Functionalization of carbon nanotubes for high-performance polymer composites

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FUNCTIONALIZATION OF CARBON NANOTUBES
FOR HIGH-PERFORMANCE POLYMER
COMPOSITES**

**YUAN WEI
SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING**

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FOR HIGH-PERFORMANCE POLYMER
COMPOSITES**

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School of Chemical and Biomedical Engineering

**A thesis submitted to the Nanyang Technological University
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List of Abbreviations

1-D	one-dimensional
2-D	two-dimensional
AFM	atomic force microscopy
AIBN	2, 2'-azobisisobutyronitrile
ATR	attenuated total reflectance
ATRP	atom transfer radical polymerization
BHT	butylated hydroxytoluene
BMI	bismaleimide
BPDA	3, 3', 4, 4'-biphenyltetracarboxylic dianhydride
CE	cyanate ester
CNTs	carbon nanotubes
CTAB	cetyltrimethylammonium bromide
CVD	chemical vapor decomposition
DMAc	<i>N, N'</i> -dimethylacetamide
DMAP	4-(dimethylamino) pyridine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
<i>d</i> ₆ -DMSO	deuterated dimethylsulfoxide
DSC	differential scanning calorimetry
EMI	electromagnetic interference
EP	epoxy
FE-SEM	field-emission scanning electron microscopy
FT-IR	fourier transform infrared
GBA	α -glycidyl terminated bisphenol A acrylate
GNE	glycidyl 4-nonylphenyl ether
GO	graphite oxide
GPC	gel permeation chromatography
HAB	3, 3'-dihydroxy-4, 4'-diaminobiphenyl
IFSS	interfacial shear strength
iPP	isotactic polypropylene
<i>m</i> -CPBA	3-chloroperoxybenzoic acid
MMA	methyl methacrylate

MWNTs	multi-walled carbon nanotubes
NMR	nuclear magnetic resonance
ODA	oxydianiline
ODPA	4, 4'-oxydiphthalic anhydride
P3HT	poly(3-alkylthiophene)
P3HT- <i>b</i> -PS	poly(3-hexylthiophene)- <i>block</i> -polystyrene
P3HT- <i>g</i> -PMMA	polythiophene- <i>graft</i> -poly(methyl methacrylate)
PA	polyamide
PAA	poly(amic acid)
PBI	polybenzimidazole
PC	polycarbonate
PDI	polydispersity index
PE	polyethylene
PEI	polyetherimide
PEO	poly(ethylene oxide)
PFO	poly(9,9-dioctylfluorenyl-2,7-diyl)
PFS	poly(pentafluorostyrene)
PI	polyimide
PI-BDA	polyimide- <i>graft</i> -bisphenol A diglyceryl acrylate
PI-GNE	polyimide- <i>graft</i> -glyceryl 4-nonylphenyl ether
PI _{OH} -BDA	hydroxyl polyimide- <i>graft</i> -bisphenol A diglyceryl acrylate
PMDA	pyromellitic dianhydride
PmPV	poly(metaphenylene vinylene)
PMMA	poly(methyl methacrylate)
POSS	polyhedral oligometric silsesquioxane
PP	polypropylene
PPE	poly(phenylene ethynylene)
PPO	poly(propylene oxide)
PS	polystyrene
PVA	polyvinyl alcohol
PVP	poly(vinylpyrrolidone)
PyMMP	(1- pyrene)methyl 2-methyl-2-propenoate
RTM	resin transfer molding

SAN	poly(styrene- <i>co</i> -acrylonitrile)
SDBS	sodium dodecylbenzenesulfonate
SDS	sodium dodecylsulfate
SWNTs	single-walled carbon nanotubes
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
Triton X-100	polyoxyethylene octylphenylether
UV–vis–NIR	ultraviolet-visible-near infrared

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Summary

Functionalization of Carbon Nanotubes for High-Performance Polymer Composites

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Supervisor: Professor Chan Bee Eng, Mary

Carbon nanotubes (CNTs) are promising nanofillers for light weight and high strength polymer composites due to their large aspect ratio, low density, and exceptional mechanical properties. Two major obstacles to the application of CNTs in polymer composites are their tendency to form bundles and aggregates, and low interfacial adhesion with polymer matrix. To solve these problems, both covalent and noncovalent strategies have been developed for functionalization of CNTs. This thesis centers on the design and synthesis of a series of polyimide dispersants to functionalize CNTs via either noncovalent approach or combination of covalent and noncovalent approaches, for fabrication of high-performance cyanate ester (CE) and polyimide (PI) composites. These dispersants effectively disperse CNTs via π - π interaction with nanotube sidewalls, and strongly interact with both CNTs and matrix to improve the nanotube/matrix interfacial adhesion, leading to significantly enhanced mechanical properties of composites.

Noncovalent functionalization of CNTs is an attractive option for compatibilization of nanotubes with the matrix as it effectively disperses CNTs and preserves the graphene structure of nanotubes. A novel comb-like polymer, polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA), was first synthesized and shown to be highly effective in dispersing and debundling single-walled carbon nanotubes (SWNTs). SWNTs dispersed with PI-BDA

were added into CE (epoxy-modified) matrix and composite fibers were successfully fabricated by reactive spinning. PI-BDA dispersant interacts noncovalently with SWNTs to produce minimal damage to the SWNTs but covalently reacts with CE matrix, resulting in high mechanical reinforcement. Only 1 wt% of PI-BDA functionalized SWNTs increased the tensile modulus and strength of composite by 80% and 70% over that of neat resin, which are higher than the results of other CNT/thermosetting composites.

We further investigated the effect of the side-chain structure of rigid polyimide dispersant on the dispersion of SWNTs and mechanical properties of SWNT/CE composites. Three kinds of polymer, including polyimide without side-chain (PI), polyimide-*graft*-glyceryl 4-nonylphenyl ether (PI-GNE) and PI-BDA, were synthesized and used to disperse SWNTs and improve the mechanical properties of CE. PI-BDA and PI-GNE are equally highly effective at dispersing SWNTs in dimethylformamide (DMF), whereas PI is less effective. PI-BDA functionalized SWNTs were found to be the most effective fillers for reinforcing CE due to the unique side-chain of PI-BDA, which is more compatible with CE matrix and leads to better SWNT dispersion and stronger SWNT/CE interfacial bonding.

Though noncovalent functionalization can disperse high concentration of CNTs without damaging nanotube structure, the interaction between CNTs and dispersant is relatively weak. Therefore, we developed a method to functionalize SWNTs via combination of covalent and noncovalent approaches for further improving the interfacial strength between SWNTs and CE matrix. A reactive polyimide dispersant, hydroxyl polyimide-*graft*-bisphenol A diglyceryl acrylate (PI_{OH}-BDA), was synthesized and used to disperse

epoxidized SWNTs via noncovalent π - π interaction. The phenolic hydroxyl groups in the backbone of PI_{OH}-BDA react with epoxide groups on SWNTs during thermal curing to achieve covalent functionalization. CE composites with 1 wt% of PI_{OH}-BDA functionalized epoxidized SWNTs show 57%, 71% and 124% increases in Young's modulus, tensile strength and toughness over neat CE, which are higher than these of CE composites reinforced with pristine SWNTs, epoxidized SWNTs or pristine SWNTs dispersed with PI_{OH}-BDA. These results suggest that the combination of covalent and noncovalent approaches may be the best nanotube functionalization method.

Our previous three studies have shown that using a polymeric dispersant that is distinct from the matrix tends to limit the nanotube loading in the composites to low content, which is possibly due to the incompatibility between the dispersant and matrix. In our last study, using a rigid hydroxyl-containing poly(amic acid) (PAA) as both the nanotube dispersant and polyimide matrix precursor, polyimide composite films with multi-walled carbon nanotube (MWNT) content as high as 30 wt% were fabricated by solution casting. The MWNT(30 wt%)/PI composites show electrical conductivity of 38.8 S cm⁻¹ which is the highest reported value for any conventional solution-processed nanotube composites. They also exhibit Young's modulus of 9.43 ± 0.14 GPa and tensile strength of 179.2 ± 9.7 MPa, which are higher than other reported values for CNT/PI composites.

Chapter 1 Introduction

1.1 Background

Cyanate esters (CEs) are a class of thermosetting resins with extensive applications in electronic and aerospace industry due to their good thermal, mechanical, electrical and adhesive properties.¹ They undergo polycyclotrimerization to form a network of polycyanurates during thermal curing (Figure 1.1).² A drawback of CEs is their brittleness, resulting from the highly cross-linked system, which often restricts their application as structural materials. Many methods, including preparing new cyanate ester monomers,³ blending with rubbers, thermoplastics or thermosets⁴⁻⁵ and incorporation of inorganic nanofillers,⁶⁻⁷ have been used to toughen CE. However, synthesis of CE monomers is quite complicated and difficult for large-scale applications. Blending with polymers always leads to decreased thermal properties of composites. The method of incorporation of nanofillers (e.g., silicate nanorods) is often selected because it improves both mechanical and thermal properties of CE matrix, and the nanofillers can be incorporated into polymers just using conventional polymer processing techniques.⁸⁻⁹ However, only a few studies have been done on carbon nanotube (CNT)- reinforced CE composites.^{6,10}

Figure 1.1 Polycyclotrimerization of cyanate ester.

CNTs are one-dimensional (1-D) nanomaterials that can be categorized as single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs).¹¹⁻¹³ A SWNT can be thought of as a rolled-up cylinder of a graphene sheet, whereas a MWNT consists of an array of concentric layers of SWNTs. Since their discovery, CNTs have been regarded as the most promising nanofillers for multifunctional polymer composites due to their high aspect ratio (typically 300–1000), low density ($\sim 1.3 \text{ g cm}^{-3}$), and remarkable mechanical, thermal and electrical properties.¹⁴⁻¹⁶ They have been reported to have Young's modulus as high as 1 TPa,¹⁷ tensile strength of about 30 GPa,¹⁷ electrical conductivity as high as 10^4 S cm^{-1} ,¹⁸ and theoretical thermal conductivity of $6000 \text{ W m}^{-1} \text{ K}^{-1}$.¹⁹

Many researchers²⁰⁻²³ have reported the fabrication of high strength and light weight CNT-reinforced polymer composites. Although enhanced mechanical properties of resulting composites relative to neat matrix have been demonstrated, most of these improvements have been far inferior to theoretical values.^{6,20,24} This has been attributed to several factors, including low CNT content, poor CNT dispersion, poor CNT/matrix interfacial load transfer and limited CNT alignment. The major challenges in CNT/polymer composites include poor nanotube dispersion and weak CNT/matrix interfacial strength. Due to strong van der Waals forces between the nanotubes, CNTs are usually bundled which would result in intertube slippage with applied stress and poor mechanical properties of CNT composites. Further, the graphene structure of CNTs is atomically smooth and highly hydrophobic so that stress transfer to a polymer composite matrix, which is usually relatively polar, is poor. To solve these two problems, both covalent^{20,25-26} and noncovalent²⁷⁻²⁹ functionalization of nanotubes have been employed.

The covalent approach is achieved by grafting small molecules²⁰ and polymers,²⁵⁻²⁶ which effectively enhances the CNT/matrix interfacial strength via covalent bonds. However, it only moderately improves nanotube dispersion and disrupts π -conjugation of the nanotube surface, resulting in decreased mechanical and electrical properties of both nanotubes and polymer composites. The noncovalent approach, based on physical adsorption of surfactants³⁰⁻³¹ and polymers,²⁷⁻²⁸ is an attractive option because it can individually disperse high concentration of CNTs without damaging the intrinsic structure of the nanotubes. One disadvantage is that the CNT/matrix interfacial adhesion is usually weak because of the noncovalent interaction.

I hypothesize that a promising nanotube dispersant would be a polymer that interacts with CNTs via strong π - π interaction, since the latter has been proven to be the strongest noncovalent interaction by a computer modeling study.³² Considering the advantages and disadvantages of both covalent and noncovalent strategies, I believe that it would be very promising to functionalize CNTs by a method that combines covalent and noncovalent approaches, which not only improves nanotube dispersion but also enhances the nanotube/matrix interfacial adhesion via covalent bond. Furthermore, so far, the nanotube loading in the composites has been limited low loading fractions (1 wt% for SWNT- and 5 wt% for MWNT-reinforced composites) due to difficulties in dispersing CNTs in composites by conventional processing methods,²⁴ which leads to only modest improvements in composite properties. Incorporation of high content of CNTs is believed to be a very promising method for fabrication of high-performance composites.

1.2 Objectives of thesis

The overall objective of this thesis is to develop effective CNT functionalization methods, with emphasis on the noncovalent approach, to improve CNT dispersion and CNT/matrix adhesion for the mechanical reinforcement of polymer composites. The issues of CNT content and alignment are also taken into account in this work. CE is chosen as the matrix due to its wide applications in aerospace, defense and transportation industries. This thesis has several sub-objectives.

The first sub-objective of this project is to synthesize a noncovalent polymeric dispersant for improving SWNT dispersion in CE matrix and enhancing SWNT/CE interfacial adhesion, so as to achieve high mechanical properties of composites. To realize this goal, a novel comb-like polymeric dispersant, polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA, Figure 1.2A1), was designed and synthesized to functionalize SWNTs for reinforcement of CE. The polyimide backbone in PI-BDA noncovalently interacts with the SWNT surface via π - π interaction while the side-chain provides CNTs with good solubility and reacts with CE matrix. Reactive spinning was applied to fabricate the composite fibers with aligned PI-BDA functionalized SWNTs.

The second sub-objective is to investigate the effect of the side-chain structure of the rigid polyimide dispersant on the dispersion of SWNTs and mechanical properties of SWNT/CE composites. This goal is realized by comparing the ability of three variants of polyimide dispersants, polyimide without side-chain (PI, Figure 1.2A2), polyimide-*graft*-glyceryl 4-nonylphenyl

ether (PI-GNE, Figure 1.2A3) and PI-BDA, in dispersing SWNTs in solvents and CE matrix and improving mechanical properties of CE composite films.

Noncovalent functionalization is effective for dispersing CNTs, but the interfacial strength between the CNTs and the dispersant is relatively weak due to the noncovalent bond. Our third sub-objective is to functionalize SWNTs using a method that combines covalent and noncovalent approaches for reinforcement of CE. A reactive polyimide dispersant, hydroxyl polyimide-*graft*-bisphenol A diglyceryl acrylate (PI_{OH}-BDA, Figure 1.2A4), was synthesized and used to noncovalently disperse SWNTs modified with epoxide groups on their sidewalls. The phenolic hydroxyl groups in the PI_{OH}-BDA backbone react with the epoxide groups on SWNTs to achieve the covalent functionalization.

The performance of CNT/polymer composites has also been hampered by low nanotube loading. Our fourth sub-objective is to make high-performance composites using large nanotube content. A novel poly(amic acid) (PAA, Figure 1.2B) was synthesized and used as both MWNT dispersant and polyimide matrix precursor. Using this dual-function PAA, MWNT/polyimide composites with nanotube content as high as 30 wt% were prepared by solution casting, which show high electrical conductivity and mechanical properties.

Figure 1.2 Chemical structures of (A1) PI-BDA, (A2) PI, (A3) PI-GNE, (A4) PI_{OH}-BDA and (B) PAA.

1.3 Organization of thesis

This thesis is divided into 8 Chapters. Chapter 1 covers the background and objectives of this work. Chapter 2 presents a literature review on CE CNTs, and CNT/polymer composites. Chapter 3 describes the experimental details. Chapter 4 is about the synthesis of PI-BDA dispersant for noncovalent functionalization of SWNTs, fabrication of SWNT-reinforced CE (epoxy-modified) composite fibers, and study of mechanical properties of the composites. In Chapter 5, the effect of the side-chain structure of polyimide dispersant on the mechanical properties of SWNT/CE composite is Chapter 6 describes the use of reactive PI_{OH}-BDA dispersant to realize the combination of covalent and noncovalent functionalization of SWNTs for reinforcement of CE. In Chapter 7, a novel poly(amic acid) (PAA) was synthesized and used as both a MWNT dispersant and a polyimide matrix precursor for preparation of high performance MWNT/polyimide composite

films with high nanotube content. Chapter 8 presents the conclusions of this thesis and recommendations for future work.

Chapter 2 Literature Review

2.1 Cyanate ester (CE)

Cyanate ester (CE) is a class of high-performance thermosetting resins. It possesses good mechanical properties, high glass transition temperature, good flammability characteristics, and low moisture absorption, which result in its widespread usage as functional structural materials in aerospace and electronic industry.³³⁻³⁴ Table 2.1 lists the physical properties of some commercially available CEs.

Table 2.1 Physical properties of some commercially available cyanate esters.³⁴

Properties	Commercial cyanate ester homopolymers						
	AroCy B	AroCy F	AroCy L	AroCy M	RTX- 366	XU71787	Primase
T_g (°C)	289	270	258	252	192	244	>270
% H ₂ O	2.5	1.8	2.4	1.4	0.7	1.4	3.8
Tensile (RT dry)							
Strength (MPa)	88	74	87	73	-	69	77
Modulus (GPa)	3.1	3.1	5.9	2.9	-	3.2	4.0
Elongation (%)	3.2	2.8	3.8	2.5	-	2.7	2.0
Flexural (RT dry)							
Strength (MPa)	-	-	-	-	-	124	112

T_g , glass transition temperature (DMA); % H₂O, water absorption at saturation (100 °C).

All are products of Ciba except XU71787 from Dow.

2.1.1 Chemistry of CE

Cyanate ester monomers contain reactive cyanate functional groups ($-O-C\equiv N$). Figure 2.1 shows the chemical structures and commercial trade

names of commercial cyanate ester monomers.³⁴ CE monomers cure to thermosets via polycyclotrimerization (an addition process) of three cyanate groups to form linkages of triazine rings (Figure 2.2).⁶ This highly crosslinked structure of symmetric triazine rings leads to the excellent mechanical, thermal, dielectric and moisture absorption properties of the polymer. To accelerate the curing process, a transition metal carboxylate or chelate catalyst together with nonylphenol is usually used.² Successful curing of CE without catalyst is also achieved, possibly by adventitious impurities which contain active hydrogen atoms.³³

Figure 2.1 Chemical structures and commercial names of commercial cyanate ester monomers.

Figure 2.2 Curing of CE via polycyclotrimerization.⁶

The carbon atom of the $\text{-OC}\equiv\text{N}$ group is highly electrophilic due to neighboring electronegative oxygen and nitrogen atoms. As a result, the cyanate group can react with nucleophilic reagents under mild conditions, using base or acid as catalyst.³⁵ Various kinds of chemicals containing reactive functional groups, such as alcohols,³⁶ phenols,³⁷⁻³⁸ amines,^{6,8} and epoxies,³⁹⁻⁴⁰ have been employed to react with CE and modify the ultimate properties of the network. The copolymerization between epoxy and CE has been well studied by several groups.⁴¹⁻⁴⁴ As shown in Figure 2.3, the complex reaction mechanism usually involves the formation of oxazoline, oxazolidone, cyanurate and isocyanurate.⁴⁴

Figure 2.3 Proposed reactions between epoxy and cyanate ester.⁴⁴

2.1.2 Modification of CE

Although CE is a class of high performance thermosetting resins, its structural applications are often restricted by its brittleness resulting from the highly cross-linked structure. Therefore, modification of CE is still required for broadening their applications. Structure modification of CE is usually a good way,^{3,45-47} although it is usually complicated. Laskoski et al.⁴⁵ developed a novel cyanate ester resin with enhanced processability, which is liquid at ambient temperature and exhibits high thermal stability and good mechanical properties up to about 150°C after curing. Guenther et al.³ synthesized a new kind of CE monomer from bis(4-cyanatophenyl)dimethylsilane, and found that this resin has improved thermooxidative stability and reduced moisture

absorption without significant loss in ease of processing or mechanical properties.

Techniques involving blending CE with rubbers, thermoplastics or thermosets have also been tried to reinforce CEs. These methods are much easier and more suitable for large-scale applications as compared to the structure modification approach. Gu et al.⁴⁸⁻⁴⁹ reported that carboxyl-terminated butadiene-acrylonitrile rubber was very effective for toughening CE. The impact strength of the blends increased significantly but the storage modulus decreased. They did not discuss the effect on thermal properties, which are believed to be inferior since the rubber has low glass transition temperature (T_g). Recently, several research groups have reported modification of cyanate ester using engineering thermoplastics, such as poly(etherimide),⁵⁰ polysulfone,⁵¹⁻⁵² and polyarylate.⁵³ Though the strength and toughness of these blends can be improved significantly, the modulus and thermal decomposition temperature usually decrease.

Recently, modification of CE resins by incorporation of inorganic nanofillers^{6-7,10,54-55} has been successfully utilized to improve both mechanical and thermal properties of composites. This method is often selected also because of the favorable performance-cost ratio and processability. Liang et al. synthesized polyhedral oligometric silsesquioxane (POSS) derivatives with amine⁸ and hydroxy³⁶ terminal groups, respectively, both of which were found to be able to react with cyanate esters and improve thermal and mechanical properties of the resultant composites.

However, there are a few reports of CNTs reinforcement of cyanate ester composites.^{6,10} Fang et al.¹⁰ used two types of MWNTs to fabricate MWNT/CE

composites, and found that both mechanical and thermal properties were improved to some extent compared to neat CE. Recently, Che et al.⁶ developed a reactive spinning technique to fabricate SWNT/CE composite fibers with aligned SWNTs, which showed 85% increase in tensile strength and 140% increase in elongation at break.

2.2 Carbon nanotubes (CNTs)

2.2.1 CNT structure

Carbon nanotubes (CNTs) are typical one dimensional (1-D) nanomaterials in the carbon material family. They can be viewed as single or nested concentric tubes formed by rolling two-dimensional (2-D) graphene sheets, with ends that may be capped by hemifullerenes. Based on the number of graphene sheet layers, CNTs are categorized as single-walled nanotubes (SWNTs)¹² or multi-walled nanotubes (MWNTs).¹¹ SWNTs have diameters ranging from 0.4–3 nm⁵⁶ and lengths in the order of micrometres.

SWNT chirality is dependent on the way the graphene sheet is rolled into a nanotube, which is defined by the chiral vector, $C_h = na_1 + ma_2$, where n and m are integers (Figure 2.4A).¹⁴ Based on this naming scheme, SWNTs can be divided into three types: armchair (n, n), zigzag ($n, 0$) and chiral (all others) (Figure 2.4B).⁵⁷ SWNT chirality determines their electrical properties (Figure 2.4C).⁵⁷ All armchair nanotubes (n, n) have band gaps of 0 eV and thus are metallic. For other nanotubes with chiral indices (n, m), when $n - m = 3p$ (where p is an integer and $\neq 0$), they are semimetallic, otherwise they are semiconductors.⁵⁸ MWNTs consist of an array of concentric layers of

individual carbon nanotubes¹¹ with an interlayer distance of about 0.34 nm⁵⁹ (Figure 2.4D). The MWNT diameter depends on the total number of graphene sheets making up the CNT, usually 5–20 nm, while the length can be as long as a few millimetres.

Figure 2.4 A) A schematic diagram showing formation of a SWNT by rolling-up graphene strips at various angles.¹⁴ B) Schematic representation of (a) armchair, (b) zigzag and (c) chiral SWNTs.⁵⁷ C) Chiral vectors specified by the pairs of integers (n, m) for SWNTs. Small dots represent semiconducting tubes while encircled dots are for metallic tubes.⁵⁷ D) TEM images of MWNTs with different layers.¹¹

2.2.2 CNT synthesis

Three techniques have been developed to synthesize CNTs, i.e. arc discharge,¹¹ laser ablation⁶⁰ and chemical vapor decomposition (CVD).⁶¹ In arc discharge and laser ablation techniques, solid carbon is first evaporated to form

hot gaseous carbon feedstock, which produces CNTs through condensation.^{11,60} These two methods provide good control over the quality of the produced CNTs but are difficult to scale up. Most commercially available high-quality CNTs are produced by the arc discharge technique due to its lower cost compared to the laser ablation process. The CVD method involves the decomposition of hydrocarbons over a transition metal catalyst (e.g., cobalt, nickel or iron) to form CNTs. Many CVD methods have been reported, including fixed bed,⁶⁰ fluidized bed,⁶² floating catalyst⁶³ and combination methods,⁶⁴⁻⁶⁵ etc. The CVD technique is effective for mass-preparation of both SWNTs and MWNTs, and many companies have applied it to produce large quantities of CNTs.

It should be noted that all known synthesis techniques yield mixtures with varying properties, such as nanotube diameters, lengths, chiralities, and defect densities along with various impurities, etc. Hence, nanotube properties vary significantly with the synthesis process. The impurities found in as-prepared CNTs are mainly amorphous carbon and metal catalysts.⁶⁶⁻⁶⁷ Purification of CNTs is usually carried out in two steps, involving thermal oxidation of amorphous carbon followed by acid treatment for removal of catalyst particles.⁶⁸⁻⁶⁹

2.2.3 CNT properties

The unique structure of CNTs leads to their outstanding mechanical, thermal and electrical properties, as described in Chapter 1.1. Meanwhile, they have high flexibility, large aspect ratio and low density ($\sim 1.3 \text{ g cm}^{-3}$) comparable to polymers. All these properties indicate that CNTs are ideal

nanofillers for multifunctional and light weight CNT-reinforced polymer composites.

2.2.3.1 Mechanical properties of CNTs

By analogy with graphite which has been shown to have high strength and stiffness,⁷⁰⁻⁷¹ CNTs are expected to display excellent mechanical properties. A large number of computer simulations has been conducted to evaluate the mechanical properties of CNTs.⁷²⁻⁷⁵ Overney et al.⁷² first used atomistic simulation to calculate the rigidity of short SWNTs. The Young's modulus of nanotubes was calculated to be 1.5 TPa, comparable to the value of graphite (1.06 TPa).⁷⁰ Based on an empirical lattice dynamics model, Lu et al.⁷³ obtained SWNT elastic modulus of ~ 1 TPa, bulk modulus of ~ 0.74 TPa and shear modulus of ~ 0.45 TPa, which are comparable to those of diamond.

Researchers have also performed experimental measurements on the mechanical properties of CNTs.⁷⁶⁻⁸⁰ The first measurements were conducted by Treacy et al. on MWNTs produced by the arc-discharge technique.⁷⁶ They measured the amplitude of intrinsic thermal vibrations using transmission electron microscopy (TEM), and calculated the moduli to be 0.41 to 4.15 TPa. Similar values (0.7–1.3 TPa) were also reported by Poncharal et al., achieved by measuring the electromechanical resonant vibrations of nanotubes.⁷⁷ The stress-strain measurements on individual MWNT (arc-discharge) were first carried out by Yu et al.⁷⁹ The MWNT was mounted between two opposite atomic force microscopy (AFM) tips. The top AFM tip gave tensile load to the MWNT while the lower AFM tip was used to determine the applied force on the MWNT (Figure 2.5). The modulus, strength, and elongation at break were

measured to be 0.27–0.95 TPa, 11–63 GPa and up to 12%, respectively. They also conducted the same measurement on SWNT bundles,⁸⁰ which showed Young's modulus of 0.32–1.47 TPa, tensile strength of 10–52 GPa, and elongation at break as high as 5.3%.

Figure 2.5 SEM images showing an individual MWNT mounted between two opposite AFM tips.⁷⁹

The above high mechanical property values have been obtained for arc-discharge MWNTs and high-quality SWNTs. CNTs produced by the CVD technique usually have a wide range of lower mechanical properties. For example, Salvétat et al.⁸¹ obtained a Young's modulus in the range of 12–50 GPa while Xie et al.⁸² reported a modulus of 0.45 TPa for CVD-MWNTs.

