Synthesis of Polyhedral Oligomeric Silsesquioxane (POSS) Functionalized Carbon Nanotubes for Improved Dispersion in Polyurethane Films

Xiaonan Kou

University of Southern Mississippi

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SYNTHESIS OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) FUNCTIONALIZED CARBON NANOTUBES FOR IMPROVED DISPERSION IN POLYURETHANE FILMS

by

Xiaonan Kou

Abstract of a Dissertation
Submitted to the Graduate School
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

May 2013
ABSTRACT

SYNTHESIS OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) FUNCTIONALIZED CARBON NANOTUBES FOR IMPROVED DISPERSION IN POLYURETHANE FILMS

by Xiaonan Kou

May 2013

Carbon nanotube (CNT) polymer nanocomposites are promising advanced materials. These materials exhibit the advantages of traditional polymeric materials, such as being light weight and easy to process, combined with the potential to exhibit enhanced mechanical, thermal and electrical properties compared to pure polymers. To achieve substantial improvement of composite properties at low CNT loading, uniform dispersion of CNTs in the polymer matrix and strong CNT-polymer interfacial interaction are needed. However, it is difficult to achieve adequate dispersion and interfacial interactions due to the inert nature of CNTs. In this project, polyhedral oligomeric silsequioxane (POSS) will be used as a dispersing agent for multi-walled carbon nanotubes (MWNTs) in polyurethane (PU) matrices.

This dissertation consists of six chapters. Chapter I provides a detailed introduction of the fundamental knowledge of CNTs, PU, and POSS. At the end of this chapter, the motivation and rationale of this research are given. Chapter II establishes the overall goal and specific objectives of this research. Chapter III describes the synthesis and characterization of three POSS modified CNTs and one organosilane modified CNT. Grafting efficiency of the different grafted molecules are calculated and compared. Chapter IV discusses the dispersion behavior of four covalently modified CNTs in both
solvents and PU matrices. Differences in dispersion behaviors of the modified CNTs are correlated to the solubility parameters of the grafting molecules and the surface structures of modified CNTs. Chapter V provides further discussion of the dispersion of POSS and silane modified CNTs by reviewing the assessment of the physical properties of PU composites containing the modified CNTs. Morphological, thermal, mechanical and electrical properties are used to estimate the interactions of the modified CNTs with the PU matrix. Chapter VI explores the function of the trisilanolphenyl POSS lithium salt (TSPLi) as a dispersant for CNTs in thermoplastic polyurethane (TPU) during melt extrusion. The dispersion of CNTs and TSPLi modified CNTs are estimated by mechanical and electrical property measurement of the PU/CNT and PU/CNT-POSS composites.
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A Dissertation
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Abbreviations

CNTs  Carbon nanotubes
MWNTs  Multi-walled carbon nanotubes
SWNTs  Single-walled carbon nanotubes
DWNTs  Double-walled carbon nanotubes
POSS  Polyhedral oligomeric silsesquioxane
CNT-COOH  Acidified carbon nanotube
CNT-R  Carbon nanotube with R groups on its surface
APIB  Aminopropyl isobutyl POSS
AEAPIB  Aminoethylaminopropyl isobutyl POSS
APIO  Aminopropyl isoocetyl POSS
APTS  Aminopropyltris(trimethylsiloxy)silane
TSP  Trisilanol POSS
TSPLi  The lithium salt of trisilanol POSS
CNT-g-POSS  Carbon nanotube covalently modified with amino POSS
CNT-g-silane  Carbon nanotube covalently modified with amino silane
CNT-POSS  Carbon nanotube bonded with POSS other than covalent bonds
PU  Polyurethane
TPU  Thermoplastic polyurethane
HS  Hard segment in polyurethane
SS  Soft segment in polyurethane
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<tr>
<td>HDI</td>
<td>Hexamethylene diisocyanate</td>
</tr>
<tr>
<td>PPG</td>
<td>Polypropylene glycol</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>DTGA</td>
<td>First derivative thermal gravimetric analysis</td>
</tr>
<tr>
<td>$T_o$</td>
<td>5 wt% weight loss temperature in TGA</td>
</tr>
<tr>
<td>$T_{max}$</td>
<td>Maximum weight loss rate temperature in TGA</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance-Fourier transfer infrared spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>WAXS</td>
<td>Wide angle x-ray scattering</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>CED</td>
<td>Cohesive energy density</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization or nucleation temperature</td>
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CHAPTER I
INTRODUCTION

Carbon Nanotubes (CNTs)

Structure and Properties of CNTs

Carbon materials exist in multiple forms in nature. (Figure 1) Some of the most well-known carbon allotropes are diamond, graphite and fullerenes. Among them, CNTs are quasi one dimensional carbon allotropes with cylindrical shapes.\(^1\) In general, CNTs can be divided into two categories: SWNTs and MWNTs. Both SWNTs and MWNTs were first prepared by Lijima.\(^2,3\) A SWNT can be viewed as a seamless roll of a graphene layer, generally with the diameter of 0.7-2 nm. Depending on the way the graphene sheet is rolled up, SWNTs may exist in different chiralities, which can be described by the rolled-up vectors \(n\) and \(m\). Achiral tubes exhibit values of \((n,0)\) (zigzag) or \((n,n)\) (armchair), while all the other tubes \((n, m)\) are chiral.\(^4\) A MWNT is simply a series of concentric SWNTs stacked together with \(\pi-\pi\) stacking force. The diameter of a MWNT ranges from 10 to 100 nm, depending on the number of layers it has. Generally, concentric tubes in MWNTs do not have similar chiralities. For example, if the inner tube of a MWNT is of a zigzag type, the rest of the tubes are generally armchair or chiral. Due to its special layered hollow tubing structure, a MWNT has properties similar to both SWNT and graphite.\(^1\) The interlayer spacing value of MWNT (0.34 nm) is slightly larger than the value of single-crystal graphite (0.335 nm). This is caused by the severe geometrical constraint of MWNTs when forming the concentric cylinders.\(^5\)
Although the formation of CNT structures are described as rolling up a graphene sheet, CNTs are not made is such a manner in industry. There are three major methods for the synthesis of CNTs: arc discharge, laser ablation and chemical vapor deposition (CVD), all of which can be adapted for making both SWNTs and MWNTs. All three methods use metal, such as Fe, Co, Ni, or Yr as catalysts, which remains in the tube ends after CNT formation. The CVD techniques are especially attractive due to their capabilities of producing high quality and quantity of CNTs, so they are the most commonly used methods today.

Defect formation in CNTs is inevitable using currently available techniques. Some of the common defects include the formation of pentagons, heptagons, vacancies, and kinks. Most of the time, defect sites are unwanted, because they cause discontinuity of the conjugated tube structures which reduces the electronic and mechanical properties of CNTs. In fact, unexpected defects are usually the reason why theoretically calculated properties of CNT containing devices do not match the experimental values. Sometimes defects are purposely introduced to tailor the intrinsic properties of CNT for creating novel nanodevices. In addition, more defects can be generated during the modification of CNTs before the end use. In these cases, the sacrifice of CNT intrinsic properties is unavoidable for enhanced dispersion and interfacial interaction.
In summary, with different diameters, chiralities, preparation methods and defect types, CNTs have very complex structures. The properties of a CNT are highly related to all the structural features mentioned above, which leads to difficulty in comparing research results conducted using different CNTs. Even with the massive number of studies of CNTs, development of methods to synthesize large quantities of CNTs with desired structures at a low cost is still under investigation.12-14

The special properties of CNTs come from the combination of their dimension, structure and topology. The nano-dimension provides CNTs with a large surface area (50-1315 m²/g).15 The long conjugated carbon structure provides CNTs with thermal stability, excellent mechanical properties, high thermal conductivity, and good electrical conductivity. The axial elastic modulus of CNTs is predicted to be at least 1 TPa,16 which is the highest of all the known materials. At room temperature, the thermal conductivity of a single MWNT is 3000W/ (mK), which is 5 times the value of copper.17 The conductivity of a metallic SWNT was calculated to be 5×10⁷ S/m, comparable to metals.9 In addition, the topology of CNTs, which distinguishes them from graphene, brings the specialty of CNT to a whole new level. Due to the hollow structure, the density of CNTs is significantly lower than that of other nanomaterials. The bent sp² orbitals on CNT side walls and tips are more reactive towards organic reagents than those in graphene, so CNTs are relatively easier to functionalize.11 Because of the hollow structure, CNTs perform much better under external forces compared to graphite. This is caused by the energy release from the deformation of the carbon tubes under stress.16, 18 For MWNTs, enhanced mechanical performance is believed to be related to wall sliding behavior.19
The market price of 99% pure CNTs made by CVD is about $300/g for SWNTs and $20/g for multi-walled nanotubes. Due to the interference of different layers, the electrical, magnetic and photonic properties of MWNTs are not as high as those of SWNTs. For the above reasons, the application of SWNTs is mostly explored in high end applications such as electronic devices and medicine, while MWNTs are used mostly as fillers for composite materials for property enhancement. Detailed information of CNTs application is beyond the scope of this dissertation. The reader is referred to a few comprehensive reviews.

Dispersion of CNTs

Because of their structural features, pristine CNTs are very difficult to manipulate. Some solvents such as aniline and DMF stabilize CNT suspensions better than others. Surface functionalization is usually needed for CNT processing. Covalent and non-covalent surface functionalizations have been used to improve the miscibility of CNTs with other materials.

Covalent modification is the most effect way to alter CNT dispersion. It provides the flexibility to modify the CNT surface to fit the desired environment. The most common method is to use strong oxidizing agents to generate –COOH, -C=O, and –OH groups on the tube end and side walls. These procedures usually yield defect carbons in which the hybridization state changes from $sp^2$ to $sp^3$, leading to a loss of conjugation and even worse, large reduction of aspect ratio. However, the conductivity of MWNTs is not harmed very much by covalent treatment because only the outer wall structure is affected. The generated –COOH and –OH groups are suitable for a large variety of chemical reactions, such as amidation, esterification, and zwitterion interaction.
There are other less commonly used methods targeted at $\pi$-conjugated carbon, including $[2+1]$ cycloaddition of nitrene,$^{28}$ addition of nucleophilic carbene, radical addition $^{29}$ and electrophilic addition. The reagents for these reactions are more expensive and the reaction conditions are harder to control, but they give CNT an even functionalization at both the side walls and the end tips with minor defect generation. It was shown that the aspect ratio of SWNTs remained the same after reaction.$^{29}$ Raman and UV/Vis/NIR absorption spectra also showed that the electronic properties of SWNTs were preserved upon surface modification.$^{28}$

Wet chemistry combined with sonication provides CNTs with homogenous functionalization, but the purification procedures are extremely time consuming. Therefore, methods for functionalizing dry CNTs were developed for better industrial scale-up. These techniques permit easier control over reactions at lower reaction temperatures, resulting in less pollution, and save time. Some of these methods are fluorination,$^{30}$ UV-ozone functionalization,$^{31,32}$ and plasma treatment.$^{33,34}$

The non-covalent functionalization of CNTs normally involves interactions between surfactants and/or polymers and the CNT surface such as van der Waals, $\pi-\pi$, or electrostatic interactions. The advantage of non-covalent functionalization is that it does not alter the structure of the nanotubes and, therefore, both electrical and mechanical properties should remain unchanged. Some commonly used surfactants for CNTs dispersion are sodium dodecyl sulfate (SDS), dodecyl-benzene sodium sulfonate (NaDDBS), and Pluronic surfactants.$^{35,36}$ These amphiphilic compounds are used to assist the dispersion of CNTs in water, organic solvents and polymers. Sonication is necessary to debundle CNTs during non-covalent functionalization. Surfactants bind to the CNT surface through hydrophobic interaction which is not strong enough to break
CNT bundles. If no high shear force is provided by sonication, CNTs will be stabilized as bundles instead of as individual tubes when mixed with surfactants in solution. Polymers can also stabilize CNTs by wrapping. Polymers with aromatic groups, such as polyvinyl pyrrolidone (PVP), polystyrene sulfonate (PSs), and polystyrene-b-polyacrylic acid (PS-b-PAA), are used for this purpose. However, both polymers and CNTs are very large in size compared to small molecules, so the entropy increases greatly during the mixing process. Conjugated polymers, such as poly(m-phenylene vinylene) (PmPV) and poly(3-hexylthiophene) (P3HT) show strong π interaction and can effectively disentangle CNTs, but the limitation for using them is that they have low solubility in most solvents and polymers.

**Polymer/CNT Composites**

Following surface modification of CNTs, solution mixing, melt blending and *in-situ* polymerization techniques have been used to improve the dispersion of CNTs in polymer matrices. In the solution mixing approach, CNTs are dispersed in a suitable solvent and mixed together with the polymer. The CNT/polymer composite is formed by precipitation or by evaporation of the solvent. A high power ultrasonication process is an easy and effective method used in forming a dispersion of CNTs. While solution mixing is relatively simple to process, it does not work for polymers with low solubility in the solvent. In the melt processing method, CNTs are mechanically dispersed into a polymer matrix using a high temperature and high shear force mixer or compounder. This method is particularly useful for thermoplastic polymers. It is simple and compatible with current industrial practice. However, the resulting dispersion of CNTs in a polymer matrix is quite poor compared to that obtained via solution mixing. In addition, the CNT loading is limited by increasing viscosity of the composite as the CNT loading is increased. The
The best way to achieve uniform distribution of CNTs is using *in situ* polymerization, during which the CNTs are dispersed in monomer followed by polymerization. A high percentage of CNTs may be easily dispersed with this method, and they form a strong interaction with the polymer matrices. Better dispersion can be achieved by adding reactive functional groups to CNTs to allow covalent bonding of CNTs to the polymer system.41, 42

Property enhancement of polymers from CNTs results from a change of morphology, which is shown most by the change of $T_g$ and crystallinity. There are no common rules of how CNTs affect the glass transition of a polymer. In some cases, an increase of $T_g$ is reported, attributed to the rigid CNT restraining the movement of polymer chains.43, 44 Other researchers have reported a decrease of $T_g$, attributed to an increase in free volume.45, 46 Some literature reported no change or a high variation of $T_g$ due to the heterogeneity of the samples.47 The understanding of how CNT addition affects the crystallinity of polymers is somewhat better. CNTs are generally recognized as nucleating agents for polymers, forming two types of morphologies: shish-kebab morphology, 48, 49 and transcrystallinity.50, 51 Crystallization temperature, $T_c$, was found to increase in almost all CNT-based composites in non-isothermal DSC studies.9 This was explained by the fact that CNTs can alter chain mobility as well as provide spatial impediment to growth.52, 53

Mechanical properties of polymer/CNT composites were found to generally increase, but the level of increase is highly dependent on the polymer matrix, composite preparation methods, and the property examined.54 The high reinforcement of CNTs to polymers can be explained by the rule of mixtures and Halpin-Tsai equations. Based on theory, there are four main system requirements for effective reinforcement: a large
aspect ratio, good dispersion, alignment and interfacial stress transfer. For most CNTs, the aspect ratio is in the region 30-1000, which is much bigger than that of other nanofillers. Therefore, CNTs almost reach the maximum enhancement for composite materials. Dispersion is a very fundamental requirement for composites to achieve effective load transfer. Homogenous dispersion of CNTs results in a more uniform stress distribution. Alignment is a less crucial issue. Based on the rule of mixtures theory, the difference in composite modulus for random orientation and perfect alignment is a factor of five, which is much smaller than the effect of aspect ratio. Good interfacial stress transfer is the most important requirement for a reinforced composite. It ensures that external stresses applied to the composites are efficiently transferred to CNTs, allowing them to take a disproportionate share of the load. However, it is still difficult to measure the interfacial shear strength (IFSS) directly by instrumentation. There are only a few reports of such studies using TEM and AFM. Most of the IFSS values for CNT-polymer composites are obtained by molecular dynamics simulations. The overlap between experimental and theoretical results suggest that the IFSS lies in the region of 50-100 MPa for non-covalently bonded composites.

