/w (brown), 0.5% w/w (yellow), 0.75% w/w (green) & 1.0% w/w (blue) PCPU/ SiO2 nanocomposite fiber membranes.

Figure 2.19 WAXS of 0.25% w/w (green), 0.5% w/w (pink), 0.75% w/w (yellow) & 1.0% w/w (blue) PCPU/ CB nanocomposite fiber membranes.
2.3.9.6 Tensile Testing

The graphs in figures 2.20-2.22 show the stress strain curves for the 16% w/w neat PCPU and PCPU composite fibers. For the carbon black the tensile profile initially decreased compared to the neat PCPU tensile profile, but as the % w/w increased the tensile strength profile of the fiber increased. The modulus of the 1%w/w carbon black composite fiber had a modulus of 4.3MPa which is three times the modulus of the neat PCPU fiber 1.3MPa (Table 2.3). The silver nanocomposite fibers tensile profile decreased compared to neat PCPU for 0.25% to 0.75%w/w silver whereas the 1%w/w increased only slightly. The silica fiber samples also showed reduced mechanical strength on the addition of the nanoparticles. This suggests that adding the nanoparticles adversely affected the mechanical strength when the PCPU nanocomposite was electrospun.

Figure 2.20 Stress vs strain curves for CB nanocomposite fiber membranes.
Figure 2.21 Stress vs strain curves for Ag nanocomposite fiber membranes.
Figure 2.22 Stress vs strain curves for SiO2 nanocomposite fiber membranes.
Table 2.4 Tensile strength data on electrospun PCPU and PCPU nanocomposite fiber membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic Modulus (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 wt NEAT FIBER</td>
<td>1.3</td>
<td>1.5</td>
<td>297.9</td>
</tr>
<tr>
<td>0.25 %w/w CB</td>
<td>0.5</td>
<td>0.53</td>
<td>191</td>
</tr>
<tr>
<td>0.5 %w/w CB</td>
<td>0.77</td>
<td>1.03</td>
<td>252</td>
</tr>
<tr>
<td>0.75 %w/w CB</td>
<td>0.99</td>
<td>1.4</td>
<td>219</td>
</tr>
<tr>
<td>1 %w/w CB</td>
<td>4.3</td>
<td>4.5</td>
<td>258</td>
</tr>
<tr>
<td>0.25 %w/w Ag</td>
<td>0.43</td>
<td>0.49</td>
<td>190</td>
</tr>
<tr>
<td>0.5 %w/w Ag</td>
<td>0.5</td>
<td>0.62</td>
<td>211</td>
</tr>
<tr>
<td>0.75 %w/w Ag</td>
<td>0.88</td>
<td>0.92</td>
<td>139</td>
</tr>
<tr>
<td>1 %w/w Ag</td>
<td>1.5</td>
<td>1.94</td>
<td>199</td>
</tr>
<tr>
<td>0.25 %w/w SiO2</td>
<td>0.32</td>
<td>0.5</td>
<td>209</td>
</tr>
<tr>
<td>0.5 %w/w SiO2</td>
<td>0.6</td>
<td>0.6</td>
<td>181</td>
</tr>
<tr>
<td>0.75 %w/w SiO2</td>
<td>1.01</td>
<td>1.05</td>
<td>175</td>
</tr>
<tr>
<td>1 %w/w SiO2</td>
<td>1.31</td>
<td>1.35</td>
<td>119</td>
</tr>
</tbody>
</table>

2.4 Conclusion

An ultrasoft polycarbonate polyurethane was electrospun to create fiber membranes. The resulting material showed variations in its thermal, mechanical and molecular properties when the polymer solution concentration was varied. The 18% w/v polymer membrane showed the highest thermal stability with an onset of 284 °C compared to the 14 % w/v at 279 °C. One glass transition
temperature was found to be -22.9 °C and it did not change as we moved from the bulk polymer to the fiber membranes. The enthalpy of melt showed a slight increase to suggest crystal formation. WAXS data demonstrated the presence of clearer reflections in spun samples than those obtained in solution cast films and bulk polymer. SAXS did not show any variations in the interdomain spacing which remained at 0.45 Å. Singular fiber SAXS yield a better idea of the molecular orientation of the electrospun PCPU. The mechanical properties showed that the electrospun PCPU high Young’s modulus of 3.3 MPa as well as an ultimate tensile strength of 4 MPa compared to the bulk PCPU. The 16% w/v sample had the highest elongation at break of 280% which showed that its fiber membrane has the ability to stretch to almost four times its original length.

On the addition of the nanoparticles, the fiber diameter of the PCPU nanofibers decreased well within the nm range. However, the tensile properties were greatly affected. Only the 1% w/w carbon black composite fiber showed a dramatic increase in strength by having a young’s modulus of about 3 times that of neat PCPU fiber membrane. Contrastingly the thermal performance of the nanocomposite fibers was increased on the addition of the nanoparticles by an increase in the thermal stability of the composite fibers and the decrease in the glass transition temperature. These results give us a clearer impression of how processing conditions can be modified to tune the properties of the fibers.