2.2.3.2 Electrical properties of CNTs

As discussed in Section 2.2.1, SWNTs can behave as a metal or semiconductor, depending on their chirality. MWNTs are composed of concentric SWNTs, and each SWNT ring has different chiralities, so the electrical behavior of MWNTs depends on the net results of the concentric

SWNTs. Further, nanotube diameter, nanotube length, impurities and defects in nanotubes also have serious influence on the electrical properties.⁸³

Many studies have reported on the electrical properties of nanotubes.^{18,84-86} Tans et al.⁸⁴ were the first to conduct experimental measurements on individual SWNT and find that SWNTs act as genuine quantum wires. They also reported that the electrical conductivity at room temperature was about 10^3 – 10^4 S cm⁻¹ for metallic SWNT and only about 0.1 S cm⁻¹ for semiconducting SWNT. Thess et al.¹⁸ reported that a single rope of metallic SWNTs had a electrical conductivity in the order of 10^4 S cm⁻¹ at 300 K, measured using a four-point technique. This value is close to that of metals, i.e. 10^6 S cm⁻¹ for copper and 10^5 S cm⁻¹ for iron.⁸⁷ The electrical conductivity of a single MWNT was measured to be about 10^4 S cm⁻¹ at room temperature, higher than the value of small MWNT bundles (10^3 S cm⁻¹).⁸⁸ The electrical conductivity of dense CNT networks (buckypaper) has been reported to vary from 10^2 to 10^3 S cm⁻¹,⁸⁹⁻⁹⁰ which is lower than that of individual or bundles of nanotube due to high tube-tube contact resistivity.

2.2.4 CNT functionalization

It has been well established that the properties of polymer composites strongly depend on filler dispersion and filler/matrix interfacial interaction. However, CNTs are usually bundled and entangled with each other due to their high aspect ratio and intrinsic van der Waals forces.¹⁸ Figure 2.6¹⁸ clearly shows the SWNT bundles and MWNT entanglements. The nanotube bundles and entanglements bring less nanotube surface to contact with the polymer matrix and consequently results in decreased stress transfer. Furthermore, poor

CNT/matrix interfacial adhesion, which arises from the smooth and nonreactive CNT surface, also leads to poor load transfer from matrix to CNTs. To improve nanotube dispersion and the strength of the interfacial interaction, two strategies including covalent and noncovalent approaches have been reported.^{15,91-92}

Figure 2.6 TEM images of SWNT bundles in the (A) cross-sectional and (B) side-view directions,¹⁸ and (C) MWNT entanglements (a photo taken in our group).

2.2.4.1 Covalent functionalization of CNTs

The inherent structure of CNTs, formed by pyramidization and misalignment of π -orbital of sp^2 carbon atoms, makes them relatively reactive and enables covalent attachment of small organic groups or large polymeric chains to nanotubes.⁹³ Covalent functionalization^{20,25-26} has been demonstrated to be effective at improving nanotube dispersion in many solvents and polymer matrices. In addition, it helps improve the CNT/matrix interfacial bonding. However, covalent functionalization disrupts the extended π -conjugation in nanotubes, which significantly alters the electrical, thermal and mechanical properties of nanotubes.

Covalent functionalization can be realized by two techniques: 1) acid oxidation and subsequent derivatization of defect sites and end-caps,⁹⁴⁻⁹⁷ and 2) direct sidewall functionalization using reactive species.⁹⁸⁻¹⁰² Acid oxidation is a widely reported method to introduce carboxylic acid groups onto nanotubes. Most of the carboxylic groups are at the end of nanotubes, which can act as the starting materials for further chemical reactions (Figure 2.7A).¹⁰³ A drawback of this method is that CNTs are usually shortened (with length below 1 μm) after acid oxidation. Reactive species, including atoms,⁹⁸ radicals,⁹⁹ nitrenes¹⁰² or carbenes,¹⁰¹ enable direct addition of functional groups onto the π -conjugated nanotube surface, in which the nanotube hybridization is changed from sp^2 to sp^3 . Most of these species are generated from thermally-activated reactions. Figure 2.7B lists the typical reactions for direct sidewall functionalization.¹⁰⁴ These reactions primarily occur on the nanotube sidewalls and are relatively less destructive to the length of nanotubes.

Covalent grafting of polymers to nanotubes is an important method for dispersing nanotubes in polymer matrices and for improving CNT/matrix interfacial adhesion. It includes both “grafting from” (polymerization of monomers from traditional initiating species that have been first immobilized on the nanotube surface)¹⁰⁵⁻¹⁰⁹ and “grafting to” approach (attaching pre-synthesized polymers with reactive or functional groups onto nanotubes).¹¹⁰⁻¹¹³ Figure 2.7C shows schematics of “grafting from” and “grafting to” approaches.¹¹⁴ An example of the “grafting from” method involves introducing of initiators (MWNTs-Br) onto the nanotube surface, followed by grafting polystyrene chains from these initiators via in situ polymerization of styrene monomers.¹⁰⁶ In the “grafting to” method, pre-synthesized end-functionalized

polymers are attached onto the nanotube surface via chemical reactions. For example, pre-fabricated polyamide,¹¹¹ phenoxy¹¹⁰ and polyimide¹¹²⁻¹¹³ have been successfully grafted onto CNTs.

Figure 2.7 A) Derivatization reactions of acid-treated nanotubes through the defect sites of the graphitic surface.¹⁰³ B) Typical reactions for direct sidewall functionalization of CNTs.¹⁰⁴ C) Schematic representations of “grafting from” and “grafting to” approaches for functionalization of CNTs with polymers.¹¹⁴

2.2.4.2 Noncovalent functionalization of CNTs

Noncovalent functionalization involves physical adsorption/wrapping of surfactants or polymers onto the surface of nanotubes. Many studies have confirmed that some molecules, including surfactants,¹¹⁵⁻¹¹⁶ aromatic compounds¹¹⁷⁻¹¹⁸ and conjugated polymers¹¹⁹⁻¹²¹ can adsorb onto CNT surface via noncovalent interaction (hydrophobic interaction, π - π interaction, and van der Waals interaction) both in water and organic solvents. This method can effectively disperse CNTs without disturbing the nanotube π system and therefore better preserve intrinsic properties of CNTs. However, the interaction between the CNTs and dispersants are relatively weak as compared with those in the covalent functionalization approach.

In water

To disperse CNTs in water, the most convenient way is to use surfactants, such as sodium dodecylbenzenesulfonate (SDBS),^{116,122} sodium dodecylsulfate (SDS),^{30,123} cetyltrimethylammonium bromide (CTAB)¹²⁴ and polyoxyethylene octylphenylether (Triton X-100).³¹ Figure 2.8 shows chemical structures of some surfactants.¹²⁵ The surfactant adsorbed on CNT surface provides nanotubes with electrostatic/steric repulsive forces to overcome the intertube van der Waals forces, thus preventing nanotubes from aggregation. Good dispersion of CNTs in water has also been achieved by wrapping polymers, such as poly(vinylpyrrolidone) (PVP),¹²⁶ poly(acrylic acid) (PAA),¹²⁷ and poly(ethylene oxide) (PEO) with poly(propylene oxide) (PPO) (PEO-PPO-PEO),¹²⁸ around the surfaces of CNTs and using aromatic molecules (e.g., pyrene derivatives).¹²⁹⁻¹³² Non-covalently functionalized CNTs in water can be

used to make CNT/polymer composites.¹³³⁻¹³⁷ For example, Zhang et al.¹³³ prepared polyvinyl alcohol (PVA) composites using SWNTs dispersed with PVP and SDS, which exhibited significantly improved tensile modulus and strength compared to neat PVA. Regev et al.¹³⁷ fabricated conductive SWNT/polystyrene (PS) and SWNT/poly(methyl methacrylate) (PMMA) composites by mixing the well-dispersed SWNT-SDS solution with PS or PMMA latex nanoparticles, followed by freeze-drying and molding.

Figure 2.8 Chemical structures of some surfactants for dispersing CNTs in water.

In organic solvents

Unlike in water-soluble systems, nonionic dispersants are usually proposed for dispersing CNTs in organic solvents. Two families of polymers have recently been reported to be effective dispersants for dissolving CNTs in organic solvents. The first family comprises conjugated or aromatic polymers and their derivatives, such as poly(3-alkylthiophene) (P3HT),¹³⁸⁻¹³⁹ poly(metaphenylene vinylene) (PmPV),¹⁴⁰⁻¹⁴² poly(phenylene ethynylene) (PPE),^{27,120} poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO),¹⁴³⁻¹⁴⁴ polybenzimidazole (PBI)¹⁴⁵ and polyimide (PI),¹¹⁹ which adsorb onto CNT surface via strong π - π stacking interaction. Figure 2.9a–f show the chemical structures of these

polymers. The other family comprises block copolymers,^{28,128,146-148} which are designed in such a way that one block anchors strongly to the hydrophobic CNT sidewall while the other block provides CNTs with good solubility by imparting strong repulsive forces via steric hindrance. Figure 2.9g–j show the chemical structures of some of these block copolymers. Zou et al.¹⁴⁶ reported that poly(3-hexylthiophene)-*block*-polystyrene (P3HT-*b*-PS, Figure 2.9h) was an excellent dispersant for both SWNTs and MWNTs, in which the P3HT segment formed strong π – π interaction with CNT surface while the PS segment led to the good solubility and stability of CNTs. Petrov et al.¹⁴⁸ synthesized a copolymer of methyl methacrylate (MMA) and (1-pyrene)methyl 2-methyl-2-propenoate (PyMMP) (Figure 2.9j) and found that this polymer had high capability at solubilizing MWNTs, which was attributed to π – π interaction between pyrene and MWNTs and the steric hindrance of MMA block.

Figure 2.9 Chemical structures of (a-f) conjugated or aromatic polymers, and (g-j) block copolymers used for dispersing CNTs in organic solvents.^{28,119-120,128,139,141,143,145-146,148}

2.2.4.3 Noncovalent functionalization of CNTs with polyimide

Polyimides (PIs) are high-performance glassy polymers with a unique combination of excellent mechanical properties, outstanding thermal stability and good chemical resistance. They are commonly synthesized by a two-step process developed by Dupont in the 1950s and 1960s, which includes synthesis of poly(amic acid) (PAA) by polycondensation of an aromatic diamine and dianhydride, followed by cyclodehydration of PAA to form the polyimide.^{112-113,119,149} Figure 2.10 shows the synthesis route of pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide.¹⁵⁰

Figure 2.10 Synthesis of PMDA-ODA polyimide.¹⁵⁰

One major problem in polyimide synthesis is that aromatic rings tend to result in poor solubility and high melting or softening temperature of the polyimide. To improve the solubility and processability of PIs, several methods have been applied. Perhaps the simplest way is to choose suitable diamine and dianhydride monomers to synthesize PIs. Monomers with cage, bicyclic or

multi-ring structures have been reported to be useful for synthesizing polyimides with good solubility.¹⁵¹ These structures help to increase PI solubility by inhibiting the crystal packing of PI molecules. Another method is achieved by modifying diamine or dianhydride monomers with pendant groups, such as phenyl,¹⁵²⁻¹⁵³ t-butyl,¹⁵⁴ and alkyl chain,^{119,155} before polycondensation. The third method is grafting side chains onto the polymer backbone after the synthesis of the PIs.^{149,156} For example, Fu et al.¹⁵⁶ successfully grafted polystyrene (PS) and poly(pentafluorostyrene) (PFS) side chains to presynthesized rigid polyimide backbone by atom transfer radical polymerization (ATRP), and the solubility of the grafted polyimides was significantly improved.

To date, several groups have employed polyimides to disperse CNT in organic solvents or in polymer matrix.^{119,157-158} Two strategies have been employed to design polyimides for CNT dispersion. One strategy is realized via a donor acceptor interaction between CNTs and substituent groups on polyimide. Wise et al.¹⁵⁷ reported that SWNTs dispersed well in a nitrile functionalized polyimide, (β -CN)APB/ODPA (Figure 2.11a). They attributed the stable dispersion to a donor acceptor interaction between SWNTs and the -CN groups of the polyimide. However, they did not measure the physical properties of the resultant SWNTs reinforced (β -CN)APB/ODPA composite films.

The other strategy is achieved via the π - π interaction between CNTs and the aromatic polyimide backbone. Shigeta et al.¹⁵⁸ reported that a fully aromatic polyimide possessing a sulfonic acid salt (PI-2, Figure 2.11b) had a high capability of debundling a large amount of SWNTs in organic solvents and

stabilizing for long periods of time. They attributed the high solubilization ability of PI-2 for SWNTs to the π - π interaction between the aromatic moieties on PI-2 and SWNTs. Later, Delozier et al.¹¹⁹ synthesized a series of polyimides from 2,7-diamino-9,9'-dioctylfluorene (AFDA, Figure 2.11c) and various aromatic dianhydrides (Figure 2.11d) and tested their effectiveness for dispersing SWNTs. They found that only three high molecular weight polyimides, AFDA-s-BPDA, AFDA-ODPA, and AFDA-PMDA were successful to debundle SWNTs in *N,N'*-dimethylacetamide (DMAc), while others were less effective. They suggested that rigid and unbent polyimides with high molecular weight were more effective at breaking up the SWNT agglomerates due to their stronger π - π interaction with CNTs, which was supported by computer simulation results.

Figure 2.11 Chemical structures of (a) (β -CN)APB/ODPA, (b) PI-2, (c) AFDA and (d) various dianhydrides.

2.3 CNT/polymer composites

Theoretically, CNTs are superior to conventional microfillers in polymer composites due to their outstanding electrical, mechanical and thermal properties, as well as nanoscale size and large aspect ratio which enables more surface area to be in contact with the surrounding matrix and leads to significantly improved properties at relatively low CNT loading. Furthermore, CNTs have densities ($1\text{--}2\text{ g cm}^{-3}$) comparable to polymer, which makes them attractive for light weight composites. Since the first report of CNT/polymer composites in 1994,¹⁵⁹ much work has been done to develop advanced polymer composites with CNTs.^{15,24} However, the addition of nanotubes into a polymer for reinforcement is not very easy. Challenges like homogeneous nanotube dispersion, interconnectivity between CNTs and matrix, increase in CNT content and alignment of CNTs must be considered in order to obtain composites with enhanced properties.

2.3.1 Processing techniques for CNT/polymer composites

2.3.1.1 Solution blending

Perhaps solution blending is the most common method for fabricating nanotube reinforced polymer composites. Many polymer matrices, such as polystyrene (PS), polyvinyl alcohol (PVA), poly(methyl methacrylate) and nylon, have been solution blended with CNTs to make composites.^{25,27-28,160-161} Three steps are usually involved in this method: i) dispersing CNTs in a solution by ultrasonication; ii) mixing the CNT dispersion with the soluble polymer matrix by stirring and ultrasonication; iii) evaporation of the solvent

from the composite formulation. CNTs used in this method are usually functionalized by either covalent or noncovalent approach. This method is widely used because the agitation of CNTs in a solvent facilitates CNT dispersion and prevents CNT re-aggregation.

2.3.1.2 Melt blending

Solution blending is good at dispersing CNTs, but it is not environmentally friendly and is unsuitable for large-scale industrial applications. Moreover, it cannot be easily applied to the fabrication of high molecular weight thermoplastic composites due to difficulties in the removal of solvent. In contrast, melt processing which uses high temperature and high shear forces, is simpler and more compatible with most current industrial processes. Although it is relatively less effective at dispersing CNTs than the solution method, there are still some successful examples of melt blending. Yang et al.¹⁶² reported that the stiffness, strength, ductility and toughness were all improved for polyethylene (PE) composites reinforced with PE-grafted MWNTs, which were fabricated by melt blending in an Atlas Minimax mixer. Pötschke et al.¹⁶³ prepared MWNT/polycarbonate (PC) composites by melt mixing neat PC with a masterbatch of MWNTs(15 wt%)/PC in a microcompounder, and observed excellent dispersion of MWNTs in PC by TEM. Liu et al.²¹ used a facile melt-compounding approach to prepare MWNT/nylon-6 composites and attributed the greatly improved composite mechanical properties to good nanotube dispersion and strong interfacial interaction. Recently, many research groups have reported the fabrication of CNT/polymer fibers with the melt spinning technique. These composite fibers,

such as MWNT/PC,¹⁶⁴ MWNT/polypropylene (PP),¹⁶⁵ and MWNT/polyamide (PA)^{111,166} fibers, show dramatically improved mechanical properties resulting from the alignment of nanotubes.

2.3.1.3 In situ polymerization

The in situ polymerization approach involves dispersion of CNTs in monomers or monomer solutions via sonication followed by polymerization. Homogeneous nanotube dispersion and high nanotube content can be achieved by using this method. Covalently functionalized nanotubes are usually used, which enable chemical reaction between the nanotubes and matrix, leading to high mechanical reinforcement through effective load transfer. This method has been widely used for preparing CNT/thermoplastic composites. For example, Jia et al.¹⁶⁷ used in situ polymerization method to fabricate CNT/PMMA composites using 2,2'-azobisisobutyronitrile (AIBN) as radical initiator. Gao et al.¹¹¹ developed a novel chemical-processing technique for production of SWNT/nylon-6 composites by dispersing SWNTs in caprolactam followed by ring-opening polymerization. Jiang et al.¹⁶⁸ prepared electrically conductive MWNT/polyimide composites by polycondensation of diamine and dianhydride in the presence of MWNTs to form MWNT/poly(amic acid) precursor, which converts to MWNT/polyimide composites after thermal imidization. In situ polymerization has also been used for fabrication of thermosetting composites such as epoxy,¹⁶⁹⁻¹⁷¹ cyanate ester (CE)^{6,10} and bismaleimide (BMI)¹⁷²⁻¹⁷³ composites, which is based on dispersion of CNTs in resin followed by thermal curing to form thermosets.

2.3.1.4 Other processing methods

Recently, some new techniques have been developed recently for preparing CNT/polymer composites, including latex technology,^{137,174} infiltration,¹⁷⁵⁻¹⁷⁶ densification,¹⁷⁷ coagulation spinning,^{135,178} layer-by-layer¹⁷⁹⁻¹⁸⁰ and pulverization.¹⁸¹⁻¹⁸² Table 2.2 lists details of these new methods.⁹²

Table 2.2 New methods for fabricating CNT/polymer composites.⁹²

Technique	CNTs	Fabrication process	Advantages
latex technology ^{137,174}	pre-dispersion of CNTs in water using a surfactant	mixing dispersed CNTs with a polymer latex followed by drying	relatively easy for scale-up, environmentally friendly
infiltration ¹⁷⁵⁻¹⁷⁶	pre-dispersion of CNTs in solution	infusing buckypaper with polymers	CNT loading can be as high as 60 wt%
densification ¹⁷⁷	CNT forest by self-grown	putting the CNT forest into a pool of uncured epoxy, which is infused into the CNT forest and then cured	CNT content can be controlled by varying the densification of CNT forest, aligned CNTs in composites
coagulation spinning ^{135,178}	pre-dispersion of CNTs using a surfactant solution	coagulation of CNT into a mesh by wet spinning into a polymer solution, and converting the mesh into a solid fiber via drawing	employed to CNT/polymer fiber
layer-by-layer deposition ¹⁷⁹⁻¹⁸⁰	pre-dispersion of CNTs in solvent is necessary	dipping of a solid substrate (glass slides, silicon wafers) into a CNT/polymer solution followed by curing	structural defects of the polymer/CNT can be minimized; high CNT loading
pulverization ¹⁸¹⁻¹⁸²	as-received CNTs	polymer and CNTs are mixed and pulverized by pan mill or twin screw	possible grafting of polymers on CNTs, easy for scale-up, solventless process

2.3.2 Mechanical properties of CNT/polymer composites

CNTs have been used for reinforcement of thermoplastic polymer, such as PP, PA, PS and PVA, as well as thermosetting resins, including epoxy, phenol-formaldehyde, CE and BMI. There are four main issues affecting the reinforcement of CNT/polymer composites: 1) CNT content; 2) CNT dispersion in polymer matrix; 3) CNT/matrix interfacial strength; 4) alignment of CNTs in polymer matrix.

2.3.2.1 Effect of CNT content

Based on the Halpin-Tsai model¹⁸³ and the rule of mixture,¹⁸⁴ the Young's modulus and tensile strength of CNT/polymer composites are expected to increase with CNT content in a certain range. Very high values of mechanical properties (Young's modulus of 15–169 GPa and tensile strength of 500–2000 MPa) of composites with high CNT content (> 50 wt%) have been reported.^{180,185-187} For example, Dalton et al.¹⁸⁵ fabricated SWNT(60 wt%)/PVA composite fibers by coagulation spinning, which possessed a tensile strength of 1.8 GPa. Shim et al.¹⁸⁰ reported that SWNT(60 wt%)/PVA composites prepared by a layer-by-layer deposition technique demonstrated tensile strength of 504.5 ± 67.3 MPa, stiffness of 15.6 ± 3.8 GPa, and toughness of 121.2 ± 19.2 J/g, outperforming other bulk composites by 2–10 times. However, these outstanding mechanical properties are achieved with non-conventional processing techniques^{180,185-186} and/or special kinds of CNTs.¹⁸⁶⁻¹⁸⁷ In composites prepared with conventional processing methods and commercial grade CNTs, a limiting CNT content is always observed, below which the composite mechanical properties increase with CNT content while above which

the mechanical properties start to decrease.¹⁸⁸⁻¹⁹⁰ The critical content is about 1 wt% and 5 wt% for SWNT- and MWNT-based composites, respectively. The limited improvement in mechanical properties at high CNT content can be attributed to imperfect CNT dispersion, poor load transfer, curvature of CNTs, effect of CNTs on polymerization reaction of the matrix (especially for thermosets), void defects, etc.¹⁷⁰⁻¹⁷¹

2.3.2.2 Effect of CNT dispersion

As discussed previously, as-produced CNTs tend to form bundles or entanglements consisting of more than 50 individual tubes because of van der Waals forces. CNT aggregation can act as a stress concentrator and reduce the filler surface area to interact with the matrix, both of which result in decreased mechanical properties of composites. In addition, there is tube slippage in CNT bundles or entanglements,¹⁹¹⁻¹⁹² which limits stress transfer at CNT/matrix interface, leading to poor reinforcement. Many studies^{26,91,193} have confirmed that well dispersed CNTs lead to higher composite mechanical properties than CNT aggregates. For example, Song et al.¹⁹³ prepared epoxy composites reinforced with well dispersed CNTs by using ethanol, which showed 18% increase in tensile strength at nanotube loading of 1.5 wt%, while the control composites prepared without solvent showed decreased tensile strength as compared to neat epoxy due to the poor dispersion of CNTs.

Many mechanical techniques, including ultrasonication,¹⁹⁴⁻¹⁹⁵ calendaring,¹⁹⁶⁻¹⁹⁷ ball milling,²³ and extrusion¹⁹⁸⁻¹⁹⁹ have been applied to disperse CNTs in composites.^{16,92} Ultrasonication, achieved using a bath sonicator or a probe sonicator, is widely used in laboratories to disperse CNTs

in a solution. However, it should be noted that aggressive and/or long-time ultrasonication treatment can result in serious damage to CNT length and structure,²⁰⁰⁻²⁰¹ leading to decreased mechanical and electrical properties of CNTs. This effect becomes more pronounced when a probe sonicator is employed. Several research groups have reported good CNT dispersion and improved composite mechanical properties achieved via mechanical For example, Thorstenson et al.¹⁹⁶ demonstrated a high degree of nanotube dispersion in MWTN/epoxy composites prepared by the calendering approach, which led to significantly enhanced fracture toughness in composites with low nanotube content. Gorrasi et al.²³ dispersed non-treated MWNTs into a linear low density PE by the ball milling technique at room temperature and achieved about three times increase (compared with neat PE) in elastic modulus of the composites at MWNT loading of 10 wt%. Isayev et al.¹⁹⁹ developed an ultrasound-assisted twin screw extrusion process to fabricate polyetherimide (PEI) composites with well dispersed MWNTs, which showed 14% and 60% increases in tensile strength and Young's modulus, respectively, at 10 wt% of MWNT.

Chemical functionalization which involves modification of the inherently inert nanotube surface has been demonstrated to be more effective at dispersing CNTs in matrix. It includes covalent and noncovalent functionalization, as discussed in Section 2.2.4. Chemical functionalization is usually used in combination with ultrasonication. CNT functionalization not only improves CNT dispersion but also enhances nanotube/matrix interfacial strength, thus leading to pronounced enhancement in composite mechanical properties. Some examples will be given in Section 2.3.2.3.

2.3.2.3 Effect of CNT-matrix interfacial adhesion

Many studies have proved that the nature of nanotube/matrix interface and stress transfer between matrix and nanotubes significantly affect the mechanical properties of composites.²⁰²⁻²⁰⁴ When the interfacial bonding is strong, stress can be transferred from matrix to nanotubes which leads to high strength composites. However, when the interfacial adhesion is poor, very limited load can be transferred to the nanotubes, resulting in composite failure at low load (thus low composite strength). As a result, the understanding of interfacial characteristics and mechanism of load transfer is important for manufacturing high strength composites.

Interfacial shear strength (IFSS), the critical shear stress at which the nanotube-matrix bond fails, determines the maximum load transfer to the nanotubes.²⁰⁵⁻²⁰⁶ The IFSS value is suggested to vary from 50 to 100 MPa for composites with noncovalent bond between nanotubes and matrix, based on many theoretical and experimental studies.²⁰⁵ Much higher values (for example 500 MPa estimated by Wagner et al.²⁰⁷) are expected for composites with nanotubes covalently bonded to matrix.

A number of studies indicate that the morphology and properties of polymer at the interfacial region are different from that of bulk polymer in carbon nanotube reinforced composites.²⁰⁸⁻²¹¹ Coleman et al.²⁰⁸ reported nucleation of crystallinity at nanotube/polymer interface in CNT/PVA composites, which maximized interfacial stress transfer and led to significant enhancement in tensile properties of composites. Assouline et al.²¹⁰ reported that MWNTs were α -nucleating agents in isotactic polypropylene (iPP),

resulting in fibrillar MWNT/iPP crystallites as compared to spherical in neat iPP. Ding et al.²¹¹ observed MWNTs coated with thick layers of polymer sheathing on fracture surfaces of MWNT/PC composites (Figure 2.12), which is direct evidence of strong MWNT-polymer interaction.

Figure 2.12 (a) SEM image showing the nanomanipulation experiment inside a Hitachi S4500 SEM. (b and c) SEM images of MWNTs covered with polymer at the fracture surface of MWNT/PC composites.²¹¹

Due to their “atomically smooth” surface, CNTs have little bonding or friction with the polymer matrix.²¹² To improve the nanotube-matrix interfacial strength and the mechanical properties of composites, both covalent and noncovalent functionalization of CNTs (Section 2.2.4) has been studied and reported. For example, Xie et al.²¹³ functionalized SWNTs by covalent grafting with high content of polymer chains and found that incorporation of 0.06 wt% of these SWNTs into PS matrix led to ~ 80% increases in both tensile modulus and strength. Yan et al.¹⁹⁰ recently grafted aldehyde structures to SWNTs to improve nanotube dispersion in phenolic resin. The incorporation of 1 wt% of these aldehyde-grafted SWNTs resulted in 31% and 68% increases in Young’s modulus and tensile strength of the resultant composites compared to neat phenolic resin. Okamoto et al.¹⁴⁵ reported that polybenzimidazole (PBI) can

individually disperse SWNTs through noncovalent π - π interaction with SWNT sidewall, and the resulting SWNT/PBI composite films with 0.06 wt% of SWNTs showed ca. 50% increases in tensile modulus and strength. Kim et al.²⁸ reported that MWNT/poly(styrene-*co*-acrylonitrile) (SAN) composites prepared using polythiophene-*graft*-poly(methyl methacrylate) (P3HT-*g*-PMMA) as a compatibilizer showed dramatically enhanced mechanical properties. Only 0.05 wt% of P3HT-*g*-PMMA functionalized SWNTs increased both tensile modulus and strength by more than 200%, as compared to neat SAN.

2.3.2.4 Effect of CNT alignment

The effect of CNT alignment on the mechanical properties of composites has been evaluated by theoretical studies. Using an extension of Cox's original model,²¹⁴ Krenchel showed that the strength and modulus of composites reinforced with rodlike fillers increase linearly with filler orientation efficiency factor, η_0 .²¹⁵ Experimental results have also shown that higher mechanical properties can be achieved for composites with aligned CNTs as compared to those with randomly oriented CNTs.²¹⁶ Thorstenson and his coworkers²¹⁷ showed that the improvement in elastic modulus of MWNT(5 wt%)/PS composite with aligned MWNTs (10% increase over neat PS) is about five times higher than that with randomly oriented MWNTs (49% increase over neat PS). Very recently, Blighe and Coleman et al.²¹⁸ quantitatively studied the influence of nanotube alignment on the mechanical performance of coagulation-spun SWNT/PVA composite fibers. The tensile modulus and strength per unit volume fraction (dY/dV_f and $d\sigma_B/dV_f$) of their as-spun fibers were 254 GPa and 2.8 GPa, respectively. By drawing fibers to a draw ratio of $\sim$

60%, the dY/dV_f and $d\sigma_B/dV_f$ increased to 600 GPa and 7 GPa, respectively, indicating significant effect of nanotube alignment on composite stiffness and strength.