CNT-polymer composites are either semiconductors or conductors. Electrical conductivity can be improved by adding CNTs into a polymer matrix. The conductivity of composite materials can be explained by the percolation theory. This is illustrated in Figure 2. When the conducting filler content is gradually increased, the composite undergoes an insulator-to-conductor transition. The critical filler content is referred to as the percolation threshold ($V_c$) where the measured electrical conductivity of the composite suddenly increases by several orders of magnitude due to the formation of continuous electron paths or conducting networks. The concentration of the conducting
filler must be above the percolation threshold in order to achieve conducting networks in the composite. For conventional conducting fillers such as metal powder and carbon black, the filler content needs to be as high as 10-50 wt%, resulting in poor composite mechanical properties and high density. For a statistical distribution of filler particles the excluded volume concept gives \( V_c \approx \frac{1}{\eta} \) with \( \eta \) being the aspect ratio.\(^5\) If the aspect ratio of CNTs is taken as 1000, then theoretically, if CNTs are properly dispersed, \( V_c \) for all CNT based composites should be \( \approx 0.1 \) wt\%. However, in reality \( V_c \) is very different from system to system due to varied levels of dispersion.\(^5\)

\[
\text{Figure 2} \quad \text{A schematic of the percolation phenomenon and conducting network in conducting composites (redrawn following the description in reference}\(^5\).}
\]

Polyurethane (PU)

PU is a material with superior properties that have applications in coatings, adhesives, shape memory polymers, and polymer composites.\(^5\) PU consists of hard and soft segments (HS and SS). The HS is composed of alternating diisocyanate and chain-
extender molecules, whereas the SS is formed from a linear, long-chain diol. Phase separation occurs in PUs because of the thermodynamic incompatibility of the hard and soft segments. The wide applicability of PU is due to the versatility of raw material selection. Structures of some of the most commonly used PU synthetic raw materials are listed in Figure 3 and 4.

![Hexamethylene Diisocyanate (HDI)](image1)

![Toluene Diisocyanate (TDI)](image2)

![Methylenebisphenyl Diisocyanate (MDI)](image3)

![Isophorone Diisocyanate (IPDI)](image4)

**Figure 3.** Structures of some of the most widely used diisocyanates in PU preparation.

![Polyethylene Glycol (PEG)](image5)

![Polyester Polyol](image6)

![Acrylic Polyol (ACPO)](image7)

![Poly(terephthalonate ether) Glycol (PTMEG)](image8)

![Poly(ε-caprolactone) (PCL)](image9)

**Figure 4.** Structures of some of the most widely used polyols in PU preparation.
PU coatings

Coatings provide materials with esthetic properties and are of vital importance in the protection against environmental influences. PU coatings have excellent gloss, hardness, flexibility, abrasion resistance, chemical resistance and UV durability. Because of the many advantages PU coatings offer, they have a large market share in the coatings industry for various substrates, especially in automotive refinish, wood coatings and chemical resistant coatings. The current coatings industry is dominated by solvent-borne PU coatings, which can be categorized into two-component and one-component coatings. Two-component coatings are supplied in two containers with polyisocyanate and polyol separately, and are mixed prior to application. One-component PU coatings utilize the same chemical reactants and are formulated by the same process except that the polyisocyanate is blocked. Heating (>300 °F) is needed to unblock the isocyanate groups to cure the coatings. The biggest challenge in solvent-borne coatings is the pollution caused by solvent evaporation. To address this issue, technologies such as UV-curable PU coatings and waterborne PU coatings have been developed and are now taking an increasing market share.

A wide variety of fillers are being used to reinforce the PU matrix for improved properties. For coatings applications, nanoparticles with high cohesive strength are added to the PU matrix to achieve composite films with good mechanical, thermal, barrier and flame-retardant properties. In addition, these films exhibit special electrical and dielectric properties as well as improved hardness and fracture toughness. Nanosilica, Fe₂O₃, and TiO₂ have all been used for the above purposes.
**Thermoplastic Polyurethane (TPU)**

TPUs are multi-block copolymers, consisting of alternating HS and SS. The SS domains contribute to high extension and elastic recovery, while the HS domains contribute to the high modulus and strength. Phase separation also occurs in TPUs. (Figure 5) The phase separation level depends on the solubility parameters of the phases, the crystallinity of HS and SS, temperature and thermal history. It has a strong effect on nearly all properties of TPU.

![Schematic representation of TPU chain structure and phase separation.](image)

*Figure 5.* Schematic representation of TPU chain structure and phase separation.

HS domains of PU are assembled with hydrogen bonding, which is the strongest secondary chemical bond with a strength estimated to be about 20-25 kJ/mol. The urethane group contains both a strong proton donor (N-H) as well as a proton acceptor (C=O). Another possible proton donor is the alkoxy oxygen in SS (-O-). (Figure 6) Hydrogen bond formation within the HS domain promotes phase separation, while hydrogen bonding between HS and SS domains promotes phase mixing. From IR and
DSC study, hydrogen bonding in TPU is shown to be related to the structure, type, and size of HS and SS, and the testing temperature. 66

Figure 6. Schematic representation of hydrogen bonding formation in TPU (A) within a HS domain (B) between HS and SS domains.

Polyhedral Oligomeric Silsesquioxane (POSS)

POSS molecules are organic-inorganic nanomaterials produced by Hybrid Plastics, Inc. POSS molecules have nanosized (1-3 nm) cage-like organic-inorganic core-corona structures, which can be described by the general chemical structure RSiO1.5. General fully condensed “closed-cage” and trisilanol “open cage” POSS structures are illustrated in Figure 7. The inorganic core is composed of thermally and chemically robust Si-O-Si, and the organic corona allows tailoring of compatibility and reactivity with polymers. 67

The perfectly defined structure makes POSS a versatile nano-building block in the preparation of organic-inorganic hybrid materials. 68-70 POSS/polymer hybrids may be produced by blending POSS with a polymer matrix. The properties of POSS/polymer composite materials are highly dependent on the way POSS is incorporated. When POSS
is covalently incorporated in the backbone, large increases in modulus and thermal properties are generally observed. The addition of POSS into organic polymers via blending was generally found to provide decreases in viscosity and significant modification of polymers’ surface properties, such as low friction, enhanced hardness and modulus, while the changes of bulk thermomechanical properties are not significant.\textsuperscript{71, 72} The extent and nature of the property enhancement is controlled by the POSS cage structure, organic group composition, compatibility with the polymer matrix and concentration. Due to the tailorable chemistry of POSS, incorporation of POSS molecules into polymer matrices imparts many other property improvements such as reduction of heat release rates in the event of fire and improved dielectric properties.\textsuperscript{70}

**Figure 7.** Schematic of a closed cage (left) and an open cage (right) POSS molecule.

**POSS Dispersants**

Trisilanol POSS (TSP) has been developed as a universal dispersant for nanoparticles by Hybrid Plastics, Inc.\textsuperscript{73} The mechanism of POSS dispersion is illustrated in Figure 8. The three silanol groups on TSP POSS react with hydroxyl groups on the nanoparticle by a silanol condensation reaction to tightly bind to the surface. This
reaction is quick and efficient, so no complicated pretreatment of nanomaterials is necessary. It also does not generate methanol like a typical silane coupling agent would. Each POSS molecule has three groups to bind to the particle. This chelate binding is more stable than monofunctional binding provided by traditional dispersants. There are seven commercially available TSP molecules, so POSS with R groups matching the polarity of the matrix can be chosen to maximize the dispersing efficiency.

![Figure 8. Silanol condensation between TSP and nanomaterials with hydroxyl groups on the surface.](image)

TSP has some other advantages over traditional dispersants.\textsuperscript{74} For organic dispersants, the degradation temperature is around 200 °C. TSPs have degradation temperatures up to 400 °C, which enable them to be used in melt blending of nanoparticles with high performance thermoplastic polymers such as polyether ether ketone (PEEK). Another benefit of using TSP POSS is the reduction of viscosity. POSS has been shown to have a lubricant effect in polymer processing.\textsuperscript{75} Organic dispersants are mostly surfactants with long aliphatic chains, or amphiphilic polymers. Mixing them into a polymer matrix increases the viscosity of the system due to chain entanglement. Unlike conventional dispersants, the interactions between POSS-coated nanoparticles with a polymer matrix is not based on chain entanglement, but on the interactions
provided by the five R groups extending in all directions. Therefore, using TPS POSS as a dispersant can reduce the viscosity of the system. This is especially important for making highly filled materials. Despite all the benefits of TSP POSS dispersants, there are relatively few reports in the literature, and to our knowledge these systems have not yet been reported in PU matrices.

In addition to TSP, close caged POSS molecules have been used as dispersing agents. Amino-functional POSS molecules have been covalently bonded to the surface of nanomaterials and used as dispersing agents for CNTs, graphene, and carbon fibers. After protonation, amino-functional POSS molecules have been used to intercalate stacked nanoclay with electrostatic force and assist its dispersion in polymer matrices. The study of these POSS dispersants is still in its early stages.

Motivation and Contribution of Current Research

The model matrices used in this study, PU coatings and TPU, are widely used materials in industry and daily life. Applying nanofillers into these materials can greatly improve the anti-abrasive, anticorrosive and electrostatic shielding properties, which can both extend the lifetime and broaden the application areas. Exceptional mechanical and physical properties demonstrated for CNTs, combined with their low density, make them excellent candidates for composite reinforcement. Although CNTs are relatively expensive, if they are well-dispersed only a small concentration of CNTs is necessary to greatly improve polymer properties such as thermal stability, mechanical strength, fire retardancy, conductivity, and dielectric performance. Thus, at low concentrations, incorporation of CNTs is an efficient way to prepare advanced materials.

All property improvements of CNT/polymer composites are strongly dependent on the dispersion of CNT in the polymer matrix. Recently, POSS has been reported as a
dispersant for nanoparticles, such as TiO$_2$, clay and CNTs, in preparing polymer composites.\textsuperscript{82, 83, 88, 92-94} There are two advantages to using POSS in making CNT/polymer composites over other methods. First, POSS is commercially available with a large selection of attached organic functional groups, which can be used to improve solubility in the polymer matrix to improve CNTs’ dispersion and CNT-polymer interfacial interaction. In this project, amino-functionalized POSS molecules with varying aliphatic substituents are chosen to improve CNT dispersion into PU systems. Amide bonds formed between acid functionalized CNTs and POSS mimic the urethane bonding in the PU matrix (Figure 9).

\textit{Figure 9.} Schematic illustration of CNT-g-POSS as reinforce agents for PU.

It is expected that CNT-g-POSS hybrids will have strong interactions with the hard segments of the polyurethane matrix. Meanwhile, the aliphatic R groups on POSS will have affinity for the aliphatic soft segments in the polyol. Second, POSS molecules can also be used as fillers for polymer composites to improve thermal, mechanical and fire retardant properties. We predict that POSS serves as a secondary reinforcement agent
for CNT/polymer nanocomposites and compensates for some of the properties lost due to surface modification of the CNTs.

To our knowledge, there is no report of using POSS to disperse CNTs in PU thin films and TPU. In this project, we used three types of POSS with different organic substituent groups and one organosilane as dispersing agents to study the effects of R group, spacer length between POSS and the CNT surface, and the POSS cage structure on CNT dispersion in solvents and in PU polymer matrices. We also used a modified version of TSP, the TSPLi, to disperse neat CNTs in TPU during melt extrusion. Knowledge gained from our study improved the understanding of how POSS structure affects the dispersion behavior of POSS functionalized nanomaterials, and provides useful information to enable commercial development of POSS dispersants in the future.
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CHAPTER II

OBJECTIVES OF RESEARCH

The overall goal of this research is to gain fundamental understanding of using POSS as a dispersant for CNTs in PU matrices, specifically, to understand how the degree of CNT dispersion and CNT-polymer interaction are affected by the structures and functionalities of the grafted POSS molecules. Knowledge gained from this study will benefit POSS product development for preparation PU/CNT composite coatings with advanced properties.

The main objectives of this research include

1. Define effective surface functionalization procedures for CNT-g-POSS production by varying parameters including concentration of oxidation agent, acid treatment time, and purification methods.

2. Estimate the dispersion of CNT-g-POSS in polymeric matrices by performing cohesive energy density (CED) and solubility parameter calculations utilizing macromolecular dynamics simulations.

3. Determine the effect of POSS structure on CNT dispersion and composite properties by varying POSS type (R group, spacer length, and cage structure).

4. Perform a systematic study of CNT-g-POSS dispersion as a function of structure variation by performing morphology, thermal, mechanical and electrical properties measurement.

5. Test the feasibility of using TSPLi as a dispersant of CNTs in polymer matrices.
CHAPTER III
SYNTHESIS AND CHARACTERIZATION OF POSS MODIFIED CARBON NANOTUBES

Abstract

Carbon nanotubes (CNTs), because of their high aspect ratio, nanoscale diameter, and exceptional strength, are excellent candidates for preparing high performance polymeric composites. However, their application is limited by poor dispersion and weak interfacial interaction with the polymer matrix. It has been shown that covalently attaching POSS molecules to the surface of CNTs can improve CNT dispersion in solution and enhance the interfacial interaction between the CNT and polymer interfaces. In this work, three types of POSS molecules with different organic substituent groups and one amino silane were successfully covalently bonded to the surface of modified CNTs. The structural parameters of the POSS molecules were estimated by molecular dynamics simulation. TGA was used to calculate the grafting density of the POSS and organosilane molecules. Raman spectroscopy and ATR-FTIR spectroscopy were used to confirm covalent bonding to the CNT surface. TEM and AFM were used to characterize the surface features of CNT-g-POSS. The effects of POSS structure on the functionalization process, CNT dispersion, and polymer matrix/CNT interfacial interaction will be described in subsequent chapters.

Introduction

The agglomeration and poor affinity of CNTs with the polymer matrix result in poor dispersion and reduced physical properties in CNT polymer nanocomposites. Countless surface modification methods have been developed to improve the miscibility
of CNTs with polymers.\textsuperscript{1,2} These methods can be divided into non-covalent approaches and covalent approaches. For non-covalent modification approaches, small molecule surfactants and amphiphilic polymers are used to adsorb or physically wrap around the CNT surface.\textsuperscript{3,4} One advantage of these approaches is that the conjugated surface structure of the CNT is unharmed, so the physical properties of CNTs are largely maintained after the treatment. However, the strength of the interactions between CNTs and the dispersing agents is relatively low, resulting in the possibility of instability of the dispersed structures during composite manufacturing.\textsuperscript{2}

In contrast, covalent approaches lead to much stronger binding of CNTs with the polymer matrix.\textsuperscript{2} The most common covalent approach is acid treatment of CNTs to create carboxylic acid groups on the CNT surface, which can then be further functionalized utilizing a variety of chemical reactions.\textsuperscript{5} Even though the surface structure of CNTs is damaged during covalent treatment, resulting in reduction of the electrical and mechanical properties,\textsuperscript{6} CNTs with covalent surface modification show stronger interfacial interactions with selected polymer matrices, which leads to greater improvement of mechanical properties in comparison to that achieved with non-covalent treatments.\textsuperscript{1}

Using POSS as a dispersant for CNTs has been reported by several groups. The first report was from Chen \textit{et al.}\textsuperscript{7} Aminopropylisooctyl POSS was covalently attached to the surface of COOH-functionalized multi-walled CNTs through reaction to form an amide linkage. The CNT-g-POSS was mixed with poly(L-lactide) (PLLA) by both solution blending and melt compounding. Uniform dispersion of CNT-g-POSS and enhanced mechanical properties of PLLA/CNT-g-POSS were observed. This was
attributed to grafted POSS disruption of CNT aggregates and increase in interaction with the PLLA matrix. In their follow-up work, the authors reported that PLLA/CNT-g-POSS composites yielded higher conductivity and electromagnetic interference (EMI) shielding effectiveness in comparison to composites formed with unmodified CNTs. The electric property enhancement was also ascribed to improved CNT dispersion. Zhang et al. prepared aminopropylisobutyl POSS grafted CNTs following a similar synthetic approach. The optical absorbance and scattering behavior of the CNT-g-POSS materials was measured, and the authors concluded that improved non-linear optical limiting performance was achieved. The wide selection of commercially available POSS products makes it possible to use different methods for CNT-g-POSS synthesis. Yadav et al. reported the preparation of MWNT modified with POSS using click chemistry. In this case, alkyne-functionalized CNTs were successfully reacted with epoxycyclohexylisobutyl POSS with a yield of 75-80%.

