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Morphology and Mechanical Properties of Polycarbonate / Carbon Nanotube Composites

by

Yiqun Pei, B.Sc.

Tinghua University.

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the requirements for the degree of

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Abstract

Composites of polycarbonate (PC) and carbon nanotubes (CNTs) were fabricated using various solution casting methods. CNT bundles were bought from Carbolex and purified in-house for further use. An interconnecting network of CNTs was found to form within the composite film, as revealed by scanning electron microscopy (SEM) pictures. This network was apparent especially after hot stretching the composite film at a constant strain rate in the vicinity of the glass transition temperature (T_g) of PC. The network of entangled CNTs in the fracture surface is markedly different from other conventional polymer/CNT fractures. When tested with a built-in-house miniaturized tensile testing system and TMA, these materials exhibit mechanical property improvements in comparison to a pure PC film.

Dedication

To my dad, **Huating Pei** ,

for his long-distance support

To my mom, **Yumei Xu** ,

who believes in dreams

And to all my friends and

relatives on both sides of the Pacific

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Nomenclature

C_{CELL}	Calibration coefficient of load cell (11.17/N).
C_{LVDT}	Calibration coefficient of LVDT (39.3/mm).
F_0	Load amplitude (g) in TMA.
L_0	Displacement amplitude (μm) in TMA.
L	Sample length (mm) in TMA/MTS.
L_{CNT}	Distance (mm) between CNTs in network.
$N3$	Number from data bench output channel 3.
$N5$	Number from data bench output channel 5.
R_{CNT}	Radius (mm) of CNT bundles.
S	Sample cross-section area (mm^2) in TMA/MTS.
V_f	Volume fraction of filler (%).
V_m	Volume fraction of matrix (%).
W	Weight percentage (%) of CNT in PC.
Y_c	Young's modulus composite(MPa).
Y_f	Young's modulus of filler (MPa).
Y_m	Young's modulus of matrix (MPa).
Y^*	Complex Young's modulus (MPa) in TMA.
δ	phase difference (radian) in TMA.
ρ_{CNT}	Density (g/mm^3) of CNT.
ρ_{PC}	Density (g/mm^3) of PC.

Chapter 1

Introduction

1.1 CNT /Polycarbonate composites

1.1.1 Carbon nanotube

Since their discovery in 1991 by the Japanese scientist Sumio Iijima at the NEC Laboratory [1], carbon nanotubes (CNTs) have inspired scientists in a wide range of research and potential applications.

In CNTs, all atoms are arranged into tubular fullerene molecules. They are forming a structure like that of a fine fiber with a hollow center. The diameter of CNTs can be as small as 1 to 2 nm. CNTs have very high aspect ratios, the length to diameter ratio sometimes can reach up to the millions.

Basically there are two types of CNTs: single walled carbon nanotubes (SCNTs) and multiple walled carbon nanotubes (MCNTs).

Due to their unique structure, CNTs have remarkable properties in mechanical, electrical, thermal and many other physical aspects. Their detailed properties will be discussed later in chapter 2.

1.1.2 Conventional composite materials

Definition of composite materials

A composite is a material system consisting of two or more phases on a macroscopic scale, whose mechanical performance and properties are designed to be superior to those of the constituent materials acting independently[2]. At least two different phases should exist in any composite system: the reinforcement phase and the matrix phase.

Reinforcement materials can be particles (particulate composites) or fibers (fiber composites). Particles can be divided into two groups. One is metallic particles, the other is nonmetallic particles (such as mica flakes, silicon carbide or rubber-like particles). The most common fibers include glass fibers, carbon fibers (such as graphite fibers), Kevlar 49 fibers, Boron fibers, silicon carbide, and aluminum oxide.

The major functions of the matrix are to transfer the load between fibers and protect the fibers from environmental damage. There are several different matrix materials that can be used when casting a composite material, such as thermoplastic matrix, thermoset matrix, metallic matrix and ceramic matrix.

Accordingly, there are two major kinds of commercial composite materials: one is fiber-reinforced composites, the other is particulate composites. In fiber-reinforced composites, the fibers can be incorporated into a matrix either in continuous lengths or in discontinuous lengths.

CNT/polymer composites can be categorized as discontinuous fiber-reinforced composites. More attention is given to fiber-reinforced composites in this thesis.

Advantages of composite materials

Compared with traditional materials like metals, commercial composite materials have tremendous advantages[3].

They possess both high specific strength (strength to density ratio) and superior specific stiffness (modulus to density ratio). This is mainly because they combine the properties of light weight of matrix and high strength/stiffness of fibers.

They also have higher corrosion resistance and long fatigue life. Unlike metals, some nonmetallic matrices will react really slowly with acid or alkali and thus have really low corrosion rate. And their ability to endure large scale deformation also gives them excellent energy absorbing capability and good resistance to micro-crack, which is quite important for good fatigue property.

A composite can be designed to have unique properties, for example, with zero thermal expansion. This can only be achieved by composite among all the known materials.

Limitations of composite materials

Although composite materials enable versatility, for the design, manufacture and practical applications, the limitations of composite materials are quite obvious.

High cost and complicated design are needed for composite materials compared with traditional materials like metals. Their fabrication technology is difficult to handle and sometimes the final properties are even dependent upon the manual skill of workers, such as the fiber-weaving skill. Compared with metal, ceramic and other materials, they are more sensitive to environmental heat due to the thermal degrading of matrix and sometimes moisture will cause some problems, too. To examine the final quality of composites, expensive and complicated nondestructive inspection methods are needed.

These limitations constrain the wide-spread use of composite materials and need engineering work to resolve these limitations.

Application of composite materials

Since the 1970s, applications of composites have experienced a rapid development in many industrial areas due to their unique mechanical and physical characteristics. There are many applications, mainly in aerospace, aircraft, automotive and sports goods [4].

Due to their weight saving advantage, composite materials are widely used in aerospace and aircraft. For example, in the early 1980's, the Boeing 767 used nearly 2,000 kilograms of composite material. In the A320 Airbus, 15% total weight is composite materials. And the wings in French Aerospatiale ATR72 70, are 100% made of composite materials [5]. In the space shuttle and international space station, composite materials like IM7/PPEK, and Carbon/epoxy are everywhere.

Composite materials are also used in the military , automotive and sports goods and many new areas. For example, many sports goods are now made of carbon-fiber or Kevlar composites, like helmets or tennis rackets, which combine light weight, good strength and even energy absorption. Kevlar is also used to make bullet-proof vests for the police.

1.1.3 Nano-composites

Nano-composites

In composite materials research, the study of nanocomposites has become one of the current trends in developing novel composite materials due to the recent technological improvements. Nanocomposites can be defined as a combination of two or more phases containing different compositions or structures, where at least one of the phases has characteristic lengths in the $1 \sim 100$ nm regime[6].

Usually nanoparticles should have an average grain or particle size of less than

100nm. Due to their high surface-to-volume ratio, they will exhibit some novel properties compared to traditional micro-scale structure materials. But at the same time, new design protocol and synthesis techniques are required.

Different materials have been tried as fillers and matrices in different nanocomposites. Polymer, metal and ceramic are most frequently used matrices. Metal or metal compounds (like Ag or Al nitride, etc. [7]), inorganic nanoparticles (like hydroxyapatite [8]), and CNTs[9] etc. have already been dispersed in some nanocomposites.

An ideal nanocomposite would be one in which there is no aggregation of the fillers, containing the optimum content of filler while still maintaining its physical and chemical properties. Developing ideal nanocomposites with improved bulk properties, requires understanding the following key issues, the composition of fillers; the nature of the ultrafine filler particles (this includes their chemical and physical characteristics) and the homogeneity of filler dispersion in matrix [7].

CNT/PC composites

The remarkable properties of CNTs make them a candidate for a reinforcing constituent in a polymer-based nanocomposite material. It is believed that incorporating CNTs into polymeric materials would promote both high strength and a high Young's modulus. At the same time, CNTs exhibit electronic and thermal characteristics that could be exploited in the polymer composite. PC was selected in this research due to its high impact toughness, high glass transition temperature (T_g) and high optical clarity[10]. PC is also a commodity polymer. The detailed information of CNT/polymer composite study will be discussed in chapter 2.

1.2 Research goal

In this research, efforts are focused on developing laboratory-scale methods for producing CNT-polymer composites, studying the influence of fabrication methods on the morphology and correlating morphology to the functional attributes, such as the mechanical and electronic properties. The role of specific molecular interactions between the CNT and the polymer is also of interest.

At the present stage, there are three main goals in this research:

- Production of the CNT-polymer composite,
- Microstructural characterization of the resulting CNT-polymer composite,
- Measurement of the material properties, such as mechanical and electrical properties.