Several strategies have been applied to achieve nanotube alignment in CNT/polymer nanocomposites, including mechanical stretching,²¹⁹ fiber spinning,^{6,111,220} and application of strong magnetic²²¹ and electric²²² fields. Fiber spinning methods, such as melt spinning,^{111,165} electrospinning,^{220,223} and reactive spinning,^{6,26} offer a high degree of alignment and are effective at improving the mechanical properties of resultant composite fibers or membranes. McIntosh et al.¹⁶⁵ reported improved mechanical properties of fluorinated SWNTs reinforced polypropylene composite fibers produced with a single-screw extruder; their fibers showed 151% and 111% increases in tensile strength and tensile modulus, respectively. Sen et al.²²³ reported 250% and 104% increases in tensile modulus and strength for ester functionalized SWNT/polyurethane membrane produced via electrospinning. Che et al.⁶ developed a reactive spinning technique to align SWNTs in CE composite fibers, and achieved increases of 85% and 140% in tensile strength and elongation at break, respectively.

2.3.3 Electrical properties of CNT/polymer composites

CNTs, which can be seen as one-dimensional conductors,²²⁴ have been demonstrated to be effective fillers for fabrication of electrically conductive polymer composites.^{24,225-226} These conductive composites are being explored for many applications, such as electrical dissipation, transparent conductive coating and electromagnetic interference (EMI) shielding. Due to their intrinsic

exceptional electrical conductivity (σ) and high aspect ratio, a very low content of CNTs (0.5 wt% or less) is able to enhance the electrical conductivity of the composites by several orders of magnitude.^{168,227-228} In these low nanotube content composites, other properties of the polymer matrix such as mechanical properties, transparency, easy processability, etc., are well preserved. For example, Sandler et al.²²⁸ fabricated epoxy composites based on aligned CVD-grown MWNTs and found that a nanotube loading of 0.005 wt% was enough to enhance electrical conductivity from $10^{-9} \text{ S cm}^{-1}$ for neat epoxy to about $10^{-3} \text{ S cm}^{-1}$ for CNT composites, which is sufficient for anti-static applications. Jiang et al.¹⁶⁸ fabricated MWNT/polyimide composites by in-situ polymerization which showed electrical conductivity of $10^{-4} \text{ S cm}^{-1}$ at nanotube loading of about 0.25 vol%, corresponding to increase of 11 orders of magnitude as compared to neat matrix, while mechanical properties of these composites were well maintained. Very high electrical conductivities ($> 10 \text{ S cm}^{-1}$) in composites have also been achieved by using high content of CNTs, high quality CNTs and/or special processing techniques.^{83,136,229-230} Munoz et al.¹³⁶ used a coagulation spinning technique to fabricate SWNT/polyethyleneimine composite fibers with nanotube loading of about 75 wt%, which showed electrical conductivity in the order of 100 S cm^{-1} . Kim et al.²³⁰ reported electrical conductivity of about 400 S cm^{-1} for their composites with 35 wt% of CNTs, fabricated by modifying nanotube junctions using poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in emulsion.

The percolation theory is often applied to describe the transition from insulator to conductor in composites containing conductive fillers. As shown in Figure 2.13, at very low filler content levels, fillers disperse individually or as

small clusters, so the electrical conductivity of the composite is very close to the values for neat matrix. When the filler content increases to the percolation threshold, a continuous conductive network or path is formed throughout the matrix, leading to sharp increase of the electrical conductivity by several orders of magnitude. As the nanotube content further increases, the composite electrical conductivity levels off at a certain value, due to the formation of multiple electron paths. The composite conductivity follows the following power law,²³¹

$$\sigma \propto (v - v_c)^t, \quad \text{for } v > v_c$$

where σ is the electrical conductivity of composite, v is filler volume fraction, v_c is the percolation threshold, and t is the conductivity exponent. The experimental percolation threshold of typical nanotube/polymer composites is in the range of 0.002–5 wt%,^{92,232} which is lower than the values (10–50 wt%)²³³⁻²³⁵ for the composites reinforced with conventional fillers (e.g., carbon black and carbon fibers). The wide variation in percolation threshold of nanotube filled composites stems from the differences in the nanotube aspect ratio,^{227,236} nanotube dispersion in matrix²³⁷⁻²³⁸ and nanotube alignment.²³⁹⁻²⁴⁰ It has been concluded that the percolation threshold decreases with higher nanotube aspect ratio, better nanotube dispersion and lower degree of nanotube alignment.^{15,232}

Figure 2.13 Electrical conductivity of CNT/polymer composites as a function of nanotube content and a schematic of percolating network.

Many studies^{29,146,169,241} have reported that functionalization of CNTs, including covalent^{169,241} and noncovalent^{29,146} approaches, can increase the composite electrical conductivity and decrease the percolation threshold. This is because proper functionalization improves nanotube dispersion in matrix, which leads to higher aspect ratio than nanotube aggregates and facilitates the formation of conductive pathway in composites. It has been known that covalent functionalization, especially acid treatment, can disrupt the intrinsic π -system of nanotube walls and cut nanotubes into small pieces,²⁴²⁻²⁴³ both of which are detrimental to the composites electrical conductivity. On the noncovalent functionalization, which results in little disruption to nanotube structure and length, appears to be a favorable method for fabrication of composites with low percolation threshold and high electrical conductivity. Zou et al.¹⁴⁶ reported that the percolation threshold of SWNT/PS composites, which were prepared by solution casting from a mixture of PS and P3HT-*b*-PS dispersed SWNTs, was as low as 0.03 wt%. Very recently, Kim et al.¹⁸⁹ synthesized a naphthalene-containing polymer and used it as a noncovalent

dispersant of MWNTs for reinforcement of Nylon 66 composite. The incorporation of 1 wt% of functionalized MWNTs increased the electrical conductivity of the composites by 11 orders from 10^{-15} S cm⁻¹ for neat nylon66 to 10^{-4} S cm⁻¹.

Chapter 3 Experimental Details

To avoid repeating same experimental details, the common information of CNTs, chemicals, dispersants and characterization techniques involved in this thesis are listed in this Chapter. All other relevant experimental details for each study are shown in Chapter 4-7.

3.1 Materials

SWNTs

CVD-grown SWNTs were purchased from Chengdu Research Institute of Organic Chemistry (China); they have diameters of 1–2 nm, lengths of 5–30 μm and purity of ~90%. They were purified by thermal oxidation in air at 350 $^{\circ}\text{C}$ for 2 h in a horizontal tube furnace followed by acid treatment via refluxing in 6 M HCl solution for 12 h.

MWNTs

CVD-grown MWNTs with a diameter of 10–15 nm and a length of 10–20 μm were supplied by Iljin Nano Tech, Korea. They were purified by thermal oxidation at 350 $^{\circ}\text{C}$ in a horizontal tube furnace for 2 h in air followed by refluxing in 6 M HCl solution overnight.

Matrix resin

Bisphenol A cyanate ester resin (CE, Figure 3.1a) was purchased from Shanghai Huifeng Technical & Business Co., Ltd. (Shanghai, China) with the tradename HF-1. Diglycidyl ether bisphenol A epoxy resin (EP, Figure 3.1b), was purchased from Wuxi Resin Factory (China) with the tradename E20.

Other chemicals

3, 3'-Dihydroxy-4, 4'-diaminobiphenyl (HAB, 97%) was purchased from Tokyo Chemical Industry and purified by recrystallization from *N*, *N*'-dimethylformamide (DMF)/ethanol mixture. α -glycidyl terminated bisphenol A acrylate (GBA, Figure 3.1c) with a molecular weight of 450 was supplied as Ebecryl[®] 3605 from UCB chemicals (Malaysia). It was freeze-dried at $-55\text{ }^{\circ}\text{C}$ for 2 days to remove water before use. Glycidyl 4-nonylphenyl ether (GNE, technical grade, Figure 3.1d), 4, 4'-oxydipthalic anhydride (ODPA, 97%), 4-(dimethylamino) pyridine (DMAP, 99%), butylated hydroxytoluene (BHT, 99%), 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA), polyvinylpyrrolidone (PVP, $\bar{M}_w = 29\ 000$), 3-chloroperoxybenzoic acid (*m*-CPBA, 77% max), sodium hydrogen carbonate (NaHCO_3 , 99.5%), dichloromethane (CH_2Cl_2), *N*, *N*'-dimethylacetamide (DMAc), xylene, dimethyl sulfoxide (DMSO), *N*, *N*'-dimethylformamide (DMF), methanol, tetrahydrofuran (THF), deuterated dimethylsulfoxide ($\text{DMSO-}d_6$), potassium bromide (KBr) and lithium bromide (LiBr) were obtained from Sigma-Aldrich. BPDA and ODPA were purified by sublimation under reduced pressure. DMAc and DMSO were distilled over calcium hydride and xylene over sodium wire before use. All other chemicals were used as received.

Figure 3.1 Chemical structures of (a) bisphenol A cyanate ester (CE), (b) diglycidyl ether bisphenol A epoxy (EP), (c) α -glycidyl terminated bisphenol A acrylate (GBA), and (d) glycidyl 4-nonylphenyl ether (GNE).

3.2 Synthesis of polyimide dispersants

Polyimide backbone (PI)

The reaction for synthesis of PI is shown in Step 1–2 in Figure 3.2. In a typical experiment, HAB (1.080 g, 5.00 mmol) was dissolved in 40 mL freshly distilled DMAc in a round-bottom flask under argon protection. After the solution was cooled at 0 °C for 15 min, ODPA (1.550 g, 5.00 mmol) was added under vigorous stirring. The mixture was then mechanically stirred at room temperature for 24 h under argon atmosphere to form poly(amic acid) (PAA) solution. Then xylene (40 mL) was added to this solution and stirred at 160 °C for 3 h to eliminate the water formed in the imidization reaction. After cooling down, the mixture was added dropwise into a large excess of methanol to precipitate the PI. The precipitate was filtered and repeatedly washed with methanol and then with THF. The resultant polymer was dried at 80 °C for 24 h in a vacuum oven. The yield was 2.040 g (83% yield). The weight-average molecular weight ($\bar{M}_w$) and the polydispersity index (PDI) of PI were measured

by gel permeation chromatography (GPC) to be 2.7×10^4 g/mol and 1.38, respectively.

Polyimide-graft-bisphenol A diglyceryl acrylate (PI-BDA), polyimide-graft-glyceryl 4-nonylphenyl ether (PI-GNE), and hydroxyl polyimide-graft-bisphenol A diglyceryl acrylate (PI_{OH}-BDA) Dispersants

The reaction for synthesis of PI-BDA is shown in Step 3 in Figure 3.2. DMAP was added as the catalyst²⁴⁴ and BHT was added to prevent homopolymerization of acrylate double bond on the BDA side chain.²⁴⁵ The yield of side chain grafting was designed to be 100%. Typically, PI (0.588 g, 1.20 mmol of repeat unit) was dissolved in 40 mL of dry DMSO at 60 °C in a round-bottom flask with a water condenser under argon atmosphere. After dissolution of DMAP (0.293 g, 2.40 mmol), a solution of GBA (1.188 g, 2.64 mmol) together with BHT (0.018 g, 0.08 mmol) in 20 mL of dry DMSO was added, and the resulting mixture was stirred at 100 °C for 48 h. After removal of ~10 mL of DMSO with a rotary evaporator, the resulting solution was added dropwise into a large quantity of methanol (500 mL) to obtain the brown PI-BDA. The polymer was further purified by washing successively with 0.2 M HCl solution, 5 wt% NaHCO₃ solution and DI water. The polymer was dried under vacuum at 30 °C for 48 h. The yield was 0.850 g (51% yield). PI-BDA had a $\bar{M}_w$ of 3.9×10^4 g/mol with a PDI of 1.35, measured by GPC.

PI-GNE was synthesized following the same procedure for preparation of PI-BDA, but using GNE (0.730 g, 2.64 mmol) instead of GBA (1.188 g, 2.64 mmol) and BHT (0.018 g, 0.08 mmol). The yield of side chain grafting was also designed to be 100%. The yield of PI-GNE was 0.778 g (62% yield). The

$\bar{M}_w$ and PDI of the PI-GNE were determined by GPC to be 5.5×10^4 g/mol and 1.35, respectively.

PI_{OH}-BDA was also synthesized by the same method for preparation of PI-BDA, but using half the amount of GBA, i.e. 0.594 g (corresponding to 1.32 mmol) GBA was added, to achieve a side-chain grafting yield of 50%. The yield of PI_{OH}-BDA was 0.654 g (58% yield). The $\bar{M}_w$ determined by GPC was 6.3×10^4 g/mol with a PDI of 1.73. It should be noted that the $\bar{M}_w$ of PI_{OH}-BDA is even higher than that of PI-BDA. This contradiction can be attributed to the inaccuracy of GPC measurement of rigid grafted polymers (in this case PI-BDA and PI_{OH}-BDA) using soft and linear polystyrenes as standards.

Figure 3.2 Synthesis of PI, PI-BDA, PI-GNE and PI_{OH}-BDA.

Poly(amic acid) (PAA) dispersant

The reaction scheme of the synthesis of PAA is shown in Figure 3.3. Typically, a solution of HAB (2.16 g, 10 mmol) in freshly distilled DMAc (51 mL) was added into a 100 mL three-necked flask under flowing argon. After the HAB was completely dissolved, BPDA (2.94 g, 10 mmol) was added at 0

0 °C and the mixture was mechanically stirred at room temperature for 24 h. The resulting viscous poly(amic acid) (PAA) solution was kept in a freezer until use. The molecular weight of PAA was determined by GPC to be 10^5 g/mol with a PDI of 1.96.

Figure 3.3 Synthesis of PAA.

3.3 Characterization techniques

Proton nuclear magnetic resonance ($^1\text{H-NMR}$)

$^1\text{H-NMR}$ analysis was performed to confirm the chemical structures of the dispersants, and also to study the reaction between PI-BDA and CE. $^1\text{H-NMR}$ spectra were recorded on a Bruker (300 MHz) NMR instrument using deuterated dimethylsulfoxide ($d_6\text{-DMSO}$) as solvent.

Fourier transform infrared (FT-IR)

FT-IR spectra were obtained on a Nicolet 5700 FT-IR instrument equipped with attenuated reflectance (ATR) accessory. All measurements were taken over the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , averaged over 64 scans. Background subtraction was performed for each

sample analysis in order to eliminate the effects of IR-active atmospheric components such as CO₂ and H₂O. For powder samples (nanotubes, dispersants and nanotube/dispersant mixtures), the sample and KBr were grinded together in a mortar with pestle, and the mixture was loaded in a press cell and made into a KBr pellet using a manual hydraulic press (Specas Atlas series). For GNE (liquid) and composite fiber samples, the FT-IR spectra were obtained with ATR accessory.

Gel permeation chromatography (GPC)

GPC was used to measure the molecular weight and polydispersity index of polymeric dispersants. The measurements were carried out on a Shimadzu LC-20A Series GPC system equipped with a pump, BC-PL gel mixed columns (Agilent PLgel Mixed-C gel column with linear molecular weight operating range of 200–2×10⁶) and a refractive index detector (RID-10A). DMF with 0.02 M LiBr was used as the eluting solvent working at a flow rate of 1 mL/min. The column temperature was 60 °C and the sample concentration was about 1 mg/mL. Polystyrene standards were used as the reference materials.

Thermogravimetric analysis (TGA)

TGA was employed to characterize the decomposition and thermal stability of composites and to measure the percentage of dispersant in nanotube/dispersant complex. The thermal experiment was performed on a Netzsch STA 409 PG/PC instrument under a nitrogen atmosphere, with a heating rate of 10 °C/min from 50–800 °C. The sample weight of each measurement was 5–10 mg.

Differential scanning calorimetry (DSC)

DSC characterization was performed on a Mettler Toledo DSC 822e instrument under N₂ at a heating/cooling rate of 20 °C/min from 50 to 230 °C. The T_g of composites was calculated from the midpoint of the change in slope of the second heating run.

Raman spectra

Raman spectra were obtained with a Renishaw Ramanscope with HeNe laser at an excitation wavelength of 633 nm. Samples of CNTs, CNT/dispersant mixtures, and composite fibers/films were measured on a glass slide using a 633nm laser focused to approximately 1 μm through a 50 x objective. Laser power density at the sample was maintained below 3 kW/cm² to avoid laser induced heating effects.

Ultraviolet-visible-near infrared (UV-vis-NIR)

UV-vis-NIR absorption spectra of pristine nanotubes and nanotube/dispersant dispersions were used to calculate the concentration of nanotubes based on Beer-Lambert law. The spectra were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer.

Optical microscope

The dispersion of nanotubes in CE-EP, CE and PI composites were evaluated by optical microscope. The characterization was carried out on an Olympus SZX12 microscope using transmission model. Composite fibers or films were observed directly without pre-treatment.

Atomic force microscope (AFM)

The dispersion of pristine and dispersant-functionalized CNTs in organic solvents was studied by AFM. The images were obtained from a MFP 3D

microscope in ac mode. Nanotube dispersions were deposited onto clean silicon wafers (treated by oxygen plasma at 100 W for 120 s) by spin coating. The single crystal plane of the silicon wafer is $\langle 1-0-0 \rangle$ and the thickness of oxide surface formed by thermal oxidation is 300 nm.

Transmission electron microscope (TEM)

TEM images of pristine and dispersant-functionalized CNTs were obtained from a JEOL 2100F high-resolution scanning electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by placing several drops of dilute nanotube dispersion on a carbon-coated copper grid (400 mesh) followed by solvent evaporation at room temperature.

Field-emission scanning electron microscope (FE-SEM)

FE-SEM images were obtained from a JEOL JSM-6700F microscope operating at 5 kV. Samples were coated with gold from a sputtering machine (JEOL JFC-1600 Auto Fine Coater, Japan) in order to suppress surface charging effects. To study the morphological features and size dispersion of nanotubes in composites, the cross-sections of composites sputtered with gold at 20 mA for 70 s were observed. To evaluate the alignment of nanotubes in composite fibers, the longitudinal surfaces of partially cured spun fibers were sputtered with gold at 20 mA for 70 s and observed. To observe the nanotube samples on the Al_2O_3 membrane, a sputtering condition of 20 mA for 30 s was applied.

Tensile properties

Young's modulus (E), tensile strength (σ), elongation at break (ϵ) and toughness (T) of composites were determined using an Instron Model 5543 mechanical tester at room temperature. The gauge length was 20 mm and the

crosshead speed was 2.54 mm/min. A 10 N load cell was used for fiber samples while a 100 N load cell was used for film samples. The fiber samples have lengths of 40 mm and their diameters were estimated by optical microscope. The film samples were cut into strips of 40 mm by 5 mm with varying thickness ($\sim 40\ \mu\text{m}$ for CE composites and $\sim 15\ \mu\text{m}$ for PI composites). A thick paper frame was used to mount the sample. Two ends of the sample were fixed to the end tabs of the frame by super glue, and two small pieces of paper made from the same material as the frame were placed on top of the end tabs to encapsulate the sample ends. At least 5 measurements were made for each sample and the results were averaged.

The strain was measured with a strain gauge and the tensile stress was obtained from Instron software (Blue Hill). Young's modulus was calculated from the slope of the stress-strain curve in the low strain linear region. The toughness, defined as the energy absorbed by the material prior to failure, is an important property for thermosetting polymers. In this thesis, the toughness of composite was measured as the area under the stress-strain curve (also known as the work of fracture).

Electrical conductivity

The electrical conductivity of polyimide composites was measured by a two-probe electrical resistance method using a Keithley 610C electrometer at room temperature. The film samples were cut into a rectangular shape with dimensions of $40\ \text{mm} \times 5\ \text{mm} \times 15\ \mu\text{m}$. To ensure good electrical contact between the electrodes and the sample, both ends of measured samples were painted with silver paste to achieve a contact area of $5\ \text{mm} \times 5\ \text{mm}$. Five tests were made for each sample, and the average value was reported.

The volume resistance was measured from Keithley electrometer, and the electrical conductivity can be calculated through the equation given below:

$$\sigma = \frac{L}{R \times A}$$

where σ is the bulk electrical conductivity, R is the electrical resistance, A is the cross-section area of the specimen, and L is the distance between the two electrodes.

Chapter 4 Synthesis of Polyimide-*graft*-Bisphenol A Diglyceryl Acrylate as a Noncovalent Dispersant of SWNTs for Reinforcement of Cyanate Ester/Epoxy Composite

4.1 Introduction

Dispersion of SWNTs into individual or small bundles of nanotubes and strong nanotube/matrix interfacial strength remain challenges in exploiting the excellent mechanical properties of SWNTs in polymer composites. Noncovalent functionalization of SWNTs using surfactants or polymers has been shown to be an attractive option for compatibilization of nanotubes with matrix as it effectively disperses nanotubes without compromising the nanotube graphene structure.^{30,146,246} Conjugated and aromatic condensation polymers, such as poly(phenylene ethynylenes),²⁷ polythiophene,^{28,247} polybenzimidazole¹⁴⁵ and polyimide,^{119,248} which interact with CNTs via strong π - π interaction, have been used to disperse CNTs and reinforce polymers in previous studies. The π - π interaction has been suggested to be the strongest non-covalent interaction by a recent theoretical modeling study.³² However, these studies mainly focus on thermoplastic matrices and only a few studies using noncovalently functionalized CNTs to reinforce thermosets have been reported.²⁴⁹

So far, in most of the CNT-reinforced thermosetting composite studies, the nanotubes were covalently functionalized, and the properties of resultant

composites have generally been modest.^{20,26,170,250} For example, Zhu et al.²⁰ reported 30% and 14% increases in tensile modulus (from 2.03 to 2.63 GPa) and strength (from 83.2 to 95.0 MPa), respectively, for epoxy composites reinforced with 1 wt% of fluorinated SWNTs which can react with the hardener of epoxy. Recently, our group reported 39% and 18% increases in tensile strength and modulus, respectively, for epoxy composites reinforced with 0.5 wt% of dendrimer-modified SWNTs.²⁶

As discussed in Section 2.3.2.4, alignment of CNTs in the polymer matrix is another requirement to achieve high reinforcement.^{165,221,223} Fiber spinning has been proven to be a facile and effective method to achieve a high degree of nanotube alignment.^{111,220} Recently, our group has developed a reactive spinning technique to fabricate thermosetting composite fibers reinforced with aligned SWNTs.^{6,26} The nanotubes used in our previous two studies were covalently functionalized via grafting of organic molecules.

Cyanate ester (CE) resins are high-performance structural thermosets but are very brittle. Copolymerizing CE with other thermosetting resins such as epoxy has been proven to be effective in toughening CE with enhanced processability and at low cost.²⁵¹ This thermostable, processable and relatively tough cyanate ester/epoxy blend is a favorable matrix widely used in electronic and aerospace applications.

This chapter reports the design and synthesis of a reactive non-covalent polymeric dispersant for SWNTs: polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA). The polyimide backbone can strongly interact with nanotubes via non-covalent interaction, while the side chain facilitates dispersion and the hydroxyl group on the graft enables reaction with the matrix.

The high efficacy of PI-BDA at dispersing SWNTs in DMF was assessed with TEM and UV–vis–NIR absorption spectra. PI-BDA was used to disperse SWNTs in a thermosetting resin blend of cyanate ester and epoxy (CE-EP) (70/30, w/w). Two series of SWNT composite fibers, one with PI-BDA dispersed-SWNTs and one without, with a nanotube content ranging from 0 to 1.5 wt% were fabricated by reactive spinning to achieve nanotube alignment. For convenience, SWNT/Resin and SWNT/PI-BDA/Resin composites are hereafter denoted as SWNTs/R and SWNTs/PI-BDA/R, respectively. The nanotube dispersion, alignment and nanotube/matrix interaction were examined by FE-SEM, Raman spectra, FT-IR and ¹H-NMR. The tensile and thermal properties of the cured composites with various contents of SWNTs were measured.

4.2 Experimental section

Materials

SWNTs were used as fillers. CE blended with 30 wt% of epoxy which was prepared by mixing them at 90 °C for 0.5 h was used as matrix. Other chemicals were obtained from Sigma-Aldrich. The details of these materials are described in Section 3.1. PI-BDA was synthesized and used as a dispersant for SWNTs. The synthetic route is described in Section 3.2.

Preparation of SWNT dispersions

To prepare SWNT/PI-BDA dispersion, 10 mg purified SWNTs and 10 mg PI-BDA were first added into 10 mL DMF. Then the mixture was sonicated with a tip sonicator for 10 min followed by further sonication in a sonicator bath for 30 min. The resulting stable and homogeneous solution has a SWNT

concentration of 1 mg/mL. Pristine SWNT suspension in DMF was prepared by same procedure without the addition of PI-BDA. For Raman characterization, the SWNT/PI-BDA solution was filtered and washed thoroughly with DMF to remove any free surfactant, and the resultant powder was dried. For visual observation, pristine SWNTs and SWNT/PI-BDA solutions with nanotube concentrations of 0.02 and 1 mg/mL were left standing for different times (immediately, 7 days and 6 months) and the homogeneity was evaluated by eye for rough analysis.

Fabrication of composite fibers

Figure 4.1 shows a schematic of the processing route used for fabrication of the SWNT-reinforced CE-EP composite fibers. SWNT/PI-BDA solution (1 mg SWNTs/mL) was first prepared via the method described above. CE-EP matrix was prepared by mixing CE (70 wt%) and EP (30 wt%) at 110 °C for 30 min (polymerization may occur during this process). 2 g CE-EP matrix was added to measured quantities of SWNT/PI-BDA dispersion to produce solutions of SWNTs/PI-BDA/R with different SWNT loadings. After sonication in a sonicator bath for 10 min, the solution was cast onto glass substrates, which were placed on a hotplate at about 50 °C for 1 h, to slowly remove most of the dimethylformamide (DMF). The glass substrates were then transferred to a vacuum oven and dried under vacuum at 90 °C for 1 h and 100 °C for 2 h. Subsequently, the blend was collected from the glass substrates and the bubbles were removed by heating the blend under vacuum. After pre-polymerization at 110 °C for about 30 min to achieve a suitable viscosity for fiber spinning, which was experimentally found to be 50–80 Pa·s, SWNT/PI-

BDA/R composite fibers were fabricated using a custom-made reactive spinning device.^{6,26} After spinning, the fibers were pre-cured for 6 h under a UV lamp (intensity of 30 mW/cm², with on/off cycle of 15 min/15 min) which was filtered with a dish of water, and then further thermal cured at 100 °C/1d under vacuum followed by 120 °C/2 h, 150 °C/2 h, 180 °C/2 h and post-curing of 200 °C/4 h at atmospheric pressure. Neat CE-EP fibers and pristine SWNTs-reinforced fibers (SWNTs/R) were also prepared by same method.

Figure 4.1 Processing route used to fabricate composite fibers.

Verifying the reaction between PI-BDA and CE

To verify, with FT-IR, the addition reaction between –OH on PI-BDA with the CE, the PI-BDA/CE blend (30/70, w/w) was first dissolved in DMF, then several drops were cast onto a blank potassium bromide (KBr) pellet. The

DMF was removed by heating at 80 °C for 2 h under vacuum. Then the sample was characterized by FT-IR before and after heating at 120 °C for 1 h. To verify the reaction using $^1\text{H-NMR}$, PI-BDA/CE blend (30/70, w/w) was dissolved in d_6 -DMSO, and $^1\text{H-NMR}$ spectra of the sample were collected before and after heating at 120 °C for 1 h.

Characterization of PI-BDA, nanotubes and composites

$^1\text{H-NMR}$, FT-IR, GPC, TGA, DSC, Raman, UV-vis-NIR, optical microscopy, TEM, FE-SEM, tensile testing were used to characterize polymers, SWNT and composite samples, as described in Section 3.3.

