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PROCESSING AND CHARACTERIZATION OF MULTIFUNCTIONAL THERMOPLASTIC NANOCOMPOSITE FILMS

by

XIN WANG
B.S. Donghua University, China, 2012

A thesis submitted in partial fulfillment of the requirements
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Major Professor: Jihua Gou
ABSTRACT

Nanoparticles reinforced polymer composite films have been widely studied for their enhanced mechanical, electrical and thermal properties compared with host polymer matrix. However, most research was conducted on incorporation of nanoparticles in polymer films to improve single property and there is a lack of research on the multifunctional polymer nanocomposite films. In this work, a scalable and continuous spray deposition process was developed for the production of nanoparticles reinforced multifunctional thermoplastic nanocomposite films. This process is capable of making a thin sheet of thermoplastic nanocomposites with high nanoparticle loadings. The smallest thickness can be 40um.

The objective of this study is to design and optimize the thermoplastic nanocomposite films by utilizing nanoclay and helical carbon nanotube for multifunctional application: a) high electrical conductivity and thermal stability. Helical carbon nanotube paper based thermoplastic polyurethane nanocomposite films have been studied. The electrical conductivity and thermal stability of nanocomposite films increase a lot due to the incorporation of helical carbon nanotube paper with high electrical and thermal conductivity. The peculiar helical configuration of carbon nanotubes could greatly improve the interfacial bonding between carbon nanotubes and polymer matrix. b) High wear resistance and thermal stability. A nanoclay reinforced thermoplastic polyurethane nanocomposite coating was applied on the surface of leather. Due to the high hardness and thermal stability of nanoclay, the leather coated with nanocomposite film showed an improvement of wear resistance and thermal stability.
ACKNOWLEDGMENTS

I would first like to express my appreciation to my research director, Dr. Jan Gou, for giving me great opportunity to explore the world of nanocomposites. His technical guidance and continuous support provided an invaluable learning experience for me over the past two years. I have received many constructive suggestions from him. These suggestions give me a better understanding of composites and help me made the completion of this thesis.

I would like to thank my thesis committee members, Dr. Yunjun Xu and Dr. Suryanarayana Challapalli for their interest in my research and their time spend on evaluating my thesis. I would also like to thank Dr. Fei Liang and Dr. Jason Gibson for their help during the beginning of my work. They provide me a lot of foundational knowledge in my research fields.

My appreciation also extends to John Sparkman, our lab manager, for designing the experimental machine and helping me carry out the experiment. Special thanks also need to be given to material facility characterization center, for their help to do the characterization of samples. Furthermore, I am grateful for all of my colleagues’ contributions to my work. Thank you, Donovan Lui and Hongjiang Yang. Thanks to Jeffery Gambrell and Amy Callaghan for their initial design of the deposition machine.

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CHAPTER ONE: INTRODUCTION

1.1 Motivation

Composite materials consist of two or more materials and combine the properties of the constituent materials. Generally, the constituent materials have with significantly different mechanical, thermal or electrical properties. When they combine with each other, a composite material with characteristics better than individual component can be produced. Usually, the new composite materials are much stronger, lighter or less expensive when compared to individual material. There is a large field of research pertaining to thermoset composites. However, relatively little research has been conducted on thermoplastic composites. While thermoset composites have many beneficial properties such as good mechanical properties combined with good resistance to heat and excellent resistance to solvents and corrosion, they suffered from difficulty to process and recycle. Thermoplastic composites do not suffer from this problem. The major advantage of thermoplastic composites is their ability to reform. When heated they soften and can be reshaped without degradation. This is also allowed for the easy recycling of thermoplastic composites.

Traditionally, polymeric materials are reinforced with carbon or glass fibers to improve their mechanical properties and a variety of micro-size metallic particles for electrical and thermal properties enhancements. These composite materials have been widely used in many fields, such as automotive and aerospace industry. However, traditional fillers are not able to significantly improve a combination of these properties. As time progressed, nanocomposites began to attract tremendous attentions, because they could take advantage of combination of excellent properties of nanofillers. Polymer nanocomposites are a class of materials with the
The addition of small fractions of nano-sized particle to achieve a substantial improvement of various properties compared to polymer matrix. The extremely reduced filler size and largely increased interfacial area filler present to matrix could lead to a dramatic enhancement in mechanical, thermal and electrical properties of nanocomposite.

The processing of nanocomposites materials into films allows easy integration into various types of devices. The concept of thermoplastic nanocomposite films entails various applications such as coatings, free-standing films and laminates. The potential functions of these films are numerous, e.g. to protect, to be thermal or electrical conductive or to provide anti-reflection property. Therefore, we want to develop optimal processes for production of multifunctional thermoplastic nanocomposite films for various applications.

1.2 Research Methods

The methodology behind this research consists of the introduction of nanoparticles into thermoplastic resin matrix for the purpose of increasing its mechanical, thermal and electrical properties.

In this research, helical carbon nanotubes (HCNTs) were introduced into thermoplastic resin by spray deposition methods. A single layer HCNT paper was made first. The HCNT paper-manufacturing process involves two essential steps. The HCNTs are initially pre-mixed in water by sonication to get HCNT water suspension. With the aid of sonication, HCNTs can uniformly disperse throughout the suspension. Proper and completely dispersion of HCNT is vital to producing high quality HCNT paper. The sonicated suspension is then sprayed on a cellulose membrane filter to form a single layer of HCNT nanopaper. The paper can be manufactured thinner than 5um. After the fabrication of HCNT nanopaper, polymer resin was
sprayed on the HCNT paper. Processing is completed by resin solidifying in an oven. The smallest thickness of helical carbon nanopaper based thermoplastic nanocomposite films can be 40um.

Nanoclay thermoplastic nanocomposite coatings were fabricated by a continuous spray deposition machine. The prepared nanoclay/polymer solution was sprayed on leather substrates. The resulting thickness for coatings was around 15um.

