Synthesis and Characterization of Self-Healing Poly (Carbonate Urethane) Carbon-Nanotube Composites

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Synthesis and Characterization of Self-Healing Poly (Carbonate Urethane) Carbon-Nanotube Composites

by

Roger Bass

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Chemistry College of Arts and Sciences University of South Florida

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DEDICATION

To the love of my life, thank you for always being there
   To my children, follow your dreams
   To mom and dad, you made it all possible
   I love you all a bushel and a peck, peck…
ACKNOWLEDGMENTS

I would like to express my deepest gratitude to Dr. Julie Harmon for giving me this incredible opportunity and allowing me to “hit the ground running”. I know that may be an ARMY phrase but remember, go AIRFORCE!!!

I would like to thank my committee members: Dr. Sheryl Li for her Raman expertise that is crucial for understand our material’s unique properties, Dr. Norma Alcantar for allowing me to use her FTIR and providing incredible insight into surface science, and Dr. Jianfeng Cai, for teaching me that no matter how much you learn, spelling a three letter word can still be difficult, I still owe you lunch.
# TABLE OF CONTENTS

LIST OF TABLES ................................................................................................. iv

LIST OF FIGURES .............................................................................................. v

ABSTRACT ........................................................................................................... x

CHAPTER 1: INTRODUCTION .............................................................................. 1
  POLYURETHANE (PU) CHEMISTRY AND STRUCTURE ............................................. 1
  CARBON NANOTUBE COMPOSITES ...................................................................... 6
  SELF-HEALING POLYMERS ................................................................................ 9

CHAPTER 2: ULTRA-FLEXIBLE AUTONOMOUSLY SELF-HEALING
  HIGH MOLAR MASS POLYURETHANES ............................................................. 15
  INTRODUCTION .................................................................................................. 15
  EXPERIMENTAL .................................................................................................. 19
    Materials ............................................................................................................. 19
    Methods ............................................................................................................. 20
      Polyurethane Synthesis .................................................................................. 20
      Carbon Nanotube Composites ....................................................................... 21
      Differential Scanning Calorimetry (DSC) ....................................................... 22
      Tensile Test ..................................................................................................... 23
      Gel Permeation Chromatography .................................................................. 24
      Raman ............................................................................................................. 25
  RESULTS AND DISCUSSION .............................................................................. 26
    Reduced Elastomeric Crystallization .................................................................. 26
    Mechanical Evaluation of Self-healing PCPU and CNT Composites ............... 29
Healing Dynamics ................................................................. 63
CONCLUSION .............................................................................. 70
CNT affect on mechanical properties .................................. 70
CNT affect on self-healing properties ................................. 70

CHAPTER 3: MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CARBON NANOTUBE REINFORCED ULTRASOFT POLY (CARBONATE URETHANE) COMPOSITES .............................................................................. 72
INTRODUCTION ........................................................................... 72
EXPERIMENTAL ........................................................................ 77
Materials .................................................................................... 77
Methods ..................................................................................... 77
Carbon Nanotube Composite Materials ............................. 77
Solution casting method ......................................................... 77
Water coagulation method ...................................................... 78
Differential Scanning Calorimetry (DSC) ......................... 78
Tensile Test .............................................................................. 79
Hardness testing ...................................................................... 79
Microstructures ...................................................................... 80
Rheometry ............................................................................... 80
RESULTS AND DISCUSSION .................................................. 81
Agglomeration measurement and control ......................... 81
Tensile Testing ........................................................................ 88
Rheometry ............................................................................... 92
Hardness .................................................................................. 94
CONCLUSION ........................................................................... 95

CHAPTER 4: ESTIMATION OF SURFACE ENERGIES OF SELF-HEALING POLY (CARBONATE URETHANE) CARBON NANOTUBE COMPOSITES .............................................................................. 96
INTRODUCTION ........................................................................... 96
EXPERIMENTAL ................................................................. 101
Materials ................................................................................. 101
Methods ........................................................................................................ 101
  PCPU/CNT Composites .............................................................................. 101
  Contact Angle Measurements ................................................................. 102
  Fourier Transform Infrared Spectroscopy (FTIR) .................................... 102
RESULTS AND DISCUSSION ........................................................................ 103
  Contact Angle Measurements ................................................................. 103
  Fourier Transform Infrared Spectroscopy (FTIR) .................................... 115
CONCLUSION .................................................................................................. 117

CHAPTER 5: FUTURE WORK ......................................................................... 118
  Structure –Property Relationships ............................................................ 118
  Next Generation Filler .............................................................................. 119

REFERENCES .................................................................................................. 122
LIST OF TABLES

Table 2.1  \( T_g, T_m \), PCPU Single/Multi-wall CNT composites. .................... 43

Table 2.2  Tensile test results for neat PCPU & PCPU/CNT composites....... 56

Table 2.3  Tensile test summary for neat PCPU & PCPU/CNT composites after healing time of 24 hours................................................. 59

Table 2.4  Tensile test results for neat, 1.0wt.% PCPU/CNT composite, timed healing................................................................. 61

Table 2.5  Tensile test results for separation test. ................................. 62

Table 3.1  Average detected diameter of agglomerates present in composites at various loadings by preparation method............... 85

Table 3.2  Comparison of ultimate break stress and strain comparing water coagulation and solvent casting methods. ......................... 89

Table 3.3  Shore A values PCPU/CNT composites.................................. 94

Table 4.1  Surface tension parameters for test liquids used for test liquids used for contact angle measurements. ................................. 104

Table 4.2  Contact angle (degrees) of different liquids-PCPU samples before and after rupture ......................................................... 106

Table 4.3  Resulting total surface tensions \( \gamma_{sv} \), with corresponding dispersive \( \gamma_{sv}^d \) and polar \( \gamma_{sv}^p \) components( mN m\(^{-1}\)). .......... 110
LIST OF FIGURES

Figure 1.1 An isocyanate functional group and a hydroxyl functional group combine to create a urethane linkage ........................................... 2

Figure 1.2 Basic Isocyanate reactions ........................................................................ 2

Figure 1.3 Polyurethane model indicating hard and soft segment locations. ................................................................. 3

Figure 1.4 One-shot and Two-shot methods for polyurethane systems ........... 4

Figure 1.5 Model drawing of CNT structure................................................................. 7

Figure 1.6 An example of a quadropole hydrogen bonding unit. ..................... 12

Figure 2.1 Reaction scheme for Nippollan 964. Red circles are used to highlight the pendant methyl groups. ......................... 27

Figure 2.2 GPC trace showing PCPU signal against calibration points........... 28

Figure 2.3 Stress-strain curves for 5 neat PCPU specimens. ...................... 30

Figure 2.4 Stress-strain curves for 5 neat PCPU specimens after rupture and heal. ................................................................. 30

Figure 2.5 SEM image showing Razor-cut and Pulled sample comparison ................................................................. 31

Figure 2.6 Ultimate tensile strength for cut and ruptured samples. ............. 32
Figure 2.7  DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of neat Poly (carbonate urethane) (PCPU). .................................................. 34

Figure 2.8  DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.25wt% SWCNT/ PCPU composite .................................................. 35

Figure 2.9  DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.50wt% SWCNT/ PCPU composite .................................................. 36

Figure 2.10 DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.75wt% PCPU composite .................................................. 37

Figure 2.11 DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 1.0wt% SWCNT/ PCPU composite .................................................. 38

Figure 2.12 DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.25wt% MWCNT/ PCPU composite .................................................. 39

Figure 2.13 DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.50wt% MWCNT/ PCPU composite .................................................. 40

Figure 2.14 DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.75wt% MWCNT/ PCPU composite .................................................. 41

Figure 2.15 DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 1.0wt% MWCNT/ PCPU composite .................................................. 42

Figure 2.16  XRD trace showing detection of ordered structure ...................... 44

Figure 2.17 XRD traces of polyurethane resins with different hard segment content [Trovati, Ap Sanches et al. 2010] ........................................ 45

Figure 2.18 DSC data: Result of stressing neat PCPU specimen ...................... 46
Figure 2.19  Tensile data: Stress-strain curves for 5 neat PCPU specimens.................................................................................................................. 47

Figure 2.20  Tensile data: Stress-strain curves for 5 0.25wt% SWCNT/PCPU composite specimens.......................................................... 48

Figure 2.21  Tensile data: Stress-strain curves for 5 0.50wt% SWCNT/PCPU composite specimens.......................................................... 49

Figure 2.22  Tensile data: Stress-strain curves for 5 0.75wt% SWCNT/PCPU composite specimens.......................................................... 50

Figure 2.23  Tensile data: Stress-strain curves for 5 1.0wt% SWCNT/PCPU composite specimens.......................................................... 51

Figure 2.24  Tensile data: Stress-strain curves for 5 neat 0.25wt% MWCNT/PCPU composite specimens.................................................... 52

Figure 2.25  Tensile data: Stress-strain curves for 5 0.50wt% MWCNT/PCPU composite specimens.......................................................... 53

Figure 2.26  Tensile data: Stress-strain curves for 5 0.75wt% MWCNT/PCPU composite specimens.......................................................... 54

Figure 2.27  Tensile data: Stress-strain curves for 5 1.0wt% MWCNT/PCPU composite specimens.......................................................... 55

Figure 2.28  Image showing typical rupture location. .......................................................... 58

Figure 2.29  Tensile test data: stress-strain curve for 0.25wt% SWCNT/PCPU composite after 24 hours of healing. ......................... 58

Figure 2.30  Model of healing process. .............................................................................. 65

Figure 2.31  Raman spectra PCPU/CNT composites .......................................................... 66
Figure 2.32  (A) Raman spectra of polyurethane ......................................................... 68

Figure 3.1  A) Optical micrograph example 1.0 wt% MWCNT in PCPU
B) binary image used for particle analysis, inset zoom
showing detection of CNT agglomerations....................................................... 83

Figure 3.2  A) SEM image for PCPU 1.0wt% SWCNT composite
solution cast. B) SEM image for PCPU 1.0wt% SWCNT
composite solution water cast. ................................................................. 84

Figure 3.3  A) Solution of PCPU/THF and 1wt% SWCNT................................. 86

Figure 3.4  A) Solution of PCPU/THF and 1wt% MWCNT.............................. 87

Figure 3.5  Tensile test data, typical stress-strain curves generated for
experiment for this series of tests.......................................................... 90

Figure 3.6  Conformational isomers of H$_{12}$MDI [Elabd, Sloan et al. 2000]....... 91

Figure 3.7  Rheology data: G' for SWCNT/PCPU........................................ 93

Figure 3.8  Rheology data: G' for MWCNT/PCPU........................................ 93

Figure 4.1  Model of a sessile-drop contact angle system............................. 97

Figure 4.2  Contact angle method of measuring angle on video based
system............................................................................................................. 104

Figure 4.3  Contact angles formed between Neat PCPU, H2O, ethylene
glycol and glycerol.1..................................................................................... 105

Figure 4.4  Contact angle data. Measured CA plotted against wt% for
Neat and PCPU/CNT composites before and after cutting. ........ 107
Figure 4.5  Contact angle data, typical linear fit of points plotted for three test liquids: H₂O, ethylene glycol and glycerol on 0.25wt% SWCNT/PCPU composite, before cut........................................... 109

Figure 4.6  Contact angle data, typical linear fit of points plotted for three test liquids: H₂O, ethylene glycol and glycerol on 0.25wt% SWCNT/PCPU composite after cut.................................................. 109

Figure 4.7  Surface tension parameter, $\gamma_{sv}$, for uncut and cut specimens according to the geometric mean method.............................................. 111

Figure 4.8  Surface tension parameter, $\gamma_{sv}^d$, for uncut and cut specimens according to the geometric mean method.............................................. 112

Figure 4.9  Surface tension parameter, $\gamma_{sv}^p$, for uncut and cut specimens according to the geometric mean method.............................................. 113

Figure 4.10 Sample FTIR showing peaks of interest A) Uncut B) Cut............ 115

Figure 4.11 FTIR showing time lapse collection over 24 hours for peaks of interest. ........................................................................................................ 116

Figure 5.1  Structure of graphene................................................................. 119
ABSTRACT

Synthesis of high molar mass polycarbonate polyurethanes using a novel polyol is described. The resulting elastomers demonstrate excellent mechanical properties as well as the capability to re-heal after rupture without the addition of additives or imbedded healing agents. The self-healing functionality is shown to greatly improve with the addition of up to 1% single and multi-walled carbon nanotubes. The interface of the carbon nanotubes and self-healing polymer are probed using Raman techniques and provide an insight into how the self-healing actions are improved with the addition of carbon nanotubes.

Synthesis of polycarbonate polyurethanes and carbon nanotube composites using a novel casting method is described and compared to the more traditional solution casting method. The dispersion of the carbon nanotubes is evaluated as well as the effect of effective dispersion on the composites through tensile testing, rheometry and hardness testing. Although complete agglomeration avoidance could not be achieved, significant size decrease was observed. Over 200% improvement in tensile strength is shown with conventional solution casting method which is further improved by the described novel solution casting method.

Contact angle measurements on our novel self-healing poly (carbonate urethane) and CNTs composites show that surface energies are drastically changed when CNTs are used. The most revealing finding is that $\gamma_{sv}^D$ increases in CNT composite materials from ~30% of the surface energy on average for the
samples tested, to ~80%. We have shown that surface free energies increase most likely as a result of exposing hydrogen bonding sites typically found within the bulk in polyurethanes. Our polyurethane differs from traditional polyurethanes in that it has both novel soft segments made from a novel polycarbonate polyol discussed in chapter 2 and relatively soft “hard” segments resulting from the use of H₁₂MDI, all leading to increased ability to hydrogen bond within the material. The availability of the hydrogen bonding sites is demonstrated by FTIR absorbance bands for associated and unassociated hydrogen bonding sites, which do not seem to be accessible to a large until the PCPU’s surface is disrupted. Once disrupted, the exposed hydrogen bonding sites are able to bond with other bonding sites of adjacent ruptured surfaces. This would explain why our material is non-blocking, e.g. won’t stick to itself, until the surface is ruptured. It would also explain why any two ruptured surfaces of our material will reheat, even if they were not attached previously.
CHAPTER 1

INTRODUCTION

Polyurethane (PU) Chemistry and Structure

The versatility of polyurethanes allows a wide range of applications, from tough versions that stand up to such uses as roller blade wheels and rigid insulation to very soft flexible foams, elastic fibers, or as integral coatings applied to metals as anti-corrosion. The underlying chemistry of PUs is the result of one man’s genius, Dr. Otto Bayer (1902-1982). Dr. Otto Bayer is recognized as the “father” of the polyurethane industry for his invention of the basic diisocyanate polyaddition process [Szycher 1999].

Polyurethanes are large and complex molecules produced by reacting a number of different monomers. The components of polyurethanes typically consist of an aromatic or aliphatic diisocyanate, a long chain polyester or polyether polyol, and a short chain polyol referred to as the chain extender. The formation of linear polyurethanes requires that monomers contain difunctional units of their respective functional groups, usually located at opposite ends of the monomer molecule. Figure 1.1 shows a typical reaction scheme resulting in the formation of a urethane functional group. The great diversity in PU structures results from many other functional groups appended to the polyols and chain extenders. Figure 1.2, shows typical isocyanate reactions including formation of
the desired urethane linkages, which despite the name “polyurethane” only makes up a minority of the functionality within the polymer system.