4.3 Results and discussion

4.3.1 Synthesis and characterization of PI and PI-BDA

The successful synthesis of PI and PI-BDA was confirmed by $^1\text{H-NMR}$ spectroscopy. The complete assignment of the proton signals is shown in Figure 4.2. In the spectrum of PI (Figure 4.2A), characteristic peaks of the phenolic OH and aromatic protons are shown at $\delta=10.1$ (a) and 7.1–8.2 (b–g) ppm, respectively. In the spectrum of PI-BDA (Figure 4.2B), the phenolic OH signals completely disappeared while the aromatic protons of the PI backbone appeared at $\delta=7.0$ –8.2 ppm (b–g). New peaks at $\delta=6.7$ ppm (k) and $\delta=7.0$ ppm (l) are attributed to the aromatic protons of the grafted BDA side chain. The peaks at $\delta=5.8$ (s, CH_2), 6.1 (q, CH), 6.2 ppm (r, CH_2) are attributed to the $-\text{OCOCH}=\text{CH}_2$ terminal group. The peak at $\delta=1.5$ ppm (m) is attributed to $-\text{CH}_3$ groups, while the peaks at $\delta=3.0$ –4.5 ppm are assigned to the aliphatic protons of $-\text{OCH}$ (i and o) and $-\text{OCH}_2$ (h, j, n and p) in BDA side chain. The complete disappearance of the peak at $\delta=10.1$ ppm (a) and the appearance of

new resonance peaks (h–s) confirm that BDA is 100% grafted on every pendant –OH of PI-BDA.

Figure 4.2 ^1H -NMR spectra of (A) PI and (B) PI-BDA.

4.3.2 Solubility of PI-BDA functionalized SWNTs in DMF

The dispersion stability of SWNT solutions prepared in DMF with and without PI-BDA was evaluated by visual observation at different standing times after sonication (Figure 4.3). Immediately after sonication, high SWNT concentration solutions (1 mg/mL) of both pristine SWNTs and SWNTs/PI-BDA are black (Figure 4.3A vials a and c), and I cannot tell whether there are

nanotube aggregates in these solutions due to the darkness. After dilution to 0.02 mg/mL, suspended nanotube aggregates can be clearly seen in pristine SWNT solution (Figure 4.3A, vial b), whereas the diluted SWNT/PI-BDA solution appears free from SWNT aggregates (Figure 4.3A, vial d). After 7 days pristine SWNTs completely settled the bottom of the vials (Figure 4.3B, vials a and b). The SWNT/PI-BDA solutions were very stable and did not sediment after 7 days (Figure 4.3B, vials c and d), or even after six months of standing at room temperature (photos are same as Figure 4.3B, vials c and d). These phenomena indicate that PI-BDA significantly improves the solubility and long-term stability of SWNTs in DMF.

Figure 4.3 Visual observation of (a and b) pristine SWNT and (c and d) SWNTs/PI-BDA in DMF at different standing times after sonication: (A) immediately; (B) 7 days. The SWNT concentration of a and c is 1 mg/mL and of b and d is 0.02 mg/mL.

The dispersion of pristine SWNTs and PI-BDA functionalized SWNTs in DMF was also examined by TEM (Figure 4.4). As shown in Figures 4.4A1 and A2, pristine SWNTs are highly entangled with each other and the bundle size (about 30 nm or larger) is not uniform. Figure 4.4A3 reveals that the SWNT surface is very clean. After functionalization with PI-BDA, the bundle size becomes much smaller (Figure 4.4B1), and most of the SWNTs appear to be dispersed as individual tubes or very small bundles (Figure 4.4B2). A higher resolution TEM image (Figure 4.4B3) reveals clearly that the SWNTs are covered with a layer of coating with non-uniform thickness, which is believed to be PI-BDA wrapped around the SWNT surface. A lower magnification TEM image (Figure 4.5) shows that the SWNT length (at least 1–2 μm) is not significantly reduced after noncovalent functionalization with PI-BDA, which is different from the observation of chopped CNTs (length usually less than 1 μm) after covalent modification.^{242,252} I postulate that the high efficiency of PI-BDA at dispersing SWNTs is attributed to its comb-like structure, where the PI backbone has strong π – π interaction with SWNTs wall and the BDA graft located at the out surface of SWNTs imparts strong repulsive forces to SWNTs via steric hindrance.

Figure 4.4 TEM images of (A1–A3) pristine SWNTs and (B1–B3) PI-BDA functionalized SWNTs.

Figure 4.5 Low magnification TEM image of PI-BDA functionalized SWNTs showing no significant reduction in nanotube length. The scale bar is 500 nm.

The efficacy of PI-BDA at dispersing SWNTs was quantitatively evaluated through UV–vis spectroscopy and evaluated using Beer-Lambert law

($A = \epsilon lc$), where A is the absorbance at a particular wavelength (here I chose 500 nm), ϵ is the extinction coefficient, l is the path length (1 cm for our cell), and c is the concentration. To determine the extinction coefficient (ϵ), the absorbance of very dilute SWNT/PI-BDA (mass ratio 1:1) solution at different concentrations was measured. Figure 4.6A shows a representative curve and the absorbance at 500 nm plotted against SWNT concentrations (inset in Figure 4.6A). The linear-least-squares fit to the data gave a slope of 37.60, which was used to calculate the extinction coefficient (i.e. $\epsilon = 37.60 \text{ mL mg}^{-1} \text{ cm}^{-1}$) for determination of SWNT concentration. Figure 4.6B shows the extracted SWNT concentrations of SWNT/PI-BDA dispersions prepared using different PI-BDA to SWNT mass ratio from 0.125:1 to 2:1 in different conditions: 1) immediately after sonication; 2) fresh solutions after standing for 3 days and 3) fresh solutions after centrifugation at 6000 rpm for 1 h. Immediately after sonication, all the dispersions have suspended SWNT concentrations of about 0.02 mg/mL for ease of comparison amongst various PI-BDA to SWNT ratios. After standing for 3 days or centrifugation at 6000 rpm for 1 h, there is a clear dependence of the PI-BDA to SWNTs mass ratio on the amount of dispersed SWNTs. The SWNT concentration increases first but levels off when the PI-BDA to SWNTs mass ratio reaches 1:1, suggesting that the 1:1 ratio is the optimal mass ratio for preparing SWNT/PI-BDA dispersion. The SWNT concentration of SWNT/PI-BDA (mass ratio 1:1) after centrifugation is about 0.0158 mg/mL, which is higher than that of polyvinylpyrrolidone (PVP, $\bar{M}_w = 29,000$, Sigma-Aldrich) dispersed SWNTs prepared by the same method (0.0105 mg/mL), indicating higher efficacy of PI-BDA at dispersing SWNTs than the commercial dispersant PVP.²⁵³

Figure 4.6 A) Absorption spectrum of SWNTs/PI-BDA (mass ratio 1:1) at a concentration of 0.0125 mg/mL in DMF. Inset shows absorbance at 500 nm of the SWNTs/PI-BDA (1:1) in DMF at different concentrations. The straight line is a linear-least-squares fit to the data. B) SWNT concentrations of solutions prepared using different PI-BDA to SWNT mass ratio in different conditions: immediately after sonication; after standing for 3 days and after centrifugation at 6000 rpm for 1 h.

4.3.3 Spinning of SWNT/PI-BDA/R composite fibers

Figure 4.7A and B show the spinning apparatus and a schematic of the custom-made spinning machine, respectively. To find out the optimal pre-polymerization condition, SWNT/PI-BDA/R blend after debubbling was filled into a syringe and heated at 110 °C (controlled by a heating tape, see Figure 4.7 A and B). The blends with different heating times were pulled out from the syringe with tweezers to see whether continuous fibers can be formed. Initially, fibers were not achievable due to low viscosity. After about 30 min, continuous fiber could be pulled out from the syringe, and the viscosity was measured to be in the range of 50-80 Pa·S. After about 45 min, the fibers tended to break due to a sharp increase in the viscosity. As a result, heating at 110 °C for 30 min was considered to be the optimal pre-polymerization condition.

To spin the fibers, pre-polymerized resin was filled into the syringe which was wrapped with a heating tape to control the temperature to be 110 °C. Fibers were extruded from the spinneret by syringe pump, cooled in air and collected on a rotating Teflon drum that is located about 20 cm from the syringe. The enjection rate was about 80 mL/h during the spinning process. Figure 4.7C shows some continuous spun fibers collected on the tension/take-up drum. Using pure CE as the matrix, our initial experiments showed that it was difficult to spin SWNT/CE fibers, which may be due to low molecular weight of the bisphenol A type CE ($\bar{M}_w = 278$). Using a blend of CE and epoxy (70/30, w/w) instead, SWNTs reinforced CE-EP composite fibers were successfully spun relatively easily.

Figure 4.7 A) Custom-made reactive spinning apparatus. B) Schematic of reactive spinning process. C) A spool of SWNT(1 wt%)/PI-BDA/R fiber collected on a takeup drum.

After spinning, the spun CE-EP fibers were subjected to further curing to complete the crosslinking (Step 6, Figure 4.1). Ultraviolet (UV) light was adopted to pre-cure the spun composite fibers (Step 6a, Figure 4.1) before the actual thermal curing (Step 6b, Figure 4.1). As shown in Figure 4.8A, spun fibers without UV pre-curing tended to fuse with each other at contact points at 100 °C (the thermal cure temperature, Step 6b, Figure 4.1) and their cross-sectional shape became elliptical. This resulted in fused non-usable fibers and loss of SWNT alignment within the fibers. With UV pre-curing for 6 h instead, the fibers did not fuse and retained their round shapes at 100 °C (Figure 4.8B) and after post-curing (Figure 4.8C).

Figure 4.8 Optical micrographs of SWNT (0.5 wt%) /PI-BDA/R fibers heated at 100 °C for 10 min: (A) before and (B) after UV pre-curing; and (C) after post-curing.

FT-IR was used to probe the chemical reactions during UV pre-curing. Figure 4.9 (b–d) shows FT-IR spectra of SWNT(1 wt%)/PI-BDA/R spun fiber before UV pre-curing, after UV pre-curing, and after post-curing. For comparison, the spectrum of neat CE-EP mixture without curing (a) is also presented. In the spectra of the composites before and after UV pre-curing (b and c), the intensity of --OCN at about 2235 and 2270 cm^{-1} is lower than in CE-EP resin (a) and two new bands appear, at 1364 and 1562 cm^{-1} , which are characteristic absorption bands of triazine rings.^{9,254} Compared to the spectrum

before UV pre-curing, the intensity ratio of -OCN (at 2235 and 2270 cm^{-1}) to the phenyl ring symmetric breathing vibration (at 1500 cm^{-1} , used as internal reference) after UV pre-curing is slightly decreased while the intensity ratio of absorptions due to triazine rings (at 1364 and 1562 cm^{-1}) to phenyl rings (at 1500 cm^{-1}) is slightly increased: $I_{2235\text{cm}^{-1}}/I_{1500\text{cm}^{-1}}$ changed from 0.108 to 0.080, $I_{2270\text{cm}^{-1}}/I_{1500\text{cm}^{-1}}$ changed from 0.109 to 0.090, $I_{1364\text{cm}^{-1}}/I_{1500\text{cm}^{-1}}$ from 0.680 to 0.741 and $I_{1562\text{cm}^{-1}}/I_{1500\text{cm}^{-1}}$ from 0.235 to 0.270. These indicate cyclotrimerization of cyanate ester during UV pre-curing (Figure 4.10A). No changes were observed in the epoxide band (at 916 cm^{-1}) for samples before and after UV pre-curing, suggesting no reaction between -OCN and epoxide groups during UV pre-curing. After thermal post curing, the bands of -OCN and epoxide groups completely disappeared, and two new peaks at 1693 and 1728 cm^{-1} appeared, which are attributed to isocyanurate and oxazolidinone structures resulting from the reaction between cyanate ester and epoxy (Figure 4.10B).²⁵⁴⁻²⁵⁵

Figure 4.9 FT-IR spectra of (a) neat CE-EP mixture before curing, and (b–d) SWNT(1 wt%)/PI-BDA/R spun fibers (b) before UV pre-curing, (c) after UV pre-curing, and (d) after post-curing.

Figure 4.10 (A) Schematic of cyclotrimerization of CE. (B) Schematic of possible reactions between CE and EP.

4.3.4 SWNT dispersion, alignment and interfacial adhesion in fibers

To compare the dispersion of pristine SWNTs and SWNTs/PI-BDA in composite fibers, uncured SWNT(1 wt%)/R and SWNT(1 wt%)/PI-BDA/R spun fibers were redispersed in DMF with only mild shaking followed by filtration through a $0.2 \mu\text{m}$ Al_2O_3 membrane and washing several times with large quantity of DMF to remove any free polymer. Figure 4.11 shows the FE-SEM images of these pristine SWNTs and SWNTs/PI-BDA. Pristine SWNTs form large aggregates (Figure 4.11A1) while PI-BDA functionalized SWNTs are homogeneously dispersed (Figure 4.11B1). Higher magnification images reveal that SWNTs in SWNTs/PI-BDA were debundled very well and the

nanotube bundle size (Figure 4.11B2) is much smaller than that of pristine SWNTs (Figure 4.11A2). These observations are consistent with the dispersion of pristine and PI-BDA functionalized SWNTs in the fully cured composites that will be discussed below.

Figure 4.11 FE-SEM images of SWNTs in uncured (A1 and A2) SWNT(1 wt%)/R and (B1 and B2) SWNT(1 wt%)/PI-BDA/R spun fibers after removal of free polymer on a 0.2 μm Al_2O_3 membrane.

Figure 4.12 shows optical micrographs of fully cured SWNT/R and SWNT/PI-BDA/R composite fibers with SWNT loading of 0.2 wt%. (Composites with higher SWNT loadings are opaque.) Many black spots with sizes up to 10 μm can be clearly seen in the SWNT (0.2 wt%)/R fiber (Figure 4.12A), indicating non-uniform dispersion of SWNTs. In contrast, SWNT (0.2 wt%)/PI-BDA/R shows homogeneous dispersion of SWNTs throughout the matrix, and no obvious aggregates were observed (Figure 4.12B).

Figure 4.12 Optical micrographs of (A) SWNT (0.2 wt%)/R and (B) SWNT (0.2 wt%)/PI-BDA/R composite fibers after post-curing.

To further evaluate the dispersion state of nanotubes in composites, cross-sections of SWNTs(1 wt%)/R and SWNTs(1 wt%)/PI-BDA/R after tensile testing were examined with FE-SEM (Figure 4.13). In SWNT(1 wt%)/R composite fibers, aggregates with sizes of about 1 μm can be clearly seen, indicating nonuniform dispersion (Figure 4.13A1, circled). Many SWNTs are pulled out, leaving holes on the surface (Figure 4.13A2 and A3, arrows), indicating weak interfacial adhesion between the SWNTs and the CE-EP. In contrast, PI-BDA functionalized SWNTs are homogeneously distributed in the CE-EP matrix without any large aggregates (Figure 4.13B1). Some nanotubes seem to have partially pulled out from the surface but the pull-out length of the SWNTs is significantly reduced (indicated by squares in Figure 4.13B2 and B3) compared with the nanotubes in SWNTs/R; other nanotubes are broken on the surface and the ends are tightly embedded in the matrix (indicated by circles in Figure 4.13B2 and B3). These FE-SEM images suggest that the nanotube/matrix interface between PI-BDA functionalized SWNTs and the CE-EP matrix is stronger than that in SWNT/R composites. The strong interfacial adhesion can be ascribed to two effects: i) strong π - π interaction

between nanotube and the backbone of PI-BDA and ii) the compatibility and covalent reaction between the BDA side chain and the matrix resin.

The nanotube alignment was confirmed by FE-SEM images of outer surfaces of composite fibers. In SWNT(1 wt%)/R fibers (Figure 4.13A4), it is difficult to observe nanotube alignment due to the aggregation of pristine SWNTs. In the case of SWNT(1 wt%)/PI-BDA/R fibers (Figure 4.13B4), more homogeneously distributed nanotubes are exposed and they are well aligned along the fiber axis. The reactive spinning process more effectively aligns the SWNTs along the fiber longitudinal direction with the PI-BDA dispersant.

Figure 4.13 FE-SEM images of (A1-A4) SWNT(1 wt%)/R and (B1-B4) SWNT(1 wt%)/PI-BDA/R composite fibers. Images A1-A3 and B1-B3 show cross-sectional fracture surfaces of cured fibers after tensile testing. Images A4 and B4 show the longitudinal surface of partially cured spun fibers. The arrows in image A4 and B4 indicate the fiber axis.

The π - π interaction between SWNTs and the backbone of PI-BDA was verified by Raman spectra. Figure 4.14A shows Raman spectra of pristine SWNTs, SWNTs/PI-BDA, SWNT(1 wt%)/R fiber and SWNT(1 wt%)/PI-BDA/R fiber. The peaks at around 1330 and 1590 cm^{-1} correspond to the disorder-induced mode (D-band) and the tangential mode (G-band), respectively. It is known that covalent functionalization can introduce defects into CNTs, leading to an increased intensity ratio of D-band to G-band (I_D/I_G).^{20,99} Unlike covalent functionalization, no significant increase in the I_D/I_G ratio was observed in SWNTs/PI-BDA (b) and SWNT(1 wt%)/PI-BDA/R (d), indicating that the nanotube graphene structure was well preserved after noncovalent functionalization with PI-BDA. Comparing the G-band of SWNTs/PI-BDA (b), SWNTs(1 wt%)/R (c) and SWNTs(1 wt%)/PI-BDA/R (d) to the pristine SWNTs sample (a), upshifts of about 5 cm^{-1} , 3 cm^{-1} and 7 cm^{-1} , respectively, were observed. The 3 cm^{-1} upshift in SWNTs(1 wt%)/R (c) compared to pristine SWNTs (a), and the 2 cm^{-1} higher upshift in SWNTs(1 wt%)/PI-BDA/R (d) compared to SWNTs/PI-BDA (b) can be attributed to the π -stacking of CE-EP resin molecules on the nanotubes.²⁵⁶ The 4–5 cm^{-1} Raman upshifts due to the PI-BDA (comparing d to c, and b to a) indicate that the electronic environment of the SWNT surface has changed after functionalization with PI-BDA, with or without CE-EP matrix. This is believed to be due to the strong π - π interaction between highly conjugated SWNT wall and PI-BDA backbone with high content of aromatic rings.^{28,146}

The BDA side chains also contribute to the good interfacial adhesion between SWNTs/PI-BDA and CE-EP matrix. The BDA side chain contains bisphenol A moieties like those in the cyanate ester and epoxy resins, which

increases the compatibility and miscibility between SWNTs/PI-BDA and CE-EP matrix. Moreover, the -OH groups on BDA side chains can react with -OCN groups of CE to form iminocarbonate (-OC(O-)=NH) bonds (Figure 4.15).^{36,43,257} The formation of iminocarbonate was confirmed with FT-IR and $^1\text{H-NMR}$.

To increase detectability of the reaction between PI-BDA and CE, a blend containing larger proportions of PI-BDA to CE (30/70, w/w) was heated and analyzed with FT-IR and $^1\text{H-NMR}$. Figure 4.14B shows the FT-IR spectra of (a) neat CE before curing, (b) PI-BDA, and PI-BDA/CE (30/70, w/w) (c) before and (d) after heating at 120 °C for 1 h. In spectrum 4.14B(c), the band at 1678 cm^{-1} , attributed to the formation of new -OC(O-)=NH bands,^{36,43} is present but small as the sample was heated to 80 °C (for DMF removal after casting). After further heating at 120 °C for 1 h (spectrum 4.14B(d)), the relative intensity of -OC(O-)=NH band (1678 cm^{-1}) increased, suggesting the reaction of more -OH groups with -OCN . The increased intensities of the bands at 1369 and 1567 cm^{-1} imply the formation of some triazine structures.⁹

The reaction between PI-BDA and CE was also confirmed by $^1\text{H-NMR}$ spectra. Figure 4.14C presents the $^1\text{H-NMR}$ spectra of PI-BDA/CE (30/70, mixture in d_6 -DMSO before and after heating at 120 °C for 1 h. After heating at 120 °C for 1 h (spectrum 4.14C(b)), the intensity of the peaks at around 9.2 ppm resulting from the NH protons of -OC(O-)=NH groups⁴³ significantly increased. Additional evidence of reaction is that the -CH_3 peaks (at δ around 1.6 ppm) and aromatic peaks (at δ = 6.7–7.2 ppm) of CE (overlapped with the peaks due to -CH_3 and aromatic protons in PI-BDA, respectively) split into two or more peaks, which can be attributed to unconsumed CE, and adducts

between PI-BDA and CE (or triazine oligomer) (Figure 4.15).⁴³ All these confirm that -OCN groups on CE matrix covalently react with -OH groups on PI-BDA dispersant to form -OC(O-)=NH bonds.

Figure 4.14 A) Raman spectra of (a) pristine SWNTs, (b) SWNTs/PI-BDA, (c) SWNT(1 wt%)/R composites, and (d) SWNT(1 wt%)/PI-BDA/R composites. B) FT-IR spectra of (a) neat CE before curing, (b) PI-BDA, (c and d) PI-BDA/CE (30/70, w/w) (c) before and (d) after heating at 120 °C for 1 h. C) ¹H-NMR spectra of PI-BDA/CE (30/70, w/w) in *d*₆-DMSO (a) before and (b) after heating 120 °C for 1 h.

Figure 4.15 Schematic of reactions between $-OH$ groups on PI-BDA and CE (or its oligomer).

4.3.5 Mechanical properties of SWNT/PI-BDA/R composites

The tensile properties for neat CE-EP, SWNT/R and SWNT/PI-BDA/R composites with different nanotube loadings are summarized in Table 4.1 and Figure 4.16. Representative tensile stress versus strain curves are shown in Figure 4.16A. Without adding PI-BDA dispersant, SWNTs/R composites show limited increases in tensile properties. The highest increase in tensile modulus (E) is 33% (from 2.61 ± 0.14 to 3.47 ± 0.18 GPa) at SWNT loading of 1 wt%, and the highest increase in tensile strength (σ) is 28% (from 83.7 ± 3.3 to 107.0 ± 11.0 MPa) at SWNT loading of 0.5 wt%. Further increase in SWNT content impairs tensile properties. The elongation at break (ϵ) decreases continuously from 5.0 ± 0.4 to 2.5 ± 0.4 % as the nanotube loading increases to 1.5 wt%, while the toughness (T) calculated from the stress-strain curve has no significant improvement. With SWNTs dispersed by PI-BDA, increasing nanotube loading from 0 to 1 wt% results in continuously enhanced tensile

modulus and strength. For SWNT(1 wt%)/PI-BDA/R composite, the tensile modulus and strength increased by 80% and 70%, respectively, from 2.61 ± 0.14 to 4.70 ± 0.24 GPa and 83.7 ± 3.3 to 142.3 ± 6.9 MPa (relative to neat CE-EP resin). 1.5 wt% SWNTs/PI-BDA resulted in decreased tensile modulus and strength, which may be due to the poor wetting of SWNTs, as reflected from more pulled-out SWNTs on the fracture surface of the SWNT(1.5 wt%)/PI-BDA/R composite (Figure 4.17). Others have calculated that 1 vol% (~ 1 wt%) of SWNTs is sufficient to ensure that every polymer is within one radius of gyration (5 nm) of a SWNT, implying difficulties in complete wetting of SWNTs in composites with high nanotube content (> 1 wt%).^{17,258} This theoretical estimate is consistent with the observation of poor wetting in SWNT(1.5 wt%)/PI-BDA/R composites. The elongation at break of SWNT/PI-BDA/R composite increases initially at SWNT loading of 0.2 wt% (from 5.0 ± 0.4 to 6.2 ± 0.7 %) and then decreases gradually to 3.7 ± 0.4 % for the 1.5 wt% composite. All the SWNT/PI-BDA/R composites with SWNT loading ranging from 0.2 to 1.5 wt% show higher toughness than neat CE-EP resin. Increases of 100% and 58% in toughness are achieved at SWNT loading of 0.2 wt% and 1 wt%, respectively. As manifested in the FE-SEM fractograph of the SWNT(1 wt%)/PI-BDA/R composite (Figure 4.13B1), well-dispersed SWNTs and strong SWNT-matrix bonding effectively resist the propagation of cracks during deformation,⁹ thus increasing the fracture toughness. The poor reinforcement effect of SWNTs without dispersant can be attributed to the aggregation of nanotubes, weak nanotube/matrix interfacial adhesion and limited nanotube alignment as discussed previously. This is corroborated by greater

improvements of the tensile modulus, strength and toughness of the composites with the PI-BDA dispersant.

Table 4.1 Mechanical (E , σ , ε and T) and thermal (T_g and T_d) properties of neat CE-EP and its nanocomposites.

Samples	E (GPa)	σ (MPa)	ε (%)	T^a (MJ m ⁻³)	T_g^b (°C)	T_d^c (°C)
Neat CE-EP	2.61 ± 0.14	83.7 ± 3.3	5.0±0.4	2.6 ± 0.2	167	305
SWNTs (0.2 wt%)/R	3.37 ± 0.07	103.1 ± 8.5	4.7±0.7	3.0 ± 0.4	167	307
SWNTs(0.5 wt%)/R	3.38 ± 0.10	107.0 ± 11.0	4.7±0.6	2.9 ± 0.2	165	311
SWNTs(1wt %)/R	3.47 ± 0.18	100.1 ± 6.5	3.9±0.4	2.5 ± 0.3	162	317
SWNTs(1.5 wt%)/R	3.10 ± 0.19	70.6 ± 4.6	2.5±0.4	1.0 ± 0.2	159	318
SWNTs(0.2wt%)/PI-BDA/R	3.48 ± 0.15	120.1 ± 2.7	6.2±0.7	5.2 ± 0.6	175	308
SWNTs(0.5wt%)/PI-BDA/R	3.87 ± 0.09	124.3 ± 2.2	4.8±0.4	4.2 ± 0.3	170	317
SWNTs(1 wt%)/PI-BDA/R	4.70 ± 0.24	142.3 ± 6.9	4.2 ± 0.8	4.1 ± 0.4	164	323
SWNTs(1.5wt%)/PI-BDA/R	4.40 ± 0.34	124.8 ± 9.6	3.7±0.4	2.9 ± 0.3	160	320

^a Calculated from the area under the stress-strain curve.

^b Determined by DSC.

^c Thermal decomposition at 5 wt% weight loss.

Figure 4.16 A) Representative stress-strain curves of neat CE-EP, SWNT(1 wt%)/R and SWNT(1 wt%)/PI-BDA/R composites. B) Tensile modulus, C) tensile strength, D) elongation at break and E) toughness of SWNT/PI-BDA/R and SWNT/R composites with different SWNT loadings.

Figure 4.17 FE-SEM image of cross-sectional fracture surface of the SWNT(1.5 wt%)/PI-BDA/R composite.

Using only 1 wt% PI-BDA functionalized SWNTs, the absolute tensile properties of SWNT(1 wt%)/PI-BDA/R composites ($E = 4.70 \pm 0.24$ GPa and $\sigma = 142.3 \pm 6.9$ MPa) are higher than most other CNT reinforced thermoplastics and thermosets, including CNT/CE⁶ and CNT/epoxy^{20,24,26,170-171,259} thermosetting composites. Since no published work appears about CNTs reinforced CE-EP composite, here we compare our results with that of solution-processed CNTs reinforced epoxy composites. The detailed comparison is summarized in Table 4.2.^{20,26,169-171,193,197,250,259-262} It should be noted that the comparisons are only approximate as the nanotubes used, matrices, processing technique etc which are listed in Table 4.2 differ. Nanotubes used could be single-walled, double-walled or multi-walled.^{20,250,259} From Table 4.2, we can see that most tensile properties are reported for low CNT contents (about 1 as the mechanical properties usually deteriorate with higher loadings. While the epoxy resins used differ chemically, most have strength and modulus of about 60–90 MPa and 2–3 GPa, respectively. The reported nanotube dispersion

methods for the tabulated composites involve covalent functionalizations.^{20,26} my absolute values and percent increases for both tensile strength and modulus achieved with 1 wt% of SWNTs/PI-BDA ($E = 4.70 \pm 0.24$ GPa (80% increase) and $\sigma = 142.3 \pm 6.9$ MPa (70 % increase)) are higher than the tabulated increases for E and σ which are usually less than 30–40%^{26,170-171} The tensile reinforcement efficacy can also be quantitatively evaluated by calculating the Young's modulus and tensile strength per unit weight fraction (dE/dW_{NT} and $d\sigma/dW_{NT}$).^{26,190} In this study, dE/dW_{NT} and $d\sigma/dW_{NT}$ reach to 252 GPa and 8120 MPa, respectively, at 0.5 wt% of SWNTs and to 209 GPa and 5860 MPa at 1 of SWNTs. These values are also superior compared to the results of CNT/epoxy composites reported recently (Table 4.2).^{20,26,170-171,259} The significant mechanical improvements achieved here can be attributed to the: i) high aspect ratio of SWNTs with well-preserved graphene structure surface due to noncovalent functionalization; ii) homogeneous dispersion of SWNTs/PI-BDA in CE-EP matrix; iii) strong π - π interaction between SWNTs and PI-BDA backbone, and covalent reaction between PI-BDA and the matrix; and iv) alignment of SWNTs along the fiber axis.