2.5 References


36. A. Baji, Y. Mai, S. Wong, M. Abtahi, P. Chen (2010), Electrospinning of polymer nanofibers: Effects on oriented morphology, structures and tensile properties, Composites Science and Technology 70, 703–718

CHAPTER 3

Rheological and Electrical Characterization of Thermoplastic and Thermoset Polymer

Lithium electrolyte.

3.1 Introduction

When it comes to electronic devices and other electronic consumer goods, lithium ion batteries are the main system used to power them. This is because lithium ion batteries possess high energy density, a long lifespan and is flexible [1]. However, lithium ions have the propensity to form dendrites during charge-discharge routes which can lead to explosive hazards. Therefore, the idea of using lithium ions within polymers as an alternative was proposed. The demand for lithium ion batteries in numerous devices have increased, therefore, polymer electrolytes research has gained widespread notoriety due to their technological uses in solid state electrochemical devices, electrochromic devices, rechargeable lithium batteries, fuel cells, super capacitors, biosensors [2-7]. Moreover, solid polymer electrolytes (SPEs) are an advantage over liquid or gel electrolytes as the SPEs have the added mechanical property which would allow for better maintenance. These electrolytes are important for electronic materials for our everyday use. The earliest work on ions within a solid came from Armand et al [8] as well as Fenton et al [9] which prompted further study metal salts in polymers.

Polymers range from highly crystalline stiff polymers to blend polymers, however highly crystalline polymers are not well suited to become electrolytes as the highly crystalline nature would not allow for the lithium ions to flow within the polymer matrix. Therefore, a
A semicrystalline polymer with low crystallinity is better suited. Polyethylene oxide (PEO) is one of the most sought after polymer used as an electrolyte but PEO tends to crystallize at ambient temperatures which would hinder the migration and movement of the lithium resulting in a low conductive electrolyte [3,10-12]. Therefore, polymers need to have good thermal stability; its polymer backbone needs to be mobile at ambient temperatures and should not crystallize. Many studies have been executed to show modifications of PEO to develop an improved high conductive polymer electrolyte [6, 13-16]. These modifications came from linear polymers [17-19, 27] comb-branched copolymers [20-21], block copolymers [22-23], cross-linked network polymers [24] and polymer blends [25-26]. Parveen et al [3] used an amorphous polyurethane to incorporate into PEO to reduce the crystallinity of the polymer to create an electrolyte fiber.

PCPU has a characteristic two-phase morphology that shows mixing of its hard and soft segments. PCPU above is Tg makes for a mobile backbone that allows the ions to flow within the matrix. Polycarbonate polyurethane (PCPU) combined with lithium salt was analyzed for its ability to be a highly conductive electrolyte that does not easily degrade. PCPU has a Shore A hardness of 64, whereas not many polyurethanes can reach such soft grades and maintain processability. This is due to the PCPU’s composition of a hard segment, providing stability, and soft segment allowing the polymer to flow at high temperatures instead of degrading.

Polyimides are also good contenders for lithium applications. They are high-performance polymers that possess excellent thermal stability, outstanding mechanical properties, and low dielectric constants [28]. Moreover, highly aligned polyimide nanofiber membranes prepared by electrospinning, showed excellent mechanical and thermal properties [33-34]. Electrospun PI nanofiber membranes which have been intensively investigated resulted in high-performance and multifunctional composite fiber membranes [32-34]. Cho et al [29], Yang et al [30] and Wu et al
investigated and evaluated electrospun polyacrylonitrile (PAN) and poly(vinylidene fluoride) (PVF) nanofiber based nonwovens in LIBs and exhibited outstanding battery performances, such as large capacity, high-rate capability and long cycle life. PI has the ability to avoid short circuiting because it is thermally stable at temperatures above 500°C whereas conventional separators can only go as high as 150°C. PI nanofiber nanomembranes’ extraordinary thermal, mechanical and electrochemical properties demonstrate its capability to be used as an ideal separator for Lithium ion batteries to achieve high battery performance, such as large capacity, high-rate capability and long cycle life [28].

An ultrasoft thermally stable molded and fibrous polymer electrolyte with lithium salts was developed by direct addition of industrial grade Lithium phosphate (LiPF₆) to novel polycarbonate polyurethane (PCPU) via ultrasonication. LiPF₆ of varying concentration from 12w/w% - 16w/w% was investigated which covers the industrial amount (14 w/w%) used in electrolytes. The thermal and electrical properties of varying concentrations of PCPU/LiPF₆ molded and fibrous electrolytes were investigated using Dynamic Mechanical Analysis (DMA) and four point probe. DMA showed a high interaction between lithium salts and the polymer matrix which resulted in a decrease in glass transition temperature of more than ten degrees. Greater interaction of the PCPU and the lithium salts resulted in an increase in ionic conductivity.