<table>
<thead>
<tr>
<th>N=C=O</th>
<th>+</th>
<th>H-O</th>
<th>→</th>
<th>NHCOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>isocyanate group</td>
<td>hydroxyl group</td>
<td>urethane linkage</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.1. An isocyanate functional group and a hydroxyl functional group combine to create a urethane linkage

Figure 1.2. Basic Isocyanate reactions

PU typically exists as a segmented copolymer of hard and soft segments and can be represented by the following form:
P-(D(CD)n-P)n

Where P is derived from the polyol, D is derived from the diisocyanate and C is derived from the chain extender. As schematically shown in figure 3, PU contains alternating regions of hard and soft segments, separation due to thermodynamic incompatibility of the two segments [Li, Gao et al. 1992]. The soft segments are formed by the polyol component, and the combination of the chain extender and diisocyanate form the hard segments. Soft segments are amorphous and control low temperature characteristics whereas hard segments are semi crystalline to crystalline and control properties such as hardness and tensile strength [Li, Kang et al. 1994].

Figure 1.3. Polyurethane model indicating hard and soft segment locations.
Starting materials can be reacted employing one of two different methods, summarized in Figure 1.4. The one shot method consists of reacting the hydroxyl (-OH) groups of both the polyol and chain extender with the cyanate (-NCO) groups of the diisocyanate in the appropriate equivalent weight ratios in a single step resulting in a polyurethane with randomized hard and soft segment placement [Szycher 1999].

The two-shot method consists of making a prepolymer by reacting a portion of the polyol with the diisocyanate to achieve a –NCO terminated prepolymer that is formulated to have a desired –NCO percentage in one step by the following:

Required Diisocyanate: \[ (X + N (X + Y))/\left(\frac{42}{X} - N\right) \] (eq. 1.1)
Where:

\[ N = \text{desired NCO\% of the prepolymer (expressed as decimal fraction)} \]

\[ X = \text{weight equivalent of the isocyanate (\% NCO by weight per molecule)} \]

\[ Y = \text{weight equivalent of the polyol (or average equivalent weight of the polyol blend)} \]

In the second step, the prepolymer is reacted with additional polyol and chain extender to achieve a polyurethane of desired hard segment ratio according to the following [Szycher 1999]:

Total weight of diisocyanate required =

\[
\text{(index)}(-\text{NCO eq. wt.}) \left( \frac{pbw\ polyol\ A}{eq.wt.A} + \frac{pbw\ polyol\ B}{eq.wt.B} + \ldots + \frac{pbw\ polyol\ N}{eq.wt.N} + \frac{pbw\ H_2O}{eq.wt.H_2O} \right)
\]

(eq 1.2)

A systematic study was accomplished by L. H. Peebles [Peebles 1974] which showed that the one-shot method results in a more polydispersed polymer in which hard and soft segment blocks are highly randomized. The two-shot method leads to an increase in order between the alternating microphase segments, which directly affects resulting characteristics [Koberstein and Galambos 1992].

**Carbon Nanotube Composites**

A composite is a material that consists of two or more physically or chemically different components separated by an interface [Miller 1996]. Composites are characterized by having unique final properties which are not exhibited by any of
the constituents when they are considered solely. The two main constituents of composite materials are the matrix and the reinforcement. Based on the type of matrix they are classified into metal matrix composites, polymer matrix composites and ceramic matrix composites. Polymer nanocomposites are a class of materials where at least one of the dimensions of the filler material is of the order of a nanometer. The unique combination of the nanomaterial's characteristics, such as size, electrical, thermal and mechanical properties, low concentrations necessary to change the composite properties coupled with advanced characterization techniques has made them one of the most sought after materials for a variety of applications. There are dramatic changes in physical properties due to reduction to the nanoscale dimension of the filler material. Some of the most common nanomaterials employed in producing polymeric composites are silica nanoparticles, carbon black, carbon nanotubes, nanofibers etc. One of the largest advantages of using nanomaterials is their large surface area [Khudyakov, Zopf et al. 2009]. The surface area per unit volume is inversely proportional to the diameter. Since most of the physical and chemical interactions are governed by the surface properties, surface area plays a major role in the determining the ultimate properties of a composite material. Surface area and quantum effects are two main factors that distinguish the nanomaterials from other materials [Hussain, Hojjati et al. 2006]. Since the discovery of carbon nanotubes (CNT) in 1991 by Iijima [Iijima 1991] CNTs have attracted considerable attention for a wide variety of applications.
Their remarkable electrical, mechanical and thermal properties combined with their large aspect ratios make them the most sought after nanofillers for multifunctional polymer composites research [Ajayan and Tour 2007]. There are two basic types of CNTs, single-wall carbon nanotubes (SWCNT) and multiwall carbon nanotubes (MWCNT). Their structure is as the name implies, SWCNTs can be thought of as a single graphene sheet that has been rolled into a seamless cylinder. MWCNTs consist of similar cylinders that are nested inside one another, however a hollow core is maintained (Figure 1.5).

**Figure 1.5. Model drawing of CNT structure.**

Despite extensive research, the full potential has not yet been realized in imparting superior properties to CNT/polymer composites because of a number of factors including the purity of CNTs, their difficulty to disperse in a polymer matrix, interfacial bonding and alignment. Research has focused on improving nanotube dispersion; better nanotube dispersion in the polymer matrices has been shown to improve properties including several hundred percent increase in mechanical strength [Gong, Liu et al. 2000] and electrical conductivity [Ramasubramaniam, Chen et al. 2003].
The ability to control the dispersion of CNTs has proven to be challenging, as of yet the perfect solvent for CNTs remains undiscovered [McClory, Chin et al. 2009]. Solution-phase processing is exceptionally useful for many of carbon nanotubes applications. To date, the best solvents reported for generating CNT dispersions are amides, particularly N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP), however the dispersions are subject to aggregation on a time-scale of days.

Ausman et al. investigated the room-temperature solubility of SWNTs in a variety of solvents. It was found that a class of non-hydrogen-bonding Lewis bases could provide better solubility, but solubility was still relatively low [Ausman, Piner et al. 2000]. With the aid of surfactants, CNTs that have not been chemically modified can be dispersed in water with some success. The surfactants deposit on the surface of nanotubes, modify the particle-suspending medium interface and prevent aggregation [Moore, Strano et al. 2003].

Surfactants provide an additional repulsive force and lower the surface energy. Suspension in surfactants can be a useful method for purification of nanotubes. A polyelectrolyte-surfactant-MWNTs complex can help micrometer-length multiwalled carbon nanotubes suspend in organic solvents by forming a lamellar structure [Jin, Huang et al. 2000].

Of all the methods used, one of the most common methods that successfully disperses CNTs is low-viscosity liquids is ultrasonication [Grady 2010]. Ultrasonication is widely employed in CNT dispersion, where separation and functionalization of the tubes can be greatly enhanced.
The two main instruments used are ultrasonic bath (40–50 kHz), and ultrasonic horn/tip (25 kHz) [Hilding, Grulke et al. 2003]. The conditions which control chemical and mechanical effects of sonication include: the ultrasound intensity and frequency; the pulsing interval and duration; the presence of gases; the external pressure and temperature; the location of the ultrasound source and the container geometry; and the concentration of solute, all of which must be taken into careful consideration [Paulusse and Sijbesma 2006].

**Self-Healing Polymers**

Self-healing materials (SHM) are able to partially or fully repair their damage, with the ultimate goal of returning all of the pre-damage characteristics after the healing process occurs. Human skin provides an excellent example of how artificial self-healing materials are required to work. Once ruptured, the body self-protects the area to stop additional damage, and then provides the necessary building blocks through vascular systems to return the damaged skin to an undamaged state. Self-healing materials can be divided into two different classes based on the required stimuli and type of response: Non-autonomous and autonomous. Non-autonomous SHMs require an external trigger, such as heat or light to initiate or provide energy for the healing process. Autonomic SHMs on the other hand, do not require an external trigger as the damage itself is the stimulus for the healing [Picken, Mookhoek et al. 2010].

The earliest reviews (in 2003 and 2006) focused on comparisons with repair in living organisms [Hiroo 2001; Fang Zheng-ping, Yang Hai-tang et al. 2006]. A
significant book of review articles on self-healing materials was published in 2007 [Zwaag 2007], and since that time a momentum has continued to build. Intrinsic self-healing polymers function via reversible bonding in the polymer matrix. This bonding is the result of equilibrium reactions, hydrogen bonding, ionomer binding, a meltable, dispersed thermoplastic phase, or can occur as a result of molecular diffusion [Blaiszik, Kramer et al. 2010]. In autonomous systems, healing occurs without intervention from heat, light, electrical signal or other stimuli. Healing in these systems is often reversible, that is, the polymer can reversibly form monomer, oligomer or non-cross-linked structures [Bergman and Wudl 2008]. Extrinsic self-healing polymers contain external components such as microcapsules or vascular healing systems that contain healing agents [Hager, Greil et al. 2010]. Damage ruptures the healing structures and the material undergoes autonomous healing. Extrinsic processes are usually not reversible.

This research focuses on intrinsic healing polymers and recent advances in this area are briefly discussed here. Two excellent reviews summarize systems that self-heal via reversible covalent bonds [Bergman and Wudl 2008; Bergman and Wudl 2008]. Several covalent systems are discussed: Diels –Alder based polymers, Thiol-based polymers, N-O-based polymers and photodimerization polymers (i.e. polyurethanes with disulfide bonds). Bergman and Wudl point out the advantages and disadvantages of these systems; advantages are that systems fail and re-heal multiple times, reversible polymerizations are simple in nature, and no added components are needed. Disadvantages are that the
processes involved are not autonomous (for example, heat or light is required), there are commercial systems are not at hand, and the monomers will likely be costly. Interest in supramolecular chemistry spurred researchers to investigate re-mendable polymers based on non-covalent interactions. Many of these structures are composed of low molecular weight units that self-assemble into highly ordered reversible structures [Brunsveld, Folmer et al. 2001; Burattini, Colquhoun et al. 2009]. One such system of interest to those studying thermoplastic, high molar mass, mendable materials uses a stable, self-complimentary, quadropole hydrogen bonding unit (figure 1.6) based on 2-ureido-4[1H]-pyrimidinones (UPys) and was developed by Zimmerman in 1998 [Kolotuchin and Zimmerman 1998]. This quadropole has a very high dimerization constant and Meijer took advantage of this and went on to develop polymers based on these structures.

![Figure 1.6. An example of a quadropole hydrogen bonding unit.](image-url)
These materials are stable to near 90°C and are thermoreversible. A company named SupraPolix was started in order to market polymer systems incorporating quadropole structures into polymer networks [Suprapolix 2011]. UPy units were linked to reactive isocyanate groups and reacted with telechelic polymers containing hydroxyl or amine groups. For example, OH telechelic poly(ethylene/butylene) was functionalized with UPy isocyanate structure [Folmer, Sijbesma et al. 2000]. The authors demonstrated that the telechelic polymer was a viscous liquid at room temperature, whereas, the UPy functionalized telechelic was an elastic solid. The material exhibited viscoelastic properties of a high polymer and melt viscosity dropped rapidly with temperature. Another UPy functionalized oligomer was made using telechelic hydroxyl trifunctional block copolymers of propylene oxide and ethylene oxide polyethers with molar masses of 6,000 [Lange, Gurp et al. 1999]. This reversible, hydrogen-bonded network exhibited a higher “virtual” molecular weight and shear modulus than an irreversible, covalently bonded polymer network analogue. The ureido-pyrimidone network exhibited high polymer behavior without requiring crystallization and also exhibited viscoelastic properties. In yet another study, polyesters were functionalized with UPy units both at chain ends and within the backbone [Dankers, van Leeuwen et al. 2006]. End functionalized polymers were more brittle that the chain extended polymers; chain extended polymers were more elastic and softer. Blending both species resulted in polymers with tunable mechanical properties.
Self-complementary multiple hydrogen-bonded (SCMHB) polymers containing pendant 2-ureido-4[1H]-pyrimidone (UPy) units were synthesized by appending methacrylate (MA) to UPy units and copolymerizing the units with butyl methacrylate [Yamaguchi, Ono et al. 2007]. Glass transition temperatures increased in a linear fashion as the SCMHB MA content increased. SCMHB pendant polymers exhibited thermoreversible characteristics, and dissociation in the melt state was observed at 80 °C. Peel strength also increased with SCMHB content. This important series of experiments illustrated that supramolecular systems have great promise in the field self-healing polymers.

A 2008 publication in *Nature* described another amazing supramolecular oligomer system [Cordier, Tournilhac et al. 2008]. Cordier et al used a mixture of fatty diacids and triacids obtained from vegetable oil and condensed it with diethylene triamine and then reacted it with urea. This resulted in a mixture of oligomers with complementary hydrogen bonding groups: amidoethyl imidazolidone, di(amidoethyl) urea and diamido tetraethyl triurea. The material could be stretched up to several hundred per cent and recovered completely. It can be torn and recovered at room temperatures multiple times. Repaired samples recover their strength as well. The self-healing properties diminished when the materials were aged at room temperature after failure and before re-healing. We observe this behavior in our polymers and discuss this under the experimental section. These materials were designed to contain branched units that hydrogen bond forming a supramolecular network. Crystallinity was avoided to allow the mobility needed for healing. It is a goal of the present research to
design a material that has minimized crystallinity in order to affect chain mobility and maintain high molar mass and have hydrogen bonding units throughout the length of the chains, which should, if successful, have a much higher inherent tensile strength and improved characteristics.

Several reviews on self-healing polymer composites have been published in recent years [Bond, Trask et al. 2008; Blaiszik, Kramer et al. 2010; Picken, Mookhoek et al. 2010; Syrett, Becer et al. 2010]. The current work focuses on using carbon nanotubes for reinforcement and to enhance self-healing without using the nanotubes to release any type of healing agent into the matrix. There are no reports that the author is aware of that detail any enhancements in self-healing due to nanotubes in systems where the nanotubes are not releasing healing agents, however there is a publication that discusses using nanotubes as sensors to detect damage and self-healing [Thostenson and Chou 2006].
CHAPTER 2
Ultra-flexible Autonomously Self-Healing High Molar Mass Polyurethanes

INTRODUCTION

Research in self-healing polymer systems has transitioned from earlier studied extrinsic self-healing systems,[Bergman and Wudl 2008; Wu, Meure et al. 2008] to more recently developed intrinsic self-healing systems[Blaiszik, Kramer et al. 2010]. Intrinsic materials are one type of autonomous self-healing materials that heal through polymeric chain interdiffusion, hydrogen bonding, use of incorporated ionomers, or the use of thermally reversible or equilibrium controlled reactions. The advantage of autonomous systems is that healing processes start relatively soon after material failure without the intervention of heat, light, electrical signal or other stimuli [Hager, Greil et al. 2010]. Some autonomous self-healing materials have microencapsulated healing agents stored in the material’s matrix either in spherical or vascular forms in order to mimic biological systems [Pang and Bond 2005; Keller, White et al. 2007; Andersson, Keller et al. 2008; Yuan, Rong et al. 2008; Chipara, Chipara et al. 2009]. Bergman and Wudl point out the advantages and disadvantages of these systems[Bergman and Wudl 2008]. Advantages are that systems fail and re-heal multiple times, reversible polymerizations are simple in nature, and no added components are needed. Disadvantages are that the processes involved are not autonomous (for example, heat or light is required), there are not commercially
available systems at hand and the monomers will likely be costly. Although these systems do have success in returning intrinsic mechanical properties to the damaged material, there is some work yet to do before being industrially viable [Andersson, Keller et al. 2008; Wu, Meure et al. 2008; Coillot, Méar et al. 2010].