Table 4.2 Comparison of tensile properties with reported data for CNT/epoxy composites.

Ref. and year	CNT type	CNT treatment ^a	Processing Technique	CNT content (wt%)	Neat epoxy		CNT/epoxy		dσ/dW _{NT} (MPa)	dE/dW _{NT} (GPa)
					σ (Mpa)	E (Gpa)	σ (Mpa) ^b	E (GPa) ^b		
2003 ²⁰	HiPco SWNTs	fluorination (cf)	solution mixing	1	83.2	2.026	95.0 (14%)	2.632 (30%)	1180	61
2004 ¹⁷¹	HiPco SWNTs	amino-modified (cf)	solution mixing	1	83	2.026	104 (25%)	2.650 (31%)	2100	62
2004 ¹⁹⁷	DWNTs	amino-modified (cf)	calendering	1	63.8	3.29	65.2 (2%)	3.51 (7%)	140	22
2005 ²⁵⁹	CVD DWNTs	amino-modified (cf)	calendering	0.5	63.8	2.5999	69.13 (8%)	2.978 (15%)	1066	76
2005 ¹⁹³	CVD MWNTs	no treatment (cf)	solution mixing direct	1.5	68	NA	80 (18%)	NA	800	NA
2006 ²⁶⁰	CVD MWNTs	plasma treatment (cf)	mixing	1	26	1.21	58 (123%)	1.61 (33%)	3200	40
2006 ²⁶¹	SWNTs	acid treatment (cf)	solution mixing direct	0.1	64.8	2.875	68.4 (6%)	2.910 (1%)	3600	35
2007 ¹⁶⁹	CVD MWNTs	maleic anhydride grafted (cf)	mixing	1	45	0.62	67.5 (50%)	1.25 (102%)	2250	63
2008 ¹⁷⁰	SWNTs	poly(amidoamine) modified (cf)	solution mixing	1	64.1	2.76	74.7 (17%)	3.49 (26%)	1060	73
2009 ²⁶	CVD SWNTs	poly(amidoamine) grafted (cf)	solution mixing	0.5	90	3.3	125.1 (39%)	3.89 (18%)	7020	118
2009 ²⁵⁰	MWNTs	acid treatment (cf)	solution mixing direct	0.5	73.4	2.67	74.4 (1%)	3.09 (16%)	200	84
2010 ²⁶²	CVD MWNTs	no treatment (cf)	mixing	10	64.51	3.11	110.1 (71%)	5.41 (74%)	456	23
our results	CVD SWNTs	Non-covalent functionalization	solution mixing	1	83.7	2.61	142.3 (70%)	4.70 (80%)	5860	209
				0.5					8120	252

^acf in the bracket represents “covalent functionalization”.

^bThe values in the bracket mean the increase of tensile modulus or strength over neat matrix.

The theoretical tensile strength of CE-EP composites reinforced with SWNTs can be predicted by a standard model for composite reinforced with short aligned fibers:^{6,263}

$$\sigma_c = \left(1 - \frac{\sigma_f r}{2l_f \tau}\right) \sigma_f V_f + \sigma_m (1 - V_f)$$

where σ_c , σ_f , σ_m are the composite, the nanotube and the polymer matrix strengths, respectively. r is average SWNT radius, l_f is average SWNT length, V_f is the SWNT volume fraction (estimated from the SWNT mass fraction, the SWNT density (1.5 g cm^{-3}) and the matrix density (1.2 g cm^{-3})), and τ is the nanotube-matrix interfacial shear strength. Based on the values $\sigma_f = 30 \text{ GPa}$,¹⁵ $\sigma_m = 83.7 \text{ MPa}$, $r = 5 \text{ nm}$, $l_f = 5 \text{ }\mu\text{m}$ and $\tau = 150 \text{ MPa}$ (guestimate theoretical value),²⁶⁴ the theoretical tensile strengths of composites with SWNTs loading of 0.2, 0.5, 1.0 and 1.5 wt% are 129, 197, 311 and 425 MPa, respectively. By comparing with the respective measured strength values of 120.1 ± 2.7 , 124.3 ± 2.2 , 142.3 ± 6.9 and $124.8 \pm 9.6 \text{ MPa}$, we see that our measured strength is very close to the calculated value only for SWNT(0.2 wt%)/PI-BDA/R. The measured strength values diverge from the calculated data as the SWNT loading increases beyond 0.2 wt%. The possible reason may include limited alignment of SWNTs in the composite fiber, relatively weak interaction between SWNTs and PI-BDA, inevitable SWNT bundling, fiber defects and so on. The interfacial strength between the matrix and the nanotube in this study is believed to be smaller than the theoretical value ($\tau = 150 \text{ MPa}$) since the nanotube-matrix interaction is noncovalent. These negative influences become severe at high SWNT loadings.

To make further improvements in the mechanical properties with nanotube, especially at high loading of the latter, several criteria need to be simultaneously achieved: good nanotube wetting and dispersion, low nanotube defect, nanotube alignment and good stress transfer from the matrix. It appears that for multi-walled carbon nanotubes with diameters of about 10 nm, the theoretical limit of nanotube content for good wetting is around 30 wt%.¹⁷ Ensuring good stress transfer to the atomically smooth nanotube surface may be another major challenge that needs to be overcome. Also, it will be ideal to have a matrix that is also nanotube-dispersing without involving a dispersant or surfactant that is different from the matrix as the compatibility of the matrix and dispersant/surfactant is usually poor.

4.3.6 Thermal properties of SWNT/PI-BDA/R composites

With addition of the PI-BDA dispersant, the thermal properties (specifically glass transition temperature (T_g) and decomposition temperature (T_d)) of the SWNT/PI-BDA/R composites were improved compared with SWNT/R composites or neat resin (Table 4.1). The T_g values of neat CE-EP and SWNTs reinforced composites were determined from DSC scans, shown in Figure 4.18. Good nanotube dispersion and improved interfacial reaction (especially at low nanotube loadings) between CE matrix and SWNT/PI-BDA restricts the segmental motion of CE-EP molecules, leading to increased T_g .^{169,265} The reduction in T_g with further increase in CNT content may be possibly due to SWNT disruption of the cross-linking network of the matrix to reduce the effective cross-link density.²⁶⁶ The 5 wt% weight loss temperatures (T_d) of all the samples were calculated from their TGA curves. Figure 4.19

shows typical TGA curves of neat CE-EP, SWNT(1 wt%)/PI-BDA/R and SWNT(1 wt%)/R composites. The improved thermal stability with addition of nanotubes is postulated to be due to a nanotube barrier effect which retards the volatilization of polymer decomposition products, and the higher heat capacity of CNTs compared to polymer.

Figure 4.18 Comparison of T_g values for (a) neat CE-EP fiber, (b–e) SWNT/R and (f–i) SWNT/PI-BDA/R composite fibers with various SWNT loadings: 0.2 wt% (b and f), 0.5 wt% (c and g), 1 wt% (d and h) and 1.5 wt% (e and i).

Figure 4.19 TGA curves of neat CE-EP, SWNT(1 wt%)/PI-BDA/R and SWNT(1 wt%)/R composites.

4.4 Conclusions

We have designed and successfully synthesized PI-BDA, a reactive comb-like polymer, and have shown it to be highly effective in individually dispersing SWNTs and improving the mechanical and thermal properties of the SWNT-reinforced CE-EP composite fibers. The thermosetting composite fibers were prepared by reactive spinning which led to nanotube alignment in matrix. Only 1 wt% of PI-BDA functionalized SWNTs increased the tensile modulus, strength and toughness of composite by 80% (to 4.70 ± 0.24 GPa), 70% (to 142.3 ± 6.9 MPa) and 58% (to 4.1 ± 0.4 MJ m⁻³) over that of neat resin blend (with $E = 2.61 \pm 0.14$ GPa, $\sigma = 83.7 \pm 3.3$ MPa and $T = 2.6 \pm 0.2$ MJ m⁻³). Without PI-BDA dispersant, the corresponding changes in mechanical properties when reinforced with 1 wt% SWNTs were 33%, 28% and -4%. The polyimide backbone has strong π - π interaction with nanotubes to anchor the PI-BDA dispersant to them while the reactive BDA side chain provides steric stabilization and reacts with the CE resin during the thermal cure. Our novel dispersant covalently reacts with the CE matrix through the side chain but strongly noncovalently interacts with nanotube surface to produce good nanotube dispersion with minimal damage to the CNTs, resulting in hence excellent reinforcement.

4.5 Declaration

Part of the work presented in this chapter has been published in the *Chemistry of Materials*.

Yuan, W., Feng, J. L., Judeh, Z., Dai, J., Chan-Park, M. B. Use of polyimide-graft-bisphenol A diglyceryl acrylate as a reactive noncovalent dispersant of

single-walled carbon nanotubes for reinforcement of cyanate ester/epoxy composite. *Chemistry of Materials*, 2010, 22, 6542-6554.

Chapter 5 Effect of Side-Chain Structure of a Rigid Polyimide Dispersant on Dispersion of SWNTs and Mechanical Properties of SWNT/Cyanate Ester Composite

5.1 Introduction

Two families of polymers, conjugated or aromatic polymers^{138,142,145} and block copolymers,^{28,146,148} have been reported to be effective at dispersing CNTs, and improving the mechanical properties of CNT/polymer composites. The conjugated or aromatic polymers debundle and stabilize CNTs by forming strong π - π interactions with CNT sidewalls. The block copolymers disperse CNTs via a method that one block forms strong interaction with nanotube sidewalls while the other block located at the outer surface of the nanotubes provides nanotubes with good solubility in solvents and polymer matrices. Recently, Zou et al.^{146,267} showed that a conjugated block copolymer, poly(3-hexylthiophene)-*block*-polystyrene (P3HT-*b*-PS), is a good dispersant for dispersing CNTs, in which the conjugated P3HT block interacts with nanotubes via π - π interaction while the nonconjugated PS block interacts with solvents or PS matrix. They reported that the P3HT-*b*-PS is more efficient than homopolymer, P3HT, in dispersing carbon nanotubes in polystyrene solution, which is possibly due to the higher compatibility and miscibility of the PS segment with the polystyrene matrix. Their findings suggest that the structure

of the nonconjugated block would significantly influence the dispersion of nanotubes in polymer matrix.

In Chapter 4, I showed that a graft copolymer, PI-BDA, was very effective at dispersing SWNTs in DMF and CE-EP matrix, and in improving the mechanical properties of the resulting composites. I attributed the high efficacy of PI-BDA at dispersing CNTs to its unique structure, in which the polyimide backbone strongly adsorbs onto nanotube surface via π - π interaction whereas the side-chain provides nanotubes with good solubility in both DMF and CE-EP matrix. This dispersing mechanism is quite similar to that of block copolymers such as P3HT-*b*-PS. As a result, it is reasonable to hypothesize that the side-chain structure of the rigid polyimide dispersant may affect their ability to disperse CNTs in a particular matrix and to improve the mechanical properties of composites.

In this chapter, to demonstrate the hypothesis, three polymers: PI, PI-GNE, and PI-BDA, were synthesized. The dispersion of SWNTs, PI functionalized SWNTs (SWNTs/PI), PI-GNE functionalized SWNTs (SWNTs/PI-GNE) and PI-BDA functionalized SWNTs (SWNTs/PI-BDA) in DMF were characterized and compared. Furthermore, CE composite films with different contents of SWNTs, SWNTs/PI, SWNTs/PI-GNE and SWNTs/PI-BDA as reinforcement were prepared by solution casting. The nanotube dispersion in CE, nanotube/CE interfacial adhesion, and mechanical properties of these composites were investigated and compared. SWNTs/PI-BDA disperse best in CE matrix and show the greatest improvement in composite mechanical properties due to the unique side-chain structure of PI-BDA.

5.2 Experimental section

Materials

SWNTs were used as nanofillers and CE was used as matrix resin in this chapter. Other chemicals were purchased from Sigma-Aldrich. The details of these chemicals are listed in Section 3.1. Three polymers including PI, PI-BDA and PI-GNE, were synthesized and used as noncovalent dispersants for SWNTs (Section 3.2).

Preparation of composite films

To make composite films, various nanotube dispersions were first prepared. It has been demonstrated in Section 4.3.2 that 1:1 ratio is the optimal mass ratio of PI-BDA to SWNTs for preparing nanotube dispersion, so in this study we also use the 1:1 mass ratio of dispersant (PI, PI-BDA or PI-GNE) to SWNTs. In a typical protocol used to prepare SWNTs/PI dispersion, 10 mg of SWNTs and 10 mg of PI were first added into 10 mL of DMF. Then the mixture was sonicated with a high-power tip sonicator (500 W, 35%, Vibra-Cell, Sonics) for 10 min followed by further sonication in a low-power sonic bath (S30H, Elma) for 30 min at 0 °C to produce a homogeneous SWNT/PI dispersion (1 mg/mL SWNTs; the mass ratio of SWNTs to PI is 1:1). SWNT/PI-GNE and SWNT/PI-BDA dispersions were prepared following the same procedure by changing PI to PI-GNE or PI-BDA. Pristine SWNT suspension was prepared without the addition of polymeric dispersant.

Composite films with different contents of SWNTs were prepared by solution casting. A typical procedure for preparing SWNT/PI/CE composite films was as follows: 0.1 g of CE that had been precured at 180 °C for 1 h was

first dissolved in 0.1 mL of DMF. Then the CE solution was mixed with measured quantities of SWNT/PI dispersion prepared as above. After sonication in a sonic bath for 10 min, the solution of SWNTs/PI/CE in DMF was cast onto a horizontal glass slide. The slide was warmed on a hot plate at ~ 50 °C to slowly remove most of the DMF. Then the slide was transferred to a vacuum oven and dried under vacuum at 80, 100, and 120 °C for 2 h each. Finally, the films were cured in a convection oven. The curing cycle was 3 h at 180 °C, 2 h at 200 °C and 2 h at 250 °C. After cooling down, the films were carefully peeled off the glass substrates which were without release-agent. The thickness of the resulting film was about 40 μm , measured with a low torque digital micrometer. Neat CE films and CE composite films reinforced with SWNTs (SWNTs/CE), PI-GNE functionalized SWNTs (SWNTs/PI-GNE/CE), and PI-BDA functionalized SWNTs (SWNTs/PI-BDA/CE) were also prepared by a similar method.

Computer simulation of SWNT-dispersant systems in DMF

A (10, 10) SWNT model (diameter ~ 1.4 nm) at length of 5 nm was first built. For the all three polymers, PI, PI-GNE and PI-BDA, two repeating units were built. All-atom AMBER²⁶⁸ general force field was used to represent SWNT, polymer, and DMF molecule. The atomic charges of polymer and DMF were generated using RED software.²⁶⁹ The validity of parameters of DMF was checked through calculating the density of pure DMF liquid, 0.92 g/cm³, which is close to the experimental value of 0.95 g/cm³. The simulation box was dodecahedral and contained one SWNT, one polymer and around 1500 DMF molecules. GROMACS²⁷⁰ package combined with Amb2gmx²⁷¹ conversion

utility tool was used to perform the simulation. LINCS²⁷² protocol was employed to constrain all bonds involving hydrogen atoms in length. In all simulations, an integration step of 2 fs was used and nonbonded pair lists were updated every 10 fs. Particle mesh Ewald method²⁷³ with a cut-off of 9 Å was used to treat electrostatic interactions. A cut-off of 12 Å was used to calculate the van der Waals interactions. The binding free energy was estimated based on GB implicit solvent model,²⁷⁴ which is provided by the sander module in AMBER 9.²⁶⁸ The distance between SWNT and polymer at beginning was larger than 1 nm. For each SWNT-polymer system, three independent simulation trajectories were conducted up to 60 ns. The last 30 ns trajectories were used for analysis.

Characterization of dispersants, nanotubes and composites

FT-IR, GPC, Raman, UV-vis-NIR, optical microscopy, AFM, FE-SEM, tensile testing were used for characterizing samples as described in Section 3.3.

5.3 Results and discussion

5.3.1 Synthesis of PI, PI-GNE and PI-BDA

The synthesis and characterization of PI and PI-BDA has been discussed in Chapter 4. Similarly to the synthesis of PI-BDA, the synthesis of PI-GNE was realized via reaction between the pendant hydroxyl groups on PI and epoxy groups on GNE with DMAP as catalyst. Figure 5.1 shows the FTIR-ATR spectra of PI, GNE, and PI-GNE. The spectrum of GNE shows characteristic absorption bands of epoxy group at 917 cm⁻¹. The bands at 2871, 2927, and 2957 cm⁻¹ are identified as the C-H stretching mode of methyl and methylene groups. The spectrum of PI-GNE shows the characteristic bands of its precursor

PI, i.e. at 1772, 1699, and 1373 cm^{-1} , corresponding to the imide group, and at 1604, 1568, 1502, 1475 cm^{-1} , corresponding to the aromatic C=C bands. After grafting the GNE side chain, new bands at 2956, 2924, and 2870 cm^{-1} appear clearly, which can be assigned to the C–H stretches of $-\text{CH}_2$ and $-\text{CH}_3$ groups in the GNE side chain. A broad band at 3700–3100 cm^{-1} in the spectrum of PI-GNE is attributed to the $-\text{OH}$ group generated in the ring-opening reaction of epoxy groups. No characteristic band of epoxy group ($\sim 917 \text{ cm}^{-1}$) appears in the spectrum. All these confirm successful grafting of GNE onto the PI backbone via reaction between $-\text{OH}$ groups on PI and epoxy groups on GNE.

Figure 5.1 FTIR-ATR spectra of (a) PI, (b) GNE, and (c) PI-GNE.

5.3.2 Dispersion of nanotubes in DMF

Figure 5.2 compares the dispersion stability of SWNTs, SWNTs/PI, SWNTs/PI-GNE, and SWNTs/PI-BDA in DMF, at different standing times after sonication. Pristine SWNTs aggregated and settled within 10 days (Figure 5.2-2, vial A). SWNTs/PI partially aggregated but remained in suspension after 2 months (Figure 5.2-3, vial B). SWNTs modified with PI-GNE and PI-BDA

were still well-dispersed and suspended even after 2 months (Figure 5.2-3, vials C and D). These results indicate that the side chain grafted on the backbone of the PI imparts strongly repulsive forces to SWNTs/PI-GNE and -BDA via steric hindrance.²⁷⁵ It is very important to the long-term dispersion stability of the functionalized SWNTs in DMF. However, there was no obvious difference between the SWNT/PI-GNE and SWNT/PI-BDA dispersions.

Figure 5.2 Visual observation of (A) SWNTs, (B) SWNTs/PI, (C) SWNTs/PI-GNE, and (D) SWNTs/PI-BDA in DMF at different standing times after sonication: (1) 0 min, (2) 10 days, and (3) 2 months.

Similar to our previous study (Chapter 4), the efficacy of PI, PI-GNE and PI-BDA at dispersing SWNTs was quantitatively compared using absorbance measurement and the Beer–Lambert law ($A = \epsilon lc$).²⁷⁶⁻²⁷⁷ The extinction coefficient (ϵ), which is strongly depended on naotube type, solvent type and wavelength of the measured absorbance, was determined in our previous study

to be about $37.60 \text{ mL mg}^{-1} \text{ cm}^{-1}$ at 500 nm for our SWNTs in DMF. Figure 5.3 shows the nanotube concentrations of SWNT/PI, SWNT/PI-GNE, and SWNT/PI-BDA dispersions (mass ratio of SWNTs to polymer was fixed at 1:1) in different conditions, determined by measuring absorbance at 500 nm and the Beer–Lambert law. Immediately after sonication, all three of the dispersions are homogeneous and have a suspended SWNT concentration of about 20 mg/L (the initial concentration we chose). After standing for 3 days, centrifugation at 6000 rpm for 1 h, and centrifugation at 14000 rpm for 1 h, the SWNT concentrations of SWNTs/PI-GNE (19.8, 15.2 and 9.0 mg/L, respectively) and SWNTs/PI-BDA (20, 15.8 and 9.3 mg/L, respectively) are quite similar and are much higher than that of SWNT/PI dispersion (18.7, 9.9 and 5.1 mg/L, respectively). These measurements are consistent with the results of visual observation.

Figure 5.3 SWNT concentrations of SWNT/PI, SWNT/PI-GNE and SWNT/PI-BDA dispersions (mass ratio of SWNTs to polymer is 1:1) in different conditions: immediately after sonication, standing for 3 days, centrifugation at 6000 rpm for 1 h, and centrifugation at 14 000 for 1 h.

The dispersions of SWNTs/PI, SWNTs/PI-GNE and SWNTs/PI-BDA were also deposited onto silicon wafers and characterized by AFM (Figure 5.4). SWNTs were observed as large bundles with diameters of about 8–15 nm (Figure 5.4A). In SWNTs/PI (Figure 5.4B), the nanotube bundle diameters were reduced to be about 5 nm, and some individual tubes were also present. The measured heights of SWNTs/PI-GEN were in the range of 1–3 nm, indicating that they were dispersed as individual tubes as well as very small bundles (Figure 5.4C). SWNTs/PI-BDA (Figure 5.4D) are present similar as SWNTs/PI-GEN. Combined with the results of visual observation and UV–vis–NIR characterization, It can be concluded that PI-GNE and PI-BDA have similar efficacy at dispersing and debundling SWNTs in DMF.

Figure 5.4 AFM images of (A) SWNTs, (B) SWNTs/PI, (C) SWNTs/PI-GNE and (D) SWNTs/PI-BDA deposited on silicon wafers by spin coating.

To investigate the dispersion of SWNTs, SWNTs/PI, SWNTs/PI-GNE, and SWNTs/PI-BDA in CE matrix in DMF, 100 mg partially prepolymerized CE (180 °C for 1 h) were added into 2 mL of nanotube/DMF dispersions (concentration fixed at 0.5 mg/mL, with dispersant to SWNT mass ratio of 1:1). In data not shown, after about 1 h, the SWNT/PI/CE dispersion showed coagulation or agglomeration of the suspended nanotubes, while the SWNT/PI-GNE/CE and SWNT/PI-BDA/CE dispersions were very homogeneous. The

quick precipitation of SWNTs/PI may be due to the poor stability of nanotubes dispersed with PI (Figure 5.2). After about 6 h, fine aggregates appeared in the SWNT/PI-GNE/CE dispersion, while the PI-BDA functionalized nanotubes showed no visible evidence of gross aggregation after 24 h. The dramatic variation in behavior is further evidence that the precise nature of the side-chain is important in the design of polymer surfactants to disperse carbon nanotubes in a polymer (in this case, CE). The structure of the PI-BDA side-chain is more similar to CE than is the PI-GNE side chain. This higher compatibility between the BDA side-chain and CE matrix results in higher efficiency of PI-BDA than PI-GNE in dispersing nanotubes in CE solution. A similar phenomenon has been recently reported by Zou et al.,¹⁴⁶ who showed that a conjugated block copolymer, P3HT-*b*-PS, better disperses nanotubes in polystyrene solution than homopolymer, P3HT.

5.3.3 Computer simulation of SWNT-dispersant systems in DMF

Molecular dynamics simulations were employed to study the interaction between SWNT and polymers PI, PI-GNE and PI-BDA in DMF. In the beginning of the simulations, the minimum distance between each polymer and the SWNT was more than 1.0 nm. For PI-GNE and PI-BDA, within a simulation time of 10 ns, the polymers formed close contacts with the SWNT, with the minimum distance between the polymer and SWNT being less than 0.3 nm. The contacts were very stable, no dissociation events happened in all simulations. However, in the case of PI, dissociation occurred frequently. During the total simulation time of 180 ns, the percentage of the SWNT-PI contacts formed was only 42%.

The strength of binding was estimated by calculating the binding energy which is defined as:

$$E_B = E_C^{GB} - (E_P^{GB} + E_{CNT}^{GB}) \quad (5.1)$$

where E_C^{GB} , E_P^{GB} and E_{CNT}^{GB} are the energies of polymer-SWNT complex, polymer and SWNT, respectively. The binding energy of PI to SWNT is -12.9($\pm$ 10.6) kcal/mol. In comparison, the binding energy of PI-GNE and PI-BDA to SWNT reaches -75.4($\pm$ 16.7) kcal/mol and -78.3($\pm$ 10.8) kcal/mol, respectively. The adding of side chains enhances the binding strength significantly. The binding patterns are illustrated by the complexes snapshots shown in Figure 5.5. It is evident that a small part of the PI, usually one or two rings, makes contacts with the SWNT surface, whereas the majority part of the molecule is solvated by the DMF solvent. The binding patterns are different for PI-GNE and PI-BDA, which adsorb well onto the SWNT surface. Clearly, the presence of side chains is essential to the intimate binding. The difference in the bonding strength and bonding pattern of PI, PI-GNE and PI-BDA to SWNT is consistent with the observation of dispersion state of SWNTs/dispersant in DMF.

Figure 5.5 Snapshots of the complex of a (10, 10) SWNT and (a) PI, (b) PI-GNE, (c) PI-BDA. All structures are taken at the end of one trajectory (60 ns).

5.3.4 SWNT dispersion and interfacial adhesion in composites

Optical micrographs can show the microscale state of the nanotube dispersion in the CE matrix. A representative optical micrograph of SWNT/CE composites (Figure 5.6A) shows many aggregated clusters of SWNTs, suggesting nonuniform dispersion of SWNTs. The nanotube dispersion was improved for PI functionalized SWNTs, though some SWNT aggregates with sizes as large as 10 μm can be clearly seen (Figure 5.6B). In SWNT/PI-GNE/CE composites (Figure 5.6C), dense aggregates are still apparent but the aggregate size is much smaller than that in the SWNT/PI/CE composites, indicating much improved SWNT dispersion. By comparison, SWNT/PI-BDA/CE composites show uniform dispersion of SWNTs throughout the matrix, and no obvious SWNT aggregates were observed (Figure 5.6D). It is interesting that SWNTs/PI-GNE and SWNTs/PI-BDA have similar dispersion in DMF, but the dispersion of SWNTs/PI-BDA in CE was much better than that of SWNTs/PI-GNE. In fact, the observation of a significant degree of SWNT aggregation in SWNT/PI-GNE/CE composites is quite similar to the results reported by Delozier et al.,¹¹⁹ who found that rigid polyimides grafted with alkyl side chains were good at dispersing SWNTs in DMAc but less effective in distributing SWNTs in polyimide composite films, especially at high CNT loading. The mechanical properties of their resultant SWNT/polyimide composites thus improved only very slightly. Comparing PI-BDA and PI-GNE, we attribute their different ability to disperse SWNTs in CE matrix to the different structures of their side chains. The structure of PI-BDA side-chain is more similar to that of CE monomer than is that of PI-GNE. This compatibility

reduces the likelihood of SWNT aggregation during film preparation. Because reduced aggregation and improved dispersion is expected to correlate with reinforcement efficacy of the filler, side-chain compatibility with the matrix is an important consideration in the design of effective SWNT-functionalizing materials.

Figure 5.6 Optical micrographs of (A) SWNT/CE, (B) SWNT/PI/CE, (C) SWNT/PI-GNE/CE, and (D) SWNT/PI-BDA/CE composites with 1 wt% SWNT loading. Scale bars are 50 μm .