1.3 Thesis outline

Chapter 1 introduces some simple concepts of CNT and polymer composites. The research goal and outline of thesis are also included in this chapter.

Chapter 2 outlines a background to CNTs manufacturing, developments and several research directions among CNT study. This chapter also describes the current knowledge of CNT composites regarding strengthening mechanisms, casting methods, and properties testing results.

Chapter 3 demonstrates the various methods used in this work for casting CNT/PC films. CNT purification, solvent selection and thermal characterization are also included as a part of the sample casting processing. In this chapter, it also describes the work to determine the morphology. The morphologies of pure PC and CNT/PC

composites with different casting methods at different fracture temperatures are compared. Some interesting SEM pictures are also discussed in this chapter.

Chapter 4 presents mechanical test results of CNT/PC network films. Thickness measurement, tensile strength testing and Young's modulus testing are key issues of this chapter. A mechanical testing system built-in-house is also introduced here.

Chapter 5 concludes the results of the reaserch, it also gives the recommendations for future work.

Additionally, there are four appendices A ~ E mainly for introducing the detailed different experiment procedures.

Chapter 2

Literature review

2.1 Carbon nanotube

Carbon nanotubes(CNTs) were formed as by-products during the discovery of fullerenes in the 1980s, but were first identified in 1991 by the Japanese scientist Sumio Iijima of NEC Laboratory in Tsukuba, Japan [1]. These were the so-called multi-wall carbon nanotubes (MCNTs). Then in 1993, single-wall carbon nanotubes (SCNTs) were observed independently both by Iijima and Bethure's group at IBM Almaden Research Center in California, U.S.[11]. In 1996, bundles of aligned SCNTs were first synthesized by Smalley's group at Rice University in Texas, U.S. [12].

Since then, CNTs have attracted the attention from the researchers all over the world and millions of dollars have been used to support CNT technology aimed at their potential use in mechanical and electronic areas.

2.1.1 Structure of CNTs

There are 3 common allotropic forms of elemental carbon : diamond, graphite and amorphous carbon. In the last few decades, scientists have found another form,

namely fullerenes “buckyballs”. CNTs and nanofibers are among this category.

The molecular structure of CNTs is totally different from the other three forms of elemental carbon. They are composed of only hexagonally or pentagonally arranged carbon. All atoms are at the surface, which is formed into a tubular fullerene molecule. It can be considered as a rather fine fiber with a hollow center. The length of the molecule usually can be millions of times greater than the tiny diameter. There are two basic types of CNTs: SCNTs and MCNTs.

SCNT is the common abbreviation for “Single-wall carbon nanotube”. This type of CNT contains carbon atoms self knitted together, with ~ 0.14 nm between neighboring carbons, rolled up in a seamless cylinder with a closed carbon cap on each end, see figure 2.1. The diameter of SCNTs is usually around $1 \sim 10$ nm, the length roughly several micrometers.

MCNTs is the common abbreviation for “Multi-wall carbon nanotube”. This type of CNT contains multiple walls arranged as concentric cylinders around inner tube, See Figure 2.2. The diameter of MCNTs is usually around $2 \sim 50$ nm, the length normally ranges between $0.2 \sim 2 \mu\text{m}$, and the distance between individual tubes is roughly ~ 0.34 nm.

Using high resolution microscopy techniques, some results about the cylindrical structure of CNTs have been obtained. It is suggested by Smalley [12] that there are three basic shapes of CNTs classified according to the angles with respect to the hexagonal lattice of CNTs forming the CNT surface.

A vector $\mathbf{v}$ (see Figure 2.3), was used to map an atom from the left hand border onto an atom on the right border line, and this vector can not be arbitrary. It has to be an integer multiple of the two graphite basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, i.e., $\mathbf{v} = \mathbf{n} \mathbf{a}_1 + \mathbf{m} \mathbf{a}_2$ with $\mathbf{n}$ and $\mathbf{m}$ are integers. The nanotube which constructed in this way is called a $(\mathbf{n}, \mathbf{m})$ nanotube.

According to the pattern of the chain of carbon atoms along the direction of the

Figure 2.1: Schematic representation of SCNTs

Figure 2.2: Schematic representation of MCNTs

Figure 2.3: Schematic representation of vectors for mapping carbon atoms

vector $\mathbf{v}$ in the graphite plane, or according to the circumference of CNT itself, the CNTs can be divided into three basic shapes(chirality): armchair CNT if $n = m$, zigzag CNT if $m = 0$ and chiral CNT for any other values of n and m , see Figure 2.4.

The properties of CNTs are mainly dependant on the CNTs' dimension and chirality. SCNTs and MSCTs share some common properties, but also have individual characteristic behavior.

2.1.2 Unique Properties of CNTs

Mechanical properties

CNTs are ranked the toughest materials ever known, they possess both high elasticity and plasticity. CNTs have the highest Young's modulus: $1 \sim 5$ TPa [13]. Their tensile strength is known to be $50 \sim 200$ GPa [14], the best performing carbon fibers can reach

Figure 2.4: Schematic representation of carbon chains around the tube circumference

the order of 650 GPa for Young's modulus and 4GPa for tensile strength[15]. They can sustain high rate bending and twisting, and can survive extremely large distortion without breaking the carbon bonds.

Electric and electronic properties

In CNTs, electrons can move freely just like in metals. They can pass currents 100 times higher than standard metal wires and can transport a high current density up to 10^9 Acm^{-2} [16]. It is quite easy to propose that the electric properties of CNTs mainly depend on chirality and diameter. A specific CNT can be conductive or semi-conductive. It has been proven that small diameter armchair CNTs are metallic while small diameter zigzag CNTs behave as semiconductors [17].

Thermal properties

Due to their high length to diameter ratio (aspect ratio), CNTs have very good thermal properties along the longitudinal direction. It is found that the thermal conductivity of aligned CNTs can transmit heat better than diamond, which is the

highest thermal conductor at present [17]. Yet in the perpendicular direction, the heat transport is much lower.

Field emission properties

Field emission plays an increasingly important role in modern life, especially in electronic displays and lighting. The tiny tubular structure of CNTs makes it ideal for field emission. Some measurements showed that the CNT emission current ranges up to 100 mA/cm², and emission site density reaches 10⁷cm⁻² at 5V/ μ m field [18]. It is also found that closed MCNTs are much more efficient than the open ones.

Other properties

There are also other promising properties of CNTs in the field of magnetic and hydrogen storage. Under certain condition, CNTs can store up to 67%wt% of hydrogen with an effective surface treatment. The pure un-doped CNTs display diamagnetic behavior while the co-doped CNTs exhibits similarities to a "super" paramagnetic nature [19].

2.1.3 Production methods

Chemical vapor decomposition

Chemical vapor decomposition is based on the theory of diffusion [20]. Under a certain pressure, a quartz tube is mounted across a flow furnace. A ceramic container with prepared catalyst is seated inside the tube. The reaction mixture (90% nitrogen and 10% acetylene) is passed over the container for hours at a temperature ranging from 500°C ~ 1100°C. Several forms of carbon are generated after cooling, amongst which CNTs can be formed.

The key parameters for generating CNTs by catalytic decomposition are the temperature and catalysts. Usually this method will produce imperfect MCNTs in high yields. But there are cases in which high quality SCNTs can also be attained with certain specified parameters.

It is suggested that this method has a possibility of mass-production of CNTs and will be the most promising production method for commercial purposes. It is simple, can be scaled up to kilograms, and the resulting length of CNTs is very long, up to 50 μm [21].

Laser ablation

This method is the first successful technique applied to synthesize SCNTs [22]. The laser beam is concentrated on a long quartz tube which is sealed and fixed in a special furnace. The tube needs to be evacuated before reaching temperatures above 1200 $^{\circ}\text{C}$. The vaporized carbon species can be carried away by the flowing gas and collected by a water-cool copper apparatus.

There are several parameters which may affect the quality and quantity of CNTs: the power of laser light, the radiation time, the graphite target, the inert gas composition. This method can operate continuously and has a higher yield than other methods. The highest yield is up to 10g/day.

Electric arc discharge

Electric arc discharge is the most widely used method [23]. In a water-cooled reaction chamber, which is evacuated first and then filled with an inert gas, two graphite rods are used as electrodes. As the distance between them becomes very small, they generate an electric arc discharge. This will result in a plasma and an extremely high temperature (3000K $\sim$ 4000K). By adding catalysts, various diameters of CNTs are

yielded.

Two kinds of current can be used in this method: direct current(DC) and alternating current(AC). DC method is most common. And many catalysts can assist the formation of CNTs, including Fe, Ni, Co, Y, La, and Pr. This method is easy to set up, but the CNT length is limited and the production cost is high.