Figure 3.1 Polyimide GPI 15.
at room temperature. The resulting polymer electrolyte is highly flexible, thermally stable and has biocompatible properties which can be useful as biosensors. Through incorporation of lithium salts, lithium hexafluorophosphate (LiPF₆), this composite could lead to an innovative, ultra-soft, conductive polymer electrolyte film.

Additionally, the research herein looks at variations of an unprocessable polyimide powder GPI 15, and transforms it into polyimide membranes. Very little literature shows the ability to electrospin a polyimide. Rather the studies show the electrospinning of the PI precursor which is a polyamine acid (PAA) and then imidization. Here this study illustrates the ability to electrospin polyimide powders. The membranes formed are then doped in two concentrations of lithium salt solutions to create polyimide lithium electrolytes. TGA was used to characterize the thermal ability of the polyimide fiber and morphological studies were done using SEM. The characterization methods done on the lithium polyimide fibers include, Fourier transform infrared spectroscopy (FTIR), and Four Point Probe.

3.2 Experimental

3.2.1 Polymer-Lithium composite synthesis

The solvents used (DMF and THF), to create the polymer lithium composite were dried using molecular sieves and sealed with parafilm until ready for use. Polycarbonate polyurethane/lithium composites were prepared by dispersing the lithium salt using a sonicator. 10g of the purified PCPU was dissolved in 100 ml dried THF (ACS reagent, 99.9% sigma Aldrich) and then the desired amount of Lithium hexafluorophosphate salt (12-16% w/w) was introduced to the solution and then mixed by ultrasonication (Fisher Scientific Sonic Dismembrator 550) at a mixing rate of 10 minutes with 3 second rest intervals for two hours to ensure homogeneity of composites. The composite was the solution cast and the resulting
material was dried overnight under vacuum. The material was then molded using a carver press and characterized using the following methods.

3.2.2 Electrospinning of Polyimide

For the electrospinning process, each of the solutions was filled up in a 3ml syringe. A 20 gauge needle with a flat tip was used as a spinneret. A collection distance of 20cm was done and a fixed voltage of 23kV was applied at a feeding rate of 50μl/min. The resulting nanomembrane was left to dry under vacuum.

3.2.3 Polyimide/Lithium nanomembrane electrolyte

The polymer electrolytes were prepared by soaking the PI fiber membranes in 14 and 16 w/v LiPF₆ solutions (DMF: THF) at room temperature for 12 hours in a glove box under nitrogen atmosphere. The resulting electrolyte was dried under vacuum for two days to ensure complete dryness.

3.2.4 Dynamic Mechanic Analysis (DMA)

In order to investigate the dynamic viscoelasticity of the PCPU/Lithium electrolyte composite, dynamic mechanical tests were carried out with a TA Instruments AR-2000 was used to explore changes in the glass transition, Tg, storage modulus, G', loss modulus, G” and tan δ. Temperature sweep tests and isothermal frequency sweep tests were performed at a strain within the materials linear viscoelastic region.

The temperature sweep tests were planned to explore the frequency dependent glass transition temperature Tg of the material. They were carried out from -120°C to 100°C, using a ramp rate of 5°C/min, and repeated at frequencies 0.2 to 10Hz. The isothermal frequency sweep tests were conducted in the range from 1 to 20 Hz and repeated at various temperatures ranging from -50 to 55°C, with an interval of 5°C. The stress responses to the strain excitations in these
isothermal frequency sweep measurements were recorded automatically, and $G', G''$ and $\tan \delta$ were calculated from these measurements.

### 3.2.5 Four-Point Probe conductivity

Four-point probe is a known instrument used to perform reliable measurements of electronic transport properties in semiconductors and electrical materials. Conventional four-point probes are millimeter sized devices with spring loaded electrodes of tungsten carbide [35-36]. The typical set up is shown in figure 3.2. Two of the probes are used to source the current from the AC/DC current source and the other two inner probes are used to measure voltage from the electrometer. The idea of using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the semiconductor material. This technique involves bringing four equally spaced probes into contact with the material of unknown resistance.

![Figure 3.2 Four Point probe set-up.](image)
The volume resistivity is calculated with this equation:

$$\rho = \frac{\pi}{ln2} \times \frac{V}{I} \times t \times s$$  \hspace{1cm} (3.1)

where: $\rho$ = volume resistivity (Ω-cm), $V$ = the measured voltage (volts), $I$ = the current applied (amperes), $t$ = the sample thickness (cm), $s$ = the probe spacing. Conductivity can then be calculated by taking the reciprocal of the resistivity.