The fracture surfaces of composites after mechanical testing were characterized with FE-SEM. In SWNT(1 wt%)/CE nanocomposites, SWNTs are observed as agglomerated ropes divided by regions containing no SWNTs (Figure 5.7A1). Many nanotubes have been pulled out (Figure 5.7A2), leaving holes between nanotubes and CE matrix (indicated by arrows in Figure 5.7A3), which indicates weak interfacial bonding between SWNTs and CE matrix. PI functionalized SWNTs (Figure 5.7B1–B3) are also dispersed as aggregates in the CE matrix, and many of the tubes are found to be pulled out. However, the aggregate size is much smaller and the nanotube/matrix adhesion seems better when compared with SWNTs/CE. The fracture surface of SWNT(1 wt%)/PI-

GNE/CE composite films (Figure 5.7C1–C3) show much better SWNT dispersion in CE matrix compared to SWNTs/CE and SWNTs/PI/CE. But there is still some degree of SWNTs sliding and pulling out of the surface, although other SWNTs are found to have broken at the surface. Figure 5.7C3 clearly shows some big SWNT bundles were pulled out (indicated by arrows). In SWNT(1 wt%)/PI-BDA/CE composites (Figure 5.7D1–D3), SWNTs are homogeneously dispersed on the fracture surface and most of them are broken or only slightly pulled out from the surface. Figure 5.7D3 shows the diffuse character of the edges of the functionalized SWNTs, and some nanotubes with the exposed break tip smaller than the end embedded in matrix (indicated by arrows). These suggest that the SWNTs are covered with a polymer shell and tightly embedded in the matrix, which would indicate effective load transfer from matrix to SWNTs. All these fracture surface characteristics are in accordance with the mechanical properties of the corresponding composites, discussed below.

Figure 5.7 FE-SEM images of fracture surfaces of (A1–A3) SWNT/CE, (B1–B3) SWNT/PI/CE, (C1–C3) SWNT/PI-GNE/CE, and (D1–D3) SWNT/PI-BDA/CE composites. The SWNT loading in these composites is 1 wt%.

Raman spectroscopy is a useful technique for studying the interactions between carbon nanotubes and molecules based on the changes in the position of spectral features due to mechanical modes of the SWNTs.²⁷⁸ Figure 5.8 shows the Raman spectra of SWNTs, and SWNT/PI, SWNT/CE, SWNT/PI-GNE/CE and SWNT/PI-BDA/CE composite films. The D-band and the G-band are observed at $\sim 1330\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$, respectively. As compared to pristine SWNTs, no significant increase in the I_D/I_G ratio was observed in the

spectra of SWNTs/PI, SWNTs/PI-GNE and SWNTs/PI-BDA, indicating that few defects were introduced into the SWNTs and the nanotube length was well preserved. This is expected since the dispersants interact noncovalently with the SWNTs and the sonication applied for composite preparation was not very severe. The intact SWNT surfaces and long length contributes to the mechanical properties of the nanotube-reinforced composites. The G-bands of SWNT/CE (1588 cm^{-1}), SWNT/PI/CE (1590 cm^{-1}), SWNT/PI-GNE/CE (1591 cm^{-1}), and SWNT/PI-BDA/CE (1592 cm^{-1}) composites were respectively upshifted by 3, 5, 6 and 7 cm^{-1} from the G-band of neat SWNTs (1585 cm^{-1}). The 3 cm^{-1} upshift of G-band in SWNT/CE composites is due to the interaction between SWNTs and CE matrix which contains a large amount of triazine and benzene rings.²⁵⁶ The $2\text{--}4\text{ cm}^{-1}$ higher upshifts in the SWNTs/PI/CE, SWNTs/PI-BDA/CE and SWNTs/PI-GNE/CE compared to SWNTs/CE suggest that the electronic environment of the SWNT surfaces was changed by the polymeric dispersants. Aromatic compounds have been reported to interact with the graphitic sidewalls of CNTs via π -stacking.^{256,279} The upshifts of G-band observed here clearly indicate the π - π interaction between the SWNTs and the dispersants.^{28,146} PI-BDA functionalized SWNTs were upshifted more than SWNTs/PI and SWNTs/PI-GNE, which may be attributed to their better dispersion resulting a greater degree of contact of SWNT sidewall with dispersant.

Figure 5.8 Raman spectra of (a) SWNTs, (b) SWNT/CE, (c) SWNT/PI/CE, (d) SWNT/PI-GNE/CE, and (e) SWNT/PI-BDA/CE composites with 5 wt% of SWNTs.

I believe that the stronger nanotube/matrix interfacial adhesion in SWNT/PI/CE, SWNT/PI-GNE/CE and SWNT/PI-BDA/CE composites than in SWNT/CE composite is due to polymeric dispersant adsorbed on nanotube surface, which not only improves the compatibility between nanotube and matrix but also reacts with CE matrix. The covalent reaction is realized via the reaction between $-OH$ group on dispersants and $-OCN$ group on CE matrix, which has been proved in Chapter 4. The stronger interfacial adhesion in SWNTs/PI-BDA/CE than in SWNTs/PI/CE and SWNTs/PI-GNE/CE can be attributed to the better dispersion of SWNTs/PI-BDA, which brings more dispersant-clad nanotube surfaces into contact with the surrounding CE matrix.

5.3.5 Mechanical properties of composite films

The tensile properties, including Young's modulus (E), tensile strength elongation at break (ε) and toughness (T) of neat CE, SWNT/CE, SWNT/PI/CE, SWNT/PI-GNE/CE and SWNT/PI-BDA/CE composites with

different SWNT loadings are summarized in Table 5.1 and Figure 5.9. Figure 5.9A shows representative tensile stress versus strain curves. The E , σ , ε and T of the neat CE are 3.08 ± 0.14 GPa, 101.1 ± 6.0 MPa 4.0 ± 0.3 % and 2.1 ± 0.2 MJ m⁻³, respectively.

Table 5.1 Mechanical properties (E , σ , ε and T) of neat CE and CE nanocomposites.

Sample	E (GPa)	σ (MPa)	ε (%)	T^a (MJ m ⁻³)
Neat CE	3.08 ± 0.14	101.1 ± 6.0	4.0 ± 0.3	2.1 ± 0.2
SWNTs(0.2 wt%)/CE	3.12 ± 0.09	90.3 ± 6.8	3.4 ± 0.3	1.6 ± 0.3
SWNTs(0.5 wt%)/CE	3.18 ± 0.17	75.1 ± 7.8	3.1 ± 0.2	1.3 ± 0.2
SWNTs(1 wt%)/CE	3.25 ± 0.11	66.2 ± 7.4	2.6 ± 0.5	0.9 ± 0.3
SWNTs(2 wt%)/CE	3.27 ± 0.13	48.7 ± 4.3	2.1 ± 0.2	0.6 ± 0.1
SWNTs(5 wt%)/CE	3.29 ± 0.11	40.6 ± 8.2	1.8 ± 0.4	0.4 ± 0.2
SWNTs(0.2 wt%)/PI/CE	3.18 ± 0.04	108.3 ± 7.7	4.3 ± 0.3	2.4 ± 0.3
SWNTs(0.5 wt%)/PI/CE	3.33 ± 0.16	93.5 ± 5.5	3.6 ± 0.5	1.9 ± 0.2
SWNTs(1 wt%)/PI/CE	3.37 ± 0.10	88.4 ± 9.1	3.2 ± 0.2	1.5 ± 0.1
SWNTs(2 wt%)/PI/CE	3.41 ± 0.23	73.6 ± 6.3	2.8 ± 0.5	1.2 ± 0.2
SWNTs(5 wt%)/PI/CE	3.48 ± 0.12	64.3 ± 8.9	2.2 ± 0.6	0.8 ± 0.2
SWNTs(0.2 wt%)/PI-GNE/CE	3.30 ± 0.13	117.8 ± 4.8	4.9 ± 0.2	3.1 ± 0.1
SWNTs(0.5 wt%)/PI-GNE/CE	3.40 ± 0.16	120.2 ± 6.3	4.4 ± 0.3	2.9 ± 0.3
SWNTs(1 wt%)/PI-GNE/CE	3.48 ± 0.05	122.3 ± 5.6	3.8 ± 0.2	2.6 ± 0.2
SWNTs(2 wt%)/PI-GNE/CE	3.67 ± 0.10	117.5 ± 5.2	3.6 ± 0.3	2.4 ± 0.2
SWNTs(5 wt%)/PI-GNE/CE	3.81 ± 0.15	110.7 ± 6.8	3.0 ± 0.6	1.9 ± 0.3
SWNTs(0.2 wt%)/PI-BDA/CE	3.35 ± 0.10	123.0 ± 5.7	5.2 ± 0.2	3.5 ± 0.2
SWNTs(0.5 wt%)/PI-BDA/CE	3.54 ± 0.06	128.2 ± 3.8	5.7 ± 0.3	3.9 ± 0.3
SWNTs(1 wt%)/PI-BDA/CE	3.78 ± 0.12	136.5 ± 5.4	5.2 ± 0.3	4.0 ± 0.4
SWNTs(2 wt%)/PI-BDA/CE	4.05 ± 0.07	148.1 ± 7.6	4.2 ± 0.4	3.6 ± 0.2
SWNTs(5 wt%)/PI-BDA/CE	4.33 ± 0.14	129.4 ± 8.6	3.6 ± 0.4	2.6 ± 0.3

^a Calculated from the area under the stress-strain curve.

Figure 5.9B shows that for all four kinds of nanotubes, the Young's modulus (E) increases as the nanotube loading increases from 0 to 5 wt%, but the degree of improvement differs significantly for the different reinforcement materials. Compared with neat CE ($E = 3.08 \pm 0.14$ GPa), the highest increase in E is about 7% (to 3.29 ± 0.11 GPa), 13% (to 3.48 ± 0.12 GPa), 24% (to 3.81 ± 0.15 GPa) and 41% (to 4.33 ± 0.14 GPa), respectively, for SWNT/CE, SWNT/PI/CE, SWNT/PI-GNE/CE and SWNT/PI-BDA/CE composites with 5 wt% of nanotubes. As shown in Figure 5.9C–E, SWNTs without dispersant lead to continuous decrease in σ , ε and T as the nanotube loading increases from 0 to 5 wt%. For SWNT/PI/CE composite, a 0.2 wt% loading of SWNTs/PI gives the highest values of σ , ε and T , i.e. $\sigma = 108.3 \pm 7.7$ MPa, $\varepsilon = 4.3 \pm 0.3$ % and $T = 2.4 \pm 0.3$ MJ m⁻³, corresponding to 7%, 8% and 14% improvements over neat CE, respectively. Further increase of nanotube loading impairs tensile properties. With SWNTs/PI-GNE as reinforcement, the composites exhibit an increase in σ at low CNT loadings and a decrease at high CNT loadings. The SWNT(1 wt%)/PI-GNE/CE composite has the highest strength of 122.3 ± 5.6 MPa, corresponding to a 21% increase over neat CE. The ε and T increase initially at SWNT loading of 0.2 wt% but decrease continuously at higher SWNT loadings. The highest values of ε and T are 4.9 ± 0.2 % and 3.1 ± 0.1 MJ m⁻³, respectively, 23% and 48% above that of neat CE. The SWNT/PI-DBA/CE composite films exhibit similar increasing trends with SWNT loading of σ , ε and T to those of SWNT/PI-GNE/CE composite, but SWNTs/PI-BDA is more effective as mechanical reinforcement. The increase of σ continues up to 2 wt% of nanotube loading, the highest tensile strength at 2 wt% of nanotube is 148.1 ± 7.6 MPa, 46% above neat CE. The highest increase in ε is 43% (from $4.0 \pm$

0.3 to 5.7 ± 0.3 %) achieved at SWNT loading of 0.5 wt% whereas the highest increase in T is 90% (from 2.1 ± 0.2 to 4.0 ± 0.4 MJ m⁻³) observed at SWNT loading of 1 wt%. The tensile reinforcement efficacy of fillers can be quantitatively estimated from the variation rate of Young's modulus and tensile strength with weight fraction (dE/dW_{NT} and $d\sigma/dW_{NT}$).^{26,190} SWNT(1 wt%)/PI-BDA/CE composite possesses a dE/dW_{NT} value of 70 GPa and a $d\sigma/dW_{NT}$ value of 3540 MPa. These values compare favorably with results of CNT/thermosetting composites reported recently (dE/dW_{NT} and $d\sigma/dW_{NT}$ are 22–63 GPa and 140–2300 MPa, respectively),^{20,169,171,193,197,262} which were calculated and listed in Chapter 4 Table 4.2.

Figure 5.9 (A) Representative stress-strain curves of neat CE, SWNT(1 wt%)/CE, SWNT(1 wt%)/PI/CE, SWNT(1 wt%)/PI-GNE/CE, and SWNT(1 wt%)/PI-BDA/CE composites. Effect of SWNT content on (B) Young's modulus, (C) tensile strength, (D) elongation at break, and (E) toughness of SWNT/CE, SWNT/PI/CE, SWNT/PI-GNE/CE, and SWNT/PI-BDA/CE composites.

The poor reinforcement effect of SWNTs and SWNTs/PI is obviously due to the large SWNT aggregates and the weak interfacial adhesion between nanotubes and CE matrix, which have been discussed previously. The use of PI-GNE or PI-BDA functionalized SWNTs effectively enhances the

mechanical properties of CE matrix. The superior reinforcement of CE matrix with SWNTs/PI-BDA as compared to that of SWNTs/PI-GNE is attributable to their better dispersion in CE matrix and stronger SWNT-CE interfacial interaction (and, consequently, more effective load transfer), as demonstrated by FE-SEM images of the fracture surface of composites (Figure 5.7) and Raman spectra (Figure 5.8). SWNT/PI/CE, SWNT/PI-GNE/CE and SWNT/PI-BDA/CE composites show increase of ε at relatively low CNT loadings, which is possibly due to the particular flexible elastic behavior of SWNTs. In addition, the entangled SWNTs in matrix can be further stretched.¹⁷¹ The increase of ε is helpful for improving the fracture toughness of a composite, especially if the tensile modulus also increases. Both SWNT/PI-GNE/CE and SWNT/PI-BDA/CE composites show significantly increased toughness as compared with neat CE. This can be attributed to the homogeneous SWNT dispersion, which brings more dispersant-clad nanotube surface into contact with the CE matrix, and the strong nanotube/matrix interfacial bonding, both of which would resist the propagation of cracks during deformation, leading to increased fracture toughness.⁹ Increased toughness for CE composite is very useful because the application of CE is sometimes limited by its brittle nature. Decrease of σ at high nanotube loadings is observed in our composites, which in fact is widely reported for other nanotube/polymer composites.²⁸⁰⁻²⁸¹ This may be due to poor wetting of CNTs at high nanotube loading, which leads to weak interfacial adhesion. For thermosetting matrix, another reason may be that CNTs may inadvertently affect the curing of thermosets and alter the network of cured matrix, especially near the interface between CNTs and matrix.¹⁷⁰

Experimental results were compared with the values predicted from established models. Young's modulus data can be analyzed using the Halpin-Tsai model.^{133,160,282} For randomly distributed SWNTs in a polymer matrix, the modified Halpin-Tsai equation is written as:

$$E_C = E_P \left[\frac{3}{8} \frac{1 + 2(l_f / d_f) \eta_L V_f}{1 - \eta_L V_f} + \frac{5}{8} \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right] \quad (5.2)$$

$$\eta_L = \frac{\left(\frac{E_f}{E_P} \right) - 1}{\left(\frac{E_f}{E_P} \right) + 2(l_f / d_f)} \quad (5.3)$$

$$\eta_T = \frac{\left(\frac{E_f}{E_P} \right) - 1}{\left(\frac{E_f}{E_P} \right) + 2} \quad (5.4)$$

where E_C , E_f , and E_P are the tensile moduli of the composite, nanotube, and polymer matrix, respectively, l_f is the average SWNT length, d_f is the average SWNT or SWNT bundle diameter and V_f is the SWNT volume fraction. The SWNT mass fractions can be converted into volume fraction using the relation

$$\frac{1}{V_f} = \left(\frac{\rho_f}{\rho_P} \right) \left(\frac{1 - m_f}{m_f} \right) + 1 \quad (5.5)$$

where V_f is the SWNT volume fraction, m_f is the SWNT mass fraction in polymer matrix and ρ_f and ρ_P are the densities of CNTs and polymer matrix, respectively. On the basis of the numerical values $\rho_f = 1.5 \text{ g cm}^{-3}$, $\rho_P = 1.2 \text{ g cm}^{-3}$, $l_f / d_f = 1000$, $E_P = 3.08 \text{ GPa}$ and $E_f = 640 \text{ GPa}$,¹³³ the predicted moduli are 3.44 GPa, 3.97 GPa, 4.86 GPa, 6.66 GPa, and 12.10 GPa for composites with SWNT loadings of 0.2, 0.5, 1, 2, and 5 wt%, respectively. At low SWNT

loading (i.e., 0.2 wt%), experimental results (3.30 and 3.35 GPa for SWNT(0.2 wt%)/PI-GNE/CE and SWNT(0.2 wt%)/PI-BDA/CE composites, respectively) are very close to the predicted modulus (3.44 GPa), suggesting excellent SWNTs dispersion in the case of low nanotube loading. As the SWNT loading increases, the experimental modulus data diverge from the predicted values.

The tensile strength of CE composites reinforced with SWNTs can be predicted by the rule of mixture $\sigma_C = \sigma_f V_f + \sigma_m(1-V_f)$,¹¹¹ where σ_C , σ_f , σ_m are the composite, the nanotube, and the polymer matrix strengths, respectively. V_f is the volume fraction of SWNTs. Using this equation with $\sigma_f = 30.0$ GPa,^{6,283} $\sigma_m = 101.1$ MPa, the tensile strength of CE composites reinforced with SWNTs is calculated to be 148.9 MPa, 220.8 MPa, 340.8 MPa, 581.4 MPa, and 1309.1 MPa for CE composites with SWNT loadings of 0.2, 0.5, 1, 2, and 5 wt%, respectively. My experimental results are lower than the predicted values, and the difference becomes larger as the SWNT loading increases.

Possible reasons for the lower experimental results than theoretical values may include the inevitable nanotube bundling, weaker nanotube/matrix interfacial adhesion achieved by noncovalent functionalization than theoretical value, SWNT-induced impairment of the network of cured CE, some void defects in composites, and so on. I believe that better mechanical improvements can be achieved by optimizing these factors.

5.4 Conclusions

Three kinds of polymer, PI, PI-GNE and PI-BDA, have been successfully synthesized, all of which noncovalently react with SWNTs via π - π interaction. PI-GNE and PI-BDA have similar high efficacy at dispersing SWNTs into

individual tubes in DMF, while PI is less effective. Computer simulations and Raman spectra indicate the presence of π - π interaction between SWNTs and polymeric dispersants. Carbon nanotube-reinforced CE composites were prepared by solution casting method, using SWNTs, PI, PI-GNE and PI-BDA functionalized SWNTs as fillers. SWNTs/PI-BDA better disperse in CE matrix and have stronger interfacial adhesion with CE than do SWNTs, SWNTs/PI and SWNTs/PI-GNE, which is due to the fact that the side chain BDA is more compatible with CE matrix and has stronger covalent bonding with CE. This makes SWNTs/PI-BDA the most effective at improving the mechanical properties of CE matrix. 2 wt% of SWNTs/PI-BDA increased the tensile modulus, strength and toughness of composite by 32%, 47% and 71%, respectively. The experimental modulus and strength were lower than theoretical predicted values, especially at high nanotube loadings, which may be due to inevitable SWNT bundling, relatively weak SWNT-CE interfacial bonding and SWNT-induced impairment of the cured CE network. This study suggests that the side-chain structure of dispersant can greatly affect its ability to disperse SWNTs and to improve SWNT/polymer interfacial strength, both of which are important for effective mechanical reinforcement.

5.5 Declaration

Part of the work presented in this chapter has been published in the *ACS Applied Materials & Interfaces*.

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Chapter 6 A Reactive Polyimide Dispersant for Functionalization of SWNTs via Combination of Covalent and Noncovalent Methods and Its Application in Cyanate Ester Composite

6.1 Introduction

Both covalent and noncovalent functionalization of CNTs have been utilized to achieve good nanotube dispersion and strong nanotube/matrix interfacial adhesion.^{15,91-92} The most widely reported covalent approach is open-end functionalization through oxidant treatment^{95,284-285} to form shortened CNTs bearing carboxylic acid groups, which can be further converted to other functional groups.²⁸⁶⁻²⁸⁷ Another covalent approach is realized through sidewall reactions such as fluorination,⁹⁸ 1,3-dipolar cycloaddition,²⁸⁸ reduction of diazonium salts,²⁸⁹ and direct addition of radicals,⁹⁹ nitrenes¹⁰² and carbenes¹⁰⁰ to the unsaturated π system of nanotubes. The direct sidewall functionalization is less destructive to the nanotube length and the reactions occur on the sidewalls of carbon nanotubes, both of which are favorable to the stress transfer between CNTs and matrix. Although covalent approach improves nanotube dispersion and nanotube/matrix interfacial strength, the covalent bond inevitably disrupts the extended π system of CNTs, resulting in decreases in both mechanical and electrical properties of the CNTs.

Noncovalent functionalization, achieved by physical adsorption/wrapping of surfactants or polymers, has been shown to be highly effective in dispersing and debundling high concentrations of nanotubes in solvents and polymer

matrices without disruption of the intrinsic nanotube structure.^{27-28,146} One major drawback of the noncovalent approach is that the interfacial adhesion between the nanotubes and the dispersant is usually relatively weak.

Considering the advantages and disadvantages of both covalent and noncovalent functionalization, it is reasonable to assume that functionalization of carbon nanotubes by a method that combines covalent and noncovalent approaches should result in the most significant enhancement of the mechanical properties of composites. This method requires a dispersant that not only disperses CNTs by noncovalent interaction but can also be covalently bonded to CNTs by reactions with nanotube sidewalls or with functional groups grafted to the CNT surface. For the latter, it is preferred if the functional groups are introduced by sidewall functionalization rather than acid treatment. So far, there has been no report about functionalization of CNTs using a combination of covalent and noncovalent methods.

In Chapter 4 and 5, I showed that polyimide dispersants can effectively disperse nanotubes but the nanotube/matrix interfacial strength is relatively weak. In this chapter, we have synthesized a reactive polymeric dispersant, PI_{OH}-BDA, and used it to functionalize SWNTs via a method combining covalent and noncovalent approaches for reinforcement of CE matrix (Figure 6.1). Epoxide groups were first grafted onto SWNT sidewalls (Figure 6.2A), which was characterized by Raman, FT-IR and TGA techniques. These epoxidized SWNTs (O-SWNTs) were dispersed by PI_{OH}-BDA, and added into CE to create composites by solution casting. During thermal curing, the phenolic hydroxyl groups in PI_{OH}-BDA backbone react with the epoxide groups on O-SWNTs (Figure 6.2B) to realize the covalent functionalization, while the BDA

Legend:

- Gray rod = p-SWNTs
- Gray rod with red dots = O-SWNTs
- Blue wavy line with yellow dot = PI_{OH}-BDA
- Red wavy line = CE network
- Red dot = Covalent bond between O-SWNTs and PI_{OH}-BDA backbone
- Pink dot = Covalent bond between BDA side-chain and CE

Process steps:

- Epoxidation: p-SWNTs → O-SWNTs
- PI_{OH}-BDA addition and sonication: O-SWNTs + PI_{OH}-BDA → Dispersed intermediate
- CE addition and curing: Dispersed intermediate + CE → Final PI_{OH}-BDA/CE/SWNTs hybrid

(A)

(B)

Where R refers to

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6.2 Experimental section

Materials

SWNTs were used as fillers and CE was used as matrix in this chapter. The details of the SWNTs, CE and other chemicals are described in Section 3.1. PI_{OH}-BDA was synthesized for functionalization of SWNTs. The synthetic protocol is described in Section 3.2.

Preparation of epoxidized SWNTs (O-SWNTs)

As shown in Figure 6.2A, pristine SWNTs (100 mg) were first added into CH₂Cl₂ (50 mL) and the mixture was sonicated in a sonicator bath (60 W, S30H, Elma) at 0 °C for 30 min. Then the reaction was conducted at 50 °C for 48 h while each 12 h a solution of *m*-CPBA (2.88 g, 16.5 mmol) in CH₂Cl₂ (50 mL) was added. After completing the reaction, the suspension was filtered and washed several times with CH₂Cl₂ followed by methanol to remove any residuals. The resultant O-SWNTs powder was dried under vacuum at 60 °C for 12 h.

Fabrication of nanotube/CE composite films

Four types of CE composite films with 1 wt% of SWNTs were fabricated in this study, i.e. composites reinforced with pristine SWNTs (p-SWNTs/CE), epoxidized SWNTs (O-SWNTs/CE), p-SWNTs dispersed with PI_{OH}-BDA (p-SWNTs/PI_{OH}-BDA/CE) and O-SWNTs dispersed with PI_{OH}-BDA (O-SWNTs/PI_{OH}-BDA/CE). A typical route used to fabricate p-SWNT/CE composite films was as follows: p-SWNTs suspension in DMF (1 mg/mL) was first prepared by sonication using a high-power tip sonicator (500 W, 35%, Vibra-Cell Sonics) for 10 min at 0 °C followed by 1 h sonication in a bath

sonicator (60 W , S30H, Elma). Then measured quantity of CE (partially cured at 180 °C for 1 h) solution in DMF (1 g/mL) was added into the nanotube suspension, and the mixture was sonicated in the bath sonicator for 10 min. Composite films were prepared by solution casting of this solution onto clean glass slides. Most of the solvent was removed by warming the slides on a hot plate at ~ 50 °C for 6 h and further drying under vacuum at 80 °C, 100 °C and 120 °C for 2 h each. Finally the composites were thermally treated respectively at 180 °C for 3 h, 200 °C for 2 h and 250 °C for 2 h under air to completely remove the solvent and achieve fully cured composites. O-SWNT/CE composites were prepared by similar procedure by using O-SWNTs instead of p-SWNTs. For fabrication of p-SWNTs/PI_{OH}-BDA/CE composite film, 10 mg of p-SWNTs were dispersed with 10 mg of PI_{OH}-BDA in 10 mL of DMF by sonication. Then measured quantity of CE solution in DMF was added and the mixture was sonicated in the bath sonicator for 10 min. Composite films were fabricated by solution casting followed by thermal curing. O-SWNTs/PI_{OH}-BDA/CE composites were prepared by similar route by using O-SWNTs instead of p-SWNTs.

Characterization of PI_{OH}-BDA, nanotubes and composites

¹H-NMR, FT-IR, GPC, TGA, Raman, UV–vis–NIR, optical microscopy, AFM, TEM, FE-SEM, and tensile testing were used to characterize samples as described in Section 3.3.

6.3 Results and discussion

6.3.1 Synthesis of PI_{OH}-BDA dispersant

In Chapter 4, PI backbone reacted with 2.2 equiv (relatively to the equivalents of polymer repeat units) of GBA to yield a polyimide graft with every pendant –OH group grafted with side-chain. In this chapter, PI backbone reacted with 1.1 equiv of GBA under the same conditions to produce a new polyimide graft, PI_{OH}-BDA, in which 50% of the –OH groups were grafted with side-chains and the other 50% remained assessible. The successful synthesis of PI_{OH}-BDA was confirmed by ¹H-NMR (Figure 6.3). Characteristic peaks of aromatic protons and phenolic –OH groups in polyimide backbone are shown at $\delta=7.1\text{--}8.2$ (b–g) ppm and $\delta=10.2$ (a) ppm, respectively. The two sets of peaks at $\delta=6.7$ (k) and 7.0 (l) ppm are attributed to the aromatic protons of the BDA side-chain. Another three sets of peaks at $\delta=5.8$ (s), 6.1 (q) and 6.2 (r) ppm are assigned to the –OCOCH=CH₂ terminal group. The aliphatic protons of –OCH and –OCH₂ of BDA side-chain appear at $\delta=3.0\text{--}4.5$ (h, i, j, n, o and p) ppm, while that of –CH₃ groups are shown at $\delta=1.5$ (m) ppm. The relative ¹H-NMR integration ratio of –CH₃ peak to phenolic –OH peak is 5.7, indicating that about 50% of the –OH groups remain intact in the PI_{OH}-BDA.

Figure 6.3 ^1H -NMR spectrum of PI_{OH} -BDA.