In order to avert the intricacies associated with creating composite material from embedded healing agents, new materials are designed to repair or re-mend using the initial species and reversible chemistry[Chen, Dam et al. 2002; Chen, Wudl et al. 2003; Cordier, Tournilhac et al. 2008; Cho, White et al. 2009; Adzima, Kloxin et al. 2010]. Many of these structures are composed of low molecular weight units that self-assemble into highly ordered reversible structures [Folmer, Sijbesma et al. 2000; Brunsveld, Folmer et al. 2001; Burattini, Colquhoun et al. 2009]. The use of supramolecular structures appears particularly advantageous because these materials behave similar to conventional macromolecular elastomers and do not require covalent bond manipulation to repair damage within the material [Kersey, Loveless et al. 2007]. Hydrogen bonding, electrostatic and donor-acceptor interactions, metal-ion coordinations, etc., within intrinsic healing materials are primarily responsible for the initial mechanical characteristics and for the self-healing properties [Ciferri 2005]. Cordier et al describes an amazing supramolecular oligomer system that takes full advantage of what can be accomplished with these types of reversible networks [Cordier, Tournilhac et al. 2008]. They used a mixture of fatty diacids and triacids obtained from vegetable oil and condensed it with diethylene triamine and then reacted it with urea. This resulted in a mixture of oligomers with complementary hydrogen
bonding groups: amidoethyl imidazolidone, di (amidoethyl) urea and diamido tetraethyl triurea. The material could be stretched up to several hundred per cent and recovered completely. It can be torn and recovered at room temperatures multiple times. Repaired samples recover most of their strength as well. The self-healing properties diminished when the materials were aged at room temperature after failure and before re-healing; self-healing properties extinguish.

Even though supramolecular materials demonstrate properties close to traditional elastomers and show the ability to autonomously self-repair, the mechanical characteristics are still somewhat lower when compared to conventional elastomers. However, the ability to heal is a particularly advantageous characteristic and thought not possible to achieve in conventional cross-linked or thermoreversible rubbers.

Studies have been reported on self-healing high molar mass materials. For example, a self-healing polyurethane has been describes by Bayer [Bayer-MaterialScience 2011]. This polyurethane has been highly cross-linked with an allophanate trimer isocyanate. It can be used with a variety of polyols. Heat from sunlight repairs the materials. The application is for scratch resistant coatings such as on cars. The PUs have low glass transition temperatures 50-60°C. This poses a problem, since the coatings cannot be buffed. In addition, mechanical loads such as due to car wash brushes result in permanent damage. Science reports still another self-healing polyurethane [Ghosh and Urban 2009]. This PU contains an oxetane-substituted chitosan precursor in polyurethane. It does, however, require UV initiated cure. A self-healing polyurea was recently
discussed by Garcia et al. This high molar mass materials has a glass transition temperature of 66°C and is designed to halt crack propagation at the tip through the use of photothermal energy [Garcia, Lin et al. 2010].

Here we describe an approach using flexible, strong, high molar mass polyurethane elastomers with optimum mechanical properties that exhibit autonomous self-healing.
EXPERIMENTAL

Materials

The modified polycarbonate polyol (Nippollan 964, previous nomenclature was PES EX-619 produced by Hodogaya Chemical Co.) was provided by Nippon Polyurethane Industry Co., LTD., Tokyo Japan, and used as received. The average OH number for this polycarbonate polyol is 56.3 and the molecular weight is reported by the manufacturer to be 2000 a.m.u.

Methylene bis (4-cyclohexylisocyanate) (H\textsubscript{12} MDI or Desmodur W) was provided by Bayer, (NCO content confirmed by dibutylamine end-group analysis to be 31.8%). End group analysis was performed according to ASTM D2572-97 in the following manner: A 0.1% bromphenol blue indicator solution was prepared by mixing 0.10g of bromphenol blue indicator with 1.5 mL of 0.1N NaOH solution and diluting to 100mL with distilled water. 1 L of 0.1 N Di-n-butylamine solution was made by weighing 12.92 g and diluting to 1L with deionized water. 1 L of 0.1 N HCL solution was made by measuring out 8.2 mL of 12 N stock HCL solution and adding 250 mL deionized water, and then diluting further to 1L. .30 g diisocyanate was added to a 250 ml Erlenmeyer flask and dissolved into 25 mL of dry toluene. 25 ml of the Di-n-butylamine solution was added to this solution and allowed to react under constant agitation for 15 minutes. 100 mL of isopropyl alcohol and 6 drops of bromphenol blue indicator
was then added. This solution was titrated with the 0.1 N hydrochloric acid to a yellow end point. A blank solution was also titrated which did not include the specimen. The NCO content was calculated using the following formula:

\[
NCO, \% = \frac{[(B-V) \times N \times 0.0420]}{W} \times 100 \quad (eq. \ 2.1)
\]

Where:

- \( B \) = volume of HCL for titration of the blank, mL
- \( V \) = volume of HCL for titration of the specimen, mL
- \( N \) = normality of HCL
- 0.0420 = milliequivalent weight of the NCO group
- \( W \) = grams of specimen weight, g

1, 4 butanediol (BDO) was purchased from Sigma Aldridge and used as received as the chain extender. Single (0.7-1.3 nm diameter) and multi-walled (7-15 nm \( \times \) 0.5-10 \( \mu \)m) carbon nanotubes were purchased from Sigma-Aldrich and used without further purification.

**Methods**

**Polyurethane Synthesis**

23% hard-segment polycarbonate polyurethane used for carbon Nanotube composites was made by two-shot process, as discussed prior, the two-shot process allows for a more ordered polymer chain structure which in this particular polyurethane results in material that exhibits increased tensile strength than the
exact material made by the one-shot method [Kull, Gerasimov et al. 2005].

Mixture 1 was a prepolymer made by reacting a ratio of H$_{12}$ MDI and Nippolan 964 to achieve 20% -NCO content under constant stirring and nitrogen environment and a constant 100$^\circ$ C. The resulting NCO content of 20% was confirmed by dibutylamine end-group analysis discussed above. Mixture 2 was 95% Nippon 964 to 5% BDO. Mixtures 1 and 2 were reacted together in a ratio to achieve the targeted hard-segment content.

**Carbon Nanotube Composites**

Carbon Nanotube composites were formed by first dissolving neat polycarbonate polyurethane (23% hard-segment) into tetrahydrofuran anhydrous,( ≥99.9%, inhibitor-free (Sigma-Aldrich)) and then mixing desired amount of carbon nanotubes (0.25-1% by weight) by ultrasonication (Fisher Scientific Sonic Dismembrator 550) for 2 Hours. Materials were then solution cast under constant agitation to ensure carbon nanotube dispersion was maintained. Samples for testing were compression molded using a Carver laboratory press (model C) equipped with heating elements.
**Differential Scanning Calorimetry (DSC)**

DSC is a thermal analysis technique used to measure the heat fluxes emitted or absorbed by a sample as a function of temperature and time. When a thermal transition occurs the enthalpy change is recorded. In addition to measuring the basic phase changes like the glass transition temperature ($T_g$) and melt temperature ($T_m$) other valuable quantitative properties can be determined. These include, but are not limited to: percent crystallinity, heats of crystallization and fusion in semi-amorphous polymers and organic-inorganic compounds, degree of cure and reaction kinetics in thermosets, oxidative stability, thermal conductivity, decomposition and cross linking. DSC is a versatile technique that can be used for polymers, organic and inorganic analysis, of which the sample can be in the form of a solid, liquid, or gel.

Throughout this study, a TA instruments 2910 DSC with standard cell and cooling accessory was used. This instrument works by detecting and displaying differences in electrical power required to maintain the temperatures of two identical metal pans, one of which contains the specimen under investigation. When a transition of state occurs in the specimen, the temperature will either lag behind the reference temperature for endothermic processes, or surge for exothermic processes.
The samples were first cooled to \(-60^\circ\text{C}\) and ramped to a final temperature of \(130^\circ\text{C}\) at a rate of \(10^\circ\text{C} \text{ min}^{-1}\). Only the first runs were analyzed, as evidence of hard segment melting disappeared during the second runs.

**Tensile Test**

Stress-strain curves can be obtained under a static load which could be compressive or tensile, with at a low applied strain rate, uniformly over the material cross-section. Tensile tests are commonly done to obtain the relevant mechanical properties of a material, such as Young’s modulus, strain-to-failure, ultimate tensile strength and toughness.

The engineering stress and engineering strain in the material are used to avoid the use of a geometry factor. The engineering stress \(\sigma\) is given by:

\[
\sigma = \frac{F}{A} \quad (\text{eq. 2.2})
\]

where \(F\) is the instantaneous load applied perpendicular to the sample and \(A\) is the original cross-sectional area of the sample.

The engineering strain \(\varepsilon\) is given by:

\[
\varepsilon = \frac{L - L_0}{L_0} \quad (\text{eq. 2.3})
\]

where \(L\) is the final sample length and \(L_0\) is the original sample length.
Young’s modulus measures the ability of a material to resist elastic deformation under applied stress, given by the slope of the stress-strain curve below the yield point. It is given by Hooke’s law between $\sigma$ and $\varepsilon$:

$$E = \frac{\sigma}{\varepsilon} \quad (\text{eq. 2.4})$$

The modulus is a direct measure of microscopic interatomic resistance to stretching. Different materials have different modulus, depending on their interatomic bonding. Polymers have a wide range of modulus varying from a few MPa (e.g. Polydimethylsiloxane) up to 3 GPa (e.g. some epoxy resins).

Tensile testing was carried out using a QTEST III (MTS) tensiometer using its extensiometer to measure the displacement. All tensile testing was conducted at a rate of 4 inches min$^{-1}$ at 25$^\circ$C in accordance with ASTM D412C. Testing articles (dog bones) were compression molded using a Carver laboratory press (model C) equipped with heating elements. Tensile testing conducted after samples were rehealed were conducted at a rate of 2 inches min$^{-1}$ to directly compare to other work conducted elsewhere.

**Gel Permeation Chromatography**

The molecular weight and molecular weight distribution of the polyurethanes were determined by gel permeation chromatography (GPC) (Polymer Laboratories PL GPC-50). The samples, dissolved in THF with concentration of $\sim$0.1 wt %, were filtered and injected at 30$^\circ$C using THF as mobile phase and at
a flow rate of 1 mL/min. GPC data reported for the molecular weights and molecular weight distributions are relative to a calibration based on monodispersed polystyrene standards (Polymer Laboratories PS-2).

Raman

Neat PCPU, 1.0wt.% SWCNT and 1.0wt. MWCNT samples were provided to Dr. Sheryl Li’s laboratory, USF Dept. of Chemistry, for Raman analysis. All Raman experiments were carried out using a Confocal Raman Microscopy (LabRam Horiba Jovin Yvon) equipped with a notch Rayleigh rejection filter, a 600 lines/mm diffraction grating and a cooled CCD detector. For all experiments, radiation at 514 nm wavelength from a Argon and Krypton laser (Coherent, Innova 70C series) was applied with a power of 40 mW to minimize possible damage to the samples. A 20X objective was used throughout the experiments which yields a spot diameter of less than 5 μm of the sample. In order to obtain high quality Raman spectra, both the exposure time and accumulation time were varied. To check the non-homogeneousness of the polymer samples, Raman spectra were collected at different spots of the sample. Even though Raman spectra were measured in the frequency range of 200 – 3300 cm⁻¹, only regions with distinguishable peaks are shown for a clear view.
RESULTS AND DISCUSSION

Reduced Elastomeric Crystallization

It is accepted that elastomeric properties of polyurethanes are due to hydrogen bonding between diisocyanate and short-diol comprised hard segments and higher molecular weight polyol soft segments [Trifan and Terenzi 1958; Tanaka, Yokoyama et al. 1968; R. W. Seymour, G. M. Estes et al. 1970]. We thought it possible to take advantage of the inherent hydrogen bonding in order to facilitate self-healing if the material were made to act as if it were made up of supramolecular structures. Cordier et al. discuss the desire to avoid crystallization by the supramolecular structures in order to achieve rubber-like properties [Cordier, Tournilhac et al. 2008]. We also considered this a requirement for our elastomers selecting novel polycarbonate diol based polyurethanes for the current study. A typical polycarbonate polyol like poly (1, 6-hexanediol carbonate) is a crystalline solid at room temperature and yields polyurethane elastomers that are tough, but also stiff due the tendency of the soft segment to crystallize. Polyurethanes made with these polycarbonate polyols are designed to producer soft, flexible, and relatively strong materials [Szycher 1999]. Synthetic efforts employing a novel modified polycarbonate polyol
resulted in an ultra-soft polycarbonate polyurethane (PCPU) [Moore, Okabe et al. 2003]. The modified polycarbonate polyol is unique in that it is a liquid at room temperature and the apparent lack of crystallinity leads to the creation of unusually soft polyurethanes (Shore A 60-70 hardness) with excellent physical and mechanical properties. The modified polyol of 2,000 a.m.u. contains several pendant methyl groups derived from the 3-methyl-1, 5-pentanediol during the polyol synthesis (figure 2.1). Appending a methyl group to the third position on the pentanediol appears to drastically alter the properties of the resulting polyol; this particular modification is primarily responsible for impeding crystallization in the polyol and in the PCPU and significantly alters the mechanical properties.

![Reaction scheme for Nippollan 964. Red circles are used to highlight the pendant methyl groups.](image)

Figure 2.1. Reaction scheme for Nippollan 964. Red circles are used to highlight the pendant methyl groups.

This liquid diol was polymerized with 1,4 butanediol chain extender and dicyclohexylmethane-4,4’-diisocyanate at hard segment content from 20-27%
(hard segment content is defined as the combined weight of the isocyanate and chain extender [Szycher 1999]). The molecular weight of the resulting material was 140,000 with a polydispersity of 1.6, figure 2.2. These materials exhibited tensile strengths from 1500-3000 psi (10-20 MPa) and reversible extensions of 500% [Kull, Gerasimov et al. 2005]. Differential scanning calorimetry (DSC) evidenced a barely discernible melting range.

Figure 2.2. GPC trace showing PCPU signal against calibration points.

This is important point, since crystallinity is not desirable in autonomous self-healing thermoplastic materials where a more “liquid” matrix is needed [Cordier, Tournilhac et al. 2008].
Mechanical Evaluation of Self-healing PCPU and CNT Composites

During the mechanical testing of the above described polycarbonate polyurethane, we documented self-healing characteristics in the neat polymer. It was discovered that the broken surfaces of the samples could be pressed back together and were somewhat difficult to pull apart by hand. This was especially intriguing because this material demonstrates superb non-blocking characteristics, e.g. will not stick to its own cured surface, even after prolonged periods of applied pressure [Kull, Gerasimov et al. 2005]. The self-healing properties of 23% hard segment PCPU were initially evaluated during mechanical testing of the neat polymer, after dog bones samples were broken during tensile testing, the two halves were pressed back together and retested after 24 hours at 25-30°C. The results showed that the PCPU did retain approximately 20% of its initial tensile strength; however, it was apparent that there was a large variance in the tensile test results. Figure 2.3 shows the resulting stress-strain curves for neat PCPU samples.

Figure 2.4 shows the resulting stress-strain curves after the samples were pressed back together and healed for 24 hours at room temperature.
The graphed data shows only two of the five retested samples were healed completely enough to register signals on the QTest III. Upon close examination of each specimen, it was noted that when the specimens were pulled until they
broke, very rough and uneven surfaces resulted. The effect of the ruptured surface on the healing was investigated by comparing pulled samples that provided a rough interface and razor-cut surfaces that provided a smooth interface (figure 2.5).