In the previously reported CNT-g-POSS studies, only a single type of POSS molecule was evaluated. To our knowledge, the effect of POSS structure and functionality on CNT dispersion and nanocomposite performance has yet to be reported. A fundamental understanding of these questions is of great importance in determining the ultimate capabilities of POSS molecules as CNT dispersants. In this study, three types of POSS molecules and one organosilane are used to modify the surface of CNTs. The CNT-g-POSS and CNT-g-silane synthesis and characterization are described. Dispersion and properties of the composite materials will be discussed in subsequent chapters.
Experimental

Materials

The CNTs used in this project are industrial grade multi-walled carbon nanotubes (>90 wt%) from CheapTube Inc. prepared by the chemical vapor deposition method. The outer diameter of the tubes is 10~30 nm, and the aspect ratio is around 1000. APIB, AEAPIB, and APIO were kindly donated by Hybrid Plastic Inc., and are used as received. APTS was purchased from Gelest Inc. and used as received. All reagents and solvents were purchased from Fisher and used without further purification.

Synthesis of CNT-COOH

CNT-g-POSS was prepared by a modified acid oxidation method as reported in the literature.9 First, CNT-COOH was prepared by oxidizing 5 g of neat CNTs with a mixture of 120 ml H₂SO₄/HNO₃=3/1 (v/v). The mixture was sonicated for 30 min at 40 ºC, refluxed at 100 ºC for 2 hours, and then poured into a 2 L mixture of DI water and methanol (v/v=1/1) with stirring. After the suspension was cooled overnight, the CNT-COOH was vacuum filtered through a 0.4 μm polycarbonate filter, and washed with DI water until the pH of the filtrate reached 7. The filter cake was vacuum dried at 60 ºC overnight. The dried powder was ground using a mortar and pestle, and further dried in vacuum at 80 ºC for another 2 days. 3.15 g (yield 63%) of CNT-COOH was generated after purification.

Synthesis of CNT-COCl

1 g CNT-COOH was suspended in anhydrous THF with 20 ml of thionyl chloride. The mixture was first sonicated at 40 ºC for 30 min before the reaction. One droplet of
DMF was added as catalyst. The suspension was stirred and refluxed at 80 ºC for 24 hours to ensure full reaction. Excess thionyl chloride was removed by vacuum distillation.

*Synthesis of CNT-g-POSS*

Immediately after its purification, CNT-COCl was transferred into a three neck round bottom flask. 100 ml THF was added. The suspension was again sonicated at 40 ºC for 30 min. In the meantime, 3 g of POSS and 1 ml of TEA were dissolved in 10 ml of THF in a scintillation vial. POSS and TEA were mixed with CNT-COCl slowly under N₂ atmosphere. The reactor was then immersed in an oil bath at 70 ºC with N₂ bubbling for 48 hours. The CNT-g-POSS was precipitated from THF in a large amount of methanol and then filtered at least 3 times for purification. A 0.22 μm nylon membrane was used for vacuum filtration. The filter cake was dried for 6 hours, ground and dried in vacuum for another 2 days at 60 ºC. By using this method, 1.30 g of CNT-g-APIB, 1.32 g of CNT-g-AEAPIB, 1.28 g of CNT-g-APIO and 1.20 g of CNT-g-APTS were generated individually.

*MD Simulation*

MD simulation was carried out using the commercial software Material Studio 5.5 developed by Accelrys Inc. The condensed phase optimization molecular potentials for atomistic simulation studies (COMPOSS) module was used to conduct force-field computations. COMPASS is a parameterized, tested, and validated *ab initio* force field, which enables an accurate prediction of various gas-phase and condensed-phase properties of most of the common organic and inorganic materials. The energy of the POSS molecules was minimized by Discover smart minimize modules.
**TGA**

TGA was performed on a TA Instrument TGA Q50 using temperature gradients of 10°C/min. Samples were equilibrated at 50 ºC for 5 min, and then ramped from 50 ºC to 800ºC at the speed of 10 ºC/min in a platinum pan with constant nitrogen flow of 40 ml/min.

**Raman Spectroscopy**

Raman spectra were obtained with a Thermo DXR confocal laser Raman microscope using a 532 nm laser as the excitation source. The laser power was set at 1 mW. The spectra were measured in backscattering configuration with a triple monochromator at intervals of 1 cm⁻¹. The spatial resolution of the microscope was approximately 1 μm. The spectra were processed by OMNIC software.

**ATR -IR**

ATR-IR spectra were collected using a Bio-Rad FTS-6000 FT-IR single-beam spectrometer set at a 4 cm⁻¹ resolution equipped with DTGS detector and a 45° face angle Ge crystal. Each spectrum represents 200 co-added scans ratioed against a reference spectrum obtained by recording 200 co-added scans of an empty ATR cell.

**TEM**

Transmission electron microscopy measurements were conducted using a Zeiss 900 electron microscope at an accelerating voltage of 60 kV. The specimens were prepared by placing a droplet of sonicated CNT suspension in THF on a carbon-coated copper grid followed by solvent evaporation at 25 ºC overnight.
Atomic Force Microscopy (AFM)

Atomic force microscopy characterization was conducted by a Dimension ICON AFM from Bruker (Santa Barbara, CA) using ScanAsyst Air technology. Height and inphase images were taken with a ScanAsyst probe in air in a temperature of 22 °C and humidity of 40-45 % controlled room. The morphology of CNT samples was studied on 2 μm x 2 μm scan areas with an image resolution of 512 x 512 pixels at a scan rate of 0.5 Hz. Multiple areas were imaged and figures show representative morphology. Samples for AFM study were prepared by spin coating 0.1 wt% CNT suspension in THF on a clean mica surface right after 5 min sonication.

Results and Discussion

POSS Structure Analysis

The structures of the POSS and the organosilane used in this project are shown in Figure 10. MD simulation was used to estimate the differences in POSS structural parameters (Figure 11, 12 and Table 1). The rigid Si-O core diameter is estimated to be 0.53 nm, which is the same for APIB, AEAPIB and APIO. The “R length” parameter describes the size of the hydrocarbon substituent groups on the POSS and silane molecules. The isobutyl substituents of APIB and AEAPIB and the trimethylsiloxy subsituents of the APTS are estimated to have similar lengths. The slightly lower estimate for the AEAPIB isobutyl groups may originate from the asymmetric structure of this molecule. The isooctyl subtiutents of the APIO POSS molecule, because they have twice the number of carbon atoms, have a substantially greater length. The “NH₂ arm length” parameter is an estimate of the length of the amine-containing substituent. It allows comparison of the accessibility of the reactive amine group and the distance
between the POSS cage and the functionalized CNT wall. APIB, APIO and APTS have similar estimated NH₂ arm lengths (three carbon atoms and one nitrogen atom in the arm), while that of AEAPIB (five carbon and two nitrogen atoms in the arm) is estimated to be almost twice as long as the others. Finally, the “diagonal length” parameter describes the maximum dimension of the molecules. The three POSS molecules are estimated to have similar diagonal lengths, but the APTS molecule is approximately one half the size of the others. The differences in the estimated structural parameters for these four molecules allow determination of the individual effects of overall size, length of the spacer group attached to the CNT, and size and type of hydrocarbon substituent on the grafting and dispersion efficiency of the modified CNT.

Figure 10. Chemical structures of POSS and silane used in this project.

Figure 11. Fully relaxed 3D MD structures of (A) APIB, (B) AEAPIB, (C) APIO and (D) APTS molecules (red for O, yellow for Si, grey for C, white for H and blue for N).
Figure 12. Definition of structural parameters of POSS estimated by MD simulation.

Table 1

Structure Parameters of POSS and APTS Measured in MD Simulation (in nm)

<table>
<thead>
<tr>
<th>Grafted Molecule</th>
<th>Core size</th>
<th>R length</th>
<th>NH₂ arm Length</th>
<th>Diagonal Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>APIB</td>
<td>0.53</td>
<td>0.42</td>
<td>0.53</td>
<td>1.5</td>
</tr>
<tr>
<td>AEAPIB</td>
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<td>0.35</td>
<td>0.90</td>
<td>1.8</td>
</tr>
<tr>
<td>APIO</td>
<td>0.53</td>
<td>0.66</td>
<td>0.53</td>
<td>1.7</td>
</tr>
<tr>
<td>APTS</td>
<td>---</td>
<td>0.37</td>
<td>0.48</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Synthesis of CNT-g-POSS

To achieve a more permanent miscibility enhancement of CNTs with solvents and polymers, covalent surface modification was chosen in this study. The modification procedure is shown schematically in Figure 13 and described in detail in the experimental section. In order to promote homogeneous surface functionalization, CNT solvent suspensions were sonicated before each reaction to promote exfoliation of CNT bundles,
and suspensions were refluxed with excess concentration of reacting reagents for extended periods of time.

**Figure 13.** Surface modification of CNT with POSS through formation of amide linkage.

**TGA and Grafting Density Calculation**

The thermal properties of POSS were examined by TGA. As shown in Figure 14, the total weight loss of all POSS molecules and the silane was close to 100 wt%, far exceeding their organic weight fraction. This is attributed to the sublimation of POSS molecules under nitrogen atmosphere.\(^{11,12}\) Both aminoisobutyl POSS molecules (APIB and AEAPIB) showed a \(T_{\text{max}}\) value of 265 °C, which was in agreement with the reported octaisobutyl POSS value.\(^{11}\) AEAPIB presented a lower \(T_o\) at 212 °C and a small second stage mass loss above 280 °C, which may be related to its longer amino substituent group.\(^{13}\) APIO exhibited the highest \(T_o\) and \(T_{\text{max}}\), and also a two stage weight loss,
attributed to the longer R group. Compared to POSS, APTS showed low thermal stability with a $T_0$ at 88 °C and $T_{max}$ at 143 °C. This indicates that the higher thermal stability of POSS is related to the Si-O core.

Figure 14. (A) TGA and (B) DTGA curves of APIB, AEAPIB, APIO and APTS in N$_2$ atmosphere. $T_0$, the temperature for 5% wt weight loss, is marked for each TGA curve in (A). $T_{max}$, the temperature for the maximum weight loss rate, is marked in each DTGA curve in (B).
TGA traces for neat and modified CNTs are shown in Figure 15. Neat CNT was thermally stable to 650 ºC, after which 5 wt% mass loss caused by defect sites and impurities was observed. After acid treatment, carboxylic acid groups along with more defect sites were evenly generated on the CNT surface. A gradual weight loss over the entire heating range was observed for CNT-COOH. All CNT-g-POSS exhibited a rapid weight loss between 100 ºC and 550 ºC, followed by a slow weight loss up to 800 ºC. The rapid weight loss is attributed to a combination of amide bond breakage and POSS molecule sublimation. The curve for CNT-g-APTS is similar to that of CNT-COOH because it does not involve the POSS cage sublimation.

Figure 15. TGA curves of CNT, CNT-COOH, CNT-g-POSS, and CNT-g-silane in N₂ atmosphere.
Table 2

*POSS Grafting Density Calculation of CNT-g-POSS and CNT-g-silane Based on TGA*

<table>
<thead>
<tr>
<th>Sample</th>
<th>MW of POSS (g/mole)</th>
<th>Weight Loss at 700 ºC</th>
<th>POSS Grafted (mole x10^4 per wt% g of CNT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>2.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT-COOH</td>
<td>12.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT-g-APIB</td>
<td>874.58</td>
<td>32.80</td>
<td>20.69</td>
</tr>
<tr>
<td>CNT-g-AEAPIB</td>
<td>917.65</td>
<td>33.97</td>
<td>21.86</td>
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<tr>
<td>CNT-g-APIO</td>
<td>1267.32</td>
<td>26.06</td>
<td>13.95</td>
</tr>
<tr>
<td>CNT-g-APTS</td>
<td>353.75</td>
<td>23.48</td>
<td>11.37</td>
</tr>
</tbody>
</table>

Figure 15 shows that all the POSS and silane molecules have complete weight loss at temperatures above 600 ºC, while CNT is shown to be thermally stable to 650 ºC in Figure 15. The difference between CNT and POSS TGA weight loss at high temperature thus can be used to estimate the grafting density of POSS. Assuming that the defect sites of CNT-g-POSS are the same as those present in CNT-COOH and that the POSS residue is totally sublimed at 700 ºC, the wt% of POSS grafted on CNT surface was calculated by subtracting the weight loss of CNT-g-POSS from the weight loss of CNT-COOH at 700 ºC, as listed in (Table 2). A slightly higher percentage of AEAPIB than APIB was estimated to be grafted to the CNTs. This can be explained by the higher
accessibility of the primary amine group in AEAPIB (due to its longer amine arm length) than that of the APIB. APIO showed lower CNT grafting density, presumably due to steric hindrance of the bulky isoctyl R groups to the amidation reaction. AEAPIB gave the highest weight grafting density and APTS gave the lowest, while APTS gave the highest molar percentage grafting and APIO gave the lowest. These results indicate that the size of the molecule and the bulkiness of the R substituent group affect the grafting efficiency to a greater degree than does the length of the reactive arm.

Covalent Modification Characterization

Raman spectroscopy has been used as a tool to characterize CNT functionalization.14-16 As shown in Figure 16, neat CNT, CNT-COOH and CNT-g-POSS all have two characteristic bands at 1342 cm\(^{-1}\) (D-band) and 1575 cm\(^{-1}\) (G-band). The D band is attributed to a disordered graphite structure or \(sp^3\) hybridized carbons of CNT, whereas the G band corresponds to a splitting of the E2g stretching mode of graphite, which reflects the structural intensity of the \(sp^2\)-hybridized carbon atoms.16 The increase in the band intensity ratio \(I_D/I_G\) of functionalized CNT reflects the number of defect sites present in the CNT, indicating covalent functionalization. For neat CNT, the \(I_D/I_G\) value is 0.88. For all 5 functionalized CNTs, the \(I_D/I_G\) value is above 1. (Figure 16). In addition, a small shoulder band at 1610 cm\(^{-1}\) is observed for all modified CNTs, while it is less apparent for the neat CNT. This peak is reported to be related to the \(sp^2\) hybridization of carbon and is used as evidence of the disruption of the aromatic system of p electrons by the grafted molecules.8
Figure 16. Raman spectra of CNT, CNT-COOH, CNT-g-POSS, and CNT-g-silane.

Figure 17. ATR-FTIR spectra of CNT, CNT-COOH, CNT-g-POSS, and CNT-g-silane.
IR spectroscopy was used as a second technique to confirm the covalent grafting of POSS molecules and the formation of the amide linkage. IR characterization is especially difficult for CNTs due to their high absorbance at all wavelengths. A Ge crystal was used due to its exceptionally high refractive index (n=4), which makes it ideal for the measurement of dark materials.\textsuperscript{17}

There are no obvious absorbances for the untreated CNTs (Figure 17). In the spectrum of CNT-COOH, three peaks are observed at 1708, 1572, and 1192 cm\textsuperscript{-1}. The peak at 1708 cm\textsuperscript{-1} is attributed to the antisymmetric stretch of the C=O in hydrogen-bonded COOH dimers. This is observed at lower frequency than the C=O band of aliphatic carboxylic acids (1740 cm\textsuperscript{-1}) due to interaction with the electron-donating aromatic carbons on the CNT wall. The band at 1572 cm\textsuperscript{-1} exists in all IR spectra of chemically modified CNTs, indicating that it is produced by functional groups that do not participate in the amidation reaction. It may be attributed to the C-O-O stretch of aromatic enol formed by ketones and hydroxyl groups during the complex oxidation. The third broad band at 1192 cm\textsuperscript{-1} is attributed to the out-of-phase stretch of the aromatic –OH.\textsuperscript{18} In conclusion, the acidification procedure of CNTs generated a mixture of carboxylic acid, carbonyl and hydroxyl functional groups on the CNT surface.