6.3.2 Preparation of epoxidized SWNTs

The grafting of epoxide groups onto SWNTs using 3-chloroperoxybenzoic acid (*m*-CPBA) was realized via a method reported by Ogrin et al.²⁹⁰ This covalent sidewall functionalization was first studied by Raman spectroscopy (Figure 6.4). The Raman spectra of SWNTs show typical D-band at $\sim 1330\text{ cm}^{-1}$ and G-band at $\sim 1585\text{ cm}^{-1}$. The $I_{\text{D}}/I_{\text{G}}$ ratio of p-SWNTs is about 0.1, while these of O-SWNTs reacted for 12 h, 24 h and 48 h increase to 0.25, 0.4 and 0.58, respectively. The increase of $I_{\text{D}}/I_{\text{G}}$ ratio after epoxidation, resulting from chemical disruption of sp^2 carbons in nanotube walls, implies that epoxide groups were covalently grafted onto the nanotube surface.^{99,290-291} The $I_{\text{D}}/I_{\text{G}}$ ratio increases gradually as the reaction time increases, indicating that more defects were introduced to the nanotube surface. We chose 24 h as the optimal reaction time in order to minimize disruption of the nanotube structure. It is worth noting that our SWNTs are less reactive than the HiPco SWNTs used by

Ogrin et al.²⁹⁰ HiPco SWNTs showed a dramatic increase in the I_D/I_G ratio even when the reaction was conducted at room temperature for 12 h, but our SWNTs showed no obvious increase in the I_D/I_G ratio after reaction at room temperature for 48 h. The higher reactivity of HiPco SWNTs may be due to their smaller diameter (~ 1 nm) and higher curvature.²⁹² For this reason, higher reaction temperature (50 °C) was applied to our SWNTs with larger diameter (1–2 nm).

Figure 6.4 Raman spectra of p-SWNTs and O-SWNTs obtained from different reaction times: 12 h, 24 h and 48 h.

The epoxidation of SWNTs was further confirmed by FT-IR spectra and TGA curves. As compared with the FT-IR spectrum of p-SWNTs (Figure 6.5, spectrum a), O-SWNTs show a new peak at 1210 cm^{-1} (Figure 6.5, spectrum b), which is characteristic of an epoxide moiety.^{290,293} TGA (Figure 6.6) showed that the weight loss of p-SWNTs and O-SWNTs at 800 °C under N_2 atmosphere were 4% and 12%, respectively. Thus the amount of epoxide groups grafted on the nanotube surface was calculated to be about 8%.

Figure 6.5 FT-IR spectra of (a) p-SWNTs and (b) O-SWNTs.

Figure 6.6 TGA curves of p-SWNTs and O-SWNTs.

6.3.3 Comparison of nanotube dispersion in DMF

Figure 6.7 compares the visual observation of the different nanotubes dispersed in DMF: p-SWNTs, O-SWNTs, p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA. Immediately after sonication (Figure 6.7A), black nanotube aggregates can be clearly seen in the p-SWNTs dispersion while the dispersions of O-SWNTs, p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA were homogeneous without any obvious aggregates. After about 1 week (Figure

6.7B), all p-SWNTs settled to the bottom of the vial whereas O-SWNTs only partially settled. Complete sedimentation of O-SWNTs occurred after about 1 month. The better solubility of O-SWNTs than p-SWNTs stems from the interaction between the solvent and the grafted epoxide groups on nanotube surface.²⁰ After functionalization with PI_{OH}-BDA, both p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA dispersions were stable and no precipitates were observed during 3 months of standing. The rigid aromatic backbone has strong affinity to the conjugated graphene surface of nanotubes via π - π interaction, while the pendant side-chain located at the outer surface of nanotubes prevents nanotubes from reaggregation by steric hindrance, leading to long-term stability of the dispersions.

Figure 6.7 Visual observation of (a) p-SWNTs, (b) O-SWNTs, (c) p-SWNTs/PI_{OH}-BDA and (d) O-SWNTs/PI_{OH}-BDA in DMF: (A) immediately after sonication and (B) after standing for 1 week.

A quantitative comparison of the solubility of p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA in DMF was performed by UV-vis-NIR. Nanotube

concentration of a dispersion can be determined from the Beer–Lambert law, $A = \epsilon lc$. The extinction coefficient (ϵ) for our SWNTs was calculated to be 0.0376 L mg⁻¹ cm⁻¹ at 500 nm in DMF (see Chapter 4). p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA dispersions (mass ratio of SWNTs to polymer is 1:1) with initial nanotube concentration of about 20 mg/L were first prepared. After standing for 3 days, centrifugation at 6000 rpm for 1 h and centrifugation at 14 000 rpm for 1 h, the nanotube concentration of p-SWNTs/PI_{OH}-BDA decreased to 19.9, 15.5 and 8.6 mg/L, respectively, which was similar to the results of O-SWNTs/PI_{OH}-BDA (19.8, 15.1 and 8.9 mg/L, respectively) (Figure 6.8), indicating that p-SWNTs and O-SWNTs have similar solubility in DMF when dispersed with PI_{OH}-BDA. This observation suggests that the epoxide groups on O-SWNTs do not affect the exfoliation of nanotubes by adsorption of PI_{OH}-BDA on nanotube surface. In fact, besides the π – π interaction between nanotube and PI_{OH}-BDA backbone, the hydrogen bonding interaction between epoxide groups on nanotubes and phenolic –OH groups on PI_{OH}-BDA also facilitates the adsorption of PI_{OH}-BDA onto O-SWNTs. The good affinity of PI_{OH}-BDA to O-SWNTs was evidenced by TEM. Figure 6.9 shows that there is clearly a layer of amorphous coating with nonuniform thickness on the surface O-SWNTs, which is believed to be the adsorbed PI_{OH}-BDA.^{146,278}

Figure 6.8 SWNT concentrations of p-SWNT/PI_{OH}-BDA and O-SWNT/PI_{OH}-BDA dispersions in different conditions: immediately after sonication, standing for 3 days, centrifugation at 6000 rpm for 1 h and centrifugation at 14 000 rpm for 1 h.

Figure 6.9 High-resolution TEM image of SWNTs/PI_{OH}-BDA.

The dispersion of p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA in DMF was further studied by AFM analysis. Figure 6.10 shows representative AFM images of p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA deposited

onto silicon wafers by spin coating. Both p-SWNTs and O-SWNTs can be dispersed well by PI_{OH}-BDA. The bundle sizes of both nanotubes are in the range of 1–3.5 nm, indicating that they are dispersed as individual tube or small bundles. It is difficult to tell the difference in the nanotube diameter between p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA. The AFM images also show that the lengths of O-SWNTs/PI_{OH}-BDA are similar to these of p-SWNTs/PI_{OH}-BDA, implying that the epoxidation of SWNTs did not shorten the SWNTs. In contrast to acid treated SWNTs, which are usually shortened and carboxyl groups mainly on the nanotube end tips. The long O-SWNTs with functional groups on nanotube sidewalls are believed to be useful for mechanical reinforcement of polymer composite.

Figure 6.10 Typical AFM images of p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA spin-coated on silicon wafers.

6.3.4 Nanotube dispersion and interfacial adhesion in composites

The dispersion state of nanotubes in composite films was initially observed by optical microscopy. In p-SWNT/CE composites, nanotubes aggregated into large clusters with sizes of several tens of micrometres (Figure 6.11A). O-SWNTs also form clusters in the CE matrix, but the cluster sizes are much smaller (Figure 6.11B), indicating improved dispersion uniformity. In contrast, both p-SWNTs/PI_{OH}-BDA (Figure 6.11C) and SWNTs/PI_{OH}-BDA (Figure 6.11D) are dispersed uniformly throughout the matrix and no obvious nanotube aggregates can be observed. These observations are consistent with the dispersibility of these nanotubes in DMF (Figure 6.7).

Figure 6.11 Optical micrographs of (A) p-SWNT/CE, (B) O-SWNT/CE, (C) p-SWNT/PI_{OH}-BDA/CE, and (D) O-SWNT/PI_{OH}-BDA/CE composites with SWNT loading of 1 wt%. Scale bars are 50 μm .

To further evaluate the nanotube dispersion and nanotube/matrix interfacial adhesion in composite films, fracture surfaces of composites were studied with FE-SEM (Figure 6.12). In p-SWNT/CE composites (Figure 6.12A1–A3), severe nanotube aggregation (indicated by circles in Figure

6.12A1) and many pulled-out nanotubes were observed. The latter indicates weak interaction between p-SWNTs and CE matrix. The nanotube dispersion in O-SWNT/CE composites (Figure 6.12B1–B3) is more homogeneous than that in p-SWNTs/CE, but nanotube aggregates with sizes of several hundreds of nanometers still can be clearly seen (Figure 6.12B1, circled). Some small bundles of O-SWNTs show only short tube ends on the surface, which indicates improved nanotube/matrix interfacial adhesion, resulting from covalent interaction between the epoxide groups on O-SWNTs and the –OCN groups in CE.⁴³⁻⁴⁴ The FE-SEM images of both p-SWNT/PI_{OH}-BDA/CE (Figure 6.12C1–C3) and O-SWNT/PI_{OH}-BDA/CE (Figure 6.12D1–D3) composites show homogeneously dispersed SWNTs. However, the pull-out length of nanotubes in O-SWNTs/PI_{OH}-BDA/CE is obviously shorter than that in p-SWNTs/PI_{OH}-BDA/CE, indicating better interfacial adhesion in O-SWNT/PI_{OH}-BDA/CE composites than in p-SWNT/PI_{OH}-BDA/CE composites.

The strong interfacial adhesion in O-SWNT/PI_{OH}-BDA/CE composites can be attributed to three effects: i) π – π interaction between PI_{OH}-BDA backbone and conjugated nanotube surface; ii) formation of covalent bonds between epoxide groups on O-SWNTs and phenolic hydroxyl groups in the backbone of PI_{OH}-BDA (Figure 6.2B); and iii) chemical reaction between the side-chain of PI_{OH}-BDA and CE matrix. The π – π interaction and the reaction between PI_{OH}-BDA side-chain and CE matrix have been proved in Chapter 4 and 5. The reaction between O-SWNTs and phenolic hydroxyl groups has been recently confirmed with FT-IR spectra by Cheng et al.²⁹³

Figure 6.12 FE-SEM images of fracture surfaces of (A1–A3) p-SWNT/CE, (B1–B3) O-SWNT/CE, (C1–C3) p-SWNT/PI_{OH}-BDA/CE, and (D1–D3) O-SWNT/PI_{OH}-BDA/CE composites. Nanotube content is 1 wt%.

6.3.5 Mechanical properties of O-SWNT/PI_{OH}-BDA/CE composites

Table 6.1 lists the Young's modulus (E), tensile strength (σ), elongation at break (ϵ) and toughness (T , calculated from the area under the stress-strain curve) of neat CE and CE composites reinforced with 1 wt% of p-SWNTs, O-SWNTs, p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA. Figure 6.13 shows

their representative stress-strain curves. The E , σ , ε and T of neat CE are 3.08 ± 0.14 GPa, 101.1 ± 6.0 MPa, 4.0 ± 0.3 % and 2.1 ± 0.2 MJ m⁻³, respectively, which are consistent with reported values.³⁴ Both p-SWNTs and O-SWNTs lead to a slight increase in E but decreases in σ , ε and T . 1 wt% of p-SWNTs increases the E , σ , ε and T by 6% (to 3.25 ± 0.11 GPa), -35% (to 66.2 ± 7.4 MPa), -35% (to 2.6 ± 0.5 %) and -57% (to 0.9 ± 0.3 MJ m⁻³) compared to the neat CE. The corresponding increases of O-SWNT/CE composite are 8% (to 3.31 ± 0.13 GPa), -10% (to 90.7 ± 5.3 MPa), -23% (to 3.1 ± 0.3 %) and -29% (to 1.5 ± 0.2 MJ m⁻³), respectively. The poor reinforcement effect of p-SWNTs and O-SWNTs is due to their nonuniform dispersion in CE matrix. The higher reinforcing efficiency of O-SWNTs compared to p-SWNTs results from their better dispersion in the matrix and more efficient stress transfer at interface, as discussed previously. Both p-SWNTs/PI_{OH}-BDA and O-SWNTs/PI_{OH}-BDA can improve the tensile properties of composites, but O-SWNTs/PI_{OH}-BDA is much more effective. The E , σ , ε and T of p-SWNTs/PI_{OH}-BDA/CE composites increase to 3.83 ± 0.09 GPa, 132.6 ± 7.2 MPa, 5.0 ± 0.3 % and 3.8 ± 0.3 MJ m⁻³ respectively, which are 24%, 31%, 25% and 81% increases over that of neat CE. The corresponding values of O-SWNTs/PI_{OH}-BDA/CE composites are 4.83 ± 0.15 GPa, 173.3 ± 8.9 MPa, 4.7 ± 0.4 % and 4.7 ± 0.4 MJ m⁻³, respectively, corresponding to increases of 57%, 71%, 18% and 124% over neat CE. The elongation at break of O-SWNTs/PI_{OH}-BDA/CE is lower than that of p-SWNTs/PI_{OH}-BDA/CE composite, because the covalent bonds did reduce pull-out length of broken nanotubes (as observed in Figure 6.12) and restrict the nanotube network deformation during loading.²⁹³

Table 6.1 Mechanical properties (E , σ , ε and T) of neat CE and its composites with 1 wt% of nanotubes.

Sample	E (GPa)	σ (MPa)	ε (%)	T^a (MJ m ⁻³)
Neat CE	3.08 ± 0.14	101.1 ± 6.0	4.0 ± 0.3	2.1 ± 0.2
p-SWNTs/CE	3.25 ± 0.11 (6%) ^b	66.2 ± 7.4 (-35%)	2.6 ± 0.5 (-35%)	0.9 ± 0.3 (-57%)
O-SWNTs/CE	3.31 ± 0.13 (8%)	90.7 ± 5.3 (-10%)	3.1 ± 0.3 (-23%)	1.5 ± 0.2 (-29%)
p-SWNTs/PI _{OH} -BDA/CE	3.83 ± 0.09 (24%)	132.6 ± 7.2 (31%)	5.0 ± 0.3 (25%)	3.8 ± 0.3 (81%)
O-SWNTs/ PI _{OH} -BDA /CE	4.83 ± 0.15 (57%)	173.3 ± 8.9 (71%)	4.7 ± 0.4 (18%)	4.7 ± 0.4 (124%)

^a Calculated from the area under the stress-strain curve.

^b The values in brackets are increases of composite tensile properties over CE.

Figure 6.13 Representative stress-strain curves of neat CE and p-SWNT/CE, O-SWNT/CE, p-SWNT/PI_{OH}-BDA/CE and O-SWNT/PI_{OH}-BDA/CE composites with nanotube loading of 1 wt%.

It is quite attractive that 1 wt% of O-SWNTs/PI_{OH}-BDA can enhance the toughness of CE by 124%. As discussed previously, the brittleness of CEs often restricts their applications as structural materials. Our O-SWNT/PI_{OH}-BDA/CE composites with significantly improved toughness are believed to have wider applications as structural materials in industries. The enhancement of tensile modulus and strength of O-SWNT/PI_{OH}-BDA/CE composites is also significant when compared to other CNTs reinforced thermosetting resins.^{20,24,26,170-171} For example, epoxy composites reinforced with 1 wt% of fluorinated SWNTs²⁰ or 1 wt% of dendrimer-functionalized SWNTs¹⁷⁰ showed less than 31% increases in both tensile modulus and strength. To quantitatively evaluate the reinforcement effect of SWNTs, the dE/dW_{NT} and $d\sigma/dW_{NT}$ were calculated.^{26,205} The dE/dW_{NT} and $d\sigma/dW_{NT}$ of O-SWNT/PI_{OH}-BDA/CE composites reach to 175 GPa and 7220 MPa, respectively, which are more than two times as high as the values of p-SWNT/PI_{OH}-BDA/CE composites ($dE/dW_{NT} = 75$ GPa and $d\sigma/dW_{NT} = 3150$ MPa), indicating much better reinforcing ability of O-SWNTs/PI_{OH}-BDA than p-SWNTs/PI_{OH}-BDA to CE. Furthermore, the mechanical improvement of O-SWNT/PI_{OH}-BDA/CE composites also compared favorably with the results of other CNT/thermosetting composites that have been reported recently, which showed dE/dW_{NT} of 22–70 GPa and $d\sigma/dW_{NT}$ of 140–3540 MPa (see Table 4.2 in Chapter 4).

For the pronounced mechanical reinforcement in the O-SWNTs/PI_{OH}-BDA/CE, it can be attributed to the homogeneous nanotube dispersion in matrix and strong chemical bonding at nanotube/matrix interface, which are achieved via the method that combines covalent and noncovalent functionalization. As shown in Figure 6.1, PI_{OH}-BDA adsorbs onto O-SWNT

surface via π - π interaction to disperse SWNTs into individual tubes or small bundles. The phenolic hydroxyl groups in the PI_{OH}-BDA backbone react with the O-SWNTs while the BDA side-chains react with the CE matrix during thermal curing, leading to strong interfacial strength. As a result, PI_{OH}-BDA, acting as both a nanotube dispersant and a bonding agent between nanotubes and CE matrix, can effectively improve the tensile properties of composites. As discussed previously, the nanotube dispersion in p-SWNTs/PI_{OH}-BDA/CE and O-SWNTs/PI_{OH}-BDA/CE composites is quite similar (Figure 6.11 and Figure 6.12). So the lower reinforcement effect of p-SWNTs/PI_{OH}-BDA to CE matrix is obviously due to the weaker strength at the interface, which involves only noncovalent π - π interaction between PI_{OH}-BDA backbone and nanotube surface.

6.4 Conclusions

In this chapter, a carbon nanotube functionalization method that combines covalent and noncovalent approaches for reinforcement of CE matrix has been developed. SWNTs were sidewall functionalized with epoxide groups and then these epoxidized SWNTs (O-SWNTs) were dispersed by PI_{OH}-BDA dispersant. O-SWNTs/PI_{OH}-BDA were added into CE resin to prepare composite films by solution casting followed by thermal curing. The phenolic hydroxyl groups in the backbone of PI_{OH}-BDA react with epoxide groups on O-SWNTs while the BDA side-chains react with CE matrix, leading to strong nanotube/matrix interfacial strength, as evidenced by FE-SEM images. Good dispersion of O-SWNTs/PI_{OH}-BDA in CE was confirmed by optical microscopy and FE-SEM images. The incorporation of 1 wt% of O-SWNTs/PI_{OH}-BDA into CE increased

the Young's modulus, tensile strength and toughness by 57%, 71% and 124%, respectively. These values are much higher than these of control samples: CE composites reinforced with p-SWNTs (6%, -35% and -57%), O-SWNTs (8%, -10% and -29%) or p-SWNTs/PI_{OH}-BDA (24%, 31% and 81%). This study suggests that functionalization of nanotube by a combination of covalent and noncovalent approaches is able to effectively improve both nanotube dispersion and nanotube/matrix interfacial strength and thus lead to high reinforcement in polymer composites.

6.5 Declaration

Part of the work presented in this chapter has been published in the *ACS Applied Materials & Interfaces*.

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Chapter 7 A Novel Polyimide Dispersant cum Matrix for Highly Electrically Conductive and Mechanically Strong MWNT/Polyimide Composite

7.1 Introduction

Due to their excellent electrical conductivity (10^3 – 10^6 S cm⁻¹), ultra-high strength (~ 30 GPa), large aspect ratio and low density, CNTs are thought to be an excellent additive for making electrically conductive and mechanically strong polymer composites.^{15,24} Many studies on increasing the electrical conductivity of CNT/polymer composites have been published.^{136,227,229,294-295} However, with traditional processing techniques such as casting, resin transfer molding, etc., the electrical conductivity achieved with CNT loading has generally been modest. Few studies^{83,294} have reported composites with electrical conductivities higher than 1 S cm⁻¹. Ramasubramaniam et al. reported a conductivity of 4.81 S cm⁻¹ with polycarbonate²⁹⁴ and Grossiord et al. reported a conductivity of 10 S cm⁻¹ with vertically-aligned nanotubes.⁸³ However, the mechanical properties of the composites were not reported in these two studies. In fact, CNT reinforced composites often show decreases of mechanical properties at relatively low content of nanotubes (1–5 wt%), which may be due to poor nanotube dispersion.

Polyimides (PIs) are an important class of structural polymers that are widely used in the defense and aerospace industries because of their outstanding mechanical properties and thermal stability. The electrical

conductivities achieved in polyimide/CNT composites have typically been low. Jiang et al.¹⁶⁸ reported a conductivity of about 10^{-1} S cm⁻¹ for nanotube/polyimide composite with 5 wt% nanotubes. Further improvement in electrical conductivity in solution-processed polyimide/CNT composites, like most other similarly processed composites, has been hampered by low CNT content (10 wt% or less)^{29,168,199,241,252,296} and poor dispersion of the CNTs. It has generally been thought that highly electrically conductive composites can be achieved if the CNT content is high and the CNTs are well distributed within the matrix, so that they form a percolation network. To debundle and disperse the CNTs as individual tubes, covalent and noncovalent approaches can be however, noncovalent functionalization is preferable as it preserves the graphene structure of the nanotubes and, consequently, their intrinsic electrical and mechanical properties.

My previous work (see Chapter 4, 5 and 6) and other researcher studies have explored polymers as noncovalent dispersants of CNTs.^{120,138,141} However, most work on CNT composites has utilized a polymeric dispersant that is distinct from the matrix.^{27,87,146,294} This approach tends to limit the CNT loading in the matrix to low content (e.g., 5 wt%) since at high CNT loading and therefore polymeric dispersant loading, incompatibility between the dispersant and matrix promotes CNTs aggregation, particularly during removal of the solvent used to dissolve the matrix and the dispersed CNTs. I hypothesize that the use of a single polymer which can serve as both nanotube dispersant and matrix (or matrix precursor) is a more effective way to achieve composites with high CNT content. The polymer must be able to disperse the CNTs and also provide the desired properties of the matrix. This method should yield the best

possible compatibility between the CNTs and the polymer matrix, and so would prevent CNT aggregation during the processing of high nanotube content composites.

In this chapter, a high nanotube content MWNT/polyimide composite film was prepared by solution-casting with excellent conductivity and high mechanical properties. A novel poly(amic acid) (PAA), was designed and synthesized to act as both the MWNT dispersant and matrix precursor. Solution-cast and thermally imidized MWNT/PI composite film with 30 wt% nanotubes has an electrical conductivity of 38.8 S cm^{-1} (compared to $3.5 \times 10^{-16} \text{ S cm}^{-1}$ for the neat polyimide). This composite has a Young's modulus of $9.43 \pm 0.14 \text{ GPa}$ and a tensile strength of $179.2 \pm 9.7 \text{ MPa}$, both of which are higher than other reported values for polyimide. Uniform MWNT(30 wt%)/PI composite coatings were also successfully deposited on glass and aluminum substrates.

7.2 Experimental section

Material

MWNTs were used as fillers in this chapter. The details of MWNTs and other chemicals are shown in Section 3.1. PAA was synthesized by the method described in Section 3.2.

Fabrication of MWNT/PI composite films

A measured quantity of MWNTs was added into DMAc (the concentration of MWNTs in DMAc was fixed at 1 mg/mL), and the mixture was sonicated with a high-power tip sonicator (500 W, 35%, Vibra-CellTM Sonics) for 5 min. Then different quantities of PAA solution were mixed with the MWNT/DMAc

suspension and sonicated with the tip sonicator for another 5 min followed by further sonication in a low-power sonication bath (S30H, Elma) for 30 min at 0 °C. MWNT/PAA dispersions with less than 10 wt% MWNTs were directly cast into films. High nanotube content (10–30 wt%) MWNT/PAA dispersions were prepared with a large amount of DMAc, some of which was slowly evaporated in a glass dish before film casting. The MWNT/PAA dispersions were cast onto glass slides which were heated on a hot plate at 50 °C. After removal of most of the DMAc, the glass slides were transferred to a vacuum oven and dried at 80 °C under vacuum for 3 h to remove residual solvent. Finally, the as-prepared MWNT/PAA films were imidized under argon at 100 °C for 2 h, 200 °C for 1 h, 300 °C for 1 h and 350 °C for 20 min. The thickness of the resulting films was measured to be $15 \pm 1 \mu\text{m}$.

Fabrication of MWNT/PI composite coatings

Ultra-thin MWNT/PAA coatings on the glass and aluminum substrates were fabricated from MWNT(30 wt%)/PAA dispersion (nanotube concentration of 0.1 mg/mL) using an air brush (Badger, model 100LG). During the spray process, the substrates were kept on a hot plate at about 170 °C in order to accelerate the evaporation of DMAc. The nozzle was kept 20–30 cm from the substrates, and the dispersion was sprayed, one spray of the dispersion at a time, onto the substrates. Thick MWNT(30 wt%)/PAA coating on aluminum was prepared by solution casting. MWNT/PI coatings were obtained after thermal imidization.

Characterization of MWNT dispersion and composite properties

¹H-NMR, FT-IR, GPC, TGA, Raman, UV–vis–NIR, optical microscopy, AFM, TEM, FE-SEM, tensile testing, and electrical conductivity measurement were used for characterizing samples, as described in Section 3.3.

7.3 Results and discussion

7.3.1 Design and synthesis of PAA

The PAA (Figure 7.1A) was synthesized from 3, 3'-dihydroxy-4, 4'-diaminobiphenyl (HAB) and 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA) using stoichiometric amounts of these in order to achieve the highest molecular weight possible. Higher molecular weight enables more contact points between the polymer molecules and CNTs so as to increase the CNT dispersion efficacy.^{139,277} The biphenyl diamine and dianhydride polymerise to a rigid and unbent PAA backbone, which facilitates the stacking of the dispersant molecules onto the conjugated MWNT surface via π – π interaction,¹¹⁹ so as to promote PAA adsorption and produce a relatively strong bonds between the dispersant and the MWNTs. The pendent –OH and –COOH groups provide the functionalized MWNTs with good solubility in organic solvents and polymer matrix precursor.

The ¹H-NMR spectrum of PAA in *d*₆-DMSO (Figure 7.1B) confirms its successful synthesis of PAA with the characteristic aromatic proton peaks at δ =7.1–7.2 ppm (b and c) and 7.8–8.3 ppm (d, f, g and h), the phenolic –OH and –NH protons peaks at δ =9.7–9.9 ppm (a and e) and the –COOH proton peak at δ =13.0 ppm (i). Interaction with the nanotube π cloud is known to cause ¹H-NMR signal broadening.^{120,146,297} Such broadening is evident in the MWNTs/PAA (mass ratio 1:2) spectrum (Figure 7.1B).

Figure 7.1 A) Synthesis of poly(amic acid) (PAA) and the strategy for fabricating MWNT/polyimide composites. B) ^1H -NMR spectra of PAA and MWNTs/PAA (mass ratio 1:2) in d_6 -DMSO.

To investigate the strong interaction between MWNTs and PAA, PAA-dispersed MWNT dispersion was filtered and washed with a large quantity of DMAc to remove any free or weakly adsorbed PAA. Then the solid (denoted as MWNT/PAA complex) was collected and dried before FT-IR and TGA characterization. Figure 7.2A shows the FT-IR spectra of MWNTs, PAA and

MWNT/PAA complex. The characteristic absorption features of PAA (1738 cm^{-1} for C=O(OH) stretching, 1644 cm^{-1} for C=O(NH) stretching, 1500 cm^{-1} for phenyl ring C–C stretching, and 1240 cm^{-1} for C–O stretching) still appear in the MWNT/PAA complex after washing, indicating that the interaction between PAA and MWNTs is so strong that not all PAA can be washed away by DMAc, which is a good solvent for PAA. The percentage of PAA still strongly adsorbed on MWNT surface was calculated to be about 23% from TGA (in N_2 atmosphere) of MWNTs, PAA and MWNT/PAA complex (Figure 7.2B).

Figure 7.2 A) FT-IR spectra and B) TGA of (a) MWNTs, (b) PAA and (c) MWNT/PAA complex.

7.3.2 Dispersion of MWNTs/PAA in DMAc

When pristine MWNTs are dispersed in DMAc and left to stand for one week, the MWNTs mostly settle to the bottom of the vial (Figure 7.3, vial a). The addition of PAA (Figure 7.3, vial b) results in homogeneous dispersions of MWNTs/PAA without visible aggregates anywhere in the vial even after several months of standing (Figure 7.3, vial c and d). The maximum MWNT concentration that can be dispersed with PAA was about 2.8 mg/mL , which is

comparable to the highest reported values with other dispersants (2.5–3 mg/mL).^{139,146}

Figure 7.3 Photographs of (a) pristine MWNTs, (b) PAA solution, (c and d) PAA functionalized MWNT dispersions, (e and f) MWNT/PI composite films with nanotube loadings of (e) 0.25 wt% and (f) 30 wt%, and (g and h) MWNT/PI coatings on (g) glass and (h) aluminum substrates.