This research study focuses on examining the manufacturing process and resulting performance of nanoparticles reinforced thermoplastic nanocomposites. The improved performance will be measured through multiple methods, such as thermogravimetric analysis, electrical resistivity measurement and taber abraser test. On the micro-scale, we will use scanning electron microscope imaging to evaluate the dispersion and interlocking of HCNT in the polymer matrix and transmission electron microscope imaging to evaluate the dispersion of nanoclay in polymer matrix.

It is believed that the mechanical, thermal and electrical performance is enhanced by the incorporation of nanoparticles into composites structure. Nanocomposite films developed for good properties require a balance of proper design of spray deposition machine and accurate processing parameters. Appropriate types and amounts of reinforcements and design of structure of nanocomposite films are also necessary to produce a successful product.

1.3 Structure of the Thesis

This thesis explores a novel topic that has no direct literature review or background on its subject. This thesis will first explain the theory and behavior of materials and processes in chapter 2. The films processing method and principle of nanoparticles enhancement are
introduced. Chapter 3 discusses processing method of helical carbon nanopaper based thermoplastic polyurethane nanocomposite films and characterization of their electrical and thermal properties. Chapter 4 discusses the fabrication of nanoclay thermoplastic polyurethane coating on leather substrate. Mechanical and thermal properties of nanoclay nanocomposites coating are analyzed. Finally, the thesis concludes with a summary of the findings and future work planned to expand the data available on these new nanocomposites, including the mechanical properties, thermal properties and optimization of the manufacturing process.
CHAPTER TWO: LITERATURE REVIEW

2.1 Carbon Nanopaper

Traditionally, researchers fabricated CNT composites by directly mixing CNT into polymer matrix. However, CNT have strong tendency to aggregate to form bundles because of their high aspect ratio and strong Van der Waals interaction among CNTs. It is very difficult to uniformly disperse CNTs into polymer matrix, especially for high loading of CNTs (>10wt%) in composites. To overcome dispersion problem, carbon nanopaper is fabricated for high concentration carbon nanotube reinforced composites.

Carbon nanopaper is a thin sheet made from the entangled and aggregated carbon nanotubes, which is also called as ‘buckypaper’. The generally accepted method of making CNT nanopaper is vacuum filtration method. In vacuum filtration method, CNT was usually dispersed in solution by ultrasonication. These suspensions can then be filtered through different membranes under pressure to yield uniform carbon nanopaper with entangled carbon nanotubes network [1]. Another novel method to make carbon nanopaper is frit compression method that without the aid of surfactant[2]. Using this method, the adverse side-effects from the surfactants can be avoided, but the thickness of carbon nanopaper are typically much larger than that of carbon nanopaper made through filtration method. Generally, the carbon nanopapers made frit compression method have thickness range from 120um to 650um. ‘Domino pushing’ method is also a simple and effective method to manipulate aligned CNT arrays into CNT paper, as shown in Fig.1[3]. This method can efficiently ensure that most of CNTs are well aligned tightly in the buckypaper.
Good dispersion and dense packing of carbon nanotube in polymer matrix can be realized by fabricating a carbon nanopaper first. Nanocomposites pre-planted with a thin layer of buckypaper showed significantly improvement on its fire resistance due to the efficient reflection of heat by the dense layer of carbon nanotubes[4]. The carbon nanopaper based polymer nanocomposites demonstrated unprecedentedly high electrical conductivity with high concentration of CNTs (~60wt%), which opens a door for developing polymeric composite conductors[5].

2.2 Processing of Nanocomposite Films

Nanocomposite film is a layer of material ranging from several micrometers to hundreds micrometers in thickness. The act of applying a film to a surface is film deposition process.
There are various methods to manufacture nanocomposite films. It is possible to classify film deposition techniques in two ways: physical process and chemical process. Physical methods include the deposition techniques which depend on physical evaporation or sputtering of materials from a source. Chemical processes comprise gas-phase and solution-phase deposition techniques. Solution phase deposition technique can also be classified as two categories: direct growth of films on the substrate during deposition or film formation requires additional processing, such as solvent evaporation or heating pyrolysis. Generally, polymer nanocomposite films are fabricated through solution phase deposition technique. Several solution deposition techniques are shown in Fig.2[6].

![Depiction of various solution deposition methods.](image)

2.2.1 Chemical Bath Deposition

Chemical bath deposition method only requires a vessel to contain solution and a substrate for film to grow on. The quality of films strongly depends on growth conditions, such as the temperature of solution, surface property of substrate, deposition time and precipitation
rate of reagent in solution. The major advantage of this method is its relatively cheap equipment and good reproducibility of product. The main drawback of this method is the wastage of solution and inefficiency to convert the precursor materials into useful deposits. Hodes[7] provided detailed information of the deposition mechanism of chemical bath deposition method. Precipitation and nucleation process is dominant for the growth of films.

2.2.2 Spin Coating

Spin coating is widely used for laboratory-scale film processing due to its high accuracy control on film thickness. Spin coating process can be described in four stages, which is shown in Fig.3[8].

![Figure 3 Four stages of spin coating process.](attachment:image)

Usually a small amount of coating material is applied on the center of the substrate, which is rotated at high speed to spread the coating material on whole substrate by radial centripetal acceleration force. The applied solvent is usually volatile and films are created after
the evaporation of solvent. The thickness of films depends on the rotation speed of substrate, viscosity of solution and property of solvent. Spin coating technique is able to produce films with uniform thickness and also it is a highly reproducible method. However, spin coating technique cannot produce samples with large size. Typical spin coating processes utilize only 2-5% of the materials deposited on the substrate[9], while the remaining 95-98% is wasted. Therefore, it is not a cost-effective technique and only suitable for small scale manufacturing.

2.2.3 Doctor Blade

In the doctor blading method, a sharp blade is placed at a fixed distance from the substrate surface. Usually the ink is dropped in front of blade. The blade is dragged across the substrate at a constant speed, and then a thin film can be uniformly deposited on the substrate. Fig.4 shows the schematic illustration of doctor blading technique[10]. The thickness of films is mainly controlled by the gap size between the blade and substrate surface. Doctor blade method can fully utilize the ink materials and can realize the large area manufacturing, but optimization of coating conditions is a big challenge for doctor blade method.