![SEM image showing Razor-cut and Pulled sample comparison](image)

**Figure 2.5.** SEM image showing Razor-cut and Pulled sample comparison.

The specimens were also healed under two temperature environments, room temperature and 40°C, to investigate if the healing process was effected by heat. In all samples, smooth surfaces demonstrated more complete healing and associated tensile strengths. For the specimens healed at room temperature, the strength climbed from an average break stress of 3.5 megapascals (MPa) to over 4.2 MPa, an increase of over 40% (figure 2.6), indicating that the amount of healing does depend on the initial contact surface. Heating the specimens greatly increased the adhesion and healing, the stress at break almost doubled.
going from 3.5 MPa to 6.4 MPa. This indicates that there may be chain
dynamics involved in the healing process.

![Cut Samples vs. Pulled](image)

Figure 2.6. Ultimate tensile strength for cut and ruptured samples.

This phenomenon is well described by Wool [Wool 2006; Wool 2008]. Here
Wool discusses his theory of interface welding in which fractured polymer chain
ends diffuse through entangled polymer segments which results in a quantifiable
amount of gain in material strength. The ability of the polymer chains on the
ruptured surfaces to reentangle does depend on both the interface-interface
contact and the mobility of the polymer chains.

The 23% hard segment PCPU was used to produce single (SWCNT) and
multi-walled carbon nanotube (MWCNT) composites containing 0.25%, 0.50%,
0.75% and 1.00% nanotubes by polymer weight. Carbon nanotubes were
selected because they have been shown to reinforce material, both before and
after damage of self-healing materials as well as initiate the healing process itself
Differential scanning calorimetry was conducted on neat and filled samples to examine effects on chain configuration and to determine what, if any interfaces may be established between the polymer matrix and the carbon nanotubes. As can be summarized by comparing DSC traces of the samples (figures 2.7-2.15), a predominate transition occurs around the -24°C and there is hard segment melting occurring 61-89°C, depending on the CNT type. An interesting find is that with increasing amounts of SWCNT, hard segment melting peaks split into two distinctive regions, indicating that we may be seeing actual crystalline melting versus hard segment domain melting. Surprisingly, despite the changes in hard segment and crystalline domains seen, the carbon nanotubes had little or no effect glass transition temperatures (table 2.1). This indicates that there is not a strong association between the nanotubes and polymer or possibly that the polymer segments are so flexible that the nanotubes move in association with the segments. This is in contrast to earlier work where we observed a 14°C increase in the glass transition temperature of rigid poly (methyl methacrylate) upon the addition of 0.26 % by weight of SWCNTs [Muisener, Clayton et al. 2002; Clayton, Sikder et al. 2005]. Small, broad endotherms were noted in the melt region of the polyurethanes. Melt temperatures decreased slightly with the addition of MWCNTs and to a greater extent with SWCNTs. Endotherm area (J g⁻¹) did increase slightly with increased nanotube content.
Figure 2.7. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of neat Poly (carbonate urethane) (PCPU).
Figure 2.8. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of .25wt% SWCNT/PCPU composite.
Figure 2.9. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.50wt% SWCNT/PCPU composite.
Figure 2.10. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.75wt% PCPU composite.
Figure 2.11. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 1.0wt% SWCNT/PCPU composite.
Figure 2.12. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of .25wt% MWCNT/PCPU composite.
Figure 2.13. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.50wt% MWCNT/PCPU composite.
Figure 2.14. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 0.75wt% MWCNT/PCPU composite.
Figure 2.15. DSC data: Glass transition, $T_g$, and hard segment melt $T_m$ of 1.0wt% MWCNT/PCPU composite.
Table 2.1. \( T_g, T_m \), PCPU Single/Multi-wall CNT composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) °C</th>
<th>( T_m ) °C</th>
<th>Heat of Melt J g(^{-1})</th>
<th>DSC Trace:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PU</td>
<td>-25</td>
<td>91</td>
<td>3.9</td>
<td>Figure 2.7</td>
</tr>
<tr>
<td>0.25% SWCNT</td>
<td>-26</td>
<td>74</td>
<td>1.0</td>
<td>Figure 2.8</td>
</tr>
<tr>
<td>0.50% SWCNT</td>
<td>-26</td>
<td>67/108</td>
<td>1.3/2.7</td>
<td>Figure 2.9</td>
</tr>
<tr>
<td>0.75% SWCNT</td>
<td>-25</td>
<td>73/107</td>
<td>.48/.57</td>
<td>Figure 2.10</td>
</tr>
<tr>
<td>1.0% SWCNT</td>
<td>-26</td>
<td>74</td>
<td>3.3</td>
<td>Figure 2.11</td>
</tr>
<tr>
<td>0.25% MWCNT</td>
<td>-27</td>
<td>73</td>
<td>2.1</td>
<td>Figure 2.12</td>
</tr>
<tr>
<td>0.50% MWCNT</td>
<td>-27</td>
<td>77</td>
<td>3.3</td>
<td>Figure 2.13</td>
</tr>
<tr>
<td>0.75% MWCNT</td>
<td>-27</td>
<td>71</td>
<td>2.3</td>
<td>Figure 2.14</td>
</tr>
<tr>
<td>1.0% MWCNT</td>
<td>-27</td>
<td>72</td>
<td>1.8</td>
<td>Figure 2.15</td>
</tr>
</tbody>
</table>
We performed small angle x-ray diffraction (XRD) on neat 23% hard segment samples to evaluate if crystal structures were present and no features were noted. However, after stressing the sample for 12 hours, we obtained a trace revealing a small peak at $2\theta = 12.9^\circ$, indicating development of ordered structure, typically termed stress-induced crystallization (figure 2.16).

Figure 2.16. XRD trace showing detection of ordered structure.
Travati et al noted similar results (figure 2.17) in their polyurethane resin investigations, finding that peak height is a direct indication of crystalline content [Trovati, Ap Sanches et al. 2010]. The fact that ordered structures were observed on XRD but not easily detected during temperature cycles indicates that our polymer is most likely on the verge of crystallizing or that crystallization is not complete or that the time scale of the chain movement is less than what is detectable.

Figure 2.17. XRD traces of polyurethane resins with different hard segment content [Trovati, Ap Sanches et al. 2010].
DSCs were accomplished on samples after the samples were mechanically stressed, however we did not observe endotherm increases. Figure 2.18 provides an example DSC trace of neat PCPU before and after stressing.

Figure 2.18. DSC data: Result of stressing neat PCPU specimen.

Tensile testing was conducted to evaluate mechanical properties of the resulting composites for the reasons discussed in the introduction. Stress-strain curves are given for 5 specimens of each sample: Neat (figure 2.19), 0.25wt% SWCNT (figure 2.20), 0.50wt% SWCNT (figure 2.21), 0.75wt% SWCNT (figure 2.22), 1.0wt% SWCNT (figure 2.23), 25wt% MWCNT (figure 2.24), 0.50wt% MWCNT (figure 2.25), 0.75wt% MWCNT (figure 2.26), and 1.0wt% MWCNT (figure 2.27). The results of the tensile test including averages and statistical data is summarized in table 2.2. The results show that the tensile strength increased over 200% with addition of both single and multi-walled carbon nanotubes in our PCPU, a similar conclusion as Xia et al for a polyether PU with 26% hard segment content [Xia and Song 2005].
Figure 2.19. Tensile data: Stress-strain curves for 5 neat PCPU specimens.
Figure 2.20. Tensile data: Stress-strain curves for 5.25wt% SWCNT/PCPU composite specimens.
Figure 2.21. Tensile data: Stress-strain curves for 5 0.50wt% SWCNT/PCPU composite specimens.
Figure 2.22. Tensile data: Stress-strain curves for 5 .75wt% SWCNT/PCPU composite specimens.
Figure 2.23. Tensile data: Stress-strain curves for 5 1.0wt% SWCNT/PCPU composite specimens.
Figure 2.24. Tensile data: Stress-strain curves for 5 neat .25wt% MWCNT/PCPU composite specimens.
Figure 2.25. Tensile data: Stress-strain curves for 5 0.50wt% MWCNT/PCPU composite specimens.
Figure 2.26. Tensile data: Stress-strain curves for 5.75wt% MWCNT/PCPU composite specimens.
Figure 2.27. Tensile data: Stress-strain curves for 5 1.0wt% MWCNT/PCPU composite specimens.
Table 2.2. Tensile Test Results for Neat PCPU & PCPU CNT composites.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Average stress @100%strain(MPa)</th>
<th>Average stress @300%strain(MPa)</th>
<th>Average stress @break (MPa)</th>
<th>Average strain @break (% ini.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU</td>
<td>1.34 +/- .09</td>
<td>1.90 +/- .15</td>
<td>3.52 +/- .45</td>
<td>583.0 +/- 25.70</td>
</tr>
<tr>
<td>0.25wt% SWCNT</td>
<td>3.02 +/- .15</td>
<td>6.57 +/- .35</td>
<td>9.00 +/- .30</td>
<td>445.4 +/- 12.76</td>
</tr>
<tr>
<td>0.50wt% SWCNT</td>
<td>3.00 +/- .31</td>
<td>5.97 +/- .46</td>
<td>8.10 +/- .52</td>
<td>441.4 +/- 28.20</td>
</tr>
<tr>
<td>0.75wt% SWCNT</td>
<td>2.36 +/- .06</td>
<td>5.30 +/- .15</td>
<td>6.90 +/- .87</td>
<td>434.0 +/- 60.26</td>
</tr>
<tr>
<td>1.0wt% SWCNT</td>
<td>2.64 +/- .11</td>
<td>5.80 +/- .27</td>
<td>7.70 +/- .28</td>
<td>442.4 +/- 20.90</td>
</tr>
<tr>
<td>0.25wt% MWCNT</td>
<td>2.50 +/- .14</td>
<td>4.59 +/- .16</td>
<td>11.30 +/- 1.90</td>
<td>459.0 +/- 28.20</td>
</tr>
<tr>
<td>0.50wt% MWCNT</td>
<td>3.24 +/- .15</td>
<td>7.22 +/- .32</td>
<td>9.80 +/- .49</td>
<td>444.2 +/- 12.40</td>
</tr>
<tr>
<td>0.75wt% MWCNT</td>
<td>2.96 +/- .09</td>
<td>6.33 +/- .14</td>
<td>8.20 +/- .35</td>
<td>439.2 +/- 10.90</td>
</tr>
<tr>
<td>1.0wt% MWCNT</td>
<td>3.06 +/- .17</td>
<td>6.53 +/- .27</td>
<td>8.50 +/- .37</td>
<td>443.8 +/- 22.70</td>
</tr>
</tbody>
</table>
What is different in our results is that elongation at break was reduced slightly, from 583% for the neat PCPU to an average of 443% for all nanotube composites combined, again suggesting that the CNTs may be acting to facilitate a crystallization process during stress, which could also explain the dramatic increased in tensile strength. This is also apparent when the shape of the stress-strain curves are compared for neat PCPU against all composites. There is a large yield region presenting as a belly in the neat stress-strain curve which indicates that the polymer chains in this sample are more mobile and therefore move to a greater extent in response to the applied stress. This also suggests that the CNTs do act as anchor points for the polymer chains within the composite materials.

The healing efficiency of all neat PCPU and PCPU/CNT composites were first tested by taking the tensile test dogbone specimens and rejoining the two-halves after rupture and allowing the specimen to heal 24 hours at room temperature. It should be noted that at this point it was known that heating the specimens increased healing efficiency as discussed earlier, however, it was decided to take a “worst case” course of testing; that is to say, we tested the specimens under the conditions where we knew from initial testing that they performed at their worst. Figure 2.28 demonstrates a typical break that occurs during initial tensile testing. Figure 2.29 shows a typical set of stress-strain curves after healing. Table 2.3 summarizes tensile test results and compares with the initial tensile test results.
Figure 2.28. Image showing typical rupture location.

Figure 2.29. Tensile test data: stress-strain curve for .25wt% SWCNT/PCPU composite after 24 hours of healing.
Table 2.3. Tensile test summary for neat PCPU & PCPU/CNT composites after healing time of 24 hours.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Average stress @break (MPa)</th>
<th>Initial Value</th>
<th>Average strain @break (% ini.)</th>
<th>Initial Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU Heal 24H @ RT</td>
<td>3.4 +/- 4.74</td>
<td>3.52 +/- 0.45</td>
<td>321.6 +/- 59.60</td>
<td>583.0 +/- 25.70</td>
</tr>
<tr>
<td>0.25wt% SWCNT Heal 24H @ RT</td>
<td>3.9 +/- 1.60</td>
<td>9.00 +/- 0.30</td>
<td>476.6 +/- 237.90</td>
<td>445.4 +/- 12.76</td>
</tr>
<tr>
<td>0.50wt% SWCNT Heal 24H @ RT</td>
<td>3.5 +/- 0.55</td>
<td>8.10 +/- 0.52</td>
<td>326.4 +/- 159.20</td>
<td>441.4 +/- 28.20</td>
</tr>
<tr>
<td>0.75wt% SWCNT Heal 24H @ RT</td>
<td>4.0 +/- 1.03</td>
<td>6.90 +/- 0.87</td>
<td>326.4 +/- 99.00</td>
<td>434.0 +/- 60.26</td>
</tr>
<tr>
<td>1.0wt% SWCNT Heal 24H @ RT</td>
<td>4.1 +/- 1.30</td>
<td>7.70 +/- 0.28</td>
<td>324.2 +/- 159.20</td>
<td>442.4 +/- 20.90</td>
</tr>
<tr>
<td>0.25wt% MWCNT Heal 24H @ RT</td>
<td>3.5 +/- 1.10</td>
<td>11.30 +/- 1.90</td>
<td>620.8 +/- 262.70</td>
<td>459.0 +/- 28.20</td>
</tr>
<tr>
<td>0.50wt% MWCNT Heal 24H @ RT</td>
<td>4.6 +/- 1.23</td>
<td>9.80 +/- 0.49</td>
<td>435.6 +/- 142.50</td>
<td>444.2 +/- 12.40</td>
</tr>
<tr>
<td>0.75wt% MWCNT Heal 24H @ RT</td>
<td>4.0 +/- 1.50</td>
<td>8.20 +/- 0.35</td>
<td>346.4 +/- 217.60</td>
<td>439.2 +/- 10.90</td>
</tr>
<tr>
<td>1.0wt% MWCNT Heal 24H @ RT</td>
<td>4.7 +/- 0.63</td>
<td>8.50 +/- 0.37</td>
<td>397.6 +/- 95.01</td>
<td>443.8 +/- 22.70</td>
</tr>
</tbody>
</table>
Figure 2.26 shows the randomness of resulting stress at break for the rehealed specimens, again believed to be the roughness of the ruptured interface. New samples of neat PCPU, 1.0wt% SWCNT and 1.0wt% MWCNT composites were cut into two halves with a fresh razor to create a smooth interface and then pressed together immediately and allowed to heal for 1, 2 and 3 hours respectively to evaluate the self-healing characteristics of the carbon nanotube composites. Only the 1.0wt% CNT/PCPU composites were retest because other weight loadings were unavailable at the time of testing.

Once the appropriate healing time had elapsed, those samples were subjected to tensile testing to evaluate the efficiency of healing. For sake of comparison, our PCPU nanotube composites’ healing capability is compared with Cordier et al’s supramolecular material results for the same healing times (table 2.4).