Amides usually display three strong absorbances in IR spectra: amide I at 1680-1640 cm\textsuperscript{-1} attributed to C=O stretch, amide II at 1550-1460 cm\textsuperscript{-1} attributed to C-N stretch and C-N-H in-plane bend in the stretch-bend mode, and amide III at 1310-1250 cm\textsuperscript{-1} for the stretch-open mode absorption.\textsuperscript{18} Both Amide II and amide III bands are clearly observed in spectra of CNT-g-POSS and CNT-g-APTS, but instead of the reported amide I band, a different band at 1740 cm\textsuperscript{-1} appeared, which usually attributed to the C=O
absorbance in a carbamate or imide. Thus the IR analysis confirms the formation of the -
C(=O)-NH- bond, but how the C=O is connected to the surface of CNT is uncertain. This
uncertainty has been attributed to the complex oxidation chemistry during the
acidification of CNTs. More information could be obtained with X-ray photoelectron
spectroscopy (XPS) characterization.

**Morphology Characterization**

TEM images of the neat and modified CNTs are shown in Figure 18. The
unmodified CNT wall (Figure 18A) appears smooth and clean with nothing attached to
the surface. Dark spots observed within the tube are attributed to residual nickel catalyst
used during CNT synthesis. The CNT-COOH modified tubes (Figure 18B) appear to
have thicker walls with fuzzy edges, which can be explained by the partial destruction of
the surface structure and the generation of –COOH and -OH functionality. After
covalently grafting of POSS (Figure 18C, D, E and F), the modified CNTs appear stained
with an extra phase on the surface attributed to the grafted molecules. This assumption
appears reasonable on consideration of the dimensions of the CNTs (d=30-50 nm) and
the grafted molecules (0.3-1.5 nm).
Figure 18. TEM images of (A) neat CNT, (B) CNT-COOH, (C) CNT-g-APIB, (D) CNT-g-AEAPIB, (E) CNT-g-APIO, and (F) CNT-g-APTS.

CNT-g-APIB and CNT-g-AEAPIB systems (Figure 18C and D) consist primarily of condensed black spherical features. The CNT-g-APIO modified system (Figure 18E), on the other hand, shows both condensed black spherical features and a diffuse grey irregular features similar to structures generally reported for polymer modified CNTs. Si atoms have higher electron density than carbon, so POSS molecules generally appear darker than organic species in TEM images. In this case, the grey features are attributed
to the bulky isooctyl substituent groups of APIO. The CNT-g-APTS system (Figure 18F) lacks the dark spherical features on the CNT surface, and displays only the diffuse structures attributed to organic surface modification. Since the APTS lacks the condensed Si-O cage structure, there is insufficient electron density to produce the dark features observed in the POSS modified systems.

AFM was used as an alternative technique to characterize the surface morphology of the CNTs. The AFM height image of the unmodified CNT is shown in Figure 19A.

Figure 19. AFM height images of (A) CNT, (B) CNT-COOH, (C) CNT-g-AEAPIB, and (D) CNT-g-APIO.
The surface appears smooth and regular, the diameter of the tube is approximately 20 – 30 nm, and tube lengths are generally greater than one micron. Acidification resulted in shorter tubes, but the diameter was not significantly changed (Figure 19B). After reaction with POSS (Figure 19C and D), nodule-like features, attributed to grafted POSS molecules, are observed on the periphery and more prominently on the ends of CNTs. The higher concentration of grafted molecules at the tube ends occurs because these are the most reactive sites during CNT functionalization. The diameters of the POSS grafted CNTs appear larger than those of the neat and COOH-modified systems. This may be attributed to the grafting of POSS molecules and the folding of CNT-g-POSS during solvent evaporation in AFM sample preparation.

Conclusions

Industrial grade multi-walled CNTs were covalently modified with three amino POSS molecules and one amino silane. Raman and ATR-IR characterization demonstrated covalent bond formation of the grafted molecules with carboxylic acid groups on the CNT surface. Grafting density calculated from TGA analysis indicates that the size of the hydrocarbon substituent groups on the POSS molecule have a greater impact on the CNT grafting efficiency than the length of the amine spacer group. Neat CNT, the CNT-g-POSS systems, and CNT-g-silane showed different surface morphologies in TEM analysis. The different morphologies are ascribed to the structural differences of the grafted POSS and silane molecules. Nanosized nodule-like features were observed on the surface of CNT-g-POSS in AFM images. The dispersion of the modified CNTs and the properties of their polymeric composites will be discussed in subsequent chapters.
Acknowledgments

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REFERENCES


CHAPTER IV
DISPERSION OF POSS MODIFIED CARBON NANOTUBES IN SOLVENTS AND
POLYURETHANE FILMS

Abstract

The dispersion behaviors of CNT-g-POSS and CNT-g-silane whose synthesis was
described in the previous chapter were studied and compared. Solubility parameters of
POSS and the silane were calculated by both a group contribution method and a MD
simulation method. Dispersion of CNT-g-POSS and CNT-g-silane was first tested in
three solvents, including THF, CHCl₃ and hexane, by observation and UV-vis
microscopy. After that, the miscibility of CNT-g-POSS and CNT-g-silane with a polymer
matrix (TPU) was examined by UV-vis microscopy and TEM. Finally, the dispersion of
CNT-g-POSS and CNT-g-silane within a PU coating (HDI+PPG) was studied using
TEM, TGA and rheology measurements. It was found that the dispersion level of CNT-g-
POSS is highly related to the chemical structure of the POSS molecule and the surface
morphology of the grafted nanotube.

Introduction

Dispersion of CNTs is a challenge. As with other nanomaterials, the difficulty of
CNT dispersion arises from their nano-sized dimensions. As the surface area of the
material increases, the attractive force between the aggregates increases as well. But in
comparison to other nanomaterials, the special topological structure of CNTs adds extra
difficulties in their dispersion. CNTs aggregate in two forms: entanglements and bundles.
The formation of entanglements mostly results from the high aspect ratio and high
flexibility features of CNTs.¹ Breaking entanglements leads to a high entropy decrease,
and thus it is neither thermodynamically nor kinetically favorable. The best way to prevent CNTs from entangling is to align them properly during their preparation.\(^2\) If the CNTs obtained are already entangled, a “cutting” process is necessary to disentangle them. A mixture of strong acids and oxidative agents are commonly used for this purpose.\(^3,\,4\)

The bundles assembled by CNTs contain hundreds of close-packed tubes tightly bound by van der Waals interactions. In the calculation reported by Girifalco et al,\(^5\) the van der Waals interaction is estimated for a one nm diameter tube at the graphite separation distance (0.35 nm) to be 0.36 eV/Å, which is equivalent to an energy of \(5.8 \times 10^{-16}\) J to separate two tubes that are 1 μm long. A calculation based on classical mechanics estimated the energy required to separate two 10 nm diameter MWNTs is calculated to be roughly \(1/3\) of the force to separate two SWNTs.\(^6\) Some of the most widely used methods for debundling CNTs include sonication,\(^7,\,8\) high shear mixing,\(^9,\,10\) the use of dispersants,\(^11,\,12\) and surface modification\(^13\). Because the force required during the debundling process is comparable to the modulus of the CNT itself, destruction of the CNT structure is inevitable during this process.\(^14\)

Another challenge in evaluating the dispersion of CNTs stems from the lack of efficient characterization methods for these nanoscale structures. For the evaluation of dispersion of CNTs in solvents, most early studies employed a combination of photographs and microscopy images. Using these methods it is difficult to discern if the CNTs are dispersed as individual tubes or as bundles. At the meantime, dispersion levels of CNTs can be indirectly estimated by determining mechanical, electrical, and/or rheological properties of polymer/CNT nanocomposites\(^15,\,16\) It is assumed that better
dispersion leads to enhancement of nanocomposite properties, however care should be taken in drawing conclusions on the degree of CNT dispersion based merely on the measurement of CNT/polymer nanocomposite properties because other factors may also affect nanocomposite performance. These include CNT alignment, interfacial interaction of the CNT with the polymer matrix, and changes in crystallinity levels in semi-crystalline polymer systems.\textsuperscript{15, 17 18}

Solubility parameter calculation is used widely for prediction of the miscibility of materials.\textsuperscript{19} For small molecules, solubility parameters are estimated by experiments designed to measure cohesive energy density (CED), which is the increase in internal energy per mole of substance if all the intermolecular forces are eliminated.\textsuperscript{20} CED values can be obtained by measuring the heat of evaporation. Hildebrand define the value of solubility parameters as

\[ \delta = \sqrt{\text{CED}} \]  

(1)

Hildebrand solubility parameters take account all forces between structure units. Hansen further divided CED into three parts: CED contributed by dispersion forces, polar forces and hydrogen bonding.\textsuperscript{21} The corresponding equation for Hansen solubility parameter is

\[ \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]  

(2)

Where \( \delta_d \), \( \delta_p \), and \( \delta_h \) are the dispersive, polar and hydrogen bonding solubility parameters. Phase diagrams can be drawn from Hansen solubility parameters and used to precisely predict the miscibility of two components.

However, polymers and inorganic fillers do not evaporate, and therefore their solubility parameter can only be estimated theoretically. Several group contribution
methods using different additive functions have been developed to calculate solubility parameters.\textsuperscript{20} These methods can be used for both Hildebrand and Hansen solubility parameter prediction.

In this chapter, the dispersion of previously synthesized CNT-g-POSS and CNT-g-silane in solvents and a polymer matrix was evaluated by multiple morphological and property evaluation techniques. The dispersion behavior of modified CNTs was correlated to the structures and the solubility parameters of the grafted molecules. Knowledge gained from these systems will benefit POSS dispersant product design in the future, and can be used to compare performance with other functionalized CNTs.

Experimental

Materials

The synthesis of CNT-g-POSS and CNT-g-silane was described in Chapter III. An aromatic polyether based TPU, Estane 2103-80AE, was used as a model polymer matrix. It was donated by Lubrizol Corporation. Desmodur 3600 and Arcol PPG1000 used for the PU coating formulation were donated by Invista Inc. and Bayer Corporation. All solvents and reagents were purchased from Fisher and used without further purification.

Solubility Parameter Calculation

Solubility parameter ($\delta$) calculation was carried out by two methods: a group contribution method and a MD simulation method. In the first method, solubility parameters ($\delta$) based on group molar attraction constant ($F$) were calculated by the structural formula and density ($\rho$) of the material using equation 3.

\[
\delta_{Hoy} = (\rho \sum n_i F_i)M
\]  

(3)
Here $\sum n_i F_i$ is the sum of molar attraction constant in the molecule and $M$ is the molecular weight of the material. $F_i$ values were estimated from Hoy’s table of group molar attraction constants.\textsuperscript{22} The value of Si-O (278 (cal.cm\textsuperscript{3}/mol)$^{1/2}$) is used as calculated by Misra \textit{et al.}\textsuperscript{23}

Table 3

\textit{Successive Procedure for AC Energy Minimization}

<table>
<thead>
<tr>
<th>Steps</th>
<th>Ensemble</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NVT</td>
<td>650</td>
<td>--</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>NPT</td>
<td>650</td>
<td>100</td>
<td>50</td>
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<tr>
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<td>50</td>
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<tr>
<td>4</td>
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</tr>
<tr>
<td>7</td>
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<td>--</td>
<td>50</td>
</tr>
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<td>8</td>
<td>NPT</td>
<td>298</td>
<td>0.1</td>
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</table>

MD simulation calculation of solubility parameters was carried out using commercial software Material Studio 5.5 produced by Accelrys Inc. The structures of the molecules were drawn using the Visualizer module and then energy minimized to a maximum derivative of less than 0.001 with the Discover Minimization module. The Amorphous Cell (AC) module was then used to create cells of each POSS molecule (5 POSS molecules were added to each cell) and each cell was energy minimized by a series of alternating NVT/NPT runs as listed in Table 3 using Anderson thermostat. (NVT is the
Canonical ensemble, in which moles, volume and temperature are conserved. NPT is the Isothermal-isobaric ensemble, in which moles, pressure, and temperature are conserved.)\textsuperscript{24} Finally the Forcite module was used to calculate the CED and the Hildebrand solubility parameter of each POSS molecules at atmospheric pressure and ambient temperature.

Composites Preparation

TPU/CNT composites were prepared by a solution mixing approach. 10 wt% solution of TPU in DMF was prepared first and was sit at room temperature for a week. CNT or modified CNT was first dispersed in 10 ml THF assisted with 20 min sonication. After that, the CNT dispersion was added to 50 ml of the TPU solution. The mixture was stirred with a mechanical stir rod for 1 hour, and immediately poured onto a polypropylene tray. The solvent was evaporated gradually at 60 °C for 48 hours, and vacuum dried for another 6 hours. 0.1 wt% CNT loading level samples were used for optical microscopy study and UV-vis measurement. Composites with 1 wt% CNT loading level were used in cryo-microtome sample preparation for TEM observation.

PU coatings with CNT or CNT-g-APIB were prepared by an \textit{in situ} polymerization method. Desmodur 3600 and Arcol PPG 1000 from Bayer were used as the polyisocyanate and polyol for PU formulation. The stoichiometric ratio of isocyanate group to hydroxyl group was set to be 1.05:1 to compensate for the side reactions of isocyanate groups with moisture. 300 ppm of dibutyltin dilaurate (DBTL) was used as catalyst. 100 mg CNT or modified CNT was first dispersed in 2 ml of THF, sonicated for 10 min and then physically mixed with polyol by a FlackTec speed mixer for 1 min at 1700 rpm. After that, polyisocyanate was added and the whole mixture was mixed again
for another 2 min. After sitting still for 10 min, the mixture was poured onto a 90 mm glass Petri dish, and cured at 25 °C for 48 hours.

**Bulk Dispersion Measurement**

Bulk dispersion of CNT was firstly observed with the naked eye. Pictures of observation were taken with an Apple iPhone 4 camera. A Perkin Elmer Lambda 35 UV-Vis spectrometer was used to semi-quantify the dispersion of CNTs in both solvents and films. For the solvent study, 0.0025 wt% CNT or modified CNT suspensions were prepared by diluting a sonicated 0.05 wt% CNT or modified CNT suspension in solvent and sit at room temperature for 1 hour before measurement. Neat solvents were used as blanks. For the study of CNT dispersion in polymer, TPU films with similar thickness were cut to the size of the cell window of the UV-vis spectrometer and directly used to measure the transmission. In this case, a neat TPU film was used as the blank.

**Micro Level Dispersion Measurement**

A Keyence VHX-600 digital microscopy system was used to observe the dispersion of CNTs in TPU at the micron level. Nano level dispersion measurement was conducted using a TEM JEOL JEM-2100 at an accelerating voltage of 200kV. Cryo-microtome was performed for TEM sample preparation. Samples were cut into ultrathin (~100 nm), trapezoidal-shaped sections with a Porter-Blum MT-2B ultramicrotome (Ivan Sorvall, Inc.), using a single crystal diamond knife (Delaware Diamond Knives, Inc.) at -70 °C. Sections were collected on a Formvar-coated, 400 mesh copper TEM grid (Electron Microscopy Sciences) and imaged without staining.
TGA

TGA was performed on a TA Instruments TGA Q50 using temperature gradients of 10 °C/min. Samples were equilibrated at 50 °C for 5 min, and then ramped from 50 °C to 800 °C at the speed of 10 °C/min in a platinum pan with constant nitrogen flow of 40 ml/min.