Figure 4 Schematic illustration of doctor blading technique.
2.2.4 Spray Deposition

Spray deposition is an attractive non-contact and scalable deposition method. Typically, spray deposition equipment consists of a precursor solution/solution, an atomizer, a nozzle and a substrate. The atomizers usually used in spray deposition technique are: pneumatic pressure (the liquid is atomized into droplet by air blasting)[11] and ultrasonic(ultrasonic frequencies produce the short wave)[12]. In general, the prepared solution is atomized pneumatically or ultrasonically to droplets and then sprayed onto the substrate. The droplets merge on the substrate into a full wet film before drying. The film morphology depends on the atomization air pressure, solution viscosity and evaporation rate of solvent. The thickness of films is controlled by flow rate of solution, droplet size and the distance between nozzle and substrate. Spray deposition has several processing advantages such as the simplicity of the apparatus, manufacturability, and low processing cost. It offers an extremely easy and scalable technique for preparing films of controllable thickness.

2.3 Multifunctional Polymer Nanocomposites

2.3.1 Helical Carbon Nanotube Enhancement to Polymer Nanocomposites

Based on molecular-dynamics simulation, helical carbon nanotubes were theoretically proposed to exist by Ihara et al[13] and Dunlap[14]. In 1994, Zhang et al.[15] first experimentally synthesized coiled carbon nanotube. Helical carbon nanotube is usually synthesized through chemical vapor deposition (CVD) method. This method involves the pyrolysis of hydrocarbon (e.g. methane, acetylene, benzene, propane, etc.) over transition metal catalyst (e.g. Fe, Co, Ni) at high temperatures (500-1000°C) to produce helical carbon
nanotube[16]. In the past 10 years, many researchers have performed detailed experiments to investigate the synthesis of HCNT. Nujiang Tang et al.[17] synthesized HCNT with ultra-high yield via a simple, low-temperature, and environmentally friendly catalytic chemical vapor deposition method using Fe nanoparticles as catalysts. However, synthesis of HCNT with high purity and high yield is still a tremendous challenge, which also hinders the study the properties of HCNT, as well as their potential application. Thus far, studies on the properties of HCNT and their application are very limited.

Volodin et al.[18] conducted the first AFM measurement of mechanical properties of coiled multi-walled nanotubes. The Young’s modulus of coiled carbon nanotubes is around 0.7TPa, comparable to that of straight carbon nanotubes. The Young’s modulus of individual straight carbon nanotube is in the 1TPa range. Chen et al.[19] reported a direct experimental measurement of the mechanical response of coiled carbon nanotube under tensile loading. AFM cantilevers were used for test and tension was loaded to single coiled carbon nanotube to a maximum relative elongation of ~42% (Fig.5). The results indicated the coiled carbon nanotube behaves like an elastic spring with a spring constant K of 0.12N/m in the low strain region. Due to this unique property, coiled carbon nanotube can act as resonating elements and nanosprings reinforcement in high-strain composites. Chiara Daraio[20] studied the dynamic response of a foamlike forest coiled carbon nanotube under high strain rate deformation using a simple drop-ball test. After the impact test, the coiled carbon nanotube showed full recovery of their structure and did not show any plastic deformation. The coiled carbon nanotube forest form a resilient system and could find applications as coating for protection purpose.
The mechanical properties of coiled carbon nanotube reinforced epoxy composites were investigated by Kin-tak Lau[21]. Vicker’s hardness measurement indicated that the hardness of coiled nanotubes reinforced nanocomposites is three times higher than the SWNT reinforced nanocomposites. The flexural strength of the coil/epoxy composites was higher than the SWNT/epoxy composites. Possible reason for the improvement is the better interaction between coiled carbon nanotube and polymer matrix. The observation of fracture surface morphologies also revealed the better interaction between coiled carbon nanotube and polymer matrix. Thermal properties of coiled carbon nanotube reinforced epoxy composites were also studied by Kin-Tak Lau[22]. The coiled nanotube/epoxy composites showed a poor endothermic ability from their differential scanning calorimetry(DSC) examination. Therefore, the incorporation of CCNTs in polymer composites may have potential to apply in the development of heat shielding polymer-based composites.

S.H.Park[23] revealed that the addition of coiled carbon nanotube to thermoplastic polymer matrices confers a two-fold increase of the relative electrical permittivity. A four-fold augmentation of the elastic modulus and a two-fold improvement in the ultimate tensile strength (compared to the base polymer) was also observed in their experiments. The coiled carbon
nanotube reinforced nanocomposites were superior to those fabricated through the use of straight (both single-walled and multi-walled) CNTs.

2.3.2 Nanoclay Enhancement to Polymer Nanocomposites

Among various kinds of nanoclays, the most abundantly explored nanoclay is Montmorillonite (MMT). Montmorillonite is a natural clay belonging to 2:1 phyllosilicates and its crystal structure is made of two layers of silica tetrahedral sharing some vertexes with an intercalated octahedral sheet of either aluminum or magnesium hydroxide. These silicates self-organize to form stacks with van der Waals force between the galleries[24]. The diameter of individual platelets of MMT varies from 150 to 250nm. The structure of MMT is shown in Fig.6[25]. The state of dispersion of nanoclay in polymer matrix can be classified into two categories: intercalated and exfoliate, as shown in Fig.7[25].