The 1% SWCNT nanotube composite was found to return closest to its initial tensile strength, 7.70 MPa initial, 3.71 MPa after 3 hours, and 6.9 MPa after 24 hours, an overall loss of only 10%. The 1% MWCNT composites and neat samples were found to retain between 50-80% of their initial strength. Similar to Cordier’s results, stress-strain curves for our neat PCPU and composites superpose with changes occurring in the elongation at break, suggesting that given enough time (longer than the testing regime allows, e.g. greater than 24 hours) the materials could regain the initial tensile strength. Under the test conditions, neat PCPU does have improved healing than the CNT composites, but is not the typically results found from the full scale tensile test accomplished.
Table 2.4. Tensile test results for neat, 1.0wt.% PCPU/CNT composite, timed healing.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Average stress @break (MPa)</th>
<th>Average strain @break (% ini.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples pulled 50 mm/min*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCPU neat healed 1H</td>
<td>1.70</td>
<td>290</td>
</tr>
<tr>
<td>PCPU 1.0% SWCNT 1H</td>
<td>1.16</td>
<td>179</td>
</tr>
<tr>
<td>PCPU 1.0% MWCNT 1H</td>
<td>1.19</td>
<td>130</td>
</tr>
<tr>
<td>Supramolecular Rubber* 1H</td>
<td>0.88</td>
<td>340</td>
</tr>
<tr>
<td>PCPU neat healed 2H</td>
<td>2.77</td>
<td>563</td>
</tr>
<tr>
<td>PCPU 1.0% SWCNT 2H</td>
<td>2.24</td>
<td>557</td>
</tr>
<tr>
<td>PCPU 1.0% MWCNT 2H</td>
<td>1.56</td>
<td>312</td>
</tr>
<tr>
<td>Supramolecular Rubber* 2H</td>
<td>1.5</td>
<td>425</td>
</tr>
<tr>
<td>PCPU neat healed 3H</td>
<td>3.24</td>
<td>802</td>
</tr>
<tr>
<td>PCPU 1.0% SWCNT 3H</td>
<td>3.71</td>
<td>477</td>
</tr>
<tr>
<td>PCPU 1.0% MWCNT 3H</td>
<td>2.84</td>
<td>479</td>
</tr>
<tr>
<td>Supramolecular Rubber* 3H</td>
<td>2.75</td>
<td>520</td>
</tr>
</tbody>
</table>

*Crosshead speed not reported for Supramolecular Rubber samples

It was thought that high-energy hydrogen bonding sites might be responsible for the results we were seeing, at least in part responsible for the initial adhesion of the two ruptured interfaces. To test this hypothesis, specimens of 1.0 wt% SWCNT and MWCNT composites were cut into two pieces and those pieces were held apart for the time period under investigation. After the time delay the segment’s ruptured interfaces were brought into contact with each other. The time periods tested were immediately, after 1 hour of separation time, 8 hours of separation time, and 24 hours of separation time, results are located in table 2.5. 1% SWCNT composites retained the ability to reheat after time delay better than
the 1% MWCNT composites. It is interesting to note that even at the 24 hour point both the SWCNT and MWCNT composite samples retained enough affinity to remain together after light pressure was applied.

Table 2.5. Tensile test results for separation test.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Average stress @break (MPa)</th>
<th>Average strain @break(% initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>all samples healed 24h @ 30°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immediate PCPU neat</td>
<td>4.22</td>
<td>735</td>
</tr>
<tr>
<td>Immediate SWCNT</td>
<td>5.43</td>
<td>752</td>
</tr>
<tr>
<td>Immediate MWCNT</td>
<td>5.23</td>
<td>758</td>
</tr>
<tr>
<td>1 hour wait PCPU neat</td>
<td>2.20</td>
<td>353</td>
</tr>
<tr>
<td>1 hour wait SWCNT</td>
<td>5.05</td>
<td>749</td>
</tr>
<tr>
<td>1 hour wait MWCNT</td>
<td>4.96</td>
<td>857</td>
</tr>
<tr>
<td>8 hour wait PCPU neat</td>
<td>1.13</td>
<td>58</td>
</tr>
<tr>
<td>8 hour wait SWCNT</td>
<td>2.09</td>
<td>230</td>
</tr>
<tr>
<td>8 hour wait MWCNT</td>
<td>1.73</td>
<td>194</td>
</tr>
<tr>
<td>24 hour wait PCPU neat</td>
<td>1.37</td>
<td>73</td>
</tr>
<tr>
<td>24 hour wait SWCNT</td>
<td>1.37</td>
<td>151</td>
</tr>
<tr>
<td>24 hour wait MWCNT</td>
<td>1.36</td>
<td>128</td>
</tr>
</tbody>
</table>
Healing Dynamics

Several explanations exist as to what dynamics are involved in self-healing materials, however key concepts appear to control healing in our material, hydrogen bonding to stabilize chain ends and reentaglement through molecular diffusion (figure 2.30) [Kim and Wool 1983; Wool 2008]. Among direct methods that can be used to monitor these dynamic processes of the composite polymer during re-mending, spectroscopic techniques offer the advantage that they can monitor fast processes, directly measure the interaction among the polymers and simultaneous detect several key changes in real-time [Eichhorn 2009].

While Fourier transform infrared spectroscopy (FTIR) usually generates higher sensitivity than Raman spectroscopy, it is limited due to sample preparation, solvent interference and usable wavelength range [Fawcett 1996; Lefrant, Baibarac et al. 2009]. By contrast, Raman spectroscopy is a powerful technique as it offers a quick, simple and nondestructive method which requires minimal sample preparation and provides a larger frequency range. It makes Raman spectroscopy particularly useful for the in situ characterization of the self-healing process in real-time [Boerio and Wirasate 2006; Amer 2009]. Raman spectroscopy has been demonstrated to be an attractive tool in characterizing the carbon nanotubes and their interaction with various polymers [O’Connell 2006; Buffa, Abraham et al. 2007; Dresselhaus, Dresselhaus et al. 2008;
McClory, Chin et al. 2009]. Figure 2.31 shows the Raman spectra of neat material and composites with SWCNT and MWCNT. For the neat material, the strong peak observed at 1450 cm$^{-1}$ is assigned to the symmetric stretching mode of isocyanate (N=C=O) while the peak ca. 2905 cm$^{-1}$ belongs to the stretching mode of C-H of the backbone of the polymer [Parnell, Min et al. 2003].
Figure 2.30. Model of healing process. 1. Hydrogen bonds form as surface interfaces are pressed together. 2.29.2A. Once interfaces are contacting, polymer chains from each side of the interface diffuse across the interface. 2.29.2B. Polymer chains reentangle, restoring material integrity.
Interestingly, with the addition of SWCNT and MWCNT to the polymer, the intensity of those characteristic peaks of the polyurethane is strongly diminished which agrees well with a previous report [Xia and Song 2005]. Three prominent features are observed for SWCNT composites. The strong vibrational modes observed at 1309, 1586 and 2621 cm\(^{-1}\) are attributed to the D-mode, tangential G-mode and G’ mode of the carbon nanotubes, respectively. The relatively high intensity of the D-mode indicates a high degree of defects in the SWCNT used. The small blue shift of the G’ mode compared with pristine SWCNT is related to the dispersion state of the SWCNT in the polymer matrix. A strong shoulder

![Raman spectra PCPU/CNT composites](image)

Figure 2.31. Raman spectra PCPU/CNT composites: neat PCU (green spectrum), PCU with 1% wt. single-wall carbon nanotubes (violet spectrum) and PCU with 1% wt. multi-wall carbon nanotubes (red spectrum). All spectra were collected using excitation wavelength of 647 nm, laser power of 20 mW, 10 s exposure time and 1 accumulation.
observed at 1550 cm$^{-1}$ and its relatively high intensity ratio with G-mode indicates the presence of metallic nanotubes when SWCNTs are dispersed in the polyurethane matrix [Chen, Cinke et al. 2005]. With the addition of MWCNTs, two characteristic peaks at 1312 and 1596 cm$^{-1}$ are observed and assigned to the D-mode and tangential G-mode of CNTs. The peak intensity of the MWCNT is much weaker than the SWCNT.

To further investigate the interaction between the nanotubes and the polyurethane during the healing process and understand the key role the nanotubes played in the matrix, a series of Raman measurements were conducted to test the effect of SWCNTs and MWCNTs on the healing ability of the polymer. To collect Raman spectra during the healing process, the polymer was cut into two pieces and put back together while the laser was focused right at the surface of the interface. For control purposes, the same experiments were also conducted on an uncut surface of the polymer to clarify the effect of laser shining and heating on the polymer.

Figure 2.32 (A) shows the Raman spectra of 1% SWCNT composite during the healing process for the first five minutes. The spectra remain almost the same after five minutes (data not shown). No distinguishable energy shift of the characteristic peaks of both SWCNT and polyurethane were observed. This indicates that there is not much change in the SWCNT dispersion and aggregation in the PCU matrix during the healing process. Figure 2.32 (C) shows the optical images of the cut interface of 1% SWCNT composite during the healing process for the first five minutes. Right after the cut, a clear dark line
was observed across the image which corresponds to the interface between the two pieces of the polymer. Healing was observed clearly after the collection of only one Raman spectra at 1 minute with ca. 40 μm of healing distance.

Figure 2.32. (A) Raman spectra of polyurethane with 1% wt. single-wall carbon nanotubes during the healing process at 1, 2, 3, 4 and 5 minute after the cut. All spectra were collected using excitation wavelength of 647 nm, laser power of 20 mW, 10 s exposure time and 1 accumulation. The laser was focused on the cutting interface of the polymer. (B) Dependence of Raman peak intensity with time for polyurethane during healing process (cyan), polyurethane with 1% wt. single-wall carbon nanotubes during the healing process (blue) and uncut surface (red), and polyurethane with 1% wt. multi-wall carbon nanotubes with uncut surface (green). All lines are just guides to the eyes. (C) Optical images of polymer surface under laser focus during the healing process for PCU with 1% wt. single-wall carbon nanotubes. The scale bar at the right corner is 10 μm.
Due to the heating effect of the laser, the healing process is accelerated during the experiments. The dark spot observed at the center of the image is due to the laser which was also observed in the control experiments on uncut surface of the polymer. The healing distance increases as the exposure time increases and reaches a plateau at ca. 65 \( \mu \text{m} \) after five minutes. This observation agrees well with the change of Raman spectra as shown in Figure 2.32 (A) in that little change occurs after five minutes as the polymer heals. Figure 2.32 (B) shows the dependence of the peak intensity with time of the G-mode for carbon Nanotube composites and the backbone deformation at 1346 \( \text{cm}^{-1} \) for neat polymer. Interestingly, the G-mode of the SWCNT starts with a very high intensity at the cut surface of 1% SWCNT composite at the beginning of the healing process, which is almost 30% higher than that from the uncut surface despite the micrometer-scale gap between the two cut pieces. This huge boost of the peak intensity strongly suggests that the nanotubes acts differently at the interface during the healing process than at the intact surface of the same polymer. The peak intensity of SWCNT decreases dramatically initially and levels off after around four minutes which agrees well with the optical images results. As the G-mode corresponds to the stretching mode in the graphite plane, it might be due to the interaction of the SWCNT with the neat material or the realignment of the CNT during the healing process. By contrast, healing does not induce a change in the polymer spectra in neat or in SWCNT or MWCNT composites. Therefore, the impressive change observed for composite with SWCNT is specific to the presence of SWCNT.
CONCLUSION

CNT Affect On Mechanical Properties

The tensile data shows that there are substantial increases in mechanical performance to be gained by combining the neat PCPU with CNTs. The nano-composites were prepared by a solvent dispersion technique, using THF as the solvent, a head-sonicator to disperse the nano-fillers and finally high temperature and pressure curing. The nano-composites were tested for mechanical characteristics by tensile testing using the appropriate ASTM standards. Test results show between 196% and 320% gain in ultimate fracture strength over the neat PCPU, with MWCNT contributing the most gain. This gain in strength comes at the sacrifice of flexibility as determined by the approximately 20% decrease in strain at break.

CNT Affect On Self-healing Properties

Test results for the healing efficiency of the neat PCPU and PCPU/CNT composites point out that self-healing in conventional elastomers is possible. SWCNT composites contributed to the smallest loss of initial tensile strength in healed samples, however all samples averaged an 80% retention of tensile
strength after healing for 24 hours at room temperature. As discussed earlier, these results can be improved by healing the samples at elevated temperatures. Cordier et al said of supramolecular elastomers: “In striking contrast to conventional cross-linked or thermoreversible rubbers made of macromolecules, these systems, when broken or cut, can be simply repaired by bringing together fractured surfaces to self-heal at room temperature. Repaired samples recuperate their enormous extensibility [Cordier, Tournilhac et al. 2008].” The thermoreversible rubbers discussed herein forges a new path in self-healing technology. We believe that a robust set of experiments encompassing the synthesis of a series of polymers with varying 3-methyl-1, 5-pentanediol contents, varying the hard segment contents and varying nanotube contents will yield valuable information that will lead to even stronger, reversible self-healing systems for conventional elastomers that were previously thought not possible.
CHAPTER 3
Microstructure and Mechanical Properties of Carbon Nanotube Reinforced Ultrasoft Poly (carbonate urethane) Composites