Other methods

There are also other methods besides those mentioned above, such as that using solar energy method, the HiPCO method and a low-temperature microwave method, etc.

Solar energy is a method developed in France[24]. In this method, by using mirrors, sunlight can be concentrated on the graphite target filled with a mixture of graphite powder and metallic catalysts. The temperature inside this type of furnace can reach as high as 3000K, and yields soot containing fullerenes. The quality and quantity of CNTs by solar energy mainly depends on the temperature, the pressure and the catalysts. Till now, only small scale CNTs yields are produced from this method.

HiPCO (high-pressure carbon monoxide) [25] method can be regarded as a modified Laser Ablation Method. In the HiPCO process, the gaseous carbon atoms do not come from a vaporized carbon target. Instead, they come from carbon monoxide gas, which is pumped into a high-pressure reaction chamber and mixed with an gas containing the necessary catalysts to sustain the chemical reactions that create nanotubes.

The low temperature microwave method takes the advantage of the selective absorption of microwave energy and a low-melting point organic polymer used to synthesize the CNTs at atmospheric pressure, and several hundreds degrees temperature.

2.1.4 CNT Applications

Some people believe that CNTs will bring a revolution in material science. As yet, the practical impact of CNTs is not widespread although there exists many potential applications. A few of these applications are discussed below.

High strength structural materials

CNTs possess a higher modulus, hardness and stiffness. They show great stability under high temperature and vacuum. Thus they are more ideal than other reinforcement fibers.

CNT/polymer composites are one of the prospective directions for fabricating future super materials. The application of CNTs to polymer reinforcement will mainly depend on the ability of the load to be transferred from polymer matrix to CNTs. Such composites can be widely employed in the aerospace industry and in the construction of building structures.

Ropes, wires, webbing and fibers made of CNTs are especially interesting for a number of utilizations. Recently a pure CNT yarn has been woven which is roughly 30 cm long and 200 μm wide [26].

Nanoscale instruments

The small size and rigidity of CNTs make them suitable for nanoscale instruments. These include nanoscale probes [16], sensors and nanoscale tweezers [27]. It is theoretically possible to make gears for nanomachines. In Japan, there has already been an attempt to realize the idea of a “molecular engine”.

Field emitter and transistor

The CNTs can emit electrons at a lower voltage while keeping a high current density, and remaining stable. This makes CNTs desirable in field emission displays and microwave generation in wireless communications [16].

It is also possible to use CNTs to generate transistors and nanochips which are basic components for future advancement in the computer industry[28].

Energy storage devices

Due to their hollow structure and open channels between them, CNTs have a large capacity for hydrogen storage. Using CNTs to store hydrogen to power vehicles has been a high priority for some researchers [16]. This also could be a good application in battery industry.

2.2 CNT /polymer composites study

After the first synthesis of the single-layer nanotubes in 1993, a lot of money and effort has been put into the study of CNTs compared to most other new materials. Among them, much research has been focused on the use of CNTs in composite materials. A variety of matrices have been used, such as polymer, metal and ceramics. Amongst CNT composite research, CNT/ polymer is one of the most popular study topics due to the unique mechanical and electronic properties of CNTs.

In particular, CNTs are regarded as promising candidates for the mechanical reinforcement of polymers. These CNT/polymer composites may also allow electric/thermal/optical property improvements in other fields, such as electric conductivity, stability of luminescence, thermal expansion and diffusion coefficients and magnetic

properties.

For CNT/polymer composites, there are two difficulties which need to be settled before some really good material systems can be produced. One is how to improve the interaction/bond between the inert CNT surface and the polymers. The other is to determine the mechanism which is most effective in strengthening different polymer matrices. There are roughly three basic strengthening mechanisms to date: by CNT alignment[9], CNT networking[29] or CNT functionalization [30].

2.2.1 Strengthening polymer with un-functionalized CNTs

Strengthening polymers with aligned CNTs

The effective utilization of nanotubes in composite applications depends strongly on the ability to disperse the CNTs homogeneously throughout the matrix without destroying the integrity of the CNTs. Good interfacial bonding is also a necessary condition to achieve load transfer across the CNT-polymer interface. Aligning CNTs along the load direction is one of the most popular methods that have been used to strengthen the CNT/polymer composites. It follows the traditional concepts of fiber-reinforcement composites. It is always more beneficial to use SWNT than MWNTs.

For un-functionalized CNT/polymer composites, there already exists some research results, which focused on three main areas, including dispersion/distribution process, alignments/assembly of CNTs and interface/load transfer properties.

In the study of dispersion/distribution process, several researchers have published some results. At the Weizmann Institute of Science, in Israel, Cooper et al. [31] used a dry powder mixing method (polymer extrusion technique) and achieved a well dispersed CNT in PMMA(poly methyl methacrylate). The impact strength improved significantly even when adding a small amount of SWNTs. At the University of Kentucky [32], Safadi et al. used ultrasonic energy to disperse MWNTs in polystyrene,

then spun and cast thin films. The tensile modulus and strain to failure increased with MWNT loading. They also obtained some electric properties of these new composites.

To yield a homogenous dispersion of CNTs in composites, there are many other methods which can be used in dispersion and distribution process.

At the same time, much effort has been put into alignments/assembly of CNTs to try to get good alignment and thus improved mechanical properties. Some research has shown that the use of CNTs, which are aligned perpendicular to cracks, are able to slow down the crack propagation process by bridging the crack face [9]. CNT alignment has also been attained by some researchers when controlling the stretching ratio during extrusion of the composites, drawing a CNT suspension through a micro filter, aligning the CNTs on a patterned substrate or melt processing.

With the CNTs aligned in composites, an improvement in mechanical and electrical properties is shown. Most often, efforts are focused on SWNTs rather than MWNTs, since they offer superior electrical and mechanical properties.

For the study of interface/load transfer properties (wetting, stress transfer, adhesion), there is beginning to be many papers about load transfer, achieved through CNT wetting and adhesion. No significant conclusions have been obtained. The mainstream techniques used to understand the load transfer of CNTs are still being refined. These include micro-Raman spectroscopy and Kelly-Tyson approach to measure the interfacial shear stress. In epoxy composites [33], Schadler et al. found that during load transfer to MWNTs, only the outer layer are stressed in tension whereas all the inner concentric MCNT layers respond in compression. They obtained much higher compression modulus in comparison to the change in tensile modulus.

In Nanyang Technology University, Singapore, Xu et al. [34] found that in a micro-fabricated MWNT reinforced epoxy thin film, there is strong interfacial adhesion between MWNT and the matrix. This was supported by electron microscopy and also by results from molecular mechanics simulations.

Strengthening polymers with CNT networks

A CNT network is another mechanism that could strengthen polymers. Since 1995, branching of the CNT tubular structure into two-dimensional (2D) and three-dimension (3D) CNT junctions have been found in several CNT studies.

D. Zhou [35] first reported the formation of 2D L-junction, Y-junction and T-junction CNTs in an arc discharge method. But these junctions are limited to 2D and at most 3 way junctions. Then M.T. Jyh found ‘H’ or 3D junctions in CNTs manufactured by the CVD method, These junctions are important not only for mechanical properties, but also for electric and thermal applications.

As more research continues on CNT/polymer composites, there is even some network-like structure found in CNT/polymer composites. During Potschke’s [29] study, a very small-scale interwoven lattice of CNTs was found as reinforcements in polymer matrix. Some property improvements were also observed in this case.

How CNT networks can strengthen the polymer is not clear, but there are already some research results on carbon black networks strengthening an elastomer matrix [36]. For a given carbon black/elastomer composite system, filler networks play a critical role in determining the mechanical properties, especially for dynamic mechanical properties. The breakdown and reformation of the filler networks cause an additional energy dissipation, hence, high hysteresis during cyclic strain is expected.

Forming CNT networks within a polymer may improve electrical and thermal properties. Networks may also improve the mechanical strength and toughness of CNT/polymer composites.

2.2.2 Strengthening polymers with functionalized CNTs

Due to the small size of CNTs, there are very strong Van der Waals interactions between the tubes. This will force nanotubes to form CNT bundles. Thus, the advan-

tages of CNTs as fillers can not be fully achieved unless the CNTs are "un-bundled". Recent studies [37] [38] have shown that CNTs can be chemically functionalized with other chemical groups (CNT functionalization) and this will facilitate both the CNT dispersion and CNT affinity for the polymer matrix. These are key issues in improving load transfer and future composite properties.