Electrical examination of the PCPU/lithium composites were carried out using four point probes attached with Kiethley 6220/6514 electrometer. Thin film samples were run by applying 1.0mA and voltages were recorded from the electrometer over a 60 second period. To samples of thickness 0.1 cm, the surface of the PCPU/LiPF6 composite was cut and samples were run over a 24 hour period. The polyimide electrolytes were run over a 5 minute period.

### 3.2.6 Solution Rheology Measurement

A Fungilab alpha series rotational viscometer equipped with a TR8 spindle was used to measure the viscosity of the polyimide solutions. 10ml of each solution was placed in the cylindrical chamber and the spindle is immersed in the solution. The rotational speed was varied, and viscosity readings were recorded. All measurements were performed at 21°C.

### 3.2.7 Surface Enhanced Microscopy (SEM)

A Hitachi S-800 SEM was used which compromises of a magnification power of 300,000 times the actual sample size. SEM gives information about fiber diameter, bead formation, quality of the polyimide fiber membranes produced from electrospinning.
3.2.8 Fourier Transform Infrared Spectroscopy (FTIR)

Perkin Elmer spectrum two furnished with and Attenuated Total Reflection (ATR) accessory was utilized for this study. A scanning range of 400-4000cm\(^{-1}\) set at a resolution of 4cm\(^{-1}\) and 16 repetitions were done on the nanocomposites. The neat PI and PI/LiPF6 nanofiber composites were scanned.

3.2.9 Thermogravimetric Analysis (TGA)

A TA instruments Q500/50 TGA equipped with a standard furnace was used to detect the degradation temperature of the polymer membranes. A sample weight between 15-20mg was placed on a tared 100 ml platinum pan. Measurements were carried out under nitrogen atmosphere as the samples were heated to 800\({}^\circ\)C at a heating ramp rate of 10\({}^\circ\)C per minute.

3.3 Results and Discussion

3.3.1 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis can be used to quantify the viscoelastic properties of polymers. The loss modulus, G”, is a measure of the ability of a material to dispel mechanical energy by converting it into heat. This absorption of mechanical energy is often related to the movements of molecular segments within the polymer sample [37]. There were two types of DMA techniques employed, temperature sweep and isothermal frequency sweep. Temperature sweep DMA was used to determine the rheological behavior of the PCPU lithium nanocomposites as well as identify the glass transition temperature \(T_g\) which is associated with chain slippage and movement. \(T_g\) can be determined from the peak maximum of either the G’ or tan \(\delta\).
Figure 3.3, 3.4, 3.5 & 3.6 shows the temperature sweep test results for neat PCPU and PCPU composites at varying frequencies. The storage modulus of the composites displays changes in the rubbery plateau as well as the primary alpha shift. 12% w/w and 14 %w/w PCPU/LiPF6 maintain a longer rubbery plateau compared to the 16 %w/w and the neat PCPU. The 16 % w/w experiences an early melt at around 50°C which may be due to high lithium loading which may have affected the melting of the sample. Figure 3.7 gives us the loss modulus overlay for neat PCPU and PCPU lithium composites which display differences in the primary (α) and secondary (β) relaxations of the composites at low temperatures.

Figure 3.8 shows the tan δ results from the temperature sweep. It is evident that the peak tan δ, and therefore T_g, varies as the %w/w of the PCPU/LiPF6 changes, with higher % w/w causing a shift of T_g to lower temperatures. This is evidence of plasticization of the amorphous region of the PCPU matrix which would suggest that the lithium salts are interacting with the soft segments of the polyurethane as seen by [27]. Table 3.1 shows the G’’ values of T_g of the different composites. There is a shift of T_g of approximately a 10 degree difference between the neat PCPU and the 16%w/w PCPU/LiPF6 composite.
Figure 3.3 DMA Data: Temperature sweep at multiple frequencies of neat PCPU.
Figure 3.4 DMA Data: Temperature sweep at multiple frequencies of 12 wt% PCPU/LiPF6 composite.
Figure 3.5 DMA Data: Temperature sweep at multiple frequencies of 14wt% PCPU/LiPF6 composite.
Figure 3.6 DMA Data: Temperature sweep at multiple frequencies of 16 wt% PCPU/LiPF6 composite.
Figure 3.7 DMA Data: Loss modulus plot of neat PCPU and PCPU/LiPF6 composites.