INTRODUCTION

This study investigates the effect of CNT dispersion within a novel highly flexible PCPU matrix and makes use of an improved method to minimize the agglomerations associated with solution casting composites containing CNTs. The structures of polyurethanes (PU) can be manipulated to achieve materials that are thin fluid-like coatings, flexible thermoplastic elastomers, and rigid foams; all possible from the same starting ingredients. At the core of polyurethane’s diversity is the inherently strong intermolecular bonds which enable polyurethanes to withstand many harsh environments. The human body is one such environment, as such polyurethanes are the subject of increasing interest in engineering various tissues for the treatment of many types of injuries and diseases, a wide variety of polymers with desirable mechanical, degradation, and cytophilic properties are needed for medical devices used in and around the human body. One of the largest shortcomings is that the urethane functional group is susceptible to hydrolysis and biodegradation [Tanzi, Farè et al. 2000; Ioan, Grigorescu et al. 2001; Howard 2002; Christenson, Dadsetan et al. 2004; Wiggins, MacEwan et al. 2004; Khan, Smith et al. 2005]. This is being
successfully mitigated with the use of poly (carbonate urethanes) [Szycher 1999]. One of the barriers to wider use of poly (carbonate urethanes) (PCPU) has been the lack of commercial available soft grades below Shore A value of 75. In general, polyurethane’s unique properties stems from what is now generally accepted as microphase separations occurring between physically incompatible regions within the polymer.[Cooper and Tobolsky 1966; Velankar and Cooper 1998] The microphases are segregated into soft segments derived from high molecular weight polyester or polyether macrodiols and hard segments composed of diisocyanate and low molecular weight diols or diamines, collectively called chain extenders. The soft segments contribute to both the elastic and mechanical properties of polyurethanes and the hard segments serve as reinforcement sites.[Velankar and Cooper 1998; Frick and Rochman 2004] The desired material characteristics stemming from these microphase segregations can be controlled by careful selection and controlled ratios of the three precursor materials: polyols, diisocyanates, and the chain extenders with the end goal of controlling the hard and soft segment content. It was previously found that soft segment crystallization which leads to very stiff but strong PCPUs could be eliminated by utilizing a specific type of polycarbonate polyol.[Kull, Gerasimov et al. 2005] Almost all polycarbonate polyols exist as solids at room temperature, the polycarbonate polyol used in previous work differs in that it is a liquid at room temperature and resists crystallization. The resulting PCPU was found to be incredible soft (<70 Shore A) and flexible while retaining the desired
mechanical characteristics. This material was also found to be non-blocking, i.e.,
will not bond to itself even after prolonged force is applied.
The desired characteristics of the resulting material can be further achieved or
refined by the incorporation of any number of organic and inorganic fillers, the
investigations of which have entire journals dedicated to describing the results.
The usual disadvantage of adding fillers is that it often results in a detrimental
change in the material’s fatigue behavior and normally reduces the elongation at
break but does increase thermal and electronic conduction and processability
[Benli, Yilmazer et al. 1998]. In great contrast to this convention, Carbon
nanotubes (CNT) have been shown to be ideal for composites because of their
unique atomic structures, high aspect ratio and excellent mechanical strength
including thermal stability. [Ma, Siddiqui et al. 2010] CNT’s enhancement has
been shown in many types of materials including Polyacrylonitire,[Weisenberger,
Grulke et al. 2003] Poly (methyl methacrylate), [Haggenmueller, Gommans et al.
2000; Stéphan, Nguyen et al. 2000; Clayton, Sikder et al. 2005; Yao, Wu et al.
2007], Epoxy, [Sandler, Kirk et al. 2003; Sun and Sue 2010], and polystyrene
[Sundaray, Subramanian et al. 2007; Slobodian, Pavlínek et al. 2009] to name
but a few. It is interesting that more emphasis has been placed on multi-walled
carbon nanotube composites, most likely because of their reduced cost and
increased availability. It is also interesting that of all CNT composites that have
been reported, only a few exist for polyurethanes [Koerner, Price et al. 2004;
Koerner, Liu et al. 2005; Xia and Song 2005; Yoo, Jung et al. 2006]. Xia and
Song [Xia and Song 2005] credit this to the possibility that it is difficult to achieve
good dispersion of carbon nanotubes into a polyurethane matrix. There are several contributing factors that make CNTs difficult to disperse within the matrix. Due to the extended pi electron system, CNTs are highly polarizable, and therefore subject to rather large van der Waals forces. These forces are responsible for aggregations along the long axis of the tubes making what resembles ropes of CNTs. Bechinger [Bechinger, Rudhardt et al. 1999] described how this attractive force increases when CNTs are suspended in a polymer matrix where entropic forces cause the particles to be forced closer together. Hwang et al [Hwang, Nish et al. 2008] have shown that it is not just the van der Waals forces that make CNTs difficult to disperse but also depend on both structure of the polymer and solvent used to create the composites. Two major categories of methods are employed to realize fully dispersed nanotubes in a polymer matrix[Rastogi, Kaushal et al. 2008]. One such method within the mechanical approach is to disperse carbon nanotubes by ultrasonication into either a polymer solution [Ausman, Piner et al. 2000] or one of liquid monomer constituents used to make the polymer composite.[Park, Ounaies et al. 2002] Another method within the mechanical approach is high-shear mixing in which carbon nanotubes are dispersed into liquid continuous phase polymer. [Sandler, Kirk et al. 2003; Moisala, Li et al. 2006] The second major approach is through chemical methods in which the surface of the carbon nanotubes are modified, either by adding functional groups to effect solubility[Gojny, Nastalczyk et al. 2003; Vaisman, Marom et al. 2006] or through the use of surfactants[Moore, Strano et al. 2003]. The aforementioned methods of nanotube dispersion can
be used in what Grady terms the dissolution-dispersion-precipitation method [Grady 2010] in which a polymer is dissolved in a solvent that is also used to disperse the nanotubes and then combined and then the polymer composite is precipitated, usually by allowing the solvent to evaporate. [Valentini, Cardinali et al. 2008] The problem with this widely used method is that the time scale required for solvent evaporation is sufficient for carbon nanotubes to reagglomerate. [Martin, Sandler et al. 2004] Du et al describe a coagulation method for poly (methyl methacrylate) carbon nanotube composites in which the nanotubes are dispersed by mechanical means in a polymer solution and then precipitated in a non-compatible fluid, in this case purified water [Du, Fischer et al. 2003]. The composite is formed instantaneously and does not allow for the formation of agglomerates.

The impact on mechanical integrity by creating composites of both multi-walled CNTs (MWCNT) and single-walled CNTs (SWCNT) at different weight percentages and subjecting the resulting composites to tensile, hardness and differential scanning calorimetry are also reported.
EXPERIMENTAL

Materials

Poly (carbonate urethane) based on a modified polycarbonate polyol (Nippon 964) and H$_{12}$MDI was provided by TSE industries (Clearwater FL). Single (0.7-1.3 nm diameter) and multi-walled (7-15 nm × 0.5-10 μm) carbon nanotubes were purchased from Sigma-Aldrich and used without further purification. Single-walled CNTs were produced by the electric arc discharge method. Multi-walled CNTs were produced by chemical vapor disposition method.

Methods

Carbon Nanotube Composite Materials

Solution Casting Method

Carbon Nanotube composites were formed by first dissolving neat PCPU (23% hard-segment) into tetrahydrofuran anhydrous, (≥99.9%, inhibitor-free (Sigma-Aldrich)). Once polymer solutions were made, the desired amount of carbon nanotubes (0.25-1.0 wt %) was added. One half of the CNT containing PCPU solutions were mechanically stirred for 24 hours and the other one half of CNT PCPU solutions were ultrasonicated (Fisher Scientific Sonic Dismembrator...
550) for 2 Hours while submerged in an ice bath to prevent THF evaporation. The solvent was then allowed to evaporate in a hood under constant agitation at room temperature to ensure carbon nanotube dispersions were maintained. This step was incorporated during early trials when resulting CNT/PCPU composites contained very large agglomerations. It was found that by placing plates on a laboratory oscillatory shaker at less than 10 revolutions per minute, the solution was provided with enough motion to prevent the large agglomerations.

Materials were then stored in 30° C dry air under slight vacuum until used.

**Water Coagulation Method**

Carbon Nanotube composites were formed by dissolving neat PCPU (23% hard-segment) into THF, adding the desired amount of carbon nanotubes (0.25-1% by weight) and then ultrasonicating in an ice bath for 2 Hours. Deionized water was then added to the solution to crash out the hydrophobic PCPU polymer containing the carbon nanotubes. The material was then allowed to air dry for 24 hours and then the materials were then stored in 30° C dry air under slight vacuum until used.

**Differential Scanning Calorimetry (DSC)**

A TA instruments 2910 DSC with cooling accessory was used. The samples were first cooled to -60° C and ramped to a final temperature of 130° C at a rate of 10° C min⁻¹. Only the first runs were analyzed, as evidence of hard segment melting disappeared during the second runs.
Tensile Test

Tensile testing was carried out using a QTEST III (MTS) tensiometer using its extensiometer to measure the displacement. All tensile testing was conducted at a rate of 100 mm min\(^{-1}\) at 25°C in accordance with ASTM D412C. Testing articles (dog bones) were compression molded using a Carver laboratory press (model C) equipped with heating elements at a pressing temperature of 90°C and 5 metric tons of force. Tensile testing conducted after samples were rehealed were conducted at a rate of 50 mm min\(^{-1}\) to directly compare to other work conducted elsewhere, however still complies with ASTM D412C.

Hardness testing

Durometry, like many other hardness tests, measures the depth of an indentation in the material created by a given force on a standardized presser foot. This depth is dependent on the hardness of the material, its viscoelastic properties, the shape of the presser foot, and the duration of the test. ASTM D2240 durometers allows for a measurement of the initial hardness, or the indentation hardness after a given period of time. The basic test requires applying the force in a consistent manner, without shock, and measuring the hardness which is directly dependent on the depth of the indentation. If a timed hardness is desired, force is applied for the required time and then read.
Microstructures

5 thin sections (<1mm) of each PCPU composites were sliced and imaged using Leica DMRX optical microscope and JEOL 6490LV scanning electron microscope. Images were converted to binary format using ImageJ (http://rsbweb.nih.gov) and then particle size and location was analyzed using “Analyze Particle” function of ImageJ.

Rheometry

A TA instruments AR 2000 Rheometer was used with torsion fixture. Samples were 13mm wide by 54 mm long and 1.5 mm thick. Samples were prepared by compression molding in the same manner as tensile testing articles using steel plate with desired sample size cut outs. Frequency sweeps were performed from .1 to 100 Hz with a temperature range of -60 to 120 °C at 20 °C increments. Normal force was controlled to 1 N +/- .2 N.
RESULTS AND DISCUSSION

Agglomeration Measurement & Control

Fillers are normally compounded with various polymers to achieve composite materials demonstrating improved thermal, mechanical, or adhesive properties. Effective filler dispersion within a polymer matrix is cited as being incredibly important to realizing improvements provided by addition of fillers. [Bokobza 2009; Ma, Siddiqui et al. 2010] The ability to evenly disperse carbon nanotubes within a polymer matrix is something researchers have struggled with ever since Ajayan et al. first reported their carbon nanotube composite [Ajayan, Stephan et al. 1994]. A greater struggle has been determining how well carbon nanotubes are dispersed within the polymer matrix. Direct evidence can be gathered on the effect of forming carbon nanotube polymer interfaces in terms of improved mechanical characteristics, improved electronic conduction, and improved processability [Ma, Siddiqui et al. 2010]. Indirect evidence including x-ray, light and neutron scattering is used to provide spatial relations of CNTs within the polymer matrix. Another technique described by Ryszkowska enables the determination of CNT agglomeration and location within a polymer matrix by manipulating images captured using traditional means [Ryszkowska 2009]. To
examine CNT dispersions within the different weighted PCPU composites created using both solution and water casting methods, optical and SEM micrographs were acquired and processed. Figure 3.1 shows an example of the optical micrographs and converted binary images. Elliptical irregularly shaped agglomerates of various sizes are present within the images. Even though agglomerations can be seen in the optical image, the binary image allows for detection of fine particle borders making detection easier. Figure 3.2 shows examples of SEM images comparing agglomerations present in traditional solution casting and those made by crashing polymer solutions out in deionized water. The example shows the typical results found in this study, agglomerations are much smaller and present in greater numbers in the materials made by crashing the polymer CNT solution in water indicating that the tubes dispersed by ultrasonication do not have the time to reaggregate to a great degree when the composite is instantly formed. The results of all image analysis are presented in table 3.1.
Figure 3.1. A) Optical micrograph example 1.0 wt% MWCNT in PCPU B) binary image used for particle analysis, inset zoom showing detection of CNT agglomerations.
Figure 3.2. A) SEM image for PCPU 1.0wt% SWCNT composite solution cast. B) SEM image for PCPU 1.0wt% SWCNT composite solution water cast.
Solutions took on average 24 hours for all of the THF solvent to evaporate in order to form the composites, whereas solutions crashed in water were formed instantly (Figure 3.3). It is apparent from the image analysis that the time period of typical solution casting allowed van der Waals forces to be recovered and agglomerations to form. The results suggest that the composites created by water casting trapped the carbon nanotubes in place and only slight mobility occurred as remnants of solvent dissipated during the final drying step.
Figure 3.3. A) Solution of PCPU/THF and 1wt% SWCNT. B) Deionized H₂O added, drawing THF into liquid layer leaving. C) resulting PCPU/CNT composite.
The same time dependence was found when dispersion methods were compared. PCPU and CNT solutions were made representing each of the weight percentages. Half of the samples were stirred for 24 hours while the other half were sonicated for 2 hours. At the initial time, the carbon nanotubes in each solution appeared to be equally well dispersed. However after just 24 hours almost all of the solutions containing MWCNTs and the solutions containing SWCNTs that were stirred had reagglomerated and collected near the bottom of the vial. This indicates that within a 24 hour period it was possible to have agglomerations formed in large size and number (figure 3.4). This also indicates that mechanical separation via ultrasonication is a viable means to successfully disrupt intramolecular attractions.

![Figure 3.4. A) Solution of PCPU/THF and 1wt% MWCNT, ultrasonicated 2h (left) and stirred 24h (right). B) Same solutions after sitting undisturbed 24h.](image)

It was desirable to investigate effects, if any, the size and number of agglomerates have on the mechanical performance of the PCPU. As mentioned earlier, very few polyurethane CNT composites have been discussed in literature, and seeming non existent is a discussion of CNT effects of ultra-soft, highly
flexible PCPU. Koerner et al found that the improvement in tensile strength when MWCNTs are added to crystallizable polyurethanes comes from reinforcements of the polymer crystals themselves.[Koerner, Price et al. 2004] The previous chapter showed the type of PCPU under investigation derived from novel polycarbonate polyols has been shown to be relatively crystalline structure free except under certain stress-strain related conditions and that the interfaces created may be different than previously discussed.

**Tensile Testing**

Tensile testing was conducted on samples made from both solution casted and water casted composite materials, to evaluate mechanical characteristics caused by the differences in dispersion methods, results of which are summarized in table 2. All composite samples that contained CNTs showed improvements in modulus and rupture properties compared to the neat sample; figure 5 shows an example stress-strain curve. This improvement is generally expected and consistently reported.[Ma, Siddiqui et al. 2010]

What is unexpected is that even though water casted MWCNT samples showed better dispersion and reduced agglomeration size, the break stress and strain were not improved until the higher loadings of CNTs. This suggests that there is not a strong interfacial interaction between the PCPU and MWCNTs until higher ratios of CNTs to polymer chains are achieved.
Table 3.2. Comparison of Ultimate break stress and strain comparing water coagulation and solvent casting methods.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Average stress @break (MPa)</th>
<th>Average stress @break (MPa)</th>
<th>Average strain @break (% ini.)</th>
<th>Average strain @break (% ini.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU</td>
<td>3.52 +/- 0.45</td>
<td></td>
<td>583.0 +/- 25.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solution Cast</td>
<td>Water Cast</td>
<td>Solution Cast</td>
<td>Water Cast</td>
</tr>
<tr>
<td>0.25% SWCNT</td>
<td>9.00 +/- 0.30</td>
<td>11.0 +/- 2.3</td>
<td>445.4 +/- 12.76</td>
<td>579.0 +/- 21.0</td>
</tr>
<tr>
<td>0.50% SWCNT</td>
<td>8.10 +/- 0.52</td>
<td>10.3 +/- 0.60</td>
<td>441.4 +/- 28.20</td>
<td>545.0 +/- 43.60</td>
</tr>
<tr>
<td>0.75% SWCNT</td>
<td>6.90 +/- 0.87</td>
<td>8.4 +/- 2.1</td>
<td>434.0 +/- 60.26</td>
<td>466.0 +/- 121.29</td>
</tr>
<tr>
<td>1.0% SWCNT</td>
<td>7.70 +/- 0.28</td>
<td>10.3 +/- 2.3</td>
<td>442.4 +/- 20.90</td>
<td>542.0 +/- 88.70</td>
</tr>
<tr>
<td>0.25% MWCNT</td>
<td>11.30 +/- 1.90</td>
<td>7.0 +/- 3.1</td>
<td>459.0 +/- 28.20</td>
<td>546.0 +/- 45.0</td>
</tr>
<tr>
<td>0.50% MWCNT</td>
<td>9.80 +/- 0.49</td>
<td>6.0 +/- 1.1</td>
<td>444.2 +/- 12.40</td>
<td>484.0 +/- 54.8</td>
</tr>
<tr>
<td>0.75% MWCNT</td>
<td>8.20 +/- 0.35</td>
<td>8.8 +/- 1.8</td>
<td>439.2 +/- 10.90</td>
<td>441.0 +/- 56.5</td>
</tr>
<tr>
<td>1.0% MWCNT</td>
<td>8.50 +/- 0.37</td>
<td>9.8.0 +/- 1.9</td>
<td>443.8 +/- 22.70</td>
<td>583.0 +/- 23.0</td>
</tr>
</tbody>
</table>
Figure 3.5. Tensile test data, typical stress-strain curves generated for experiment for this series of tests.
These results may also be symptomatic of conformational changes that take place within the polymer structure caused by the increased interactions. The PCPU used in this investigation has its backbone hard segments derived from H_{12}MDI, 4, 4’ diisocyanato dicyclohexylmethane. This diisocyanate is known to exist as three conformational isomers, figure 3.6, which Byrne et al showed could impart very different mechanical properties to polyurethanes depending on the packing of the isomers [Byrne, Mack et al. 1985]. That group found that samples containing smaller amounts of trans-trans were better for flexible coatings where increased amounts formed tougher elastomers.