Rheology Measurement

The apparent viscosity of the mixtures of polyol with CNT and CNT-g-APIB was measured using a TA AR-G2 rheometer as a function of shear rate. Initially, the mixtures were sonicated for 30 min, followed by 48 hours stirring to ensure that the mixtures were homogenous. Then, the apparent viscosity was measured with a cone (40 mm diameter, 24 micron truncation) and plate (40 mm diameter) geometry using a steady state flow procedure at 40 °C

Results and Discussion

Solubility Parameter Calculation

The dispersion of POSS in solvents and polymers is selective, and it is highly related to the POSS structure. A few calculations of POSS solubility parameters using either a group contribution method or a MD simulation method have appeared in the literature. In our work, both methods were used to calculate the solubility parameters of POSS and the silane. (Table 4) Molar attraction constant values reported by Hoy were used, so solubility parameters obtained by group contributions methods are termed \( \delta_{\text{Hoy}} \). Because there are differing opinions in the literature on the contribution of the POSS cage itself on solubility, solubility parameters were calculated both for the core and corona and for the corona alone. Using all three methods, the solubility parameter of
AEAPIB was calculated to be the highest and the one for APIO was the lowest. This is explained by the high level of polar interactions in the secondary amine group in AEAPIB contributing to a higher CED, while the tertiary and quaternary carbons in APIO hydrocarbon substituents yield a lower CED. For all three POSS molecules, the \( \delta_{\text{Hoy}} \) calculated without the cage is smaller than \( \delta_{\text{Hoy}} \) calculated with the cage, because lower attraction energy is estimated. One drawback of the group contribution method is that the geometry of molecules is not taken into consideration. This is particularly important for POSS calculations because of the high degree of symmetry in these molecules. The MD simulation includes consideration of the POSS structural features, as it calculates all interactions between bonded atoms in the simulated molecule. Interestingly, the calculated \( \delta_{\text{MD}} \) values of POSS lie between those calculated using the Hoy method with and without the cage.

Table 4

*Hildebrand Solubility Parameter Calculation of POSS and Silane (in (J/cm\(^3\))\(^{1/2}\) Used in This Project*

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta_{\text{Hoy}} ) (with cage)</th>
<th>( \delta_{\text{Hoy}} ) (without cage)</th>
<th>( \delta_{\text{MD}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>APIB</td>
<td>18.7</td>
<td>11.4</td>
<td>13.4</td>
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<tr>
<td>AEAPIB</td>
<td>19.1</td>
<td>12.1</td>
<td>14.3</td>
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<tr>
<td>APIO</td>
<td>16.1</td>
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</tr>
<tr>
<td>APTS</td>
<td>16.5</td>
<td></td>
<td>14.2</td>
</tr>
</tbody>
</table>
Table 5

Hansen Solubility Parameters of Good and Poor Solvents of POSS Molecules Used in This Project ((J/cm³)¹/₂)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ_d</th>
<th>δ_p</th>
<th>δ_h</th>
<th>δ_t</th>
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<tr>
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<td>Hexane</td>
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<td>13.7</td>
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<td>18.7</td>
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<td>MeCN</td>
<td>13.0</td>
<td>9.8</td>
<td>11.0</td>
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</tr>
</tbody>
</table>

Note. (Values were obtained from Hansen Solubility Parameters: a user’s handbook).¹⁹

Hanson solubility parameters predict the solubility behavior of a compound more accurately than do those calculated by the Hildebrand method, because they take into account polar, dispersive and hydrogen bonding interactions in the molecules. But Hanson solubility parameters were not calculated for POSS molecules used here due to lack of reported molar attraction constant values of certain functional groups. Guenthner et al measured the Hansen solubility parameters of 5 POSS molecules using 45 test solvents.²⁹ Unfortunately, our POSS molecules were not included in his study. Using experimental information for good solvents and poor solvents of POSS, we roughly estimated the δ_p, δ_h, and δ_t values by the rule of like dissolves like. THF and CHCl₃ were proved to be good solvents for all three POSS and the silane molecules, hexane is a moderate solvent, and MeOH and MeCN are poor solvents for all four compounds. The Hansen solubility parameters of these solvents are listed in Table 5. It is thus estimated
that the Hansen solubility parameters of the POSS molecules used are similar to those of THF and CHCl₃, which are primarily determined by dispersive and polar interactions, with little contribution of hydrogen bonding.

Dispersion of CNT-g-POSS in Solvents

In addition to the solubility parameters of the grafted POSS or silane molecules, the surface morphology of the modified CNTs is also expected to affect their dispersion level. Figure 20 provides a schematic description of the proposed surface structures of the modified CNTs. The MD simulation estimations in chapter III indicate that CNT-g-APIB, CNT-g-APIO and CNT-g-APTS have the same spacer lengths between the CNT wall and the POSS cage or the silane molecule. The spacer length for CNT-g-AEAPIB molecule is twice as long. The CNT-g-APIO system differs in that it has longer and bulkier aliphatic substituent groups that extend farther into the surrounding solvent or polymer matrix, providing greater opportunity for interaction with the matrix. The CNT-g-APTS system has no POSS cage, and thus has a lower density of organic substituents.

Figure 20. Proposed surface structures of (A) CNT-g-APIB (B) CNT-g-AEAPIB (C) CNT-g-APIO, and (D) CNT-g-APTS.
Photographs of neat and modified CNTs in THF are shown in Figure 21. Figures 21 A-E represent mixtures that were shaken by hand and allowed to settle for one hour. Figures 21 F-I represent mixtures that were sonicated for ten minutes and then allowed to settle for one week. The unmodified CNTs precipitated to the bottom of the vial immediately after mixing or sonication (Figure 21A). All modified CNTs show improved dispersion in THF. Before sonication, the dispersion level follows the order: CNT-g-APIB>CNT-g-AEAPIB>CNT-g-APIO>CNT-g-APTS. After sonication, they all appear to disperse homogenously in the solvent and remain stable for one month without noted phase separation.

Figure 21. 0.05wt% of (A) CNT, (B-D, F-H) CNT-g-POSS, and (E, I) CNT-g-silane suspensions in THF (B-E) before and (F-I) after sonication.

To better observe the dispersion of CNT-g-POSS after sonication, the 0.5 wt% suspensions were diluted 20 times to obtain translucent suspensions for transmission measurement. Theoretically, the dispersion levels of CNT-g-POSS suspensions at 0.5wt% and 0.0025wt% are not the same, because adding solvent pushes the equilibrium towards greater levels of dispersion. All suspensions were diluted to the same level, so the effect of the concentration change should be equivalent. Figure 22 shows photographs of the solutions and % transmission curves obtained by UV-vis spectroscopy. For solutions of
the same concentration, lower transmission indicates increased dispersion. Percent transmission for the CNT-g-APIB is approximately half that of the other modified CNTs, indicating significantly improved dispersion. Photographs of the other three systems show precipitate in the bottom of the vials further indicating the poor solubility of these modified CNTs. The dispersion order of these modified CNT suspensions is: CNT-g-APIB>CNT-g-APIO>CNT-g-APTS>CNT-g-AEAPIB.

Figure 22. Images (left) and UV-vis transmission curves (right) of 0.0025wt% of CNT, CNT-g-POSS, and CNT-g-silane in THF after sonication

Similar dispersion behaviors of modified CNTs were observed in CHCl₃ and in hexanes. (Figure 23 to Figure 26). The slightly difference in dispersion levels results from the solubility parameter difference of the three solvents. By comparing the UV-vis spectra of CNT-g-APIB in THF, CHCl₃ and hexane, it can be seen that THF is the best solvent and hexane is the worst solvent of those three. This indicates that the Hanson solubility parameters of the POSS used are most similar to the ones of THF (Table 5).
**Figure 23.** 0.05wt% of (A) CNT, (B-D, F-H) CNT-g-POSS, and (E, I) CNT-g-silane suspensions in CHCl₃ (B-E) before and (F-I) after sonication.

![Figure 23](image)

**Figure 24.** Images (left) and UV-vis transmission curves (right) of 0.0025wt% of CNT, CNT-g-POSS, and CNT-g-silane in CHCl₃ after sonication.

![Figure 24](image)

**Figure 25.** 0.05wt% of (A) CNT, (B-D, F-H) CNT-g-POSS, and (E, I) CNT-g-silane suspensions in hexane (B-E) before and (F-I) after sonication.

![Figure 25](image)
Figure 26. Images (left) and UV-vis transmission curves (right) of 0.0025 wt% of CNT, CNT-g-POSS, and CNT-g-silane in hexane after sonication.

Modified CNTs showed different miscibility in the three solvents used, but the orders of dispersion before and after sonication are the same. This indicates that the dispersion behavior of CNT-g-POSS molecules is less dependent on the solubility parameter and more related to the surface morphology. To explain this special correlation, a mechanism is proposed that is shown schematically in Figure 27.
In general, dispersion in solvent follows the order APIB>APIO>AEAPIB>APTS. The APIB has short, branched isobutyl hydrocarbon substituents that closely and evenly cover the CNT surface. These bulky R groups interfere with the van der Waals interactions that create CNT bundles. Thus in a good solvent for APIB, nanodispersion of the CNTs is achieved (Figure 27A). The AEAPIB molecules have a longer spacer group between the CNT wall and the POSS cage. With the AEAPIB grafting density of 20 wt% and the small size of the dangling POSS cage (diameter ~1nm), there are relatively large spaces of non-grafted CNT surfaces that can interact to form bundles. The AEAPIB system allows only microdispersion in solvents that is not disrupted with sonication (Figure 27B). The APIO molecule has long isooctyl hydrocarbon substituents that form entanglements prior to stirring or sonication. After sonication, these entanglements are

Figure 27. Proposed mechanism for dispersion behaviors in solvents of (A) CNT-g-APIB, (B) CNT-g-AEAPIB, and (D) CNT-g-APIO.
disrupted, solvent molecules penetrate the bundles, and nanodispersion of the CNTs is achieved (Figure 27C). The poorer dispersion of the APTS system is attributed to its overall lower density of hydrocarbon functional groups.

Dispersion of CNT-g-POSS in TPU

The TPU used in this project is an aromatic polyether based elastomer, which means it has aromatic groups and large amount of hydrogen bonding in its HS domains and aliphatic ether groups in its SS domains. The POSS and silane molecules used in this study have aliphatic R groups and are unmixable with solvents having strong hydrogen bonding (Table 5), so modified CNTs should prefer to interact with the SS domains, while neat CNT has the capability to interact with the hard segment of TPU due to π-π interaction.

Figure 28. Images (left) and UV-vis transmission curves (right) of TPU composites film with CNT, CNT-g-POSS, and CNT-g-silane at 0.1 wt% loading level.

The dispersion level of CNT-g-POSS was evaluated by UV-vis spectroscopy (Figure 28). The absorbance follows the same order as that demonstrated by CNT-g-
POSS in solvents: CNT-g-APIB>CNT-g-APIO>CNT-g-APTS>CNT-g-AEAPIB. This indicates that the dispersion provided by POSS has a greater relationship to the morphology of the grafted CNT surface than to the nature of the solvent or polymer matrix. Neat CNT demonstrated moderate dispersion in the TPU, but since it interacts with different domains of TPU, it is difficult to compare its overall dispersion with CNT-g-POSS simply through UV-vis spectroscopy analysis. Even though CNT-g-APTS has lower transmittance than that of CNT-g-AEAPIB, agglomerates of CNT can be clearly observed in the film (Figure 28). On the other hand, no apparent CNT agglomeration was observed by the naked eye in the three CNT-g-POSS films.

Figure 29. Optical microscopy images (×100 magnification) of TPU composites with 0.01 wt% of (A) CNT, (B) CNT-g-APIB, (C) CNT-g-AEAPIB, (D) CNT-g-APIO, and (E) CNT-g-APTS.

To better evaluate the CNT aggregation size at the micron level, optical microscopy was used to observe the TPU composite thin films (Figure 29). The result is
consistent with observation by the naked eye and UV-vis spectroscopy measurement. TPU composites of CNT and CNT-g-APTS display CNT clusters as large as 100 μm. TPU/CNT-g-AEAPIB composites show a small number of some clusters with diameter of 20 μm, and no obvious CNT clusters were observed in the other two TPU/CNT-g-POSS composites. In summary, CNT-g-POSS systems showed better dispersion than both CNT-g-APTS and neat CNT in TPU.

TEM was used to observe the dispersion of CNT-g-POSS at the nano level (Figure 30). Samples for TEM were prepared by cryo-microtoming. Higher loading level composites (1 wt%) were evaluated in order to increase the probability of finding CNT structures in the microtomed sections. In Figure 30 large CNT agglomerates and heterogeneous distribution of CNT were observed in TPU/CNT, TPU/CNT-g-APTS, and TPU/CNT-g-AEAPIB composites. TPU/CNT-g-APIB and TPU/CNT-g-APIO composites showed smaller CNT aggregate sizes. The results indicate that the dispersion of CNT-g-POSS in TPU at the nano level follows the same trends as those observed in solvents and in TPU in bulk.

Most of the previously reported studies of TPU/CNT composites used CNT-COOH modified systems, so a TPU/CNT-COOH sample was included as a control. From Figure 30B, it is noticed that CNT-COOH clearly shows better dispersion and alignment in TPU than all of CNT-g-POSS samples, indicating that a hydrogen-bonding, polar system provides better dispersion than the POSS systems we have chosen.
Figure 30. TEM images of TPU composites with (A) CNT, (B) CNT-COOH, (C) CNT-g-APIB, (D) CNT-g-AEAPIB, (E) CNT-g-APIO, and (F) CNT-g-APTS at 1wt% loading level.

Dispersion of CNT-g-POSS in PU coating

Adding CNT to a coating system enhance its anti-corrosion property, wear resistance properties, conductivity, and electromagnetic interference (EMI) shielding.30 In addition, POSS has been successfully used both as a dispersant and a processing aid for pigments in coating formulations.31 It is hoped that adding POSS will help with the dispersion of CNT and thus add advanced functions to existing coating systems.

A widely used 2K clear coat system was picked as a model system. The structures of the trifunctional polyisocyanate (Desmodure 3600) and difunctional polyol (Arcol PPG 1000) are shown in Figure 31. Only CNT-g-APIB was used for this study since it
showed the best dispersion behavior in solvents and in TPU. An aliphatic polyisocyanate and polyol were chosen for their miscibility with the isobutyl R groups of POSS.

TEM was used to observe the CNT dispersion in PU/CNT and PU/CNT-g-APIB composites. (Figure 32) Agglomerates and heterogeneous dispersion of CNT were observed throughout the microtome section of the PU/CNT sample. The dispersion of CNT-g-APIB in the PU appears substantially better. However, it is also observed that the aspect ratio of CNTs is greatly reduced after the chemical modification.

\[ R = \begin{array}{c} \text{NCO} \\ \end{array} \]

*Figure 31.* Structures of the major component of (A) Desmodur 3600 (HDI trimer) and (B) Arcol PPG 1000 (PPG with weight average molecular weight of 1000).

\[ n=17 \]

*Figure 32.* TEM images of PU coating with (A) neat CNTs and (B) CNT-g-APIB at a loading level of 0.5wt%. 
TGA analysis was performed in an attempt to gain more information about the interaction of the CNTs with the hard and soft domains (Figure 33). The neat PU shows a two step degradation profile, with the first step attributed to the polyol rich SS phase and the second attributed to the HS phase. The CNT-modified samples both show an initial onset of small weight loss at around 200°C that may be attributed to accelerated thermal degradation of the SS phase by the trace amount of residual metal catalyst in the CNTs. The CNT-containing systems also show three-stage degradation profiles, which can be seen more clearly in the rate of degradation profiles (Figure 33B). Addition of CNTs leaves the $T_{max}$ for the first stage of SS phase degradation unchanged, but it reduces the peak height and width. The second stage, observed in the CNT-modified systems, is attributed to the formation of a rigid amorphous phase composed of closely-packed polymer chains associated with the CNT surface.