Figure 3.8 DMA Data: tan delta plot of neat PCPU and PCPU/LiPF6 composites.
3.3.2 Secondary-relaxation

The secondary relaxation or $\beta$-relaxation of neat PCPU and PCPU lithium composites, as measured by the loss modulus $G''$ Figure 3.7, occurs between temperature range -120 to -80 ºC. It follows Arrhenius behavior which is characteristic of secondary relaxations in polymers. Therefore, the activation energy can be obtained using the Arrhenius type relationship between the experimental frequency and the temperature range in Kelvin.

$$\ln f = \ln f_o - \frac{\Delta E_a}{RT}$$  \hspace{1cm} 3.2

The resulting linear relationship gives us a slope that is used to find the activation energies (Table 3.2). This activation energy is the amount of energy needed for the pendant methyl group to rotate. The neat PCPU was found to have an activation energy of 34.4kJ/mol which almost doubled to 63.7 kJ/mol for 12%w/w PCPU/LiPF6, 64.0 kJ/mol for the 14%w/w PCPU/LiPF6 and

<table>
<thead>
<tr>
<th>Sample</th>
<th>DMA Tg G’’ (ºC)</th>
<th>Tan $\delta$ height</th>
<th>Tan $\delta$ width (ÂºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU</td>
<td>-19.4</td>
<td>0.381</td>
<td>55.9</td>
</tr>
<tr>
<td>12%w/w LiPF6/PCPU</td>
<td>-23.6</td>
<td>0.429</td>
<td>44.8</td>
</tr>
<tr>
<td>14%w/w LiPF6/PCPU</td>
<td>-28.8</td>
<td>0.447</td>
<td>44.9</td>
</tr>
<tr>
<td>16%w/w LiPF6/PCPU</td>
<td>-29.7</td>
<td>0.456</td>
<td>50.7</td>
</tr>
</tbody>
</table>

Table 3.1 DMA Data: DMA Tg and tan $\delta$ for the PCPU and PCPU/LiPF6 composites.
65.3 kJ/mol in the 16%w/w PCPU/LiPF6 composite. This demonstrates that the lithium salts within the backbone creates a higher need for energy in order for the side groups to rotate.

Table 3.2. DMA data: Activation Energy of the β-transition for neat PCPU and PCPU lithium composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ea (kCal/mol)</th>
<th>Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU</td>
<td>8.2</td>
<td>34.4</td>
</tr>
<tr>
<td>12%w/w PCPU/LiPF6</td>
<td>15.2</td>
<td>63.7</td>
</tr>
<tr>
<td>14%w/w PCPU/LiPF6</td>
<td>15.3</td>
<td>64.0</td>
</tr>
<tr>
<td>16%w/w PCPU/LiPF6</td>
<td>15.6</td>
<td>65.3</td>
</tr>
</tbody>
</table>

3.3.3 Primary-relaxation

For PCPU and its lithium composites, the alpha transition involves micro Brownian motion in the main chain and conformational changes in the phenyl groups [38-39, 41]. The α relaxation is apparent in tan δ vs temperature plots. The maxima in tan δ for Tg occur from -14.9 to -5.05 °C for neat PCPU, -10.8 to -9.1°C for 12% w/w PCPU/LiPF6, -4.1 to -20.3 °C for 14% w/w PCPU/LiPF6 and from -20.7 to -20.1 °C for 16% w/w PCPU/LiPF6 (Figure 3.7A-D). The plots of log frequency vs inverse temperature unveiled a curved behavior predicted by the William-Landel-Ferry (WLF) equation (3.3) [40-42].

\[
\log a_T = \frac{-C_1(T-T_0)}{C_2(T-T_0)^2}
\]

Where the \(a_T\) is the shift factor that corresponds to frequency, and \(C_1\) and \(C_2\) are WLF constants. These constants can be determined using the second DMA technique which is the isothermal frequency sweeps.
Figure 3.10a, shows the isothermal frequency sweep results for $G'$ for temperatures between -50 to 55 °C. The graph demonstrates that at higher temperatures above the Tg from 0°C to 55°C, there is a frequency dependence occurring which means that there is less time for relaxation to occur but at lower temperatures a change in frequency does not change the storage modulus. Figure 3.10b shows the master curve fit after the TTS is imposed. From this the WLF graph is plotted (Figures 3.11-3.14), and the values of C1 and C2 were found to be 33.1, 217.7K, for neat PCPU. The WLF equation describes the effect of temperature on the shift factor for many
polymers near their T\textsubscript{g}. By putting the C1 and C2 values into equation 3.3 we would get the following Arrhenius relationship;

$$\Delta E_a = (-2.303) \left( \frac{C_1}{C_2} \right) RT^2$$ \hspace{1cm} (3.4)

Where, Ea is the activation energy, predicted by the temperature sweep experiments at the glass transition region. The Activation energy from the WLF showed a much higher Ea because there is a greater amount of energy needed for the polymer chains to begin moving in association with each other.

\textbf{Figure 3.10a.} Isothermal frequency sweeps for neat PCPU and 3.10b. the master curve.
Figure 3.11 DMA data: WLF plot of neat PCPU.