Some researchers believe that by functionalization, CNTs can be separated in an organic solvent or water. A CNT/polymer composite can then be easily manufactured. Nanotubes have the ability to undergo both end-cap functionalization and surface functionalization (see Figure 2.1).

Several attempts have been tried in recent years to functionalize CNTs. Professor Hirsch [37] has classified different functionalizations, namely: defect functionalization, covalent functionalization of sidewall CNTs, noncovalent exohedral functionalization and endohedral functionalization.

At the State University of New York [38], by using OPA (octadecyl phosphonic acid), MCNTs were functionalized and then mixed with PS (polystyrene) and PMMA to form a new nanocomposite materials. The nanotubes were observed to be dispersed in both the PS and PMMA phases. Thus domain size and surface roughness were dramatically reduced.

At the Foster-Miller, Inc [30], nanotubes were functionalized with PMMA. The process was straight-forward: after removing oxygen from CNTs, PMMA and AIBN (as a free radical initiator) was added to the toluene suspension. Then mechanical stirring and heating were applied which would remove excess solvent and polymer. The functionalized SWNTs were then redispersed in solution to form a CNT/epoxy composite. This procedure resulted in an 11% increase in stress at break and a 21 % increase in static modulus over the unfilled epoxy. However, this procedure also resulted in a 29% increase in stress at break and a 16.5% increase in static modulus over untreated nanotubes.

In University of North Carolina, U.S [39], CNTs were functionalized to blend with PEO (poly ethylene oxide). PEO is a semi-crystalline thermoplastic polymer. By functionalization, a uniform CNT dispersion and significant enhancement in mechanical properties was obtained. The storage modulus (E') increased 400% at the loading of 4% CNTs and yield strength became $\sim 300\%$ higher at the loading of 1% CNTs compared to that of the pure PEO.

2.2.3 Other key factors in Strengthening CNT/polymer composites

The strength of composites not only depends upon alignment or the presence of a network, it is also depends on the CNT/polymer interface and CNT dispersion quality. These will be discussed in following sections as they play an important role in this study.

In both mechanisms, a uniform dispersion of the CNTs in the polymer matrix, and a compatible interface between the two components are basic requirements for favourable polymer reinforcement.

Functionalization will be helpful in forming a compatible CNT/polymer interface and getting well-dispersed CNT/polymer composites. However, this requires complicated techniques and is not suitable for all polymers and CNTs.

The strength of CNT/polymer composites reported to date shows only a moderate increase except in some functionalization cases. Generally, this can be ascribed to unsuccessful load transfer from the polymer to the nanotube as indicated by microscopic examination of the fractured composite surface. The CNTs appear to be pulled out in most cases or aggregated, and the true benefits on mechanical properties are as yet unclear.

2.3 Dispersing CNTs in polymer

Preparing polymer/CNT composites presents many difficult processing challenges. Only when CNTs have been dispersed evenly in polymer/CNT specimens to give homogeneous composites is it possible to expect any enhanced properties and morphology. CNTs are notorious for their poor dispersion quality in most ordinary organic solvents. Several forces are related to the poor dispersion quality of CNTs. Once the key forces are known, mechanical or chemical methods can be taken to de-agglomerate CNTs in polymers.

2.3.1 Dispersing method

The methods used to prepare most CNT/polymer composites are mechanical film casting of polymer/CNT suspensions, polymerization reactions of polymer monomer/CNT suspensions or shear mixing (melt processing) polymers with CNTs. Different methods have different characteristics and were used by different researchers accordingly.

Mechanical casting

The specimens are made by dispersing CNTs in a polymer solution, then casting CNT/polymer suspension and removing the solvent[9]. Among this category, most common methods include solution casting, spin coating and simple solution evaporation method. This is usually the best option for good CNT dispersion and orientation.

Polymerization reactions

By polymerization of a monomer when covalently attached to the CNT surface, CNT/polymer composites can also be fabricated. An example is functionalization of the CNT surface with methylmethacrylate, this modified CNT surface becomes

”easier” to blend with PMMA. Then polymerization to form short PMMA segments. Finally a CNT/PMMA composite can be fabricated from this short segments.

Melt processing

Specimens are made by mixing the CNTs in molten polymers[40]. The melting process is not used frequently. However in many cases, it may be beneficial because aggregates of CNTs can be minimized by application of shear during melt mixing.

Combination method

Some researchers have also tried some methods that combine the solution casting and melt process. For example, films were cast first, then extruded between heated plates to get very thin films. These thin films were cut into small pieces and then extruded again. Repeating this whole procedure several times yielded a much better dispersed film. [41]

At the present stage, we mainly focus on methods which can produce a film thick enough that we can perform some material testing. We select the solution casting method as our major method to make films because of easy processing, low consumption of expensive raw materials, no polymer degradation during the film making, no need to purchase complicated equipment and lastly high reproducibility. It is also have good scalability which will make it easily transfer to a large scale production.

The required film thickness for mechanical testing is difficult to obtain using spin casting. Melting method is also not a good choice, for it will make PC degrade though it has some advantages in making thick films.

2.3.2 Agglomeration of CNTs in polymers:

The dispersion of particles in polymer is a very complex problem [42], as severe particle agglomeration might occur. It leads to inhomogeneous distribution of filler particles, processing problem, poor surface quality and deteriorated mechanical properties. Thus, considerable effort is concentrated on the development of particle surface treatment or processing technologies with the single goal of improving homogeneity. Since CNTs are tiny tubes, with large Van der Waals interactions, the agglomeration of CNTS in polymer is even worse than that of usual particles.

Forces leading to aggregation

Usually the force between particles and the force between particles and solvent are most important forces which determine the aggregation of particles. There are several kinds of forces which contribute to the aggregation of particles, like adhesive force, viscous force, capillary forces and some other forces[43].

Adhesive force is the most important attractive force lead to aggregation. It depends on the reversible work of adhesion and the dimension of the effective particle radius. Van del Waals force is a kind of adhesive force.

In particles dispersed in a viscous liquid, the viscous force will hinder the separation of particles. It is mainly affected by viscosity, the size of the particles, the rate of separation and initial separation distance between particles.

In the case of incomplete wetting, capillary forces act between particles connected by discrete liquid bridges. Capillary forces can be divided into two parts: one is determined by surface tension and the other is a hydrostatic component.

Several other forces may act between particles in some cases, such as electrostatically charged particles, but these are small compared to those forces mentioned above.

Forces leading to separation

Compared to the different kind of forces leading to aggrgation, only two forces can be cataloged as separating forces: hydrodynamic force and repulsion of particles[43].

When dispersed in a liquid, hydrodynamic force will act, just like during the processing of polymer melting. The shear stress is one of hydrodynamic force that will sepearate particles.

The shear forces developing under such condition depend on shear rate, viscosity and the dimension of the particles.

The same electrostatic charges may lead to separation due to the repulsion of particles, but the significance of these forces is quite limited.

Key factors for agglomeration

Thus agglomeration of CNTs in polymer is determined by the relative magnitude of attractive and separating forces and the most important factors influencing the homogeneity of polymer/CNTs composites are CNTs characteristics such as the size of the CNTs, surface tension of CNTs and the shear forces during their dispersion.

2.3.3 Techniques for de-agglomeration

Suspensions can be treated mechanically and chemically in order to get the homogeneous particle dispersion [7]. Besides chemical method and mechanical method, there is also other methods used for de-agglomeration.

Mechanical method is frequently used. The long time scale and strong force of stirring may cause a loosening of the structure in the agglomerates and create porous constructions. Thus interpenetration of the polymer chains into these porous structures may take place. Mechanical agitation and sonication are the two most frequently using method in this category.

Chemical methods such as use of a polar solvent and/or a surfactant are also quite good choices to improve dispersion quality. In a polar solvent media, the dispersion can be achieved by the dominance of electrostatic repulsion due to the interactions between the electric double layers surrounding the particles over the attractive Van der Waals force between the particles. The surfactant method involves adding a surfactant during dissolving step to enable better CNT suspension. Surfactants such as Triton or Sodium Dodecyl Sulfate (SDS) have been used when suspending CNT in other research.

Other methods include using vacuum or combination of the methods above. It will be beneficial to remove solvent under vacuum without causing agglomeration due to gravity. And combination of the methods above, in many cases, will lead to a good dispersion, too [44].

2.4 CNT/polymer interface

2.4.1 Polymer-filler interface

In a polymer composite, the mechanical properties are mainly determined by the interfacial interaction between various phases present.

Bonding between the various phases is the most important prerequisite for fillers to transfer the load and thus reinforcing the composite. Strong bonding is generally required, but sometimes a particular application may require some compromise in this interfacial strength. For example, interface decohesion will be beneficial for energy dissipation.