The mobility of these chains is restricted by the rigid structure of the CNTs. Based on the temperature at which this degradation stage occurs, the reduced area under the curve for the first stage of degradation, and the greater expected affinity of the CNTs for the SS phase, the second stage of degradation is attributed primarily to interaction of CNTs with the SS phase. The addition of CNTs results in an increase in $T_{max}$ and a narrowing of the curve. The CNT-g-APIB system shows $T_{max}$ for degradation stages two and three, which is a result of better dispersion and enhanced interfacial interaction with the polymers.
Figure 33. (A) TGA and (B) DTGA traces of neat PU, PU composites with 0.5 wt% CNT, and with 0.5 wt% CNT-g-APIB in N₂ atmosphere.
Steady state viscosity was measured for neat polyol, the polyol blend with CNT and the polyol blend with CNT-g-APIB (Figure 34) to evaluate the effect of covalently bonded POSS molecules on the rheology of the PU formulation. A blend of polyol was evaluated rather than the polyisocyanate because polyol is less reactive, allowing greater control of the reaction and more reproducibility of the test results. Addition of neat CNTs resulted in dramatic viscosity increase in the low shear region, attributed to entanglement of the CNTs with each other and with the polyol chains. Entanglements are reduced and CNT alignment increased at high shear rates, resulting in reduction in viscosity to nearly the same level as the polyol alone. Addition of CNT-g-APIB results in very little increase of viscosity over the entire shear regime. Reduction of the aspect ratio of CNT-g-APIB in comparison to that of the neat CNT may partially explain the viscosity drop. Additionally, the flow enhancement effect often observed for POSS, assumed to be a lubricant effect caused by the surface attached APIB molecules, might also contribute to the viscosity reduction.25
Figure 35. Steady state viscosity of polyol, polyol with neat CNT and with CNT-g-APIB at 40 °C measured with a 0.5 wt% loading level.

Conclusions

The dispersion of CNT-g-POSS and CNT-g-silane in solvents and PU polymers was studied. Solubility parameter calculations were carried out to estimate the miscibility of POSS with the dispersing media. VU-vis spectroscopy was used to determine CNT dispersion by transmission measurement. Optical microscopy and TEM were used to observe the CNT aggregation at the micron and the nano levels respectively. It was found that the dispersion level of CNT-g-POSS and CNT-g-silane follows the order: CNT-g-APIB>CNT-g-APIO>CNT-g-AEAPIB≈CNT-g-APTS in all dispersing media. It is concluded that the difference in dispersing behaviors for different CNT-g-POSS systems was attributed mostly to their surface morphology rather than their differences in solubility parameters. The CNT-g-APIB system showed better dispersion, improved
thermal properties and lower viscosity increase than neat CNT in a PU coating. However, it also showed lower aspect ratio, so the enhancement of mechanical and electrical properties of PU/CNT-g-POSS coating might be limited.

Acknowledgments

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REFERENCES


CHAPTER V

PROPERTIES OF THERMOPLASTIC POLYURETHANE COMPOSITES WITH POSS MODIFIED CARBON NANOTUBES

Abstract

Well-dispersed CNTs enhance multiple properties of a polymer matrix. The level of property enhancement of CNT-based polymeric composites is a function of the dispersion state of CNTs, the interfacial interactions between the polymers and the CNT surface, and the composite morphology. In this chapter, varied properties of previously synthesized TPU/CNT-g-POSS were examined. The structural and crystalline properties were studied by ATR-FTIR and WAXS. The thermal properties were evaluated by TGA and DSC measurement. DMA, tensile testing, and melt rheology measurement were used to study the mechanical properties of the TPU composites. Finally, the electric properties were assessed by the measurement of surface and volume resistivity and permittivity. The difference in properties between each sample was correlated to the structure of CNT-g-POSS systems and their dispersion level in TPU.

Introduction

PUs are widely used in the polymer industry, but are less commonly reported in the fundamental research of polymeric composites, particularly in the study of CNT composites. This is due to the complexity of their structures, difficulty in their synthesis, and the difficulty in comparing results from varied studies because of the versatility of PU systems. There are several methods used for PU/CNT composites preparation, but all of them have limitations.
The first method of composite preparation is solution mixing. This method is reserved for TPU because cross-linked PUs only swell in solvents. Both CNTs and PU are dissolved in a polar solvent and mixed with either lengthy sonication or mechanical stirring.\textsuperscript{1,2} The viscosity of TPU solutions is high and the dissolution process takes a long time. Usually the concentration of TPU is lower than 10wt\%, so a large amount of solvent evaporates to the environment and causes pollution. TPU chains align and crystallize differently depending on the solvents and film formation conditions and therefore the film morphologies are varied. In general, due to its simplicity, solvent casting is still a widely used method for small-scale TPU/CNT composite preparation.

The second method is melt mixing, which is also only applicable for TPUs. Mixing CNT with TPU by extrusion fits the current industrial processing procedures of TPU. Studies conducted by this method are the most beneficial for industrial scale-up. CNTs and TPU are mixed at a temperature above the $T_m$ of the TPU by an extruder.\textsuperscript{3,4} One limitation of this method is that extrusion of TPU is not as convenient as the extrusion of other plastics. TPU resins must be dried thoroughly before extrusion and remixed with CNTs to reduce the amount of side reactions due to water. A nitrogen environment is preferred during extrusion to minimize thermal degradation, further complicating processing.

The third widely used method is reactive mixing. This is an \textit{in situ} polymerization method for making composites. CNTs are pre-functionalized with hydroxyl, amino, or isocyanate groups, which are reactive towards the urethane bond formation reaction, and then reacted into the polymer network during PU synthesis. Both difunctional and multifunctional raw materials can be used. This method produces
thermoset PU/CNT composites as multi-functionalized CNTs serve as cross-linkers of the systems. PU/CNT composites prepared by this method were found to have greater property enhancement compared to the ones made by other methods. However, reactive mixing is very complicated. The CNTs must first be modified with multiple steps to have the desired functionality. Multi-step reactions are also necessary to prepare the final composite product. The CNTs increase the cross-link density of the material, and hence it is hard to tell whether the property enhancement is from CNTs or from the increase of cross-link density. In addition to these three methods, there are other less used methods for PU/CNT composite preparation, such as using waterborne PU dispersion, and using PU foams as the matrix.

In this project, we chose a simple solution casting method to made TPU composites containing previously synthesized CNT-g-POSS systems. The aim of this study is to further explore the differences in dispersion of CNT-g-POSS molecules of different structures in PU by assessing their physical properties. The morphological, thermal, mechanical and electrical properties of the TPU/CNT-g-POSS composite films were studied and compared.

Experimental

Preparation of TPU/CNT-g-POSS

TPU/CNT-g-POSS composites were prepared by a solution mixing method. 10 wt% solution of TPU in DMF was prepared first and allowed to sit for one week to ensure full solvation. CNT was dispersed in 10 ml THF with 20 min sonication. After that, the CNT dispersion was added to 50 ml TPU solution in DMF. The mixture was stirred mechanically for 1 hour, and immediately poured onto a polypropylene tray. The solvent
was evaporated gradually at 60 ºC for 48 hours, and vacuum dried for 6 hours to remove
the residual solvent. 1 wt% CNT loading was used for all samples.

**ATR-FTIR**

ATR-FTIR was used to determine the bonding mechanisms of the modified fillers.
IR spectra were obtained using a Thermo Scientific Nicolet 6700 in attenuated total
reflectance mode (USA). 64 scans were collected at a spectral resolution of 2 cm⁻¹. The
surfaces of the composite films was analyzed using a 2-mm Ge crystal with a 45° angle
maintaining constant contact pressure between the crystal and the film. Data analysis was
conducted using the OMNIC software suite.

**WAXS**

WAXS studies were conducted on the surface of composite films to determine the
affect of adding CNT-g-POSS on the crystallization of TPU. Diffraction patterns were
obtained using a Rigaku D/MAXUltima-III diffractometer (Woodlands, Texas). XRD
was conducted in transmission mode at room temperature using Cu Ka (λ=0.1542 nm)
radiation at a tube current of 44 mA and an acceleration voltage of 40 kV. The scan range
was 2°–40° at a step interval of 0.1 ° and a scanning rate of 2 °/min.

**TGA**

TGA was performed on a TA Instruments TGA Q50 using a temperature gradient
of 20 ºC/min. Samples were equilibrated at 50 ºC for 5 min, and then ramped from 50 ºC
to 800ºC with the speed of 20 ºC/min in a platinum pan under a constant nitrogen flow of
40 ml/min.
DSC

DSC thermograms were obtained with a TA Instruments Q200 DSC. Samples ranged from 8 to 15 mg and were sealed in aluminum pans. Nitrogen was used as purge gas. A heat-cool-heat procedure was used. The samples were first equilibrated at -70 ºC, and then heated to 220 ºC at a rate of 10 ºC/min. A cooling scan from 220 ºC to -70 ºC with the rate of 10 ºC/min was used to find the heat and temperature of crystallization. A second heating scan at the rate of 10 ºC/min was used to measure the glass transition temperatures. The tests were performed twice to ensure their accuracy. Data was processed by TA Universal Analysis 2000 software suite.

DMA

DMA was carried out on a Rheometric scientific DMTA V instrument with a frequency of 1 Hz, strain rate of 0.05%, and heating rate of 5 ºC/min. The experiments were performed in air on a small piece of polymer plaque held in a single-point cantilever clamp. Storage modulus, E’, loss modulus, E’’, and tanδ values were measured in temperature sweep studies from -100 ºC to 120 ºC.

Tensile Testing

A TA 800 DMA instrument was used to perform the tensile testing of TPU/CNT-g-POSS samples. A single-point cantilever clamp was used to obtain the Young’s modulus of the initial deformation. The composite films were cut into 10 mm × 6 mm rectangles. A displacement ramp of 10 µm/min was used and the final displacement was set to be 100 µm. All the tensile tests were performed at 25 ºC.
Melt Rheology

Parallel plate rheology was conducted in dynamic mode on a TA Instruments ARES rheometer (New Castle, Delaware). Isothermal frequency sweeps were conducted at 180 °C in the frequency range of 1 to 400 rad/s at 5% strain. Parallel plate geometry plates (8 mm diameter plates) with a gap in the range of 1.0 mm were used in order to generate the storage modulus, \( G' \), loss modulus, \( G'' \), tan \( \delta \) and complex viscosity, \( \eta^* \), with data collected at five points per decade.

Resistivity Measurements

A Keithley 4200-SCS with a custom assembly was used to measure surface and volumetric resistivity using an alternating polarity method with steps of +200V and -200V as per Keithley high resistance measurements application note. The custom probe assembly was designed to allow switching between surface and volumetric resistivity tests as per ASTM D257-07. The bottom electrode was comprised of two separate electrodes, an inner and an outer ring with a gap of 0.5 mm. Volumetric measurements were acquired by applying a potential between the top and bottom inner electrode plates, allowing current to flow through the material. Surface measurements were acquired by applying a potential between the bottom inner and outer ring electrodes. The unused electrode in both configurations was not connected. Calculations involving surface and volumetric resistivity were performed according to the previously stated ASTM standard. Instrumentation and procedural validation tests were conducted using carbon film resistors with known, verified values.
Dielectric/Capacitance Measurements

Dielectric properties were measured using a Keithley 4200 Semiconductor Characterization System (SCS) connected to a custom designed parallel plate electrode assembly at room temperature under controlled humidity. The assembly contains a circular parallel plate electrode (diameter of 1.1 cm) that was encased in an electrically grounded box to prevent interference from external sources. The sealed enclosure was designed to maintain a constant humidity through the delivery of a dry inert gas. The tests conducted measured capacitive reactance at frequencies spanning 10 kHz to 10 MHz in graduated logarithmic steps with 0 VDC bias. Capacitive reactance was then converted to capacitance which in turn was used to calculate permittivity as per ASTM standard D150-11. Instrumentation and procedural validation tests were conducted using ceramic capacitors with known, verified values.

Results and Discussion

Structure and Crystallinity Properties

The structure of the air surface of TPU/CNT-g-POSS was studied by ATR-FTIR (Figure 35). Typical IR spectra for TPU were observed for all composite air surfaces. TPU/CNT-g-APTS showed a slightly higher intensity of the band at 1100 cm\(^{-1}\), which is the stretch band for Si-O groups, and small differences in the intensity of the carbonyl groups are observed. Phase separation is an important factor for TPU physical properties. The degree of phase separation of TPU can be calculated according to a method developed by Cooper. There are several hydrogen bonding sites in PU systems, but the one used to determine phase separation is that attributed to hydrogen bonding of the -NH- in HS domains and the –O- in SS domains. The absorbance peak at \(~1705\) cm\(^{-1}\) is
attributed to the hydrogen bonded C=O stretch and the one at ~1728 cm\(^{-1}\) is attributed to that of the free C=O.

\[ \text{Figure 35. ATR-FTIR spectra of the air surface of TPU/CNT-g-POSS films: (A) full spectra and (B) spectra in 1600 - 1800 cm}^{-1} \text{ region.} \]
The degree of phase separation can be estimated by calculation of the hydrogen bonding index, $R$, using the following equation:

$$
R = \frac{C_{\text{bonded}} \varepsilon_{\text{bonded}}}{C_{\text{free}} \varepsilon_{\text{free}}} = \frac{I_{1705}}{I_{1728}}
$$

(4)

Where $C$ is the concentration and $\varepsilon$ is the respective extinction coefficient of hydrogen bonded and free carbonyl groups. Here the ratio of $\varepsilon_{\text{bonded}}/\varepsilon_{\text{free}}$ is taken as 1 according to Cooper.\(^\text{10}\) The degree of phase separation (DPS) is calculated using the following the equation:\(^\text{11}\)

$$
\text{DPS} = \frac{R}{R + 1}
$$

(5)

Table 7

*Calculation of Degree of Phase Separation of TPU/CNT-g-POSS by IR Results*

<table>
<thead>
<tr>
<th>Fillers</th>
<th>$I_{1703}$</th>
<th>$I_{1731}$</th>
<th>R</th>
<th>DPS</th>
</tr>
</thead>
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<tr>
<td>none</td>
<td>0.0264</td>
<td>0.0175</td>
<td>1.51</td>
<td>0.601</td>
</tr>
<tr>
<td>CNT</td>
<td>0.0220</td>
<td>0.0151</td>
<td>1.46</td>
<td>0.593</td>
</tr>
<tr>
<td>CNT-g-APIB</td>
<td>0.0279</td>
<td>0.0185</td>
<td>1.51</td>
<td>0.601</td>
</tr>
<tr>
<td>CNT-g-AEAPIB</td>
<td>0.0245</td>
<td>0.0169</td>
<td>1.45</td>
<td>0.592</td>
</tr>
<tr>
<td>CNT-g-APIO</td>
<td>0.0263</td>
<td>0.0182</td>
<td>1.45</td>
<td>0.591</td>
</tr>
<tr>
<td>CNT-g-APTS</td>
<td>0.0211</td>
<td>0.0143</td>
<td>1.48</td>
<td>0.596</td>
</tr>
</tbody>
</table>

The measured absorbance peaks at 1703 cm\(^{-1}\) and 1731 cm\(^{-1}\) are used for the calculations and the results are shown in Table 7. The hydrogen bonding index was
reduced in general on addition of CNTs. CNT-g-AEAPIB and CNT-g-APIO interrupt hydrogen bonding the most. This is probably due the secondary amine structure and the bulky isooctyl R groups in these molecules Only the CNT-g-APIB system showed no apparent reduction in hydrogen bonding in comparison to the neat TPU.

![WAXS curves of the air surface of TPU/CNT-g-POSS films.](image)

**Figure 36.** WAXS curves of the air surface of TPU/CNT-g-POSS films.

WAXS curves are shown in Figure 36. The curves are similar for each sample. Two peaks were observed for all curves. A wide peak at $2\theta=20^\circ$ ($d=0.44$ nm) is attributed to the amorphous section. A small sharp peak at $2\theta=5^\circ$ ($d=3.54$ nm) is attributed to part of the crystalline structure in TPU. The TPU/CNT-g-APTS system shows an additional peak at $2\theta=12.5^\circ$ ($d=0.71$ nm), which is not observed in the other systems. The degree of crystallinity of TPU can be estimated by calculating the ratio of crystalline peak and amorphous peak, but this method is not exact, however, and can lead to large error. Due to the large difference in size of the crystalline and amorphous peaks
for our systems, such a calculation was not performed. In addition, the crystalline peak observed here does not represent all the crystalline domains in TPU. TPU has crystals with different sizes and a significant number of these crystals are in the nanoscale.\(^9\) WAXS lacks the resolution to fully elucidate these big crystals, and further small angle X-ray scattering (SAXS) studies would be necessary to provide more details regarding the crystal structures of these systems.