The efficacy of PAA at dispersing MWNTs in DMAc was quantitatively evaluated and compared with that of polyvinylpyrrolidone (PVP), a commercially available dispersant for nanotubes,²⁵³ through absorbance measurements evaluated using the Beer–Lambert law ($A = \epsilon lc$).²⁷⁷ To determine the value of extinction coefficient (ϵ), absorbance spectra of very dilute and well-dispersed MWNT/PAA (mass ratio 1:2) dispersions at different concentrations were characterized (Figure 7.4A) and the absorbance at 500 nm was plotted against nanotube concentrations (inset in Figure 7.4A). The linear-least-squares fit to the data gave a slope of 0.04704, so the the extinction coefficient was calculated to be $0.04704 \text{ L mg}^{-1} \text{ cm}^{-1}$, which is in agreement with those found at 500 nm for MWNTs in chloroform ($0.04220 \text{ L mg}^{-1} \text{ cm}^{-1}$)²⁷⁷ and *o*-dichlorobenzene ($0.04600 \text{ L mg}^{-1} \text{ cm}^{-1}$).²⁹⁸ The nanotube concentrations of MWNTs/PAA (mass ratio 1:2) and MWNTs/PVP (mass ratio 1:2) in different conditions, determined using absorbance at 500 nm, are shown

in Figure 7.4B. Immediately after sonication, both MWNTs/PAA and MWNTs/PVP have nanotube concentrations of about 20.0 mg/L. After standing for 3 days, centrifugation at 6000 rpm for 1 h and centrifugation at 14000 rpm for 1 h, the nanotube concentration of MWNTs/PAA decreases to 19.3, 10.8 and 5.5 mg/L respectively, which is higher than that of MWNTs/PVP (17.5, 7.2 and 3.2 mg/L, respectively), suggesting higher efficacy of PAA over PVP to disperse MWNTs in DMAc.

Figure 7.4 A) Absorption spectra of MWNTs/PAA (mass ratio 1:2) in DMAc for different nanotube concentrations. Inset shows absorbance at 500 nm of these dispersions. The straight line is a linear-least-squares fit to the data. B) MWNT concentrations of MWNTs/PAA (mass ratio 1:2) and MWNTs/PVP (mass ratio 1:2) in different conditions: immediately after sonication; after standing for 3 days; after centrifugation at 6000 rpm for 1 h and after centrifugation at 14000 rpm for 1 h.

TEM images further prove the high efficacy of PAA at dispersing MWNTs (Figure 7.5). Pristine MWNTs, used as controls, form large aggregates (Figure 7.5A1 and A2) while the majority of the PAA-dispersed MWNTs are observed as individual nanotubes (Figure 7.5B1 and B2). At the higher magnification, the pristine MWNT surface is quite clean (Figure 7.5A3) while there is a layer of amorphous coating in MWNTs/PAA (Figure 7.5B3). The

feature of Figure 7.5B3 can be interpreted to be a layer of PAA self-assembled onto the nanotube surface which contributes to long-term stability and individually dispersed MWNTs.

Figure 7.5 TEM images of (A1–A3) pristine MWNTs and (B1–B3) PAA-functionalized MWNTs.

The capability of PAA to disperse MWNTs into individual nanotubes was also manifested by AFM images (Figure 7.6). Pristine MWNTs forms large agglomerates (Figure 7.6A). Most of the PAA-dispersed MWNTs (Figure 7.6B) have length exceeding 1 μm , indicating that noncovalent functionalization of MWNTs with PAA does not significantly reduce the nanotube length. The measured height of the PAA-dispersed MWNTs is about 5–14 nm, suggesting that the MWNTs are dispersed as individual tubes. We attribute the high efficacy of PAA at dispersing MWNTs to its unique structure. The rigid unbent highly aromatic backbone of PAA has strong affinity via π – π interaction to the highly conjugated graphene-like surface of nanotubes while the pendent

–COOH and –OH groups provide MWNTs with solubility and keep them from re-aggregation.

Figure 7.6 AFM images of (A) pristine MWNTs and (B) PAA-functionalized MWNTs deposited on silicon wafers by spin coating.

7.3.3 MWNT dispersion and adhesion to PI in composites

Figure 7.3 e and f show representative photographs of composite films containing 0.25 wt% and 30 wt% MWNTs. The composite with 0.25 wt% MWNTs possesses good transparency and uniformity, while the composite with 30 wt% of MWNTs is completely opaque. Even at 200 $\times$ magnification, no visible aggregates were observed in the MWNT/PI composite films, indicating homogeneous MWNT dispersion (Figure 7.7).

Figure 7.7 Optical micrographs of MWNT/PI composite films with MWNT loadings of (A) 0.5 wt% and (B) 0.75 wt%. The scale bar is 50 μm .

To further examine the nanotube dispersion in composite film, a MWNT(1 wt%)/PAA film without thermal imidization was redispersed in DMAc with only mild shaking. This dispersion was then filtered through a 0.2- μm Al_2O_3 membrane and washed with a large quantity of DMAc to remove free polymer. FE-SEM images of the MWNTs on the Al_2O_3 membrane (Figure 7.8) show that the MWNTs, without significant reduction in length, are distributed homogeneously on the membrane and no aggregates can be observed. The diameter of MWNTs, which were coated with a gold layer before FE-SEM observation, is about 14–20 nm. This value is only 4–5 nm higher than that of pristine MWNTs (10–15 nm), suggesting that MWNTs in Figure 7.8 were dispersed individually. We confirmed that MWNTs can not be dispersed by PAA with only mild shaking (data not shown), so Figure 7.8 exhibits the nanotube dispersion state in composite film. The nanotube morphology in Figure 7.8 suggests that MWNTs generated a conductive network for electron transport, leading to high electrical conductivity for the final MWNT/PI composite film, which will be discussed below.

Figure 7.8 FE-SEM images of MWNTs in (A and B) MWNT(1 wt%)/PAA composite film on 0.2- μm Al_2O_3 filter membranes after removal of free polymer. (B) is enlarged image of selected region in (A).

To investigate the dispersion and morphology of nanotubes in fully imidized MWNT/PI composites, composite films were dipped into liquid nitrogen and then freeze fractured. Figure 7.9 shows the FE-SEM images of the cryo-fractured surfaces of composites with nanotube contents of 1, 10 and 30 wt%. For all the three loadings, nanotubes are dispersed homogeneously throughout the surfaces without any obvious aggregates (Figure 7.9A–F). With 1 wt% MWNTs (Figure 7.9A and B), MWNTs are broken on the surface (indicated by arrows), suggesting strong polymer-nanotube interfacial adhesion. The diameter of the MWNTs in Figure 7.9B (about 40–60 nm) is much larger than that in MWNT(1 wt%)/PAA composite after removal of polymer (about 14–20 nm, Figure 7.8B), suggesting a thick polymer coating on the nanotube.^{21,299} The FE-SEM images of MWNTs(10 wt%)/PI (Figure 7.9C and D) reveal more MWNTs on the surface compared with the MWNT(1 wt%)/PI sample. Some MWNTs are partially pulled out from the surface, but most MWNTs are broken on the surface and well-wetted by PI matrix which is again reflected in the large diameter of the polymer-clad nanotubes (Figure 7.9D). As

the MWNT content increases to 30 wt% (Figure 7.9E and F), there are more MWNTs “competing” for the matrix, leading to less polymer coating on MWNT surface as reflected in the reduced diameters of the polymer-coated MWNTs (about 18–33 nm) and consequently, more pulled-out MWNTs.

Figure 7.9 FE-SEM images of cryo-fractured surfaces of MWNT/PI composite films with MWNT loadings of (A and B) 1 wt%, (C and D) 10 wt% and (E and F) 30 wt%.

It has been shown that the wrapping of polymer around nanotubes can result in a shift toward higher frequencies of the G-band,^{28,146} due to charge transfer from the CNTs to the polymer dispersant.³⁰⁰ Figure 7.10 shows the Raman spectra of pristine MWNTs and MWNT/PI composites with a nanotube content of 30 wt%, 20 wt%, 10 wt% and 5 wt%. The D-band and the G-band of

MWNTs are located at $\sim 1335\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$, respectively. The G-band of pristine MWNTs is at 1596 cm^{-1} (spectrum a) while that of MWNT/PI composites with MWNT content of 10–30 wt% are at about 1611 cm^{-1} (spectra b–d). The observed 15 cm^{-1} Raman up-shift in MWNT/PI composites confirms the presence of strong π – π interaction between PI and MWNTs. Moreover, the Raman peaks become less distinct as the MWNT content in composites decreases from 30 wt% to 10 wt%. In MWNT/PI composites with nanotube loading of 0.25–5 wt%, the Raman spectra features are overwhelmed by the strong broad luminescence background and the characteristic peaks of MWNTs are undetectable (here we show only the spectrum of 5 wt% MWNT sample, spectrum e), which has also been observed in other functionalized CNTs.³⁰¹⁻³⁰² It has been suggested that a better nanotube dispersion enhances the luminescence, leading to more significant interference in Raman measurements.³⁰³ Thus, our observations suggest good nanotube dispersion.

Figure 7.10 Raman spectra of (a) pristine MWNTs, and MWNT/PI composites with MWNT loadings of (b) 30 wt%, (c) 20 wt%, (d) 10 wt% and (e) 5 wt%.

7.3.4 Electrical conductivity of MWNT/PI composites

Figure 7.11 and Table 7.1 show the DC conductivity of MWNT/PI composites as a function of MWNT loading. The conductivity of neat PI is $3.5 \times 10^{-16} \text{ S cm}^{-1}$ and no obvious increase is observed in composites with 0.25 wt% of MWNTs. When the nanotube loading increases to 0.5 wt%, the conductivity exhibits a sharp increase of about 8 orders of magnitude from 6.8×10^{-16} to $8.3 \times 10^{-8} \text{ S cm}^{-1}$, which indicates the formation of a continuous conductive network. Percolation theory predicts that the composite conductivity versus nanotube volume fraction obeys the power law²³¹

$$\sigma \propto (\nu - \nu_c)^t, \quad \text{for } \nu > \nu_c$$

where σ is composite conductivity, ν is nanotube volume fraction, ν_c is percolation threshold, and t is the critical exponent. The best fit of our experimental electrical conductivity data to the above equation gives $\nu_c = 0.31$ vol% (i.e. 0.48 wt%) and $t = 2.8$ with a correlation coefficient of 0.9954, as shown in the plot of $\log(\sigma)$ versus $\log(\nu - \nu_c)$ in the inset in Figure 7.11.

Figure 7.11 Log DC conductivity as a function of MWNT mass fraction for MWNT/PI composites. The inset shows the best-fit to the conductivity data using the equation described in the text for the determination of percolation threshold.

Our percolation threshold, 0.48 wt%, is much lower than most reported values for CNT/polyimide composites (> 1 wt%).^{29,199,241,252,304-305} Most reported CNT/PI composites contain acid oxidized CNTs, which reduces CNT intrinsic electrical conductivity due to the introduction of structural defects. Further, decreased nanotube length and aspect ratio of acid-treated CNTs lead to a higher CNT fraction needed to form a continuous charge carrier channel in composites. As a result, relatively high percolation thresholds were observed in these studies. In my method, the designed PAA molecular chains are adsorbed onto the MWNT surface to disperse nanotube bundles into individuals without any substantial damage to the MWNT length and structure. The original aspect ratio and intrinsic electrical properties of the MWNTs are better preserved. Compared to other reported methods, the MWNTs in my research are better suited to form a conducting interconnected nanotube network in the polymer matrix.

Moreover, the absolute conductivities of our MWNT/PI composites are much higher than reported values of CNT/PI composites with the same nanotube loading. For example, for nanotube/polyimide composites with 5 wt% nanotubes, reported conductivities are in the range of 10^{-9} – 10^{-4} S cm⁻¹^{129,199,241,252,304-305} which is about 3–8 orders of magnitude lower than our value (0.27 S cm⁻¹). Our conductivity reaches 13.3 S cm⁻¹ at 20 wt% MWNT loading and 38.8 S cm⁻¹ at 30 wt% MWNT loading, about 17 orders of magnitude higher than that of neat PI. These values are the highest values yet reported for CNT/PI composites.^{199,252,305} The electrical conductivity of the composite with 30 wt% of MWNTs (38.8 S cm⁻¹), to the best of our knowledge, is the highest value ever reported for a solution-processed nanotube composite. At a loading

of 0.75 wt%, the conductivity reaches $7.2 \times 10^{-5} \text{ S cm}^{-1}$, which satisfies the requirements of electrostatic dissipation applications ($10^{-5} \text{ S cm}^{-1}$). The conductivity of the composite with 5 wt% MWNTs (0.27 S cm^{-1}) is adequate for electromagnetic interference (EMI) shielding applications (0.1 S cm^{-1}).

7.3.5 Mechanical properties of MWNT/PI composites

The tensile properties of neat PI and MWNT/PI composites are summarized in Table 7.1 and Figure 7.12. Figure 7.12A presents representative stress-strain curves. For neat PI films, the tensile modulus and strength are $6.37 \pm 0.13 \text{ GPa}$ and $151.2 \pm 5.1 \text{ MPa}$, respectively. The reported tensile values of polyimide vary widely since they depend on the diamine and dianhydride used. The modulus and strength obtained in this study are at the higher end of the published range due to the rigid monomers employed.^{199,252,306} As shown in Figure 7.12B and C, increase in MWNT loading from 0 to 10 wt% leads to a continuous increase of both tensile modulus and strength. Further increase in MWNT loading to 20 wt% and 30 wt% results in a decrease of the tensile properties. This may be due to the reduced distance between nanotubes (Figure 7.9F), which would cause highly intensified stress field between the closely spaced nanotubes³⁰⁷ and increased free volume.²⁶⁵ However, the MWNT(30 wt%)/PI composite still has better tensile properties (with modulus of $9.43 \pm 0.14 \text{ GPa}$ and strength of $179.2 \pm 9.7 \text{ MPa}$) compared to the unreinforced matrix. Figure 7.12B and C also show a comparison of the tensile properties with the values recently reported for CNT/PI composites.^{29,199,241,252,296,304-305} The absolute tensile values at all nanotube loadings (6–10 GPa and 151–228

MPa) are higher than the values reported for other CNT/PI composites, which are in the range of 3–5 GPa and 100–130 MPa, respectively.

Table 7.1 Tensile properties (modulus, strength and elongation at break) and electrical conductivity of neat PI and MWNT/PI composites.

CNT loading (wt%)	CNT loading (vol%)	Modulus (GPa)	Strength (MPa)	Elongation (%)	Conductivity (S cm ⁻¹)
0	0	6.37 ± 0.13	151.2 ± 5.1	4.5 ± 0.2	3.5×10 ⁻¹⁶
0.25	0.16	7.30 ± 0.09	175.0 ± 6.3	6.2 ± 0.3	6.8×10 ⁻¹⁶
0.5	0.33	7.68 ± 0.12	188.1 ± 3.4	5.9 ± 0.4	8.3×10 ⁻⁸
0.75	0.49	8.15 ± 0.09	193.6 ± 6.5	5.6 ± 0.2	7.2×10 ⁻⁵
1	0.65	8.47 ± 0.17	206.7 ± 6.8	5.4 ± 0.3	5.6×10 ⁻⁴
2	1.31	8.88 ± 0.11	215.4 ± 5.2	5.0 ± 0.3	1.8×10 ⁻²
5	3.31	9.21 ± 0.07	221.3 ± 6.3	4.4 ± 0.3	0.27
10	6.75	9.55 ± 0.12	228.4 ± 5.2	4.1 ± 0.2	3.5
20	14.00	9.97 ± 0.13	206.6 ± 4.0	3.2 ± 0.1	13.3
30	21.82	9.43 ± 0.14	179.2 ± 9.7	2.5 ± 0.3	38.8

Figure 7.12 A) Representative stress-strain curves of neat PI and MWNT/PI composites with MWNT loadings of 0.5, 2, 10, and 20 wt%. Comparison of B) Young's modulus and C) tensile strength of composites prepared in this study with published values for other CNT/PI composites. The tensile data for other CNT/PI composites were reprinted with permission from these references.

We believe that the excellent electrical conductivity and mechanical properties achieved in this study can be attributed to the good nanotube dispersion efficacy of the designed PAA, which functions both as the polymer matrix precursor and as the nanotube dispersant. The PAA has a good affinity for the nanotubes and also good solubility in the solvent. It interacts noncovalently with nanotube surface without severe damage to their length and conjugated π system. A single polymer functioning as both matrix precursor and dispersant avoids any incompatibility issue between matrix and dispersant, such as has been encountered in some other studies. As a result, excellent mechanical properties were obtained for composite with high nanotube loading. The uniform dispersion of MWNTs in the matrix, even at high nanotube content, leads to more effective electrical network formation and increased electrical conductivity.

7.3.6 Preparation of MWNT/PI coatings

Besides highly electrically conductive and mechanically strong free-standing composite films, the PAA-functionalized MWNT dispersions can also be used to fabricate composite coatings on various substrates. Figure 7.3g shows a transparent coating of MWNT (30 wt%)/PI on a glass substrate. The measured transmittance at 550 nm of this coating is $81 \pm 0.4 \%$, which is calculated based on 10 transmission scans of this coating at different spots. The extremely low standard deviation compared to the mean transmittance value indicates the very high uniformity of our composite coating. Similar ultra-thin composite coating (several hundreds of nm) can also be deposited on an aluminum substrate. Thicker coatings (in μm) on aluminum (Figure 7.3h) can

be prepared by solution casting due to their excellent adhesion to aluminum. Our composite coatings can be easily handled. Combined with their high electrical conductivity (about 38.8 S cm^{-1}), as well as high temperature resistance and good chemical resistance, they may have wide applications in electronics and aerospace industries.

7.4 Conclusions

In summary, I have synthesized a rigid hydroxyl-functionalized poly(amic acid), the precursor of polyimide, and have demonstrated its ability to perform the dual functions of a highly effective dispersant of MWNTs and a matrix material for polymer/MWNT composites. High-performance MWNT/PI composite films can be made by conventional solution casting technique with this dual-function PAA. The electrical conductivity of the composites reaches 38.8 S cm^{-1} at MWNT loading of 30 wt% and the nanotube concentration for percolation threshold of conductivity of MWNT/PI composites is 0.48 wt%, which are respectively the highest and among the lowest reported values for any conventional solution-processed nanotube composites. The 30 wt% MWNTs composite has higher Young's modulus ($9.43 \pm 0.14 \text{ GPa}$) and tensile strength ($179.2 \pm 9.7 \text{ MPa}$) than common polyimides. This is also the first report of MWNT/PI composites with as high as 30 wt% MWNT loading made by the solution casting technique, a simple and commonly employed method. The excellent electrical and mechanical properties, combined with the facile fabrication technique, make this MWNT/PI composite a promising material for many potential applications, including electrostatic dissipation, EMI shielding

and flexible printed circuit boards. Uniform and stable MWNT(30 wt%)/PI composite coatings have also been deposited on glass and aluminum substrates.

7.5 Declaration

Part of the work presented in this chapter has been published in the *Chemistry of Materials*.

Yuan, W., Che, J. F., Chan-Park, M. B. A novel polyimide dispersing matrix for highly electrically conductive solution-cast carbon nanotube-based composite. *Chemistry of Materials*, 2011, 23, 4149-4157.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

In this thesis, I designed and synthesized several kinds of polyimide dispersants for functionalization of CNTs to improve nanotube dispersion in polymer matrix and nanotube/matrix interfacial adhesion for reinforcement of composites. Methods to fabricate composites with aligned CNTs and high content of CNTs were also developed. The influence of CNT content, dispersion, alignment and interfacial adhesion with the matrix on the mechanical properties of composites was studied as well. These high-performance cyanate ester and polyimide composites are believed to be useful in aerospace, transportation and defense applications.

Firstly, a comb-like polymer, PI-BDA, was successfully synthesized and shown to be highly effective in individually dispersing SWNTs. CE (epoxy-modified) composite fibers reinforced with aligned and PI-BDA functionalized SWNTs were fabricated by reactive spinning. Only 1 wt% of PI-BDA functionalized SWNTs increased the tensile modulus, strength and toughness of composite by 80%, 70% and 58% over that of neat resin blend. The excellent reinforcement can be attributed to the unique structure of PI-BDA, in which the polyimide backbone noncovalently interacts with SWNTs via strong $\pi-\pi$ interaction to produce minimal damage to SWNTs, whereas the reactive BDA side-chain reacts with CE during thermal curing.

Secondly, the side-chain structure of rigid polyimide dispersant was proved to be able to greatly affect the dispersibility of CNTs, as well as the mechanical properties of CNT composites. These findings showed that PI-GNE

and PI-BDA have similar high efficacy at individually dispersing SWNTs in DMF, whereas PI is less effective. Compared with PI and PI-GNE, PI-BDA is more effective at dispersing SWNTs in CE matrix and improving interfacial strength, resulting from the side-chain structure of BDA which is more compatible with CE matrix. Thus PI-BDA functionalized SWNTs showed the highest mechanical reinforcing efficiency in CE composites. 2 wt% of SWNTs/PI-BDA increased the tensile modulus, strength and toughness of the composite by 32%, 47% and 71%, respectively.

Thirdly, using a reactive polyimide dispersant, PI_{OH}-BDA, and epoxidized SWNTs, a new nanotube functionalization method that combines covalent and noncovalent approaches was developed for reinforcement of CE composites. SWNTs were covalently sidewall-functionalized with epoxide groups, then noncovalently dispersed by PI_{OH}-BDA, and finally added into CE to make composite films. The phenolic hydroxyl groups in the backbone of PI_{OH}-BDA react with the epoxidized SWNTs while the BDA side-chains react with CE matrix during thermal curing, leading to strong interfacial strength. 1 wt% of SWNTs functionalized by this method showed increases in the Young's modulus, tensile strength and toughness of CE by 57%, 71% and 124%, respectively. These results are much higher than those of CE composites reinforced with pristine SWNTs (6%, -35% and -57%), epoxidized SWNTs (8%, -10% and -29%) and pristine SWNTs dispersed with PI_{OH}-BDA (24%, 31% and 81%).

Finally, a rigid hydroxyl-functionalized poly(amic acid) (PAA) was designed and synthesized to act as both a MWNT dispersant and a matrix precursor. High-performance MWNT/PI composites with nanotube content as

high as 30 wt% were prepared by conventional solution casting technique with this dual-function PAA. The MWNT/PI composites showed an electrical conductivity of 38.8 S cm^{-1} at MWNT loading of 30 wt% and a percolation threshold of conductivity of 0.48 wt%, which are respectively the highest and among the lowest reported values for any conventional solution-processed CNT composites. The 30 wt% MWNTs composite has higher Young's modulus ($9.43 \pm 0.14 \text{ GPa}$) and tensile strength ($179.2 \pm 9.7 \text{ MPa}$) than common polyimides. The excellent electrical conductivity, high mechanical properties, and facile processing method, make this composite very promising for applications in electrostatic dissipation, EMI shielding and flexible printed circuit boards.

8.2 Recommendations for future work

8.2.1 Fabrication of unidirectional SWNT/CE laminate

In Chapter 4, we have demonstrated the successful spinning of SWNT/CE composite fibers with aligned nanotubes by reactive spinning. We believe that unidirectional CE laminate with aligned SWNTs can also be fabricated by reactive spinning. To make the laminate, a belt of SWNT/CE composite fibers will be first fabricated by moving the takeup drum in the longitudinal direction when the fibers are spinning, which will then be precured to some extent to avoid fiber melt in the following processing steps. Using this partially cured fiber belt as the preform, SWNT/CE composite laminate can be fabricated by the resin transfer molding (RTM) technique.³⁰⁸⁻³⁰⁹ Typically, the RTM process begins with loading the belt of SWNT/CE composite fibers into a mold cavity. Then the CE resin is pumped and injected into the mold until the mold is

completely filled. After that, the mold is left closed for the cure time of CE, and the final CNT/CE composite laminate is obtained after demolding. This unidirectional laminate with aligned SWNTs in matrix is believed to have high strength and light weight, which make it a promising material for applications in defense and aerospace industries.

8.2.2 CNT-based hierarchical composites

It is reasonable to expect that the incorporation of CNTs into conventional fiber reinforced composites to create a hierarchical composite is an effective method for improving composite performance. Firstly, CNTs can provide both intralaminar and interlaminar reinforcement, so as to improve delamination resistance without reducing in-plane performance of composites.³¹⁰ Secondly, grafting CNTs on fibers can increase fiber surface area and improve stress transfer at the fiber/matrix interface, thus enhancing composite toughness. Lastly, the excellent physical properties of CNTs enable the fabrication of multi-functional structural composites. Some pioneer work³¹⁰⁻³¹² has been done in making CNT-based hierarchical composites by dispersing CNTs homogeneously in a polymer matrix³¹¹ or grafting CNTs onto fibers,³¹⁰ and improved properties have been achieved. These high-performance hierarchical composites are believed to have many applications in the near future.

8.2.3 Graphene/polymer composites

Graphene, a two-dimensional (2-D) nanofiller, has recently been considered to be another ideal reinforcement in polymer composites.³¹³⁻³¹⁵ It has a Young's modulus of ~ 1 TPa,³¹⁶ ultimate strength of ~ 130 GPa,³¹⁶ electrical conductivity as high as 6000 S cm^{-1} ,³¹⁷ and thermal conductivity of

$5000 \text{ W m}^{-1} \text{ K}^{-1}$.³¹⁸ All these properties are comparable to those of CNTs. Moreover, graphene has cheaper fabricating costs than CNTs. To fully utilize the excellent properties of graphene, great attention should be paid to the following issues: 1) preparation of graphene at low cost; 2) structure and surface characteristics of functionalized graphene prepared by different methods; 3) morphological control of dispersed graphene in matrix for target properties; 4) interfacial adhesion between graphene and polymer matrix.

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List of Publications

Journal Papers:

1. Yuan, W., Chan-Park, M. B. Covalent cum non-covalent functionalizations of carbon nanotubes for effective reinforcement of a solution cast composite film. *ACS Applied Materials & Interfaces*, 2012, 4, 2065-2073.
2. Yuan, W., Che, J. F., Chan-Park, M. B. A novel polyimide dispersing matrix for highly electrically conductive solution-cast carbon nanotube-based composite. *Chemistry of Materials*, 2011, 23, 4149-4157.
3. Yuan, W., Li, W. F., Mu, Y. G., Chan-Park, M. B. Effect of side-chain structure of rigid polyimide dispersant on mechanical properties of single-walled carbon nanotube/cyanate ester composite. *ACS Applied Materials & Interfaces*, 2011, 3, 1702-1712.
4. Yuan, W., Feng, J. L., Judeh, Z., Dai, J., Chan-Park, M. B. Use of polyimide-graft-bisphenol A diglyceryl acrylate as a reactive non-covalent dispersant of single-walled carbon nanotubes for reinforcement of cyanate ester/epoxy composite. *Chemistry of Materials*, 2010, 22, 6542-6554.
5. Che, J. F., Yuan, W., Jiang, G. H., Dai, J., Lim, S. Y., Chan-Park, M. B. Epoxy composite fibers reinforced with aligned single-walled carbon nanotubes functionalized with generation 0 to 2 dendritic poly(amidoamine). *Chemistry of Materials*, 2009, 21, 1471-1479.
6. Yuan, W., Jiang, G. H., Che, J. F., Qi, X. B., Xu, R., Chang, M. W., Chen, Y., Lim, S. Y., Dai, J., Chan-Park, M. B. Deposition of silver nanoparticles on multi-walled carbon nanotubes grafted with hyperbranched poly(amidoamine) and their antimicrobial effects. *Journal of Physical Chemistry C*, 2008, 112, 18754-18759.

Patents:

1. Chan-Park, M. B., Yuan, W., A carbon nanotube-dispersing matrix for highly electrically conductive solution cast polyimide composite film, US provisional patent, *accepted*.
2. Chan-Park, M. B., Yuan, W., Feng, J. L., Judeh, Z. Use of a reactive non-covalent dispersant of nanotubes for reinforcement of composite fibers, US provisional patent application no.: 61/302,808, 09-Feb-2010.