![Figure 6 Structure of the layered silicate clay montmorillonite](image-url)
Successful enhancement to polymer nanocomposites requires a complete exfoliation of clay platelets. Complete exfoliation is often very difficult because of the hydrophilic-hydrophobic repulsion between nanoclay and polymer matrix[26]. The high viscosity of polymer makes dispersion more difficult. To overcome dispersion problem, modification is used to render the nanoclay surface hydrophobic[27]. Modifications can also increase the gallery spacing of the nanoclay, so that nanoclay can become more compatible with polymer. A list of commercially available organic modified MMT and its counter ions is shown in Table 1[28].
Table 1 Common counter ions for organic modified clay

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Counter Ion</th>
<th>Modifier Concentration (meq/100g clay)</th>
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<tbody>
<tr>
<td>Cloisite 10A</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt; – N&lt;sup&gt;+&lt;/sup&gt; – CH&lt;sub&gt;2&lt;/sub&gt; – HT</td>
<td></td>
</tr>
<tr>
<td>Cloisite 15A</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt; – N&lt;sup&gt;+&lt;/sup&gt; – HT</td>
<td></td>
</tr>
<tr>
<td>Cloisite 20A</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt; – N&lt;sup&gt;+&lt;/sup&gt; – HT</td>
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<td>Cloisite 25A</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>95</td>
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<td>CH&lt;sub&gt;3&lt;/sub&gt; – N&lt;sup&gt;+&lt;/sup&gt; – CH&lt;sub&gt;2&lt;/sub&gt;CHCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>HT CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
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<tr>
<td>Cloisite 30B</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;3&lt;/sub&gt; – N&lt;sup&gt;+&lt;/sup&gt; – T</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td></td>
</tr>
</tbody>
</table>

Where HT is hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14), and T is Tallow (~65% C18; ~30% C16; ~5% C14)

A. Pattanayak[29] found that both clay-polymer reactions and shear stress mixing are responsible for clay exfoliation in polymer. Nanocomposites with good exfoliated nanoclay exhibited more than 100% increase in tensile strength and modulus with good optical clarity. Another interesting result was found by Dai’s group. Dai[30] used in situ polymerization method to synthesize polyurethane montmorillonite nanocomposites. Nanocomposites with 2wt% montmorillonite showed a markedly increase of tensile strength, Young’s modulus as well as a 1700% elongation at break. This is surprising because usually an increase of tensile strength
results in the decrease of elongation. The aspect ratio and orientation of nanoclay in nanocomposites can also affect the performance of nanocomposite. J.I.Weon[31] utilized shear process to alter the aspect ratio and orientation of nanoclay in nanocomposites. As clay aspect ratio and degree of orientation reduced, the modulus and strength decreased, whereas the fracture toughness and ductility increased.

Enhanced thermal stability is found for nanoclay/polymer composites. K.P.Pramoda[32] studies the thermal degradation behavior of nanoclay/polymer nanocomposites. The onset temperature is 12°C higher for PA6 with 2.5 wt% nanoclay loading, but for higher loading(5,7.5,10wt%), the onset degradation temperature remained unchanged. Morphological observation indicated that higher nanoclay loadings resulted in agglomeration so the thermal stability was not improved. Their study suggested that only exfoliated nanoclay/polymer nanocomposites can exhibit improved thermal stability. The thermal stability and degradation kinetics of polyurethane/MMT nanocomposites was reported by S.Pashaei[33]. Introduction of nanoclay into polyurethane matrix increase thermal stability and change the total heat of degradation. It suggested that the enhanced thermal stability was related to the increase of the effective activation energy of nanocomposites degradation. Enhanced flame retardancy is generally found for polymer/nanoclay composites. This is related with the char formation resulting from nanoclay platelets and the barrier effect of clay platelets to the diffusion of volatile products formed during thermal degradation[34].
CHAPTER THREE: MORPHOLOGY, THERMAL STABILITY AND ELECTRICAL PROPERTIES OF HELICAL CARBON NANOTUBE PAPER BASED THERMOPLASTIC NANOCOMPOSITE FILMS

3.1 Introduction

Carbon nanotubes are unique “one-dimensional systems” which can be envisioned as rolled sheets of graphene. The carbon nanotubes were first discovered by the Japanese researcher Sumio Iijima in 1991. From then, intensive research began to be conducted on the properties of this one-dimensional tubular molecule[35]. Theoretical and experimental studies have shown that CNTs exhibit extremely high tensile modulus(1TPa), strength(150GPa), high electrical conductivity(105~106S/m) and high thermal conductivity(6000-3000W/mK)[36]. Owing to their outstanding mechanical, thermal, and electrical properties, carbon nanotubes have played a significant role for the development of composites technology in both academic research and industry application. In the advanced composite society, substantial works have been conducted on straight carbon nanotubes. However, the uncertainty of interfacial bonding between the straight carbon nanotubes and polymer matrix may hinder the enhancement of properties of nanocomposites, i.e. the outermost layer of straight carbon nanotubes always pulls out from the matrix while all inner lays do not effectively take any load.

Recently, the development of helical carbon nanotube opens a new alternative to reinforce the traditional composite materials. Helical nanotubes are generally described by coil diameter and coil pitch, the distance between adjacent corresponding points along the axis of helix, as shown in Fig.8[16].
The helical structure of HCNT allow them to anchor themselves tightly into a polymer matrix and the better interaction of matrix can give a better improvement of the overall mechanical and electrical properties of the resulting composites. Also, helical carbon nanotube behaves like an elastic spring. By adding a small amount of helical carbon nanotube to a polymer matrix to form nanocomposites, the nanocomposites may be applied for cushioning and energy dissipation. As such, this intriguing helical structure is believed to have exceptional properties and possess great potential for applications on nanocomposites.

3.2 Experiment Method

3.2.1 Materials

Helical multi-walled carbon nanotubes (HCNT) as supplied by Cheaptubes were utilized for experimentation. The content of helical structure CNTs is about 80wt%. The rest is ordinary CNTs. The total CNTs content is more than 90wt%. Most of the HC NTs have 100~200nm outer diameter and 1~10um length. Fig.9 shows the morphology of HCNT.
Thermoplastic polyurethane utilized in this work was supplied by SMP Technologies Inc. in pellet form. DMF solvent can be used to dissolve pellets into solution. The pellets have a specific gravity of 1.25g/cm³.