Many practical and theoretical efforts have been focused on improving this interfacial interaction. The following are several key factors leading to good polymer-filler

bonding[45].

Filler surface condition is one of most important factors. It is always required clean, dust-free, crack-free and non-porous filler surface. Also moderate roughening of filler surface will help polymer-filler bonding.

Processing parameters also play a critical role in polymer-filler bonding, such as low viscosity of resin at time of application and high viscosity when cooling and curing, etc. And γ_{LV} (surface tension of liquid) should be less than γ_C (critical surface tension) for spreading of polymer on filler.

Other factors including similar coefficients of thermal expansion of polymer and fillers, this will be helpful in preventing the polymer-filler de-bonding during the thermal cycle of fabrication. Low contact angle between polymer and filler will also facilitate the polymer-filler bonding as in this case filler can be easily wetted by polymer. High temperature can increase the compatibility of the various components. Also high temperatures can be helpful to remove some impurities.

For CNT, they share some common characteristics of fillers. But they also have their specialty in CNT/polymer interface. Thus more work are needed to determine the key factors for CNT/polymer bonding.

2.4.2 Some existing CNT/polymer Composite morphology

The study of the morphology of polymer composites will help reveal some useful information about interfacial interaction between components, such as mixing quality, the interfacial bonding, reinforcing mechanism and this information even helps judge some properties like wear, friction and fatigue life.

An ideal high performance polymer or a polymer composite is a lightweight material with a high Young's modulus, which exhibits little or no deformation under the applied load, and has high strength without sacrificing ductility.

As mentioned previously in the literature review, many researchers have been trying to align CNTs and examine the SEM/TEM pictures to obtain information about the CNT/polymer morphology. Since a breakthrough on CNT dispersion is not yet been achieved, most of these pictures are of a quite small area and at a quite small scale.

By mechanical stretching, L.Jin [40] etc showed localized CNTs parallel to the stretching direction in a polyhydroxyaminoether matrix. In their TEM image, some CNTs even bridged the micro-voids or micro-cracks. But this method is only applicable to a 1D nanostructure.

Using toluene solution, Brendan etc [46] made a CNT/PmPV(poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylene vinylene)) sediment which could be tested for several properties including electrical conductivity. Among their TEM pictures, the CNT ropes were coated/wrapped with polymer.

2.5 PC/CNT composites study

Untill now, very few CNT/polymer composites use PC as a matrix. However, there does exist a few papers concerning CNT/PC composites. Research at the Natick Solider Center [47] is aimed towards finding a composite material which has potential as a high strength, high impact-resistant material. PC and CNTs were selected due to their high performance in fulfilling the above requirements.

In conjunction with Boston College, Sennett et al. dispersed both SWNTs and MWNTs in a PC matrix by mixing in a conical twin-extruder, and then aligned by a fiber-spinning apparatus. A good CNT dispersion in a PC matrix was obtained. Mixing time, fiber draw rate and type of CNTs all play an important role in dispersion and alignment.

In conjunction with MER Corporation (one of the major CNT manufacturers), Loutfy et al. [48] made samples in following steps: solution casting was first used to form a film, these films were broken into pieces and then ground, lastly the ground film was melted under pressure to form a cylindrical shape sample. This resulted in a composite sample with a significant improvement in compressive strength for low molecular weight PCs. For higher molecular weight PCs, there is less improvement or even loss of properties.

Another group researching PC/CNT is at the University of Texas at Austin [29]. Twin screw extrusion was used to obtain different CNT concentration samples and these were tested for their electrical properties. They found that as nanotube concentration increases, the viscosity of the composite also increases which means an increase in the elastic melt properties (represented by the storage modulus G').

But both these two method are far from perfect. The first method, mechanical extruder does not provide enough time for CNT to react with PC matrix. Thus there is almost no bonding between CNT and PC matrix. There is no SEM picture in this study which shows that CNT has good bonding or even wetting with PC. Porosity among the specimens is another problem for this method.

The second method, even though they use solution casting method to make film, the already aggregated CNT can not be re-dispersed (they do not introduce an effective way to disperse CNT). Repeat broken and ground film can only yield some “well-dispersed” CNT/PC composite in dozens of μ m. This is not really CNT/PC bonding and the CNTs were shortened sharply by this method. Besides compression strength can be improved even there is no bonding between CNT and polymer. For most of materials, tensile failure is much more frequent happened than compression failure. So it is important to find a way to improve tensile strength of CNT/PC composite.

2.6 Challenges in polymer/CNT composites study

Since the systematic study of CNTs is no more than 10 years old, there are still many unknowns in CNT manufacture and property characterization. There are many challenges in studying CNTs before final commercialization and utilization can be attained. At the present stage, the major challenges are low yield, specialized and expensive tools and lack of knowledge of CNT/polymer composites.

First, high purity and long length CNTs are still hard to manufacture, and the cost of high quality CNTS can be as high as \$1,000/g and present production method can only reach the scale of g/day. Even the cost of unpurified CNTs is around \$60/g, which is already 10 times more expensive than gold. The chirality of CNTs needs to be controlled since it is crucial for electric properties[49].

Secondly, specialized, expensive tools are necessary to study the microstructures due to the small CNT size. SEM, AFM (atomic force microscopy), STM (scanning tunneling microscopy) and TEM are widely used in CNT study. CNTs also demand well-defined testing systems and measurement techniques. Sometimes for more accurate property results, some built-in-house tiny tools and devices are needed which are quite difficult and complicated to complete. This makes it difficult for other researchers to duplicate and improve upon existing results.

Lack of knowledge of CNT/polymer composites is also a crucial problem in CNT/composite study. Like in other CNT related studies, there is only limited knowledge and experimental results concerning CNT/polymer composites. A lot of detailed answers are needed to questions like how to functionalize the CNTs, how to distribute CNTs in the polymer, and how to optimize the percentage of CNTs. Investigation of CNT segregation and interaction and composite processing methods remain underdeveloped. This is one area to which this thesis aims to contribute.

Chapter 3

Sample Preparation and CNT networks from CNT/PC Composites

3.1 Starting Material

There are several different commercially available CNT products. To balance the quality and cost of CNTs (which is currently almost the most expensive material in the world, the purest CNT can be as expensive as 1000 USD/gram), in this study not so pure but can be purified CNTs from CarboLex Inc. were used. Purification also allows the end-user to get familiar with CNTs, it can also have some other effects in the structure of CNTs: like shortening the CNTs and introducing some weak positions which would be beneficial the attaching chemical groups. This allows desirable interactions with the polymer matrix.

Several commercial polymers are good choices for polymer/CNT composites, and there are already some CNT/PMMA [31], CNT/PS [32] and CNT/Epoxy[33] compos-

ites. Polycarbonate(PC) was selected for this research mainly for its high mechanical properties and easy processing. The strength of PC (around 60 MPa) is 5 times higher than PS (12.8 MPa) [9]. Though the strength of PC is lower than PMMA (roughly 100 MPa), but elongation of PC (above 100%) is much higher than PMMA (below 10%). PC is an important engineering polymer in its own right, and thus any enhancements due to CNT dispersion may lead to a very useful new material.

No matter which polymer is used in CNT/polymer composite, it is always difficult to disperse CNT evenly among polymer matrix. But PC has been notoriously resistant to CNT dispersion. Although CNT/PC composites have been produced using mechanical means (see section 2.5), solution casting with CNT/PC has been unsuccessful. One important contribution of this study is the development of a new hot casting process to make CNT/PC composite.

After the selection of an appropriate polymer and CNT, the composite fabrication method should be decided according to different specimens' usage. This work focuses on the productions of CNT/PC films. Several methods were compared and used to cast these films. Temperature, solvent, CNT weight percentage, and drying time are important control parameters in making films.

During our film casting, we use a sonicator and magnetic stir bar (mechanical method) to get better dispersion of CNTs. We also tried polar solvent and surfactants (chemical method) to de-agglomerate CNTs.

3.1.1 Polycarbonate

There are two general kinds of polycarbonate resins. One is aliphatic PC and the other is aromatic PC. Aromatic PC is a common engineering thermoplastic material while aliphatic PC is not widely used. The structure of bisphenol A polycarbonate is shown in Figure 3.1. Bisphenol A Polycarbonate gets its name from the carbonate

groups in its backbone chain, it is made from bisphenol A and phosgene.

Figure 3.1: Bisphenol A polycarbonate

Aromatic PC usually has high impact toughness, high glass transition temperature (T_g) and high optical clarity. PC also has good dimensional stability which permits it to retain its shape in a range of conditions, high heat resistance and excellent processability. At room temperature, PCs have yield strength of roughly 60 MPa at a yield strain of 6% percent, See Figure 3.2 [50]. The T_g of PC is around 150°C. The high toughness of PC also allows large scale deformation compared with other polymers.