![Figure 3.6. Conformational isomers of H_{12}MDI](image-url)
Rheometry

Rheological experiments do show a nonlinear trend in the storage modulus for increasing filler loadings which does depend whether SWCNTs or MWCNTs are used. Figure 3.7 shows changes in storage modulus for SWCNT composites and 3.8 shows changes in storage modulus for MWCNT composites. The amount and direction of change suggests SWCNTs do interact with the polymer in a much different way than do the MWCNTs. In both SWCNT and MWCNT 0.25wt% samples, the lower loading did improve the rupture stress the most and demonstrated the highest storage modulus suggesting that at lower CNT to polymer chain ratios the CNTs are acting to enhance physical cross links than inherently exist between soft and hard segments in polyurethanes and depending on how these attractions are enhanced can directly influence the mechanical properties of the system[Eceiza, Martin et al. 2008].
Figure 3.7. Rheology data: G’ for SWCNT/PCPU.

Figure 3.8. Rheology data: G’ for MWCNT/PCPU.
Hardness

The influences the carbon nanotubes had on the motions of the polymer chains was only seen during dislocation when stress was applied to the material, a check of Shore A values did not show a significant change with a range of 65 for the neat sample increasing to 67 for 1.0 wt% MWCNT PCPU composites (table 3). This reiterates CNTs in the polymer matrix are most likely reinforcing the physical cross links on which polyurethane elastomers derive their strength. Considering the electronic differences in the two different CNT types, the roles and interfaces with polymers containing novel flexible soft segments of the type discussed here will need to be further investigated.

Table 3.3 Shore A values PCPU/CNT composites.

<table>
<thead>
<tr>
<th>Material:</th>
<th>Shore A:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU</td>
<td>65</td>
</tr>
<tr>
<td>0.25 wt% SWCNT</td>
<td>67</td>
</tr>
<tr>
<td>0.50 wt% SWCNT</td>
<td>69</td>
</tr>
<tr>
<td>0.75 wt% SWCNT</td>
<td>67</td>
</tr>
<tr>
<td>1.0 wt% SWCNT</td>
<td>69</td>
</tr>
<tr>
<td>0.25 wt% MWCNT</td>
<td>68</td>
</tr>
<tr>
<td>0.50 wt% MWCNT</td>
<td>68</td>
</tr>
<tr>
<td>0.75 wt% MWCNT</td>
<td>68</td>
</tr>
<tr>
<td>1.0 wt% MWCNT</td>
<td>67</td>
</tr>
</tbody>
</table>
CONCLUSION

This study shows that more complete dispersion of both SWCNTs and MWCNTs within a poly (carbonate urethane) takes place by first mechanically disrupting the cohesive forces that cause agglomerations in a polymer solution and then rapidly forming solid material. By rapidly forming the material, large agglomerations responsible for premature fatigue and rupture can be significantly reduced, if not totally avoided. There are beneficial effects to effective dispersion of CNTs, the magnitude of which is dependent on the weight loading of the CNTs. As shown here, more than 300% increase in ultimate tensile strength can be garnered with the addition of up to 1.0 wt. % MWCNTs and more than 200% for SWCNTs. The significant gain, however, comes only when large irregular shaped agglomerates are avoided by effective dispersion techniques, leading to an additional increase of 120% in ultimate tensile strength.
CHAPTER 4
Estimation of Surface Energies of Self-Healing Poly (Carbonate Urethane) Carbon Nanotube Composites

INTRODUCTION

The mechanical characteristics of the novel ultrasoft poly (carbonate urethane) PCPU and PCPU/ carbon nanotube (CNT) composites have been discussed thus far. What has not yet been provided is an explanation of what might be occurring at the surface of this unique polymeric material. Availability of hydrogen bonding sites could explain the non-blocking property of our material, e.g. the material will not adhere to itself unless the surface has been ruptured. Any two ruptured surfaces can be brought together and the healing process will take place, regardless of the origin of the material. Surface science techniques offer the ability to investigate the healing phenomenon at the surface, therefore it is where focus will now turn.

The determination of solid-vapor ($\gamma_{sv}$) and solid-liquid ($\gamma_{sl}$) interfacial tensions is of importance in a wide range of problems in pure and applied science. Because of the difficulties involved in measuring directly the surface tension involving a solid phase, indirect approaches are called for. One such approach is contact angle measurements. Contact angle measurements are easily performed by establishing the tangent of the angle that a liquid drop forms with a solid surface at the base. The possibility of estimating solid surface tensions from contact angles relies on a relation which was originally recognized by Young [Young 1805]. The contact angle formed by a liquid drop placed on a solid
surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions, solid-vapor tension ($\gamma_{sv}$), solid-liquid tension ($\gamma_{sl}$), and liquid-vapor tension ($\gamma_{lv}$) (figure 4.1).

![Figure 4.1. Model of a sessile-drop contact angle system](image)

This equilibrium relation is known as Young’s equation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} - \pi_e \quad (eq. 4.1)$$

Where $\gamma_{lv}$, $\gamma_{sv}$, and $\gamma_{sl}$ are the free energies of the liquid and solid against their saturated vapor and of the interface between liquid and solid, respectively, and $\pi_e$ is the equilibrium pressure of adsorbed vapor of the liquid on the solid.

Fowkes [Fowkes 1964] postulated that attractive forces at interfaces was the sum of contributions from the different intermolecular forces at the surface. Using this as the basis, he derived from the Young equation an expression for the contact angle of a liquid on a solid in terms of the dispersion force contributions of each:

$$1 + \cos \theta = 2 \sqrt{\frac{\gamma_{l}}{\gamma_{lv}}} \left( \frac{\gamma_{l}}{\gamma_{sv}} \right) \quad (eq \ 4.2)$$
Owens and Wendt [Owens and Wendt 1969] provide a derivative of Fowkes work to account for both polar $p$ and dispersive $d$ forces:

$$1 + \cos \theta = 2\sqrt{\gamma_s^d} \left( \sqrt{\frac{\gamma_{lv}^d}{\gamma_{lv}}} \right) + 2\sqrt{\gamma_s^p} \left( \sqrt{\frac{\gamma_{lv}^p}{\gamma_{lv}}} \right) \quad \text{(eq 4.3)}$$

This is rewritten as:

$$\frac{1 + \cos \theta}{2} \frac{\gamma_{lv}}{\sqrt{\gamma_{lv}^d}} = \sqrt{\gamma_{sv}^p} \sqrt{\frac{\gamma_{lv}^p}{\gamma_{lv}}} + \sqrt{\gamma_{sv}^d} \quad \text{(eq 4.4)}$$

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \quad \text{(eq 4.5)}$$

Where $\theta$ is the contact angle, subscripts ‘lv’ and ‘sv’ denote the interfacial liquid-vapor and surface-vapor tensions, respectively, while superscripts ‘p’ and ‘d’ denote the polar and disperse components, respectively, of total surface tension, $\gamma_{sv}$. Using geometric mean principles, free energy of adhesion is equal to the geometric mean of cohesive energy. Accordingly, the solid surface tension components $\gamma_{sv}^d$ and $\gamma_{sv}^p$ can be determined from the slope and the intercept of the linear dependence, with eq 4.4, using the known surface tension components of different liquids and the contact angles those liquids form with the solid under investigation.

Solid surfaces, i.e. metals and ceramics are much different than the polymeric surfaces under investigation. The PCPU molecules, like in most
polymer materials, can have a much greater freedom for rearrangement at the surface than in the bulk, therefore may have different properties at the surface than in bulk [Yasuda, Sharma et al. 1981]. As an example, Holley and Refujo [Holly and Refojo 1975] did contact angle measurements on a hydrogel using water as the liquid interface. Hydrogels are designed to absorb large amounts of water by weight; some hydrogel materials can contain over 99% water. Hydrogels possess a high degree of flexibility very similar to natural tissue, due to their significant water content. Holley and Refujo submerged a hydrogel sample in water and formed an air bubble beneath the surface of the hydrogel. They observed a very low contact angle, which indicated that the surface of the hydrogel at the hydrogel-water interface was hydrophilic, whereas the hydrogel-air interface was hydrophobic. Based on this they suggested that hydrophilic groups of the polymer at the hydrogel-air interface are preferentially drawn into the bulk of the hydrogel. Based on free rotation around carbon-carbon bonds and the long-range mobility of macromolecules, the explanation seems logical. It also seems a logical deduction that polymeric molecules in the solid state would also behave in much the same way.

Pike et al [Pike, Ho et al. 1996] investigated the surfaces of linear, segmented block copolymers of poly (dimethyl-siloxane-urea-urethans) by dynamic contact angle analysis. In this study, the authors systematically altered the length of soft segments formed by the poly (dimethylsiloxane) component. It was concluded that the polymer surface rearranged in response to prolonged contact with water, and the amount of rearrangement was dependent on the
molecular weight of the soft segments. The results are expected as longer segments have increased areas of gyration [Doruker and Mattice 1998]. Polyurethane surfaces have been shown to undergo rearrangements when the environment they are exposed to is changed from air to water. Chen and Ruckenstein [Chen and Ruckenstein 1990] investigated the rearrangements by wetting angle and ESCA measurements. The wetting angle measurements indicated that the polar component of the surface free energy of polyurethane increases in time, and angular-dependent ESCA experiments show that this is due to the increase in the surface density of the more polar hard segments of the polyurethane. The rearrangements affect the structure of the polymer to a depth of more than 90 Å from the surface. It was shown that the rearrangement in water can be stimulated by preimmersing the polymer for a short time in a suitable organic solvent, since this increases the mobility of the molecular chains near the surface.

The purpose of this particular effort is to determine what changes occur at the surface of our self-healing PCPU/CNT composites. It is hypothesized that high energy hydrogen-bonding sites are turned inward toward the bulk leaving the surface at a lower free energy, which would explain the non-blocking property of our material. Once the material is cut or ruptured, these bonding sites that were in bulk are now at the surface. Measured contact angles will provide insight into the free energy of these two very different surfaces.
EXPERIMENTAL

Materials

Poly (carbonate urethane) based on a modified polycarbonate polyol (Nippon 964) and H$_2$MDI was provided by TSE industries (Clearwater FL). Single (0.7-1.3 nm diameter) and multi-walled (7-15 nm × 0.5-10 μm) carbon nanotubes were purchased from Sigma-Aldrich and used without further purification. Single-walled CNTs were produced by the electric arc discharge method. Multi-walled CNTs were produced by chemical vapor disposition method.

Methods

PCPU/CNT Composites

Carbon Nanotube composites were formed by first dissolving neat polycarbonate polyurethane (PCPU) (23% hard-segment) into tetrahydrofuran anhydrous, (≥99.9%, inhibitor-free (Sigma-Aldrich)) and then mixing desired amount of carbon nanotubes (0.25-1% by weight) by ultrasonication (Fisher Scientific Sonic Dismembrator 550) for 2 Hours. Materials were then solution cast under constant agitation to ensure carbon nanotube dispersion was maintained. 20mmx 8mm discs for testing were compression molded using a Carver laboratory press (model C) equipped with heating elements using an aluminum mold of the desired dimension. 75mm x 5mm x 5mm rectangular samples were pressed for FTIR investigations.
Contact Angle Measurements

Uniform drops of the test liquids were deposited on the PCPU surface and the contact angles were measured using KSV CAM-101 video-based optical contact angle measuring device equipped with a Hamilton syringe in an environmentally controlled chamber (KSV-1 TCU). All measurements were performed in air, at a temperature of 25°C. 5 right angle and 5 left angle measurements were accomplished for each sample. Neat PCPU, 0.25wt%, 0.50wt%, 0.75wt%, and 1.0wt% of SWCNT and MWCNT composites were tested and then the samples were cut and the freshly cut surface was subjected to contact angle measurement. Each contact angle measurement was made on a freshly cut surface. As probe liquids, double-distilled water, ethylene glycol and glycerol were used, as purchased at maximum obtainable purity.

Fourier Transform Infrared Spectroscopy (FTIR)

A Thermo Scientific Nicolet 6700 spectrometer and solid was used for the study. The scan range was 400-4000 cm⁻¹ set at a resolution of 4 cm⁻¹, 32 repetitions. Neat, 1.0wt% SWCNT/PCPU, and 1.0wt% MWCNT/PCPU composites were scanned for 24 hours; each sample was cut through the middle of the thickness along the length and scanned for an additional 24 hours.
RESULTS AND DISCUSSION

Contact Angle Measurements

The method used for the determination of surface tension is based on contact angle measurements between the liquid meniscus and the materials surface. A contact angle below 90° indicates the material is easily wetted by the test liquid. When water is used as the test liquid, the indication is that the material is hydrophilic. Angles greater than 90° indicates a resistance to wetting by the test liquid, when water is used, indicates a hydrophobic surface. The contact angles formed by distilled water, ethylene glycol and glycerol on the surfaces of neat PCPU and composites containing 0.25wt%, 0.50wt. %, 0.75wt. %, and 1.0wt% CNTs were measured. The test liquids were selected because water has one polar OH group, ethylene has two, and glycerol has three. The surface tension parameters (mN m⁻¹) of each test liquid was available the KSV CAM-101 software. Figure 4.2 shows how the angle is measured from using the KSV CAM-101 video contact angle image, and figure 4.3 shows a series of typical drops formed on neat PCPU before and after cutting by each of the test liquids. Table 4.2 lists the measured contact angles between the double-distilled water, ethylene glycol and glycerol before and after cutting the material. A decrease in the contact angle shows an increase in the hydrophilicity of the material which indicates higher surface energies caused by increased hydrogen bonding sites.
Table 4.1. Surface tension parameters for test liquids used for contact angle measurements.

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>$\gamma_{lv}$</th>
<th>$\gamma_{lv}^d$</th>
<th>$\gamma_{lv}^p$</th>
<th>$\gamma_{lv}$</th>
<th>$\gamma_{lv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>72.8</td>
<td>21.80</td>
<td>51.00</td>
<td>25.50</td>
<td>25.50</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48</td>
<td>29.00</td>
<td>19.00</td>
<td>47.00</td>
<td>1.92</td>
</tr>
<tr>
<td>Glycerol</td>
<td>64</td>
<td>34.00</td>
<td>30.00</td>
<td>57.40</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Figure 4.2. Contact angle method of measuring angle on video based system.
Figure 4.3. Contact angles formed between Neat PCPU, H20, ethylene glycol and glycerol
Table 4.2. Contact angle (degrees) of different liquids-PCPU samples before and after rupture.