Figure 3.12 DMA data: WLF plot for 12% w/w LiPF₆/PCPU.
Figure 3.13 DMA data: WLF plot for 14% w/w LiPF$_6$/PCPU.
3.3.4 Conductivity

Resistivity and conductivity are fundamental properties for semiconductors and are critical parameters in materials research [43]. The four-point probe measurements on the PCPU/lithium composite electrolyte were done and the conductivity was measured. Figure 3.15 shows the conductivity for the 12%, 14% and 16% w/w PCPU/LiPF6 vs time. The neat sample had a too low conductivity to display on the chart but it was recorded in table 3.3 as 2.4 e-10 S/cm. The graph shows that the conductivity of the lithium composites increases as the % w/w of the lithium was increased. In addition, the conductivity levels out overtime. This indicates that as the current is initially passed through the polymer material there is a surge of lithium activity which then levels off after a minute to give us the final constant voltage reading.

Figure 3.14 DMA data: WLF plot for 16% w/w LiPF6/PCPU.
The conductivity was also taken of a circular mold with a thickness of 0.1cm which allowed us to cut away the surface to see if there is any change in the conductive reading over time Figures 3.16-3.18 displays the conductivity measurement over a period of 24 hours from the pristine surface to the surface being cut away and what was the conductivity after 24 hrs. What was observed is that when the surface is cut away the conductivity of the lithium composites increased. This is due to the hydrogen bonding that is known to be exposed when the surface of PCPU is cut away and this allowed for the availability of the lithium to become more accessible which lead to the surge in the conductivity from 4.0 e-3 to 1.5e-2 S/cm in the 12%w/w, 2.0e-3 to 1.7 e-2 in the 14 % w/w and 5.0e-3 to 2.8 e-2 in the 16 %w/w. After 1 hour the conductivity reduces drastically for the 12 and 14 %w/w down to 1.5 e-3 and 2.9 e-3 S/cm but there was a small reduction to 2.3e-2 for the 16 w.t.% Hence, it appears that the high lithium loading in the 16% w/w allows for the slowing of the H-bonds within the polymer matrix which permitted the conductivity of the mold to remain high. After the 24 hour period the lithium composites conductivity was closer to its starting conductive material.
Figure 3.15 Conductivity data: Conductivity of PCPU/LiPF6 thin film composites.

Figure 3.16 Conductivity vs time for 12 wt% PCPU/LiPF₆ composite for cut and uncut surface.
Figure 3.17 Conductivity vs time for 14% w/w PCPU/LiPF$_6$ composite for cut and uncut surface.

Figure 3.18 Conductivity vs time for 16wt% PCPU/LiPF$_6$ composite for cut and uncut surface.
### Table 3.3 Conductivity data: Conductivities for uncut and cut surfaces of PCPU and PCPU/LiPF6 nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity σ (S/cm)</th>
<th>Uncut</th>
<th>Cut</th>
<th>After 1 hr</th>
<th>After 24 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat PCPU</td>
<td></td>
<td>2.4 E-10</td>
<td>2.3 E-10</td>
<td>2.30E-10</td>
<td>2.30E-10</td>
</tr>
<tr>
<td>12wt% PCPU/LiPF6</td>
<td></td>
<td>9.1 E-4</td>
<td>2.60E-03</td>
<td>1.5 E-3</td>
<td>9.90E-04</td>
</tr>
<tr>
<td>14wt% PCPU/LiPF6</td>
<td></td>
<td>1.4 E-3</td>
<td>4.40E-03</td>
<td>2.9 E-3</td>
<td>1.40E-03</td>
</tr>
<tr>
<td>16wt% PCPU/ LiPF6</td>
<td></td>
<td>1.70E-03</td>
<td>3.2 E-3</td>
<td>3.2 E-3</td>
<td>2.0 E-3</td>
</tr>
</tbody>
</table>

### 3.3.5 Polyimide nanomembrane electrolyte

#### 3.3.5.1 Solution Rheology

Figure 3.19 shows the solution viscosity as a function of shear rate for the 20% w/v polyimides before electrospinning. Viscosity vs shear rate graphs tells us the different the behavior of fluids. For a dilitant fluid there would be shear thickening with increasing shear stress meaning that the viscosity would be increasing. For a pseudo plastic fluid there would be gradual decrease in viscosity with changing stress through shear thinning and for a newtonian fluid, the viscosity would be independent of the changing shear rate. The polyimide solutions demonstrates pseudoplastic behavior as the shear rates goes from 9s-1 to 170s-1 the viscosity of the polymer solutions decrease from 97mPa (XP02691) to 12 mPa (P347). Another aspect realised by the graph identifies an increase in Mw allows for a higher viscosity of the solutions from 25 mPa (R127), whose Mw is ~68,000, to 37 mPa ( P347) whose Mw is ~78,000 and to 80 mPa (XP02691) whose Mw ia 79,500. The polyimide solutions are low in viscosities which was also evident by Liu et al [45] but they also exhibited pseudo plastic fluid behavior which suggest that the orientation of the polymer chains influences the behavior of the fluid.
The polyimide nanofibers were successfully electrospun and the SEM images are shown in figure 3.20. The P347 PI showed fibers with diameters ranging from 155 to 650 nm and it was easily plied from the foil collector. The R127 had fiber sizes of 341 nm but the membrane itself could not be taken off of the foil to be used in the doping step. The XP0291 contained fiber diameter sizes ranging from 297 to 800 nm but the pore sizes were too large for testing for battery separator purposes. Hence polyimide P347 was used as the material to be characterized as well as to be doped in lithium salt solution to form an electrolyte.