Aromatic PCs also have wide applications ranging from consumer products such as beer glasses, safety optical spectacle lenses, medical syringes, to instrument panels in automobiles. Since its discovery in the 1930s worldwide capacity for PCs has grown to more than 1 billion pounds per year.

T_g can be determined by a thermal analysis method. Usually the thermal analysis are techniques by which the physical and chemical properties of a substance, a mixture and/or reaction mixtures are determined as a function of temperature or

Figure 3.2: Engineering stress-strain behavior of aromatic polycarbonate at room temperature and an initial strain rate of $3 \times 10^{-4} \text{ sec}^{-1}$

time, while the sample is subjected to a controlled temperature program. The program may involve heating or cooling (dynamic), or holding the temperature constant (isothermal), or any combination of these.

DSC is the thermal analysis methods selected to measure the T_g . In DSC, the difference in heat flow from a sample or a reference is monitored as a function of temperature or time, while the sample is subjected to a controlled temperature program.

In this study, a DuPont 990 DSC calibrated for temperature and area using indium was used. The 910-module measures temperature and heat flow associated with transitions in the state of materials, such as boiling points, glass transition and heat capacity etc. Glass transition temperatures were obtained using 7~10 mg of sample and a heating rate of 10 °C/min under a nitrogen flow (50~70 mL/min).

The parameters of DSC are as follows: isothermal for 5 minutes at room temperature, then ramp 10.0 °C/min to 300.0 °C and at last ramp 30.0 °C/min to 30.0 °C.

We use in our lab as-received Aldrich PC, its molecular weight is 64 kg/mol and T_g is around 144 °C to 147 °C, see Figure 3.3. From Figure, there is one sharply changed slope of heat flow which corresponding to the T_g of PC. It starts from 141.86 °C and ends at 147.37 °C. 144.86 °C is taken as the T_g of this pure PC sample. This T_g matches the value from Encyclopaedia of Polymer Science.

3.1.2 Carbon Nanotubes

Due to economical reasons and research purposes, we used CNTs which was purchased from CarboLex Inc. with purity range from 50 to 70 vol%, We do not manufacture CNTs ourselves but we do purify the CarboLex CNTs in-house.

CarboLex CNTs are generated by the electric-arc discharge technique, see Figure 3.4. They are single-walled nanotubes (SWNT) with diameter around 1.4 nm,

Sample: PC pure (RT cast/CH₂Cl₂)
Size: 10.1000 mg
Method: DSC
Comment: made Mar18/03, Al spreader, thin side

DSC

File: C:\...purePC\PC-pure.007
Operator: Shanti
Run Date: 21-Mar-03 05:14

Figure 3.3: DSC of pure PC

which form rope-like bundles with an average final diameter of 30 nm as measured from SEM micrographs. The measured lengths of these entwined rope-like bundles (RCNTs) range from one to two microns in the dry state. However, upon SEM sample preparation, the bulk of the RCNTs are trapped within large flakes so the entire length is not resolved.

Figure 3.4: as-received CarboLex CNTs

To purify CNTs (Carbolex), we use procedures previously reported [51] for small-scale batches of CNTs. These RCNTs were oxidatively purified using HNO_3 , repetitively washed with water then centrifuged (15,000 x g for 35 minutes) until a neutral supernatant¹ solution was obtained. Thus, residual catalyst, oxides and carbon species were removed (amorphous carbon or carbon nanoparticles are removed with acid reflux but are not resolved when using SEM). Starting with 109.5 mg of CNTs, we

¹supernatant: the clear fluid above a sediment or precipitate

recovered a very low yield of pure CNTs, approximately 11 mg trapped in a filtration membrane and 6 mg in “loose flaks”.

SEM showed that all supernatant solutions also contain a high concentration of CNTs, see Figure 3.5 . The final neutral supernatant solution is used in our composite formation. Figure 3.5(a)~(d) are supernatants 1 to 4. A lot of tiny ropes exist especially among supernatants 2 to 4. In supernatant 1, only isolated ropes can be found. Figure 3.5(e) are CNT layers and flake. In the upper part of image, there are purified CNT layers. In the bottom part, there is a filtration membrane with trapped CNTs. This is also some residue, mainly metal catalyst and carbon salt from the acid wash, is not shown in this figure.

This CNT/water supernatant suspension shows no sedimentation or aggregation after 8 months, see Figure 3.6. Figure 3.6(a) is the bottle of HNO_3 after 3 months, and impurities were removed by acid or dissolved in this bottle, Figure 3.6(b) are supernatant 1 to 4 after 3 months. Figure 3.6(c) is washed water left.

Free/pure SWNTs do not suspend in water - they are bundled i.e., ropes. These ropes are held together by inter-tube Van der Waals forces, and the final diameter does not change after our purification steps, see Figure 3.7 and figure 3.8. These diameters are calculated from SEM image. By measuring the diameters of a bunch of (around 50) CNT ropes in SEM image, the average diameter can be calculated. By calculation, we can be 95 % confident that with a sample size of 50, the average diameter is off less than 0.083 [52].

From Figure 3.7 and figure 3.8, we can conclude that purification has no effects on diameter of CNTs. Before and after purification, the diameters of CNTs are the same value: around 30 nm.

Figure 3.5: SEMs of purified supernatant and CNTs in membrane

Figure 3.6: Supernatant vial after 3 months (a) acid and impurities; (b) supernatant 1 to 4; (c) washed water solution

From the literature, purification usually shortens the CNTs. But due to the limitation of our SEM, we can not get the actual CNT length. Although it is difficult to judge how the length varied after purification, we can estimate that the final average length is around 5 to 10 μm .

Figure 3.7: Diameter distribution of CNI and CarboLEX CNTs before purification

Figure 3.8: Diameter distribution of CarboLEX CNTs after purification

3.2 Solution casting procedure of CNT/PC film

To make a CNT/PC film, the general steps are as follows: First, we find a common solvent which can dissolve both CNT and PC. There are many solvents that can dissolve PC, but only DCB and Chloroform can dissolve useful quantities of CNTs. Secondly, both PC and CNT are dissolved in separate solutions. Finally, the solution are mixed and the films are cast. At last, the film is cured to let solvent escape.

3.2.1 Room temperature casting and solvent selection

At first, we used the following procedure to make our CNT/PC films and selected dichloromethane as solvent mainly due to easy processing of PC and accumulation of experience we already have in dichloromethane films. We used the following procedure:

- Dissolve PC in dichloromethane (Caledon, laboratory grade)
- Stir CNT with CH_2Cl_2 in sonicator (1510 Branson Ultrasonic Cleaner, output power is 70W) for 15 minutes
- Sonicate the mixture of PC, CNT and CH_2Cl_2 for another 15 minutes
- Cast onto glass plate using solution casting apparatus, see Figure 3.9². The drag speed is around 60 mm/minute
- Cure at room temperature for another 30 minutes with cover

²Solution casting apparatus is a equipment that films can be dragged automatically at a constant speed/uniform thickness. There is a platform with two guided rods where a glass can be put on and films can be made above the glass. Below the platform, there are motor and other parts which can provide constant speed in one direction. There is also a transformer there, so the speed can be selected.

- Vacuum dry 24h at 120°C
- DSC examination to make sure all solvent all removed

Figure 3.9: Picture of solution casting apparatus and spreader

Following this procedure, CNT/PC films which were cast resulted in a poor CNT dispersion quality. See Figure 3.10. In these figures, Figure 3.10 (a) is as-received CarboLex CNT/PC film; Figure 3.10(b) is purified CarboLex CNT/PC film; Figure 3.10(c) is as-received CNI CNT/PC film.(All magnification used here: 2.5 times).

Besides CarboLex CNTs, we also try to make films from highly purified CNI SWNTs. In CNI SWNTs, the raw sample typically contains less than 5% metal catalyst. The length of CNI CNTs is longer than CarboLex CNTs.

It seems that the purer the CNTs, the worse the dispersion quality. We concluded that during the removal of solvent, CNTs aggregate. All films had some large

Figure 3.10: Optical microscope of CNT/PC film (dichloromethane)

CNT aggregates. For making well-dispersed CNT/PC film, room temperature casting method does not work.

3.2.2 High temperature casting and solvent selection

Our final and most successful film production involved using a high temperature casting method with 1,2 dichlorobenzene (DCB) to make films.