### 3.2.2 Manufacturing of Helical Carbon Nanotube Paper Based Nanocomposite Films

#### 3.2.2.1 Helical Carbon Nanotubes Treatment

The main reason for purification was the removal of amorphous carbon and metallic catalyst impurities used to the growth of HCNT. Thus 1g HCNTs were refluxed in 200mL concentrated H₂SO₄(98%)/HNO₃(70%) mixture at the optimized temperature 50°C for 2h. The mixture was kept under a mechanical stirring rate of 180 rpm. The solution was then filtered through a PTFE membrane and rinsed with distilled water, until the pH of the filtrate was neutral. The sample was finally dried in an oven at 120°C for 2 hr. After drying, cleaned HCNTs were obtained.
3.2.2.2 Preparation of HCNTs Water Suspension

The purified carbon nanotube powder needed to be dispersed in water to form a suspension before making into paper. Generally, 1g HCNTs is used to make a 6x6 inch carbon nanopaper. The HCNTs is added to 1L water within a glass beaker. The surfactant was added to the solvent to help dispersion. 10 single drops of Triton X-100 were used for 1L water. This mixture was then sonicated using a high intensity sonicator (1375-watts sonicator from Qsonica. LLC.) for a prescribed amount of time under designated input power. 30 minutes of sonication was required for 1 gram of HCNT. It is important to control the input energy and sonication time carefully to achieve optimized dispersion quality. Since short sonication time and less energy cannot fully disperse HCNT in solvent, while too long sonication time and too much power may damage HCNT.

3.2.2.3 Preparation of Helical Carbon Nanotubes Paper

HCNT nanopaper was processed through spray deposition technique. Unlike many other deposition techniques, spray deposition technique represents a very simple and relatively cost-effective processing. It is a continuous process, which uses a slow moving belt. The process begins with HCNTs water suspension after sonication. A high accuracy controlled flow rate pump delivered the suspension to nozzle at the rate of 0.14L/min. An atomizing nozzle operated with cleaned compressed air at 50psi. The dispersion was atomized continuously into droplet and then sprayed onto cellulose membrane. The cellulose membrane sat on a moving belt with the speed of 9 in/min. The suspension flow rate, atomizing gas pressure and the moving speed of belt were optimized to ensure the stability of spray deposition process. Vacuum is used to pull the HCNT strongly onto the cellulose filter membrane. By controlling all related parameter, the
thickness of deposited HCNT nanopaper is in the range of 2-10μm. The as-deposited HCNT nanopaper was then heated in an oven at 120°C for 30min.

3.2.2.4 Preparation of Helical Carbon Nanotubes Paper Based Thermoplastic Nanocomposites

The thermoplastic polyurethane (TPU) was first dissolve in N,N-dimethyl formamide (DMF) at 50°C for 3 hrs and a 10wt% TPU solution was prepared. HCNT/TPU nanocomposite films were processed by spray deposition technique. A cleaned compressed air under 50 psi was injected to spray nozzle. The droplets were born in the nozzle and sprayed onto the previous fabricated HCNT nanopaper. Then HCNT/TPU thin film nanocomposites were heated in an oven at 60°C for 10min. During the spraying process, DMF solvent dissolved the cellulose membrane which supported HCNT nanopaper and evaporated during heating. TPU solidified when heated in the oven, thus HCNT/TPU nanocomposites films were received.

3.2.3 Characterization and Evaluation

3.2.3.1 Four Point Probe Resistivity Measurement

The electrical resistivity of composites was measure with a four point probe apparatus (Signatone Quadpro system), which consist of a combination of four probes in a straight line with a constant inter-probe spacing of 1.56mm. Fig.10 shows a schematic representation for electrical resistivity measurement.
3.2.3.2 Differential Scanning Calorimetry

Netzsch Sta 449C was used to measure the glass transition temperature and melting temperature of nanocomposite films. Each sample having weight around 10mg was scanned from 30 to 250°C at a scanning rate of 10°C/min under nitrogen purge.

3.2.3.3 Thermal Gravimetric Analysis

Thermo-gravimetric analysis (TGA) experiments were carried out using a TGA Q5000 analyzer. The characterization of the sample was conducted in nitrogen flow from 50 to 700°C at a heating rate of 10°C/min. The weight of the sample was about 10mg.
3.2.3.4 Scanning Electron Microscope

A scanning electron microscope (SEM) Zeiss-Ultra 55 takes images of a sample by scanning with high-energy beam of electrons in a raster scan pattern. Because the samples must be electrically conductive, nanocomposites are given a thin coating of platinum-gold.

3.3 Results and Discussions

3.3.1 Processing Parameter Effect

3.3.1.1 Thickness Control of Helical Carbon Nanopaper

Spray deposition process for fabrication HCNT nanopaper involves atomizing the suspension to fine droplets, which is then directly sprayed onto a cellulose filter set on the moving belt. Vacuum was used to pull water out and deposit HCNT on cellulose filter (Fig.11).

![Schematic illustration of HCNT nanopaper processsing](image)

Figure 11 Schematic illustration of HCNT nanopaper processsing
The thickness of HCNT nanopapaper is controlled by the composition of suspension, flow rate, speed of moving belt and the amount of waste go through vacuum. Typical thickness of HCNT nanopaper deposited on cellulose filter is around 2~10um. At constant flow rate 0.14L/min, the dependence of film thicknesses on the deposition time is shown in Table 2.

Table 2 Deposition time versus thickness for HCNT nanopaper

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Thickness (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Scanning electron microscopy was used to measure the thickness of films. The film thickness increases not linearly with deposition time. As time progresses, deposition rate turns to be slower due to the reduced permeability of HCNT nanopapaer, which results in difficulty for HCNT to further deposit.