**Figure 3.19** Viscosity vs shear rate for pre-spun polyimide solutions.

### 3.3.5.2 Scanning Electron Microscopy (SEM)

The polyimide nanofibers were successfully electrospun and the SEM images are shown in figure 3.20. The P347 PI showed fibers with diameters ranging from 155 to 650 nm and it was easily plied from the foil collector. The R127 had fiber sizes of 341 nm but the membrane itself could not be taken off of the foil to be used in the doping step. The XP0291 contained fiber diameter sizes ranging from 297 to 800 nm but the pore sizes were too large for testing for battery separator purposes. Hence polyimide P347 was used as the material to be characterized as well as to be doped in lithium salt solution to form an electrolyte.
Figure 3.20 A-C. SEM images of neat polyimide fibers P347, R127 & XP02691. D-F. Images of the resultant fiber membranes collected.

3.3.5.3 Thermogravimetric Analysis (TGA)

Figure 3.21 shows the thermal gravimetric curves for PI P347 at different 15 and 20wt%. The initial weight lost is likely due to packing of the fibers in the weight pan. The weight losses in the 100–200 °C range are likely due to solvent effects, as the boiling point of DMF occurs at 153°C which happened to Liu et al [44]. The onset temperature of decomposition for the 15wt% and 20wt% PI fiber ensued at 436°C and 475 °C respectively. Additionally, the PI fibers held 40% and 50% of their weight at the highest temperature run of 800°C. This demonstrates the thermal stability of the polymer at high temperatures under nitrogen atmosphere.
The FTIR spectra for the polyimide fiber and fiber membrane electrolytes are shown in figure 3.22. The spectra show the typical layout for polyimides, the absence of the N-O and –OH peak [28]. The spectra appear very similar for the three composites but there are peaks found in the PI/Li composite membranes. They are, 1658 cm⁻¹ which is indicative of lithium interaction between the C-N bonds of the PI, 1455 cm⁻¹, 1355 cm⁻¹, 1298, 1138 cm⁻¹, 511 cm⁻¹ in the fingerprint region all may be attributed to lithium salts added that is not in the neat polyimide fiber.

**Figure 3.21** TGA Data: Thermogravimetric curves of 15wt% and 20wt% PI fibers membranes.

### 3.3.5.4 Fourier-transform Infrared Spectroscopy (FTIR)

The FTIR spectra for the polyimide fiber and fiber membrane electrolytes are shown in figure 3.22. The spectra show the typical layout for polyimides, the absence of the N-O and –OH peak [28]. The spectra appear very similar for the three composites but there are peaks found in the PI/Li composite membranes. They are, 1658 cm⁻¹ which is indicative of lithium interaction between the C-N bonds of the PI, 1455 cm⁻¹, 1355 cm⁻¹, 1298, 1138 cm⁻¹, 511 cm⁻¹ in the fingerprint region all may be attributed to lithium salts added that is not in the neat polyimide fiber.
3.3.5.5 Conductivity of Polyimide fibers

The conductivity, \( \sigma \), at room temperature of the PI/LiPF6 nanomembranes, over a five-minute period, is shown in figure 3.23. It took five minutes of testing for the samples to level to a constant voltage. The conductivity of the polyimide fibers increased tremendously with increasing lithium hexafluorophosphate. The room temperature conductivity of the PI/LiPF6 fiber membranes with 14% w/w LiPF6 was \( 9.3 \times 10^{-3} \) S/cm after the five-minute period. Moreover, when the LiPF6 salt increased to a concentration of 16% w/w the conductivity improved to \( 1.3 \times 10^2 \) S/cm. This is indicative that the addition of the lithium salts creates a conductive polyimide fiber composite.
3.4 Conclusion

Lithium hexafluorophosphate salts were successfully incorporated into an ultrasoft PCPU as well as a polyimide nanofiber membrane. Thermal and rheological analysis of the PCPU/lithium composite electrolyte showed Arrhenius behavior in the beta transition and WLF behavior around the Tg. The Activation energies in the beta transition from PCPU/LiPF6 composites dramatically increased compared to the neat PCPU. The possibility exists that the structure and arrangement of the lithium salt may have attributed to the high activation energies.

The polyimide nanofiber was successfully transformed from an unusable polyimide powder to a nanomembrane for use as a lithium battery separator. The nanofiber did not possess the ability to be thermally characterized via DSC as there were no Tg present. However, TGA shows

Figure 3.23 Conductivity vs time graph of neat polyimide (red) and 14% w/w (green), 16% w/w (purple) PI/LiPF6 fiber membranes.
that the polyimide membrane is thermally stable in fiber form and conductivity measurements show that the addition of the lithium salts created a highly conductive membrane.