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>Neat PCPU Uncut</th>
<th>Neat PCPU Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>Av CA 85.32 ± 1.36</td>
<td>77.29 ± 3.31</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Av CA 66.54 ± 4.16</td>
<td>55.852 ± 11.2</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Av CA 76.76 ± 2.32</td>
<td>71.82 ± 7.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>0.25wt% SW Uncut</th>
<th>0.25wt% SW Cut</th>
<th>0.50wt% SW Uncut</th>
<th>0.50wt% SW Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>Av CA 91.00 ± 3.61</td>
<td>90.65 ± 4.21</td>
<td>102.44 ± 4.13</td>
<td>88.37 ± 1.88</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Av CA 79.96 ± 5.59</td>
<td>63.77 ± 5.60</td>
<td>92.27 ± 2.96</td>
<td>70.05 ± 2.61</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Av CA 88.91 ± 1.75</td>
<td>76.39 ± 3.33</td>
<td>100.33 ± 4.67</td>
<td>81.19 ± 3.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>0.75wt% SW Uncut</th>
<th>0.75wt% SW Cut</th>
<th>1.0wt% SW Uncut</th>
<th>1.0wt% SW Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>Av CA 95.18 ± 3.39</td>
<td>78.06 ± 3.92</td>
<td>94.10 ± 2.87</td>
<td>84.579 ± 1.96</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Av CA 86.49 ± 1.48</td>
<td>59.01 ± 2.88</td>
<td>80.42 ± 2.52</td>
<td>63.56 ± 6.92</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Av CA 93.74 ± 1.74</td>
<td>74.8 ± 3.57</td>
<td>91.52 ± 1.90</td>
<td>78.61 ± 10.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>0.25wt% MW Uncut</th>
<th>0.25wt% MW Cut</th>
<th>0.50wt% MW Uncut</th>
<th>0.50wt% MW Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>Av CA 94.97 ± 3.88</td>
<td>88.32 ± 4.03</td>
<td>92.80 ± 3.86</td>
<td>82.11 ± 2.36</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Av CA 90.20 ± 4.33</td>
<td>67.53 ± 5.64</td>
<td>77.48 ± 3.35</td>
<td>54.90 ± 4.65</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Av CA 91.08 ± 2.65</td>
<td>77.08 ± 11.21</td>
<td>82.27 ± 3.99</td>
<td>71.5 ± 6.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Liquid</th>
<th>0.75wt% MW Uncut</th>
<th>0.75wt% MW Cut</th>
<th>1.0wt% MW Uncut</th>
<th>1.0wt% MW Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>Av CA 93.81 ± 9.61</td>
<td>73.52 ± 5.18</td>
<td>97.40 ± 8.71</td>
<td>70.30 ± 4.96</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>Av CA 86.49 ± 6.36</td>
<td>54.06 ± 5.70</td>
<td>80.96 ± 7.87</td>
<td>53.72 ± 2.92</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Av CA 91.1 ± 1.83</td>
<td>63.52 ± 5.18</td>
<td>86.51 ± 3.47</td>
<td>71.20 ± 9.76</td>
</tr>
</tbody>
</table>
Interesting trends become apparent when the measured contact angles for the three test liquids are plotted against the weight loadings for the SWCNT and MWCNT composites, figure 4.4.

![Figure 4.4. Contact angle data. Measured CA plotted against wt% for Neat and PCPU/CNT composites before and after cutting.](image)

The testing fluids are listed in polarity order, water having one polar group, ethylene glycol having two and glycerol having three. The contact angle for water on PCPU/SWCNT composites increases up to the 0.75wt%, and then decreases slightly. The same trend is noted for the ethylene glycol, however for glycerol, the contact angles increase and decrease for each increase in weight percentage of the CNTs, however, overall the contact angles moved from below 90° to approaching 90°, meaning the PCPU/CNT composite materials became more
hydrophobic as the CNTs were increased in loading. The same general trend occurs the PCPU/MWCNT composite samples as well; the 1.0 wt.% PCPU/MWCNT sample is more hydrophobic than is the neat PCPU. The contact angles significantly drop for all cut samples, meaning the surface is more hydrophilic after cutting and the drop in measured contact angle is more significant with higher CNT loading.

One possible explanation for this is that the CNTs are acting as anchor sites and preventing the hydrogen bonding sites from turning in to the bulk. As discussed in the introduction to this chapter, both the dispersive \( \gamma_{SV}^d \) and polar \( \gamma_{SV}^p \) forces can be determined by plotting \( ((1 + \cos \theta)/2)(\gamma_{LV}/\gamma_{LV})^{0.5} \) against \( \gamma_{LV}/\gamma_{LV}^{0.5} \) using the data for the three test liquids. The slope of the resulting points is the \( \gamma_{SV}^d \) and the intercept of the linear dependence is the \( \gamma_{SV}^p \) value.

Figure 4.4 shows an example curve and best fit line for 0.25wt.% PCPU/SWCNT composite before cut. Figure 4.5 shows an example curve and best fit line for the same sample after cutting the sample.
Figure 4.5. Contact angle data, typical linear fit of points plotted for three test liquids: H$_2$O, ethylene glycol and glycerol on .25wt% SWCNT/PCPU composite, before cut.

Figure 4.6. Contact angle data, typical linear fit of points plotted for three test liquids: H$_2$O, ethylene glycol and glycerol on .25wt% SWCNT/PCPU composite after cut.
Table 4.3 provides total surface tensions $\gamma_{sv}$, with corresponding dispersive $\gamma_{sv}^d$ and polar $\gamma_{sv}^p$ components (mN m$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_{sv}$</th>
<th>$\gamma_{sv}^d$</th>
<th>$\gamma_{sv}^p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PCPU uncut</td>
<td>23.89</td>
<td>8.98</td>
<td>14.91</td>
</tr>
<tr>
<td>Neat PCPU cut</td>
<td>27.81</td>
<td>15.10</td>
<td>12.71</td>
</tr>
<tr>
<td>0.25 SW uncut</td>
<td>17.65</td>
<td>11.63</td>
<td>6.02</td>
</tr>
<tr>
<td>0.25 SW cut</td>
<td>28.91</td>
<td>2.94</td>
<td>25.97</td>
</tr>
<tr>
<td>0.50 SW uncut</td>
<td>11.28</td>
<td>6.80</td>
<td>4.49</td>
</tr>
<tr>
<td>0.50 SW Cut</td>
<td>21.53</td>
<td>8.07</td>
<td>13.47</td>
</tr>
<tr>
<td>0.75 SW Uncut</td>
<td>15.06</td>
<td>10.85</td>
<td>4.20</td>
</tr>
<tr>
<td>0.75 SW Cut</td>
<td>26.99</td>
<td>12.17</td>
<td>14.82</td>
</tr>
<tr>
<td>1.0 SW Uncut</td>
<td>16.01</td>
<td>8.71</td>
<td>7.30</td>
</tr>
<tr>
<td>1.0 SW Cut</td>
<td>24.16</td>
<td>9.20</td>
<td>14.96</td>
</tr>
<tr>
<td>0.25 MW uncut</td>
<td>15.52</td>
<td>12.11</td>
<td>3.41</td>
</tr>
<tr>
<td>0.25 MW cut</td>
<td>24.29</td>
<td>6.13</td>
<td>18.16</td>
</tr>
<tr>
<td>0.50 MW uncut</td>
<td>19.28</td>
<td>6.43</td>
<td>12.85</td>
</tr>
<tr>
<td>0.50 MW Cut</td>
<td>30.26</td>
<td>6.92</td>
<td>23.34</td>
</tr>
<tr>
<td>0.75 MW Uncut</td>
<td>15.98</td>
<td>11.82</td>
<td>4.16</td>
</tr>
<tr>
<td>0.75 MW Cut</td>
<td>31.83</td>
<td>15.23</td>
<td>16.60</td>
</tr>
<tr>
<td>1.0 MW Uncut</td>
<td>17.66</td>
<td>13.34</td>
<td>4.32</td>
</tr>
<tr>
<td>1.0 MW Cut</td>
<td>32.29</td>
<td>8.73</td>
<td>23.56</td>
</tr>
</tbody>
</table>

Table 4.3 provides total surface tensions derived from the geometric mean relationship as described earlier in the introduction of this chapter. Figure 4.7, figure 4.8, and figure 4.9 show the trends for total surface tension, dispersive forces and polar forces, neat PCPU and PCPU/CNT composites before and after rupturing the surface, respectively. It can be determined from these graphs that there is not a linear relationship between CNT loading in the composites and the surface tension value. There is a general trend for decreased surface tension with wt.% loading, all composite samples had lower surface tensions than the neat sample before cutting and higher surface tensions than the neat sample after cutting.
It is also interesting that in all cases, the polar component, $\gamma_{sv}^P$, was equivalent in the pre and post cut neat PCPU samples but was the smallest component prior to cutting and was the largest after for all of the CNT composites.

Figure 4.7. Surface tension parameter, $\gamma_{sv}$, for uncut and cut specimens according to the geometric mean method.
Figure 4.8. Surface tension parameter, $\gamma_{sv}^d$, for uncut and cut specimens according to the geometric mean method.
Figure 4.9. Surface tension parameter, $\gamma_{sv}^p$, for uncut and cut specimens according to the geometric mean method.
Fourier Transform Infrared Spectroscopy (FTIR)

The contact angle data provided convincing evidence that hydrogen bonding sites that are located within the bulk of the material become exposed upon rupture. Commonly, the formation of hydrogen bonding between proton acceptor, for example, C=O, and proton donor, such as the N-H located in a urethane group within a polyurethane, play a critical role in determining the way a polymer behaves, including mechanical properties [Na, Lv et al. 2009]. As discussed in chapter 1, it is widely accepted that hydrogen bonding between polyurethane hard segments is responsible for the establishment of microphase separation responsible imparting stiffness and strength. Bonding between the hard and soft segments promotes microphase mixing which imparts flexibility and elasticity.

Several studies [Tanaka, Yokoyama et al. 1968; R. W. Seymour, G. M. Estes et al. 1970; Boerio and Wirasate 2006; Na, Lv et al. 2009] have shown the ability to detect both associated and unassociated hydrogen bonding sites using FTIR. The surfaces of solid samples of 1.0 wt.% PCPU/SWCNT, PCPU/MWCNT composites and neat PCPU were scanned for 24 hours each and then the surface was cut away and the scans were repeated for another 24 hours. Figure 4.10 shows FTIR absorbance for the neat sample before and after cutting. The expected absorbances for associated N-H groups is 3318-3338 cm⁻¹ and associated C=O 1704 cm⁻¹ and unassociated C=O is 1740 cm⁻¹.
Figure 4.10. Sample FTIR showing peaks of interest A) Uncut  B) Cut

Figure 4.11 shows example peaks for associated and unassociated N-H and C=O peaks for PCPU/ 1.0wt% MWCNT composites, the PCPU/ 1.0wt.% SWCNT composite resulted in the same peak structure. When neat and
composite materials were cut, absorbance bands associated with unassociated N-H and C=O bonds increased, and returned to relatively the starting absorbances after 24 hours. This indicates that hydrogen bonding sites are available when the PCPU is first rupture and turn inward away from the surface of some period of time. The time period of 24 hours may not be long enough to view the entire relaxation process.

Figure 4.1. FTIR showing time lapse collection over 24 hours for peaks of interest.
CONCLUSION

Contact angle measurements on our novel self-healing poly (carbonate urethane) and CNTs composites show that surface energies are drastically changed when CNTs are used. The most revealing finding is that $\gamma_{sv}^p$ increases in CNT composite materials from ~30% of the surface energy on average for the samples tested, to ~80%. We have shown that surface free energies increase most likely as a result of exposing hydrogen bonding sites typically found within the bulk in polyurethanes. Our polyurethane differs from traditional polyurethanes in that it has both novel soft segments made from a novel polycarbonate polyol discussed in chapter 2 and relatively soft “hard' segments resulting from the use of H$_{12}$MDI, all leading to increased ability to hydrogen bond within the material. The availability of the hydrogen bonding sites is demonstrated by FTIR absorbance bands for associated and unassociated hydrogen bonding sites, which do not seem to be accessible to a large until the PCPU’s surface is disrupted. Once disrupted, the exposed hydrogen bonding sites are able to bond with other bonding sites of adjacent ruptured surfaces. This would explain why our material is non-blocking, e.g. won’t stick to itself, until the surface is ruptured. It would also explain why any two ruptured surfaces of our material will reheat, even if they were not attached previously.
CHAPTER 5
FUTURE WORK

Structure –property relationships

The next generation of fillers holds promise for increasing performance for already existing materials. The novel composite material discussed throughout this body of work represents an unoptimized polymer system. An effort needs to be initiated to determine the effects of adding, deleting or moving the pendant methyl groups present in our material along the backbone of the polymer. Preliminary work in this direction is already underway, as Nippolan 964, the novel polycarbonate polyol, was replaced in a recent formulation with a Duranol T5652, a C5/C6 copolymer polycarbonate polyol of 2000 a.m.u. This polyol is a liquid at room temperature like the Nippolan 964, indicating that we should be able to avoid crystallization within polyurethanes made from this polyol. This seems to be key in allowing enough mobility within the polymer chain to facilitate the intermolecular hydrogen bonding necessary for the self-healing process. The pendant methyl groups found in the backbone come from the polyol, making up the soft segment of the polyurethane. This pendant group can be moved to the hard segment domain by using a chain extender, like 2-methyl-1,3-propanediol, that has a pendant methyl group resembling those found in the polycarbonate polyol currently being used in our formulations. Polyurethanes resulting from
new formulations will be subject to the suite of mechanical testing described herein to determine the resulting characteristics.

**Next Generation Filler**

The work presented here demonstrates that it is possible to synthesize an autonomous self-healing material that has relatively useful properties. These properties can be improved by incorporating CNTs, both single and multi-walled varieties. There exist a new frontier where the unrolled variety of CNTs, namely graphene (figure 5.1).

![Figure 5.1. Structure of graphene.](image)

Graphene sheets are one-atom-thick 2-D layers of sp2-bonded carbon and are predicted to have a range of unusual properties. Their thermal conductivity and mechanical stiffness may rival the remarkable in-plane values for graphite (approximately 3,000 W m(-1) K(-1) and 1,060 GPa, respectively); their fracture strength is comparable to carbon nanotubes for similar types of defects. Recent studies have shown that individual graphene sheets have extraordinary
electronic transport properties. One possible route to harnessing these properties for applications would be to incorporate graphene sheets in a composite material. The manufacturing of such composites requires not only that graphene sheets be produced on a sufficient scale but that they also be incorporated, and homogeneously distributed, into various matrices. Graphite, inexpensive and available in large quantity, unfortunately does not readily exfoliate to yield individual graphene sheets [Stankovich, Dikin et al. 2006].

Graphene has three distinct advantages over carbon nanotubes. The first advantage is the rough and wrinkled surface texture of graphene, caused by a very high density of surface defects. These defects are a result of the thermal exfoliation process that is used to manufacture bulk quantities of graphene from graphite. These wrinkly surfaces interlock extremely well with the surrounding polymer material, helping to boost the interfacial load transfer between graphene and the host material.

The second advantage is surface area. As a planer sheet, graphene benefits from considerably more contact with the polymer material than the tube-shaped carbon nanotubes. This is because the polymer chains are unable to enter the interior of the nanotubes, but both the top and bottom surfaces of the graphene sheet can be in close contact with the polymer matrix.
The third benefit is geometry. When microcracks in the composite structure encounter a two-dimensional graphene sheet, they are deflected, or forced to tilt and twist around the sheet. This process helps to absorb the energy that is responsible for propagating the crack. Crack deflection processes are far more effective for two-dimensional sheets with a high aspect ratio such as graphene, as compared to carbon nanotubes.
REFERENCES