3.3.1.2 Thickness Control of Helical Carbon Nanopaper Based Nanocomposite Films

After the fabrication of HCNT nanopaper, TPU solution was sprayed at a constant flow rate of 1.3ml/s on the HCNT nanopaper. HCNT nanopaper was set on the moving belt(Fig.12).
At the constant flow rate and fixed composition, the thickness of HCNT/TPU nanocomposite films is only controlled by moving speed of the belt. Thickness can be controlled by the following equation:

\[ t = \frac{V}{b \times v} \]

Where: \( V \) : volumetric flow rate of polyurethane resin

\( t \) : thickness of sample

\( v \) : belt moving speed

\( b \) : width of the spray system is 18cm

Scanning electron microscopy was used to measure the thickness of films. The smallest thickness of smooth and homogeneous film is 40um, as shown in Fig.13.
3.3.1.3 Temperature Effect on Morphology of Nanocomposite Films

Drying temperature is an important processing parameter for manufacturing HCNT/TPU nanocomposite films. Fig.14 shows different morphologies of deposited films at different drying temperature. At temperature below 50°C, DMF evaporates slowly so the films deposited are still rich in solvent. The liquid flowable DMF solvent breaks up the network of HCNT and subsequent results in the cracking of nanocomposites films. At high temperature(>70°C), DMF evaporates too fast, which results in the air bubble forming on the surface of nanocomposite films. High drying temperature also results in too fast solidifying of TPU resin and the air bubbles may get trapped in the solidified TPU resin. In this case, a temperature of 60°C results in films with good quality.
3.3.2 Differential Scanning Calorimetry Analysis

DSC is a standard method to measure the glass transition temperature and melting temperature of samples. Fig.15 plotted the DSC curve of HCNT/TPU nanocomposite films. Glass transition temperature is determined as 78°C. Moreover, DSC results indicated that HCNT/TPU nanocomposite films are semi-crystalline nanocomposites, which experience both glass transition and melting period in the heating ramp. The melting temperature was determined by the melting peak points as 188°C.
The thermal properties of TPU film and HCNT/TPU nanocomposites film were showed in Fig. 16.

The decomposition of TPU and TPU/HCNT film samples occurred in two steps. The decomposition occurred around 280-300°C may belong to the disruption of urethane groups, which is the hard segments of TPU. The urethane groups will dissociate to the original polyol and isocyanate, which then dissociate to primary amine, alkene and carbon dioxide. The weight loss around 400-500°C could be attributed to the decomposition of soft segment[37]. If the onset degradation temperature was taken as the criterion of thermal stability, TPU/HCNT nanocomposite films have better thermal stability(degrade at 304°C) than the pure TPU.
film (degrade at 274°C). The reason for improvement in thermal stability of HCNT/TPU nanocomposite films is the enhancement of thermal conductivity of nanocomposites. HCNT can facilitate heat transfer and thus heat will not accumulate around polymer matrix.

Figure 16 TGA curve of pure TPU film and HCNT/TPU nanocomposite film

3.3.4 Electrical Resistivity Measurement

Four Point Probe apparatus uses pairs of current-carrying and voltage sensing electrodes to measure electrical resistivity. By passing a current through two outer probes and measuring the voltage through the inner probes allows the measurement of sample resistivity.

The characteristic electrical resistivity was measured for HCNT/TPU nanocomposites film with the thickness of 30μm at room temperature. The electrical resistivity at different film locations was tested. Fig.17(a) shows a schematic illustration of different test locations. Electrical Resistivity was calculated by the followed equation[38]:

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\[ \rho = \frac{\pi \cdot t \cdot V}{\ln(2) \cdot I} \]

Where: 

- \( V \): voltage read from test machine 
- \( I \): current read from test machine 
- \( t \): thickness of sample 
- \( \rho \): electrical resistivity

The electrical resistivity of HCNT/TPU nanocomposite films in different locations was plotted in Fig.17(b). Nine locations were chosen to determine the electrical resistivity for tested HCNT/TPU nanocomposite films. In the experiment, we found that the average value of electrical resistivity is 1.13 \( \Omega \cdot cm \). Compared with the electrical resistivity of pure TPU films, which is 1016 \( \Omega \cdot cm \) [39], the electrical resistivity of HCNT/TPU nanocomposites decreased a lot. It is expected that the HCNTs in TPU matrix form conductive paths, leading to a greatly reduced electrical resistivity. In addition, all nine locations have similar electrical resistivity, which indicates that the HCNTs were uniformly dispersed in TPU matrix.

![Figure 17 a)Schematic illustration of different test locations b)electrical resistivity of HCNT/TPU nanocomposite films in different locations.](image-url)
3.3.5 Morphologies of Helical Carbon Nanotube Paper Based Nanocomposite Films

Cross-sectional SEM image of HCNT/TPU nanocomposite film is showed in Fig.12(a). HCNT/TPU thin film has a even thickness of 40\(\mu m\). In order to investigate carefully the dispersion and interlocking properties of HCNT in TPU, SEM images of HCNT/TPU nanocomposites films are shown in Fig.18(b). In Fig.18(b), HCNT were well dispersed without any clusters which indicates the nanocomposite films were homogenous. Observing from the cross-sectional image of nanocomposites, it can be easily seen that the HCNTs interlock tightly with TPU matrix, which governed their enhancement of electrical and thermal properties. Furthermore, HCNTs can act as micro-crack reducer through stopping the propagation of cracks in the polymer matrix, because of their high strength and high toughness.
Figure 18 a) Cross-sectional SEM image of HCNT/TPU nanocomposite films b) SEM image of HCNT in TPU resin matrix
CHAPTER FOUR: MORPHOLOGY, THERMAL STABILITY AND TRIBOLOGICAL PROPERTIES OF HELICAL CARBON NANOTUBE PAPER BASED THERMOPLASTIC NANOCOMPOSITE FILMS

4.1 Introduction

Nanoclay is also a popularly used nanomaterial to reinforce nanocomposites because of its unique layered structure and low cost compared to other nanomaterials. The high mechanical strength, hardness and fire retardancy of nanoclay make it a good reinforcement to polymer matrix.

The properties of polymer/nanoclay nanocomposites are significantly associated with the clay morphology in polymer matrix. Particle agglomeration decreases the surface area and effective interaction with polymer matrix, resulting in the deterioration of desired properties. Intercalated and exfoliated states are two common morphologies. Intercalated clay morphology occurs when polymer chains are stacked into the gallery spacing of clay layered structure. If layered nanoclay completely separate into single platelet and disperse randomly in polymer, the nanoclay is considered to be exfoliated. The homogeneous dispersion of nanoclay and resulting significant properties improvements are achieved only when nanoclay is exfoliated in polymer matrix.