To improve both CNT dispersion concentration and quality, we introduced 1,2-dichlorobenzene as the solvent following the results of literature[53]. Among common solvents solubility of CNTs in DCB is the highest, roughly ~ 95 mg/L. (Chloroform is 31 mg/L, DMF around 7.2 mg/L and dichloromethane solubility is unknown), but PC will not dissolve in DCB at room temperature. A much high temperature is needed to dissolve PC in DCB (In room temperature, PC/DCB solution is just gel-like mixture and hard to get clear solution). The detailed procedure is as follows:

- Dissolve PC in DCB (Labcor reagent grade, as-received) at 90°C using a digital hot plate and covered with Al foil to maintain an even temperature
- Stir CNT/DCB with magnetic stir bar for 15 minutes
- Stir the mixture of PC, CNT and DCB for another 15 minutes upon hot plate
- Cast onto Al plate by manual using the same spreading tools as RT casting method
- Cure at 90°C for another 3 hours.
- Vacuum dry 24~48h at 120°C
- DSC examination to make sure the solvent is completely removed

From this method, we obtained some opaque films which were ~ 0.026 %w/w CNT in PC. The dispersion quality is much better than RT casting films. These films could be used later in our high temperature strength tests and also used for TEM and SEM analysis. It could also be used to make some samples to study the bond between PC and CNTs, since there is more CNTs dissolved in PC and therefore a better chance to find their interaction using microscopy.

3.3 Network Found in CNT/PC Composites

Based on the literature review, there are different mechanisms in strengthening polymer with CNTs. Since CNT alignment is always connected with complicated techniques and CNT functionalization needs a more comprehensive circumstance. Network attracts our interests.

Whereas most previous research emphasis has been placed on aligning CNTs during fabrication of the composite to increase tensile strength, we tried to use current simple solution casting method to form some CNT network, which combined with the properties of PC, can lead to a new material which possesses both good mechanical properties and electrical properties from the CNT network.

The method developed here takes advantage of the naturally occurring entanglements between the nanotubes (perhaps stemming from the purification of CarboLex CNTs). The formation of a clear two-dimensional CNT network was found within a PC matrix using a simple technique (high temperature fracture method). Some SEM pictures are included in this section for the purpose of indicating how this technique was developed. The morphologies of pure PC and PC/CNT films fabricated using different methods will also be compared.

3.3.1 Structures from room temperature fracture method

Fracturing the composite allows the study of the boundary between the fillers and the matrix. The morphology of fractured cross-sectional surfaces may be examined using scanning electron microscopy (SEM). The filler and matrix bonding quality can easily be judged to have either a good or a poor bonding depending upon the resolution of these SEM images.

SEM is also a good way to check the filler dispersion quality. Since most fractures happen over a short time frame and at a relative low temperature, the distribution should represent the actual CNT dispersion conditions within the polymer film.

In the very beginning, some PC/CNT films using a room temperature casting procedure were made. Even with high energy sonication over a long time, the aggregates were persistently found.

When these samples were fractured at room temperature and examined by SEM, there were obvious aggregates in some place, see Figure 3.11 (a) and (c).

From the pictures, bundles of CNTs were showed to gather together in some spots, while the majority of the cross-sectional areas were just pure PC microstructure. This is not an efficient way to reinforce the PCs with CNTs.

Besides aggregates, some places where the CNTs were wetted with PC were also found in these samples. This means that there should be a possibility for CNT to have a bonding interface with PCs even at room temperature. From SEM pictures, see Figure 3.11 (b), CNTs were showed to penetrate deeply into PC with no vacancy between CNTs and PC even after stretching.

The room temperature film casting method was then changed to a high temperature casting procedure for the purpose of getting well-dispersed CNT films. Due to the high temperature and associated high energy, and also from the higher CNT solubility in DCB, much better CNT dispersion quality PC films were obtained.

Figure 3.11: SEM images of room temperature cast CNT/PC films fractured at room temperature

CNT aggregates are rarely found in these films under this procedure. These films were fractured again at room temperature. This time only a few nanotubes were exposed, see Figure 3.12.

It is difficult to form any conclusion from these isolated CNTs (see Figure 3.12(b) and (c)) about the reinforcement mechanism. It is believed that in these films CNTs are much better dispersed than room temperature casting, hence fewer CNTs show up in SEM pictures. This result is comparable to previous studies on room temperature fracture surfaces of polymer/CNT composites [9].

In order to better view the micro-structure of these films, a high temperature fracture technique was explored.

3.3.2 CNT network found from high temperature fracture method

After blending CNT with PCs, a lot of observations on these films were done using SEM to examine how CNTs reinforce PC matrices. The clear DCB PC/CNT films were especially helpful in these observations.

Some DCB PC/CNT films were fractured at room temperature. Few interesting images were seen due to the thickness of these films. Usually the thicknesses of these films are roughly 10 microns, which are quite thick for present SEM imaging. SEM images therefore really showed only the actual surface of these films.

At room temperature, the fracture surface does not give much useful information about the action between PC and CNTs when applying a load. This is partly due to the use of SEM (only surface images are possible to observe); partly due to the fracture time which is too short (no chance for CNTs to carry the load and then be pulled out); partly due to the CNTs still imbedded at the large fracture area of samples.

Figure 3.12: SEM images of Tg-cast CNT/PC films fractured at high temperature

To study the properties of CNT/PC composites, an efficient way needs to be found to make the films thin enough, to expand the fracture processing and to increase the plasticity of PC/CNT composite.

Based on these ideas, a high temperature stretch method was developed to fracture the samples at a constant slow strain rate above the glass transition temperature in order to examine these films. Then SEM was used to check these fractured surfaces.

Using this technique, a network was revealed as we expected, see figure 3.13. As shown, it is quite clear that there is an entangled CNT network in the PC matrix.

Figure 3.13: SEM images of CNT/PC network

This clear network image has never been seen in previous literature, notably at micron length scale. A network-like structure has been viewed by at a nanometer scale in TEM [29], but a network has never been reported using SEM at a micron scale.

The detailed procedure for manual stretching is as follow. A 2.5cm × 1.5cm trans-

parent section of the film was clamped in a manual stretching device, and maintained in an oven at around 150°C, five degrees above the T_g of polycarbonate. The sample was then slowly stretched at a low strain rate, with care taken to maintain the oven temperature (< 2% strain for each load and heat cycle). The film was stretched in this manner until it fractured, usually at an elongation of average 30%.

The high temperature, several degrees above glass transition temperature and the slow strain rate will make PC become more mobile and have more time to coat the CNTs and to keep CNT structures constant. The bulk of the PC matrix not involved in the network will become separate at this high temperature. The high temperature will make film become some kind of thinner, which will also facilitate the observation of CNT network. SEM is mainly a surface microscope technique. Too thick film will bury the CNT network and hard to find in SEM. Thus some phenomenon appeared which is difficult to notice at room temperature. Here, films from the high temperature casting procedure which yielded well-dispersed CNT/PC clear films were used to manually stretch around the T_g of PC (150°C).

Figure 3.14 shows a series of SEM pictures of a fractured sample. Images from magnification of 40×, to 2,200× to 8,500× were showed one by one. as shown, the fracture surface is quite rough, implying a lot of deformation of PC.

From these SEM pictures, it is also found that the thickness of film was reduced to 1 micron at the fracture edge. This edge contains fibrils with an average diameter of 130 nm. Based on the diameter of 30 nm for the RCNTs after purification (CarboLex CNTs), the larger diameter observed in Figure 3.13 suggests that these fibrils contain CNTs which are coated with polycarbonate.

Additionally, these fibrils are joined by nodules spaced approximately one micron apart, which is similar to the measured average length of the RCNTs after purification. However, these fibrils are not pulled out of the polymer matrix, as commonly noted with room temperature composite fractures. The fibrils are shown to bridge the

Figure 3.14: SEM images of network fractured at high temperature

fracture, which might lead to enhanced strength of the composite.

3.3.3 Fracture surfaces of pure PC under microscope

For comparison, some pure PC film samples were also made and fractured both at room temperature and at high temperature (above the glass transition temperature). The same method which was used for CNT/PC film samples was used, The fractured surfaces were checked in SEM to compare what the different morphologies the pure PC films should have. It is hoped that these sample pictures will facilitate the understanding of CNTs network in PC matrices.

Figure 3.15 is the picture of pure PC fractured in both room and high temperature. In Figure 3.15, most of the pictures just shows some typically polymer structures. The different structures for different temperatures is also quite obvious: at room temperature the PC films are more brittle and the fractured surfaces there are more flat, see Figure 3.15(a) .

Since PC is a good engineering polymer, it is quite stiff at room temperature and does not have much elongation when broken at room temperature. However, at high temperature, the films showed more plasticity and thus gave more rough fractured surfaces, see Figure 3.15(b) and Figure 3.15(c). Importantly, neither of them has networks which were found in PC/CNT films.