3.5 References


31. N. Wu, Q. Cao, X. Wang, S. Li, X. Li and H. Deng (2011), In situ ceramic fillers of electrospun thermoplastic polyurethane/poly(vinylidene fluoride) based gel polymer electrolytes for Li-ion batteries, J.Power Sources, 196, 9751-9756.


43. CAPRES Vancouver (2002) Micro Four-Point Probe Application note, CAPRES A/S.

APPENDIX A: CHAPTER 1

Complex Viscosity of PCPU/ Nano Ag at Different Temperatures
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.1wt%Ag.

\[ y = 7527.6x - 8.045 \]
\[ R^2 = 0.9996 \]
\[ Ea = 14.9 \text{ kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.25wt%Ag.

\[ y = 7518.3x - 8.1573 \]
\[ R^2 = 0.9981 \]
\[ Ea = 14.9 \text{ kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.375wt%Ag.

\[ y = 7665.6x - 8.1405 \]
\[ R^2 = 0.9946 \]
\[ Ea = 15.2 \text{ kCal/mol} \]
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.5wt%Ag.

\[ y = 7746.5x - 8.4454 \quad R^2 = 0.9974 \]

\[ Ea = 15.4 \text{kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.75wt%Ag.

\[ y = 7486x - 8.2354 \quad R^2 = 1 \]

\[ Ea = 14.9 \text{kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/1.0wt%Ag.

\[ y = 7489.7x - 8.409 \quad R^2 = 0.9998 \]

\[ Ea = 14.9 \text{kCal/mol} \]
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.1wt%SiO2.

\[ y = 8398.3x - 9.8813 \]
\[ R^2 = 0.9993 \]
\[ E_a = 16.7 \] kCal/mol

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.25wt%SiO2.

\[ y = 8735.4x - 10.789 \]
\[ R^2 = 0.9964 \]
\[ E_a = 17.3 \] kCal/mol

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.375wt%SiO2.

\[ y = 8442.9x - 10.468 \]
\[ R^2 = 0.9995 \]
\[ E_a = 16.8 \]
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.5wt%SiO2.

\[ y = 8351.7x - 10.303 \]
\[ R^2 = 1 \]
\[ E_a = 16.6 \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.75wt%SiO2.

\[ y = 6716.5x - 6.4602 \]
\[ R^2 = 0.9899 \]
\[ E_a = 13.3 \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/1.0wt%SiO2.

\[ y = 7327.7x - 7.376 \]
\[ R^2 = 0.9987 \]
\[ E_a = 14.6 \text{ kCal/mol} \]
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.1wt%cb.

\[ y = 8390.8x - 10.308 \]

\[ R^2 = 0.999 \]

\[ \text{Ea} = 16.7 \text{ kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.25wt%cb.

\[ y = 8056.2x - 9.0602 \]

\[ R^2 = 0.9976 \]

\[ \text{Ea} = 16.0 \text{ kCal/mol} \]
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.375wt%cb.

\[ y = 7677.3x - 8.253 \]
\[ R^2 = 0.996 \]
\[ Ea = 16.4 \text{ kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.5wt%cb.

\[ y = 14977x - 25.725 \]
\[ R^2 = 0.9949 \]
\[ Ea = 29.7 \text{ kCal/mol} \]
Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/0.75wt%cb.

\[ y = 13325x - 21.832 \]
\[ R^2 = 0.9922 \]
\[ E_a = 26.4 \text{ kCal/mol} \]

Melt Rheology Data: Arrhenius plot of melt viscosity for PCPU/1.0wt%cb.

\[ y = 14060x - 23.578 \]
\[ R^2 = 1 \]
\[ E_a = 27.9 \text{ kCal/mol} \]
APPENDIX B: Chapter 2

Figure B1. WAXS on nanosilver powder.

Figure B2. WAXS on nanosilica powder.
Figure B3. WAXS on carbon black nanoparticle powder.
ABOUT THE AUTHOR

Tamalia Julien received a B.S. Degree in Chemistry from Florida A&M University in 2011. She entered the Ph.D. Chemistry program at the University of South Florida in Fall 2011 and officially joined Dr. Julie Harmon’s polymer materials research lab in Spring 2012.

While in the Ph.D. program at the University of South Florida, Tamalia was awarded the Fred L & Helen M Tharp Endowed Scholarship Award (2015, 2017), the NOBCChE Advancing Science Travel Grant (2015, 2017) and placed first at the 15th Annual Raymond Castle Conference Poster Presentation.

Tamalia has co-authored three publications in various peer-reviewed scientific journals and has participated in nine conference presentations at several regional chemical meetings.