Polyurethane/nanoclay nanocomposites are relative new class of composite materials. These nanocomposites are expected to show excellent mechanical and thermal properties. In 1998, first development of polyurethane/nanoclay nanocomposites was reported by Wang[40]. The nanocomposites exhibited an unusual improvement in modulus and strength, as well as the toughness. A fully intercalated nanoclay material was observed in their experiment and a nanocomposite with good optical transparency and was obtained. A complete exfoliation of
nanoclay with high concentration of nanoclay (~40%) was observed in polyurethane/nanoclay nanocomposites [41]. In this work, when the nanoclay content was 5%, the tensile strength and elongation achieved maximums. Thermal properties of nanoclay/polyurethane nanocomposites were also higher than pure polyurethane. Also, it is documented that the flexural strength and abrasion resistance was significantly enhanced in the nanocomposites compared to the plain polyurethane [42].

4.2 Experimental Method

4.2.1 Materials

An organo-modified nanoclay (Cloisite 30B) was obtained from Southern Clay Product Inc. It is a natural montmorillonite modified with a quaternary ammonium salt. Typical dry particle size is about 5um.

Thermoplastic polyurethane utilized in this work was supplied by SMP Technologies Inc. in pellet form. DMF solvent can be used to dissolve pellets into solution. The pellets have a specific gravity of 1.25g/cm³.

4.2.2 Manufacturing of Nanoclay/Thermoplastic Polyurethane Coating

4.2.2.1 Preparation of Nanoclay/Thermoplastic Polyurethane Solution

Thermoplastic polyurethane (TPU) was first dissolved in N,N-dimethyl formamide (DMF) at 50°C for 3 hours and a 10wt% TPU solution was prepared. Different loadings of nanoclay were then added into TPU solution. Thinky centrifugal mixer was utilized for dispersion of nanoclay in TPU solution. Mixing cycles were run at 2,000rmp for 20min. The nanoclay contents in solutions were 0, 3, 5, 7 wt%, respectively.
4.2.2.2 Preparation of Nanoclay/Thermoplastic Polyurethane Nanocomposite Coatings

TPU/nanoclay nanocomposite coatings were fabricated by a continuous spray deposition machine. The prepared TPU/nanoclay solution was delivered to an atomizing spray nozzle, which operated with cleaned compressed air at 50psi. The solution was atomized continuously into droplet and sprayed onto leather substrates. The leather substrate sat on a moving belt with the speed of 10.5in/min. After the spray deposition process, the received samples were dried in an oven. The DMF solvent got evaporated slowly at 80°C and then the SMP/nanoclay coating solidified on leather substrate. The resulting thickness for all coatings was around 15um.

4.2.3 Characterization and Evaluation

4.2.3.1 Abrasion Resistance Test

Abrasion properties of prepared TPU/nanoclay coating on leather substrate were evaluated by Taber Abraser Test. All the tests were performed with CS-10 wheels and 500g weight.

4.2.3.2 Thermogravimetric Analysis

Thermo-gravimetric analysis(TGA) experiments were carried out using a TGA Q5000 analyzer. The characterization of the sample was conducted in nitrogen flow from 50 to 500°C at a heating rate of 10°C/min. The weight of the sample used for test was about 10mg.

4.2.3.3 SEM Analysis

Scanning electron microspopy(SEM) images were recorded using a Zeiss-Ultra 55 microscope. Because the samples must be electrically conductive, TPU/nanoclay coatings were given a thin coating of platinum-gold layer by sputtering technology.
4.2.3.4 TEM Analysis

The dispersible morphology of TPU/nanoclay coatings was further observed using transmission electron microscopy (JEOL TEM-1011) under an accelerating voltage of 100kV.

4.3 Results and Discussions

4.3.1 Abrasion Resistance Analysis

The wear cycles to reach tear points of different samples have been reported in Table 3. As shown in Table 3, the wear cycles of samples with TPU/nanoclay coatings have been significantly improved. In addition, the leather samples with no coating or pure TPU coatings showed minor damage when test was finished, but for samples with TPU/nanoclay coatings, the top coat was only slightly worn off and the samples appeared intact. Results show that the samples containing 5wt% of nanoclay have maximum improvement of wear cycles.

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Wear Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>8500</td>
</tr>
<tr>
<td>TPU only</td>
<td>11000</td>
</tr>
<tr>
<td>TPU+3%Nanoclay</td>
<td>14000</td>
</tr>
<tr>
<td>TPU+5%Nanoclay</td>
<td>15500</td>
</tr>
<tr>
<td>TPU+7%Nanoclay</td>
<td>13000</td>
</tr>
</tbody>
</table>
4.3.2 Thermal Gravimetric Analysis

The TGA and derivative TGA thermograms of 0%, 3%, 5% and 7% nanoclay loaded SMP/nanoclay coatings are shown in Fig.19(a and b). Temperatures at different weight loss are analyzed from the TGA thermograms and are given in Table 4. It is observed that the incorporation of nanoclay into TPU coatings increases the decomposition temperature. Especially obvious is the decreasing of weight decomposition rate when nanoclay is added into TPU coatings. For pure TPU coating, the maximum weight loss rate is 1.05 %/°C, but for sample with nanoclay, the maximum weight loss rate is around 0.6~0.7 %/°C. It indicates a considerable improvement of thermal stability.
Figure 19 a) weight loss dependence on temperature for TPU/nanoclay coating b) derivative weight loss dependence on temperature for TPU/nanoclay coating.