**Thermal Properties**

PUs generally show a two stage degradation process caused by different degradation pathways of the SS phase and HS phase.\(^9\) For aromatic polyether PU, stage 1 degradation (c.a. 350 °C) results from degradation of the polyether SS phase while stage 2 degradation (c.a. 430 °C) results from the degradation of the aromatic HS phase.\(^12\) The results in Figure 37 show that the effect of CNT-g-POSS on the thermal degradation of TPU is complicated. The TPU/CNT-g-APIO shows a slightly earlier onset of degradation than the other samples, and the lowest \(T_{\text{max}}\) for both stages. APIO and APIB appear to show 3-stage degradation profiles, with one \(T_{\text{max}}\) at slightly lower temperature than that of stage 1 degradation in neat TPU, and a second at slightly higher temperature. This intermediate degradation stage is attributed to formation of a rigid amorphous phase of highly constrained molecules closely associated with CNTs.\(^{13,14}\) The AEAPIB and APTS systems do not show the intermediate degradation phase, but do exhibit decreased \(T_{\text{max}}\) for stage 1. \(T_{\text{max}}\) of stage 2 is reduced slightly (1 – 4 °) for all systems except neat CNT and CNT-g-APIB in comparison to the neat TPU. The changes in the stage 1 degradation pathway indicate that the POSS-modified CNTs selectively interact with the soft segments of TPU. This is attributed to the non-polar hydrocarbon substituents of the
POSS molecules used in this study, which preferentially reside in the SS domain rather than the hydrogen bonding rich HS domains. In general, the thermal stability of TPU decreases slightly on incorporation CNT-g-POSS.

Figure 37. (A) TGA and (B) DTGA curves of TPU/CNT-g-POSS films.
CNTs can induce complicated melting/recrystallization phenomena. During the crystallization process, CNTs serve as nucleating agents and polymer chains crystallize parallel to the nanotube’s axis. This process has been shown to cause an increase in nucleating temperature ($T_c$) in non-isothermal DSC experiments for a number of polymers.

Similar results were obtained in this study as shown in Figure 38. Systems with neat CNTs and CNT-g-POSS show two stage nucleation curves and an increase in the $T_c$ (taken as the higher transition temperature). The neat CNT results in a $50^\circ C$ increase in CNT, while CNT-g-APIB, CNT-g-AEAPIB and CNT-g-APTS cause increases of $27^\circ C$, $31^\circ C$ and $37^\circ C$ respectively. The CNT-g-APIO shows a single stage nucleation mechanism and a slight reduction in $T_c$ in comparison to that of the neat TPU. The difference in $T_c$ are attributed to the accessibility of the CNT side walls. Neat CNT is uncovered, and it gives the highest increase of $T_c$. Though CNT-g-APIO has the lowest mole percentage grafting density (chapter I), the bulky APIO molecules keep CNT side walls from interacting with the polymer matrix so the crystallization behavior of TPU chains remain unchanged. The other three CNT-g-POSS samples have moderate accessibility of CNT side walls, so the level of $T_c$ increase is between that of CNT-g-APIO and neat CNT. The difference in crystallization rate can be further studied by isothermal DSC at the $T_c$ of each system.
Figure 38. DSC cooling scan of TPU/CNT-g-POSS films.

Figure 39. DSC second heating scan of TPU/CNT-g-POSS films.
The second DSC heating scan is used to observe the $T_g$ and $T_m$ differences between samples. (Figure 39) No obvious $T_g$ was noticed in all curves. TPU/CNT composites are very complex systems with multiple phases, including the hard segment dominated phase, soft segment dominated phase, and CNT induced extra phase. A wide $T_g$ could be the result of different phases mixing in TPU after the thermal annealing during the first heating and cooling scan. The differences in $T_m$ follow the same trend as that observed in $T_c$, but only single stage mechanism is observed.

Table 8

<table>
<thead>
<tr>
<th>Fillers</th>
<th>$T_c$</th>
<th>Heat of crystallization</th>
<th>Heat of fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(J/g)</td>
<td>(J/g)</td>
</tr>
<tr>
<td>None</td>
<td>74</td>
<td>8.44</td>
<td>152</td>
</tr>
<tr>
<td>CNT</td>
<td>124</td>
<td>8.04</td>
<td>176</td>
</tr>
<tr>
<td>CNT-g-APiB</td>
<td>101</td>
<td>7.36</td>
<td>158</td>
</tr>
<tr>
<td>CNT-g-AEAPiB</td>
<td>103</td>
<td>9.53</td>
<td>154</td>
</tr>
<tr>
<td>CNT-g-APIO</td>
<td>72</td>
<td>8.13</td>
<td>153</td>
</tr>
<tr>
<td>CNT-g-APTS</td>
<td>111</td>
<td>8.20</td>
<td>155</td>
</tr>
</tbody>
</table>

Integrated heats of crystallization and fusion are shown in Table 8. The heat of fusion is lower for all CNT containing composites than for TPU alone, and the POSS-modified systems show lower values than those of the neat CNT system. This is
attributed to the interruption of hydrogen bonding caused by CNT-g-POSS and CNT-g-silane. With less hydrogen bonding, less heat is required to melt the polymers.

**Mechanical Properties**

Mechanical properties of TPU/CNT-g-POSS films were assessed by tensile testing at room temperature, rheology measurement above $T_m$, and DMA tests at low temperature. The performance of the materials was found to be different at different temperatures.

![Figure 40. Young’s moduli of TPU and TPU/CNT, and TPU/CNT-g-POSS measured by DMA tensile tests.](image)

A simple tensile test performed by DMA was used to obtain the initial Young’s modulus of the film at room temperature. The results are shown in Figure 40. Addition of 1 wt% of CNT or CNT-g-POSS improves the Young’s moduli in all systems, but the
extent of improvement and standard deviation is different for each sample. The modulus and its standard deviation are related to the dispersion level of CNTs in the TPU composites. TPU/CNT-g-APIB and TPU/CNT-g-APIO show higher modulus improvement and lower standard deviation. This is attributed to better CNT dispersion in these two systems. On the other hand, TPU/CNT-g-AEAPIB and TPU/CNT-g-APTS which showed poor dispersion of CNTs, show lowers modulus improvement and high standard deviation in tensile testing.

Minimal differences are observed for CNT and CNT-g-POSS TPU composites in melt oscillatory rheology measurements, but all composites show differences in comparison to neat TPU (Figure 41). For TPU composites, both the storage modulus and loss modulus at 180 °C show higher frequency dependence than the neat TPU, and this trend is magnified in the tan δ curves. In reported rheology studies of CNT based composites, lower frequency dependence is usually observed due to the restriction of polymer chain movement caused by the formation a rigid CNT network. It appears that in our system CNTs do not connect to each other to form a rigid network, but are non-continuously dispersed. In addition, TPU is a more complex matrix compared to the other widely studied systems, such as PS and PMMA. In TPU there are a large number of hydrogen bonded segments which behave as physical crosslinks and contribute greatly to TPU’s high modulus. As shown in our IR study, adding CNT-g-POSS disrupts the hydrogen bonding within TPU, and promotes chain movement instead of restricting it. However, this effect does not reduce the viscosity of the composite melt. From Figure 41, a slight increase of Eta* is observed upon the addition of CNTs.
A

\begin{align*}
G'(\text{Pa}) & \\
\text{Frequency (rad/s)} & \\
\end{align*}

B

\begin{align*}
G''(\text{Pa}) & \\
\text{Frequency (rad/s)} & \\
\end{align*}
Figure 41. (A) Storage modulus, (B) loss modulus, (C) tanδ, and (D) complex viscosity $\eta^*$ of TPU/CNT-g-POSS composites films at 180°C.
Figure 42. DMA storage moduli $E'$ of TPU, TPU/CNT, and TPU/CNT-g-POSS (A) below 0 ºC and (B) above 0 ºC.
Figure 43. DMA loss moduli $E''$ of TPU, TPU/CNT, and TPU/CNT-g-POSS (A) below 0 °C and (B) above 0 °C.
Dynamic mechanical behavior of the composites below $T_g$ and at room temperature was studied by DMA measurement. (Figure 42 and 43) The order of storage modulus $E'$ is: APIO ≈ APIB > AEAPIB. The order of Loss modulus $E''$ is: APIB > APIO > AEAPIB. This result is in agreement with the order of CNT-g-POSS dispersion level as shown in Chapter IV. The difference in loss modulus between samples is less significant than the difference in storage modulus. An interesting phenomenon observed for TPU composites with CNTs is a reduction of storage modulus and an increase of loss modulus at reduced temperatures at low temperature. This phenomenon is more obvious for CNT-g-POSS systems, but is not observed in neat TPU. The position and the broadness of the $\alpha$ transition (glass transition) peaks of TPU composites are not affected by CNT-g-POSS addition. (Figure 44) A $T_g$ of -25 °C is obtained for all samples.
Electrical Properties

Figure 45. DC (A) surface resistance and (B) volume resistivity of TPU, TPU/CNT, and TPU/CNT-g-POSS.
Both the surface and volume conductivity of the TPU/CNT-g-POSS were measured under DC current by a custom assembled instrument. The results are shown in Figure 45. After adding CNTs, the surface resistance increased for all samples except TPU/CNT-g-APIO. The volume resistivity of the material is in the range of $10^5 \, \Omega \cdot m$, which is lower than the surface resistance in number. However no significant difference is observed between samples. A potential explanation for this behavior is that 1 wt% loading is below the percolation threshold of this system.

The real permittivity of the composite samples was obtained from dielectric property measurements. (Figure 46) At low frequency, the permittivity of composites is higher than that of neat TPU. The frequency dependence of the samples, however, is very different. For the neat TPU sample permittivity was found to increase with increasing frequency. The curves for composites with CNT, CNT-g-AEAPIB and CNT-g-APTS all show the same trend. They all decrease slightly as the frequency increases. Curves for TPU composites with CNT-g-APIB and CNT-g-APIO show a greater drop of permittivity at higher frequency. Based on study shown in Chapter VI, 1wt% loading level is far below the percolation threshold of TPU/CNT system. There is no clear plateau region at the applied frequency. At this loading, the frequency dependency of $\varepsilon'$ is more related to the structural properties of the polymer than to CNT dispersion. Measurement of loss permittivity and tan$\delta$ is needed to further elucidate these effects.
Figure 46. Permittivity of TPU, TPU/CNT, and TPU/CNT-g-POSS.

Conclusions

Analysis of the physical properties of TPU/CNT-g-POSS shows that adding 1 wt% of CNT-g-POSS to a TPU matrix does not enhance the properties of the TPU matrix significantly. Minor differences in hydrogen bonding and phase separation levels were estimated by ATR-FTIR analysis. The thermal stability of the composites is slightly reduced compared to that of neat TPU. CNT-g-POSS was found to interact primarily with the soft-segment TPU domain. CNT-g-POSS influences the nucleation of crystallization of TPU but the effect is not as significant as that of neat CNT. The crystallization of TPU is affected by adding CNT-g-POSS and the increase of $T_c$ and $T_m$ is dependent on the amount of non-grafted CNT surface in the system. At the melting point the storage and loss modulus of the composites are more frequency dependent than that of neat TPU. This is attributed to the disturbance of hydrogen bonding by CNT-g-
POSS as observed in IR study. Mechanical properties measured at room temperature were enhanced on addition of CNTs. Both the storage modulus and Young’s modulus were increased in comparison to that of neat TPU, and the extent of property increase is correlated to the dispersion efficiency of CNT-g-POSS.

Acknowledgments

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REFERENCES


CHAPTER VI
TRISILANOLPHENYL POSS LITHIUM SALT (TSPLi) AS A DISPERSANT FOR
CARBON NANOTUBES IN THERMOPLASTIC POLYURETHANE

Abstract

A POSS product TSPLi was used as a dispersing agent for MWNTs in TPU. A series of CNT-TPU composites were prepared with gradient CNT loading levels and their properties were compared to controls made without TSPLi. Mechanical properties of the composites were determined by tensile testing. Young’s modulus, ultimate strength, ultimate elongation, and toughness were obtained from the tensile stress-strain curves. Conductivity and permittivity measurements were used to test the electrical properties of the composites. TPU/CNT-POSS composites were found to have a higher Young’s modulus and a lower percolation threshold compared to TPU/CNT samples at the same CNT loading level.

Introduction

TSP was developed as dispersing agents by Hybrid Plastics, as discussed in Chapter I. TSPLi is the lithium salt of phenyl TSP, and is a synthetic intermediate obtained during TSP production. TSPLi is commercially available from Hybrid Plastics with the name Trisilanolphenyl POSS Lithium Salt or SO1457. Although it is easier to make, it has not been widely used, and to our knowledge there has been no research published on this compound.

There are limited literature reports of the use of lithium salt to assist with the dispersion of CNTs. Billups and coworkers reported a reductive alkylation of SWNTs using lithium and alkyl halides in liquid ammonia. High efficiency of this reaction is
attributed to the capability of Li\(^+\) cations to intercalate SWNT bundles. Catterjee \textit{et al.} reported a dispersion study of SWNTs using a lithium-based anionic surfactant in PEO.\(^3\) Very low electrical and geometric percolation thresholds were demonstrated for this system. Meyer, \textit{et al}, proposed from Raman spectroscopy and MD simulations that LiCl directed the formation of a supermolecular system with PEO-b-PLLA copolymer and CNTs.\(^4\) Combining Li\(^+\) cations with functionalized CNTs has also been found to result in a high electric capacity and the potential to be used for high power delivery lithium-ion batteries.\(^5\)

Based on the above information, it was propose that TSPLi has the potential to be used as a dispersing agent for CNTs and to enhance the electrical properties of CNT-based composites. In this work, TSPLi was employed to assist the dispersing of CNTs in a TPU during melt extrusion. Gradient loading ratios of CNTs were used to determine the percolation threshold for this system. The electrical and mechanical properties of the TPU/CNT and TPU/CNT-POSS composites were compared. This is the first known report of TSPLi as a dispersing agent for CNTs. Experimental information provided by this study will provide the fundamental information necessary to enable future development of POSS dispersant products.

\textbf{Experimental}

\textit{Materials}

Industrial purity (90 wt \%) MWNTs were purchased from Cheaptubes.com. TSPLi was donated by Hybrid Plastics, Inc.. TPU with the commercial name Estane 2103-80AE was used as the polymer matrix, and it was kindly donated by Lubrizol Corporation. All reagents were purchased from Fisher and used without purification.
Preparation of CNT-POSS

CNTs were blended with POSS at different weight ratios in solvents. CNTs and TSPLi were mixed in methylene chloride at a ratio of 20 milliliters of methylene chloride per gram of CNTs and subjected to 30 minutes of sonication. The suspension was then refluxed at 60 °C for one hour before the solvent was slowly removed by rotary evaporation. Finally, POSS treated CNTs were vacuum dried at 80 °C for 4 hours to remove the residual solvent.

Preparation of TPU/CNT Composites

TPU/CNT composites were prepared by melt mixing at 180 °C. TPU resins were thoroughly dried before each extrusion. Composites at low CNT loading levels were prepared using a PRISM TSP bench top twin screw extruder. The composites were extruded twice to ensure homogeneous mixing. CNT-PU composites with 5 compositions were prepared at 0.5, 1.0, 1.5, 2.0, and 2.5 wt%. CNT-PU Composites with high CNT loading levels were prepared using a Haake minilab twin extruder at screw speed of 50 min⁻¹ and were mixed 3 times to ensure homogenous mixing. CNT-PU composites with 2 compositions were prepared at 6wt% and 14wt%.

TEM

Dispersion of CNTs in TPU composites was analyzed by a TEM JEOL JEM-2100 at an accelerating voltage of 200kV. Cryo-microtoming was performed for TEM sample preparation. Samples were cut into ultrathin (~100 nm), trapezoidal-shaped sections with a Porter-Blum MT-2B ultramicrotome (Ivan Sorvall, Inc.), using a single crystal diamond knife (Delaware Diamond Knives, Inc.) at -70 °C. Sections were collected on a Formvar-
coated, 400 mesh copper TEM grid (Electron Microscopy Sciences) and imaged without staining.

**Tensile Testing**

An MTS Insight (Eden Prairie, Minnesota) was used to perform tensile testing to obtain stress-strain curves of TPU composites with loading levels from 0.5 wt% to 2.5 wt% following a modified method of ASTM D638. “Dog bone” test parts with a width of 4.8 mm and a thickness of 1.1 mm of the testing region were stamped out from a compression molded TPU sheet. The initial gap distance was set at 15 mm. The crosshead speed was set at 50 mm/min and tests were conducted at room temperature. The average of 5 tests for each composite is reported. Data were processed by the Origin 8 software suite.

Tensile testing of composites with loading levels of 6 wt% and 14 wt% was performed using a TA 800 DMA instrument with a tension clamp due to the small quantity of samples. The composite films were cut into a 10 mm×6 mm rectangle. A displacement ramp of 10 μm/min was used and the final displacement was set to be 100 μm. All tests were performed at 25 ºC. Four samples were tested and the average reported.

**Conductivity Measurement**

A Keithley 4200-SCS with a custom probe assembly was used to measure surface and volumetric resistivity using an alternating polarity method with steps of +200V and -200V. The custom probe assembly was designed to allow switching between surface and volumetric resistivity tests as per ASTM D257-07. The bottom electrode was comprised of two separate electrodes, an inner and an outer ring with a gap of 0.5 mm. Volumetric measurements were acquired by applying a potential between the top and bottom inner electrode plates, and allowing current to flow through the material. Surface
measurements were acquired by applying a potential between the bottom inner and outer ring electrodes. The unused electrode in both configurations was not connected. Calculations involving surface and volumetric resistivity were performed according to the previously stated ASTM standard. Instrumentation and procedural validation tests were conducted using carbon film resistors with known, verified values.

**Permittivity Measurement**

Dielectric properties were measured using a Keithley 4200 Semiconductor Characterization System (SCS) connected to a custom designed parallel plate electrode assembly at room temperature under controlled humidity. The assembly contains a circular parallel plate electrode (diameter of 1.1 cm) that was encased in an electrically grounded box to prevent interference from external sources. The sealed enclosure was designed to maintain a constant humidity through the delivery of a dry inert gas. The tests conducted measured capacitive reactance at frequencies spanning 10 kHz to 10 MHz in graduated logarithmic steps with 0 VDC bias. Capacitive reactance was then converted to capacitance which in turn was used to calculate permittivity as per ASTM standard D150-11. Instrumentation and procedural validation tests were conducted using ceramic capacitors with known, verified values.

**Results and Discussion**

**Composite Preparation**

The proposed mechanism of TSPLi adhesion to the CNT surface is illustrated in Figure 47. The three Li\(^+\) cations on the POSS cage bond to the surface of the CNT side walls by electrostatic force, which provide it with a higher affinity than a monofunctional dispersant. The specific area of the CNTs used in this work is estimated to be 233 m\(^2\)/g,
and the specific area for POSS is estimated to be 3600 m²/g. It is assumed that one quarter of the POSS surface interacts with the CNT surface, and that there is a 25% chance for POSS to interact with the CNTs, taking into account the efficiency of collision and steric hindrance of the phenyl R groups. Thus a ratio of 10 g CNT to 1 g of POSS molecules was used for this study to increase the likelihood of interaction. It is expected that the phenyl organic substituents of the TSPLi molecules will enhance interaction the aromatic-group-rich HS phase of TPU.

![Structure of TSPLi and a proposed mechanism of TSPLi interaction with CNT side walls](image)

*Figure 47. Structure of TSPLi (left) and a proposed mechanism of TSPLi interaction with CNT side walls (right).*

TEM results indicate that CNTs are well dispersed in TPU at a 1.5 wt% loading level (Figure 48) for both the POSS-containing and the POSS-free samples. The microtomed sections in these images are prepared as cross sections from a compression molded TPU composite sheet, and thus many of the CNTs appear to be transected. It would be preferable to obtain microtomed sections in the direction parallel to the long axis of the TPU sheet, but such samples are difficult to obtain in thin films. There is not
clear difference in the CNT dispersion for samples with and without POSS observed in the TEM images, but the dispersion and alignment in the current samples is noticeably better than that obtained in the composites prepared by solution mixing and \textit{in situ} polymerization methods described in the previous chapters. This indicates that the CNT bundles were broken during the high shear twin screw extrusion process. Unfortunately, it is not possible to obtain much information concerning POSS distribution in the current TEM images. Energy-dispersive X-ray spectroscopy (EDAX) 2D mapping analysis of Si or Li elements could be used for this purpose in the future.

![Figure 48. TEM microtome section images of (A) TPU/CNT and (B) TPU/CNT-POSS composites with 1.5 wt% CNT.](image)

\textit{Mechanical Properties}

TPU is an elastomer, which means it has a low Young’s modulus, high yield strength, and high shape recovery after stress is removed.\textsuperscript{7} All these features are seen in the tensile testing of TPU and its composite samples. Figure 49 gives a typical stress-strain curve for the TPU/CNT-POSS composites. Initially the TPU composite shows
elastic deformation. At a certain deformation, it starts to show viscoelastic behavior, and finally it breaks before reaching a yield point. Young’s modulus of the elastic region, strength and elongation at breakage, and toughness were gathered from the stress-strain curves of TPU and its composites.

![Stress-strain curve](image)

**Figure 49.** A typical stress-strain curve for TPU composites and its analysis (CNT-POSS 1.5 wt %). The initial slope is used as Young’s modulus; stress and elongation at breakage are used as ultimate strength and elongation; and the area under the curve is used as tensile test toughness value.

Before data analysis, Young’s modulus of the composites was first predicted by calculation. According to the Halpin-Tsai Theory

\[
\frac{E_c}{E_m} = \frac{3}{8} \left[ \frac{1 + 2(l/D)\eta L V_f}{1 - \eta L V_f} \right] + \frac{5}{8} \left[ \frac{1 + 2\eta T V_f}{1 - \eta T V_f} \right]
\]

(6)

Where
\[ \eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l/D)} \]
\[ \eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \]

\(E_c, E_f\) and \(E_m\) are the moduli of the composite, fiber and matrix, respectively; \(l\) and \(D\) are the length and diameter of the fiber; \(V_f\) is the volume fraction of the fiber. In our calculation, 20 nm was used as the average diameter \((D)\) of the CNTs based on our observation from TEM in previous chapters, 2 \(\mu\)m was used as the length of CNTs \((l)\) considering the breakage of CNTs during multiple extrusions, 2.1 g/cm\(^3\) was used as the density of CNTs, and 1.28 TPa was used as the modulus of MWNTs \((E_f)\).\(^9\) The density of Estane is 1.13 g/cm\(^3\) as provided in its material data sheet. The measured modulus of the neat TPU sample was used as \(E_m\).

The predicted modulus and experimental modulus of TPU and its composites are shown in Figure 50. Theoretical values show a good fit of data below 1.5 wt% CNT loading level. Above 1.5 wt%, the experimental values start to deviate from the predicted value to the lower modulus region, which is very common in CNT-based composites.\(^9\) It is caused by a smaller surface area of CNTs than the theoretical value due to the formation of CNT clusters. At less than 1.5 wt% CNT concentration, there is no difference in modulus between TPU/CNT and TPU/CNT-POSS considering the standard deviation values of the tests. However, above 1.5 wt%, TPU/CNT-POSS showed a higher modulus than TPU/CNT.
Figure 50. Young’s modulus of TPU/CNT and TPU/CNT-POSS at low CNT loading levels.

Prediction of mechanical properties other than modulus is more difficult, because the interfacial shear strength needs to be taken into consideration. Computational simulation is commonly used for such a purpose.\textsuperscript{10,11} It is possible that similar types of studies may be conducted in the future, but for this project, we only summarized the experimental results and observed the trend. Ultimate strength values are shown in Figure 51. The strength of the material decreases upon the addition of CNTs, and the strength of the CNT-POSS samples decreased slightly more than that of the CNT samples, however differences are minor when the standard deviation is taken into consideration. The decrease of strength after CNT addition could be related to the interruption of hydrogen bonding in HS domains, as discussed in chapter V. $T_g$ of the SS of TPU is -25 °C as measured by DMA (Chapter V). Breaking TPU at room temperature is breaking the
physically cross-linked HS domains which are held together by hydrogen bonding. With the interruption of hydrogen bonding, the bonding energy between chains in HS is reduced along with the ultimate strength of the material. This result indicates that the interfacial forces between TPU chains with CNT and CNT-POSS surfaces are weaker than hydrogen bonding in TPU.

**Figure 51.** Ultimate strength of TPU/CNT and TPU/CNT-POSS samples at low CNT loading levels.

The ultimate elongation of TPU increased after the addition of CNTs. (Figure 52) There is no trend of increasing extension with CNT concentration, but for all concentrations, TPU/CNT samples show higher elongation values than TPU/CNT-POSS samples. As discussed in the last paragraph, neither the interaction between CNT with TPU nor that of CNT-POSS with TPU is stronger than hydrogen bonding. The difference in ultimate strength between the two systems is very minor. This combined with the
results of the ultimate elongation measurements of these two systems indicate that the interfacial interaction between the CNT-POSS surface and the TPU molecules is higher than that of the neat CNT with TPU.

![Graph showing ultimate elongation vs. CNT concentration]

*Figure 52.* Ultimate elongation of TPU/CNT and TPU/CNT-POSS samples at low CNT loading levels.

One phenomenon related to the results of ultimate elongation measurement is the shape recovery of the sample (Figure 53). After the neat TPU sample is broken, the length is 125% of its original length. TPU composite samples were found to have less shape recovery than that of the neat TPU. The length of TPU composites sample is 200% of its original length. There is no noticeable difference between TPU/CNT and TPU/CNT-POSS behavior. The recovery of TPU is related to both the cross-link density and the crystallization level of the SS domains. From the IR study in chapter V, it is known that CNT interrupts hydrogen bonding, which provides physical cross-linking of
TPU. CNTs also serve as a nucleating agent in the composites and affect the crystallization behavior of the SS domains, according to the DSC study in chapter V. In this system we believe the loss of shape recovery is a combination of the reduction of cross-linking cause by hydrogen bonding interruption in HS domains and disturbed crystallization of SS domains.

![Images of TPU, TPU/CNT, and TPU/CNT-POSS](image)

*Figure 53. Shape recovery of (A) TPU, (B) TPU/CNT, and (C) TPU/CNT-POSS with 1.5 wt% CNT loading level after tensile test.*

Toughness increases slightly for TPU/CNT composites, but within one standard deviation appears unchanged for TPU/CNT-POSS samples (Figure 54). Toughness is related to the ultimate strength and ultimate elongation, because it is calculated as the area under the stress-strain curve. The lower toughness value of the TPU/CNT-POSS samples could be the reason for their lower ultimate elongation values. (Figure 52) Another explanation for this result may be based on the definition of toughness. Toughness measures the capability of a material to absorb energy before fracture. The interfacial interaction between CNT-POSS and TPU is higher than that for CNT with
TPU based on our earlier discussion, so neat CNTs slide more easily in the TPU matrix under stress, which leads to better energy dissipation and a higher toughness value.

![Graph showing Toughness vs CNT concentration](image)

*Figure 54.* Toughness of TPU/CNT and TPU/CNT-POSS samples at low CNT loading levels.

Due to a limited number of samples, only tensile modulus of composites with high CNT loading level was studied. A new $E_m$ based on this test was used in a theoretical modulus calculation because the value of the tensile modulus is highly dependent on testing procedures. The modulus of composites with a high CNT concentration shows a further deviation from theoretical values than that of TPU composites with low CNT concentration. (Figure 55) This is due to the poorer dispersion of CNTs at high loading levels. As was observed for the low CNT concentration samples, the modulus of TPU/CNT-POSS samples is higher than that of the TPU/CNT samples. Taking into account the Young’s modulus measurement of composites at all CNT
concentrations, it is concluded that CNT-POSS has better dispersion in TPU and stronger interfacial interactions with the TPU matrix than neat CNT, particularly at high CNT loading levels.

![Graph showing Young's modulus vs CNT concentration](image)

*Figure 55.* Young’s modulus of TPU/CNT and TPU/CNT-POSS samples at high CNT loading levels.

**Electrical Properties**

The surface and volume resistance of TPU composites are shown in Figure 56 and 57. At low CNT loading levels, little difference is observed in the surface resistance of the TPU/CNT and TPU/CNT-POSS composites, but the TPU/CNT-POSS samples show slightly lower volume resistivity values. At high loading levels, TPU/CNT-POSS samples show an earlier drop in surface resistance and volume resistivity than the TPU/CNT samples, indicating a lower percolation threshold for the POSS-containing samples. However, a larger number of data points are needed to fully describe the trend. There are
two possible explanations for this phenomenon. The first is that better dispersion of CNTs is achieved by using TSPLi as a dispersion agent, so a conductive CNT network is formed at lower CNT concentrations. The second is that the Li$^+$ in POSS also contributes to the conductivity of the system. Li$^+$ is small and has high mobility under direct current, so the fast movement of Li$^+$ could also assist in the early formation of a conductive network. Permittivity values for the CNT and CNT-POSS TPU composites shows similar trends with CNT concentration (Figure 58) for both systems, the permittivity threshold is between 6 wt% and 14 wt%. Evaluation of more samples in this concentration range is necessary to fully describe the trends.
Figure 56. (A) Surface resistance and (B) Volume resistivity of TPU composites at low loading levels.
Figure 57. (A) Surface resistance and (B) Volume resistivity of TPU composites at high loading levels.
Figure 58. Real permittivity of (A) TPU/CNT and (B) TPU/CNT-POSS.
Conclusions

TSPLi appears to improve CNT dispersion in a melt blended TPU system. Improved Young’s modulus and lower percolation thresholds were observed for the CNT-TSPLi/TPU systems in comparison to those of the neat CNTs. The property enhancements in the TPU/CNT-POSS composites are attributed to a combination of better dispersion of CNTs, a higher interfacial interaction between the modified CNTs and the TPU matrix, and the presence of high mobility of lithium ions in the composites.

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CHAPTER VII

CONCLUSIONS AND RECOMMENDED FUTURE WORK

This research successfully demonstrated the synthesis of three POSS modified CNTs and one organosilane modified CNT. The correlations between modified CNT structures and their dispersion behaviors both in solvents and in polyurethane matrices were established. It was found that the difference in dispersing behaviors for different CNT-g-POSS systems was attributed primarily to their surface morphologies rather than to their differences in solubility parameters. Predicted levels of enhancement in physical properties for TPU/CNT-g-POSS composites were not achieved. This was attributed to disruption of hydrogen bonding by the CNTs and CNT-g-POSS systems during TPU composite preparation.

CNTs and modified CNTs displayed different interactions with both the HS domains and SS domains of PU. These interactions were studied using IR, TGA and DSC analysis. However, the mechanism of the interactions between modified CNTs and different domains of the TPU matrix was not fully elucidated. In the future, advanced imaging techniques, such as TEM-EDAX, AFM, and nanoindentation 2D mapping could be used to observe the sizes and distribution of the different domains as well as locate the position of CNTs. X-ray diffraction was used to study the effect of CNTs on the degree of crystallinity of TPU, however it was not possible to fully evaluate the wide range of crystallite sizes by wide angle x-ray scattering. In the future, small angle x-ray scattering (SAXS) could be used to study the effect of CNTs and POSS functionalized CNTs on the crystallinity of TPU.
In Chapter VI, better CNT dispersion and higher interfacial interaction between the filler and the TPU matrix were observed for CNT-g-POSS systems in comparison to neat CNT systems. However, the mechanism of the property enhancement of the TPU/CNT-g-POSS composites was not well understood due to the complex interaction between CNTs with both the HS domains and SS domains. To exclude the influence from a complicated polymeric matrix such as TPU, amorphous polymer matrices with simple structure, such as epoxy, acrylates, and atactic polystyrene, could be used to better delineate the mechanism of POSS assisted dispersion in the future.