Table 4 Temperatures at different weight loss of SMP/nanoclay coating

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature at different weight loss(°C)</th>
<th>Temperature at maximum weight loss rate (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{30}$</td>
<td>$T_{50}$</td>
</tr>
<tr>
<td>TPU</td>
<td>338.0</td>
<td>358.1</td>
</tr>
<tr>
<td>TPU+3%Nanoclay</td>
<td>334.9</td>
<td>362.8</td>
</tr>
<tr>
<td>TPU+5%Nanoclay</td>
<td>338.5</td>
<td>370.6</td>
</tr>
<tr>
<td>TPU+7%Nanoclay</td>
<td>331.0</td>
<td>366.2</td>
</tr>
</tbody>
</table>
4.3.3 Morphologies of Nanoclay/Thermoplastic Polyurethane Coating

4.3.3.1 SEM Analysis

To investigate the homogeneity of coatings, the observation of TPU/nanoclay coating through the use of SEM was conducted. The thickness of smooth and homogeneous nanocomposite coating is around 15µm, as shown in Fig.20. Fig.21 displays the SEM images of TPU/nanoclay coating surface with 5% nanoclay contents. In the image, the regions with gray color indicate the TPU polymer matrix and the brighter spot indicate the distribution of nanoclay particle. All nano-sized nanoclay clusters were found uniformly dispersed in the TPU polymer matrix. It proves that the uniformly-dispersed samples were achieved.

![Cross-sectional SEM image of TPU/nanoclay nanocomposite coating](image)

Figure 20  Cross-sectional SEM image of TPU/nanoclay nanocomposite coating
4.3.3.2 TEM Analysis

The dispersible morphology of TPU/nanoclay coatings was further observed using transmission electron microscopy (JEOL TEM-1011) under an accelerating voltage of 100kV.

The homogeneity of nanoclay particles in TPU matrix was confirmed through TEM analysis of coatings as shown in Fig. 22. In the TEM photographs, the morphologies of nanoclay clearly showed high clay exfoliation in TPU matrix and single nanoclay platelets were randomly distributed throughout the polymer matrix.
Figure 22 TEM micrograph of dispersed nanoclay particles in SMP matrix with 5 wt% content
CHAPTER FIVE: CONCLUSIONS AND FUTURE WORK

This thesis discusses a new method to fabricate multifunctional nanocomposite films. Spray deposition is a versatile and effective technique to deposit HCNT nanopaper, HCNT/TPU nanocomposite films and TPU/nanoclay nanocomposite coatings. The quality and properties of the nanocomposites films depend largely on the process parameters. To ensure the smoothness of film surface without wrinkles or air bubbles, aluminum plate is used to hold the spray substrate. Oven temperature is also adjusted to control the settling time of polymer resin as solvents evaporate. Thickness of the polymer resin and HCNT nanopaper is adjusted to avoid the deformation of films when resin dries. Flow rate of solution, air flow rate and moving speed of melt is required to be constant during the processing so that even thickness of films/coatings is achieved. The most important processing parameter is the drying temperature. If temperature is too high, DMF evaporate fast and air bubbles appear on the films. The drying temperature also influences the porosity and physical properties of the deposited nanocomposite films. In our work, a drying temperature of 60°C results in films with good quality. Thickness of the films/coatings is controlled by solution/suspension flow rate and moving speed of the belt. Typical thickness of HCNT nanopaper deposited on cellulose filter is around 2~10um. The smallest thickness of smooth and homogeneous HCNT/TPU nanocomposite film is 40um.

Four point probe resistivity test results show that the electrical resistivity of HCNT/TPU films decreases significantly. The average value of electrical resistivity is $1.13 \ \Omega \cdot cm$. The highly conductive HCNTs provide conductive path for the nanocomposite films. The results of SEM images indicate that HCNTs have tight interfacial bonding with polymer matrix which would result in tremendous enhancement to properties. It was also found that the addition of HCNTs could enhance the thermal stability of the TPU-based nanocomposite. If the onset degradation
temperature was taken as the criterion of thermal stability, TPU/HCNT nanocomposite films show a 30°C improvement on degradation temperature. The HCNTs with high thermal conductivity effectively facilitates the heat transfer in nanocomposites, which leads to an improvement of thermal stability.

A series of experiments were conducted to study the properties of TPU/nanoclay nanocomposite coating. From the abrasion test, it can be observed that the abrasion resistance increases (wear cycle to reach tear points increases) when nanoclay is added into TPU matrix. TPU/nanoclay nanocomposite coating with 5wt% content of nanoclay shows the maximum improvement in abrasion resistance. The wear cycles increase by 40% from 11000 to 15500. The higher hardness of nanoclay is a possible reason for the improvement of abrasion resistance. The thermal stability of TPU/nanoclay nanocomposite coatings was evaluated by TGA test. TGA thermogram indicates that all TPU/nanoclay nanocomposite films are stable up to 250°C and then undergo thermal degradation. It can be observed that the thermal stability of TPU/nanoclay nanocomposite coating is high compared to pure TPU. The maximum degradation rate of nanocomposite decreases from 1.05%/°C for pure TPU to 0.65%/°C, a 38% decrease. The improvement of thermal stability is related with the barrier effect of clay platelets to the diffusion of volatile products formed during thermal degradation. The nanoclay with layered structure hinders the diffusion of volatile product so that the degradation rate decreases a lot. Evaluation of morphologies of TPU/nanoclay nanocomposite coating shows clearly that nanoclay is exfoliated in polymer matrix, which is responsible for the significant improvement of properties.

There are a few notable and potentially rewarding directions for which the future research may take. For the equipment improvement, real-time control on the thickness of nanocomposites should be realized by modifying the design of machine. Moving speed of the belt on spray
deposition should be increased for fabrication of thinner sample. Rolling mill can be added to improve the surface quality of nanocomposite films. For the processing, currently cellulose filter cannot be fully removed from nanocomposite films. More work should be done to totally get rid of this cellulose filter. Currently, HCNT nanopapers contain randomly dispersed HCNT. Alignment of HCNT in nanopaper should be researched. With the ability to align HCNT in a desired direction, nanocomposites can better take advantage of the ‘spring’ structure of HCNT. Lastly, mechanical properties of HCNT/TPU nanocomposite films should be evaluated. Tensile test and dynamic mechanical analysis test could be done to study their mechanical properties, such as Young’s modulus, tensile strength, storage modulus and loss modulus.
LIST OF REFERENCES


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