3.4 PC reinforcement with CNT network

3.4.1 CNT Weight percentage calculation

One limitation of SEM observation is that it is only possible to view a small representation sample of material. Thus, it is difficult to be certain that the network is

Figure 3.15: SEM images of pure PC fractured surface

truly uniform throughout the sample. To build confidence that a uniform dispersion exists everywhere in the film, we estimated the required CNT concentration for such a network and compared it to the actual concentration in the sample.

In the following calculation, we obtained a rough estimate for the minimum CNT concentration necessary to form a uniform network like that observed in Fig 3.13 throughout the film. We will see that the actual CNT concentration is very close to that estimate, leading confidence to the assertion that the network exists throughout the film.

Some assumptions were made in this estimate process. First, the network is formed in 3 dimension. Secondly, in each direction the distance between nodes in the network is the same as the average distance we observed. Last, CNT length is the same and the density of CNT ropes is the same as the single wall CNT.

For a 3-D calculation, a cubic arrangement of CNT ropes was used, see Figure 3.16. In this model, the volume of cubic PC is L^3 (L: the distance between CNT nodes in network). The volume of CNTs is $3L \times 3.14 \times R^2$ (R: the radius of CNT bundles)³. For CarboLex CNTs, R is 15 nm and $\rho_{CNT} = 1.34$ (g/mm³). For PC/CNT network, the L we obtained from SEM is roughly 2 microns and $\rho_{PC} = 1.20$ (g/mm³).

Thus, weight percentage (W%) of CNT in PC:

$$W\% = \frac{3L_{CNT} \times 3.14 \times R_{CNT}^2 \times \rho_{CNT}}{L_{CNT}^3 \times \rho_{PC}} = \frac{3 \times 3.14 \times R_{CNT}^2 \times \rho_{CNT}}{L_{CNT}^2 \times \rho_{PC}} \quad (3.1)$$

So W % of CNTs needed to form a network is 0.059%

For most films that have been made in this research, the W % ranges from 0.026% to 0.26%, which is quite near this percentage. This implies there should be a high chance to form a networks over significant areas if the casting technique is properly controlled.

³There should be 12 CNT edges in each cubic, but each edge is always shared by 4 cubes

Figure 3.16: Network model structure

3.4.2 Network reinforcement in PC/CNT composite

Although previous studies used much higher concentration of CNTs in composites [54], very rarely was the formation of a network suggested. For PC/CNT composites previously reported in literature, a concentration of 20 wt% CNTs (considerably above the CNT percolation threshold) in a melt-blended polycarbonate/CNT composite showed the formation of a randomly oriented interconnected lattice of CNTs within the PC matrix[29].

Percolation theory usually deals with the effects of varying, in a random system, the amount of interconnections present [55]. In a two-phase or a multi-phase system, as the connectedness, density, or concentration of one phase increases, long range connectivity of this phase will suddenly appear. This is the percolation transition. Conductivity, network formation and glass transition are all believed to experience this kind of transition. For a polymer composite, the percolation threshold mainly depends on the particle size, fractal dimension, assistant agent and casting parameters,

such as shearing rate used to disperse the fillers in the matrix.

In another polymer/CNT composite, a multi-walled CNT/epoxy resin composite containing 5 wt% CNTs (ultrasonically dispersed), the nanotubes remain curved and interwoven, essentially forming a network again above the percolation limit [33].

The image of fibrils obtained in this research was joined by nodules spaced approximately one micron apart (Figure 3.14). It was also found that these fibrils were not pulled out of the polymer matrix, as commonly noted with room temperature fractures. Rather the fibrils were shown to bridge the fracture, which might lead to enhanced strength of the composite. This bridging mechanism could be an effective route for load transfer that is necessary for PC/CNT composites [56].

The estimate described above showed that a CNT network is possible with only 0.06% weight loading of nanotubes. This network might have formed from a critical amount of CNT entanglements generated at the water/DCB phase boundary when re-dispersing CNTs in DCB. Some entanglement points may even be retained from the purification process when the CNTs sediment was extracted after the acid reflux and suspended in the highly concentrated supernatant phase. These nanotube-nanotube interactions in solution are stable and cause connectivity between tubes.

CNTs of a critical length naturally form inter-tube entanglements that have been compared to the critical entanglement length associated with polymer chains [57]. The energetics of formation of a random CNT network structure within the PC matrix may be considered to be more favourable than incorporating aligned CNTs over the same macroscopic scale. The randomly dispersed system is entropically more favourable. Pre-existing entanglements may even act as “nucleation sites” where further entanglements are trapped during the mechanics of hot casting and kinetics of slow evaporation of the solvent (90 °C for 3hrs). The measured diameter of the networked fibrils is 3-4 times that of the pure RCNTs, suggesting a thick adsorbed layer of polycarbonate. Stretching above the T_g of the polymer may have enhanced this

adsorption since there may be sufficient motion along the polycarbonate backbone to wet the RCNT surface.

Besides the appearance of a network, two other features are also of interest, the appearance of nodules and the complete curvature of a CNT rope, see Figure 3.17 and Figure 3.18.

These nodules and curved CNTs may connect the fibrils. It is believed that the nodules are junction points where the RCNTs have crossed or bundled together. The tensile strength of the composite may be affected by the polycarbonate/RCNT interaction at these points. The nature of the adhesion between polycarbonate and the RCNT is difficult to characterise. The outer surface of the RCNTs may contain debris from oxidized SWNTs [58] and, after acid reflux, the surface of the RCNT may have COOH groups [59], which all aid the PC/CNT interaction.

Figure 3.17 shows evidence of wetting which appears as a few droplets adhering to a single RCNT that extends from the fracture after stretching. This indicates that the simple method described here for preparing films yields the same intimate polymer/CNT blend when compared to more intricate techniques reported previously by various authors. The morphology is then dependent upon the method of composite preparation. The formation of a network of entangled CNTs in the fracture surface, as have been shown here, is markedly different than the morphology of conventional polymer/CNT fracture surfaces reported to date.

3.5 Annealing after high temperature casting

There were some limitations on the high temperature casting method described above. The films always turned brittle during the processing of drying and the films were not so even in thickness, nor were the films completely transparent. Upon attaining the

Figure 3.17: SEM image of CNT nodules

Figure 3.18: SEM image of curved CNT at fractured edge

network in PC/CNT films using high temperature casting, modifications were needed to ensure an easily reproduced procedure and to yield more uniform films, which in future could be used in mechanical testing.

Since DCB is not so an easy solvent to handle for PC, the films always have some defects (air bubbles, uneven thickness and sometimes cracks). So an effective way is needed to keep both the network formation constant and also have a good film quality. Based on this, we thus introduced an annealing step after casting and before the 3 hour cure at 90°C. The annealing temperature is around T_g and lasts 1 to 2 hours.

This is helpful to get a much thicker and even film, and the films are much clear than the films which are not annealed. See Figure 3.19, which shows clear film on the non-stick casting plate and no perceptible CNT aggregates under the magnification of 2.5 and 10 times. Transparent film also indicated a good dispersion of the CNTs in the matrix.

Drying the films above the T_g of the matrix perhaps also facilitates the interaction between the polycarbonate and the CNT. The previous studies on PVA and PVK involved vinyl polymers, the preferred conformation of which is either an extended chain or a tightly wound helical form. However, polycarbonate can form a range of energetically favourable conformations, from an extended zig-zag to flat helical conformations, with a large radius [60]. An example of an amylose chain (with a flat helical conformation) wrapping around a CNT was reported recently [61]. Whether such wrapping of the CNT by polycarbonate chains occurs in the present study is not confirmed. However, drying at a temperature slightly above the T_g of the matrix does seem to improve the compatibility and give a more clear film.

By imposing this annealing procedure, some very good quality films were cast. From these films much bigger specimens could be easily obtained. Since the film thickness is quite even and specimens are much bigger, mechanical testing becomes

Figure 3.19: Optical microscope image of high temperature cast CNT/PC film (The rough texture of films here mainly comes from the unevenness of glass plate surface.)

possible. As shown in Figure 3.20, a network was also present using this annealing procedure and while the overall PC/CNT film quality was improved.

In this film, CNT dispersed really well and it has excellent transparency. This clear film has never been obtained by any researcher before in CNT/PC composite, or even in most of CNT/polymer composite. Many people using solution casting method to make films, but most of time their films show some severe aggregation at micrometer scale. Untill now, we can make some well-dispersed CNT/PC composite specimens big enough for mechanical property testing with possible chemical bonding between CNT and PC(though the weight percentage of CNT is quite low).

CNTs were blended quite evenly among PC in the present research and it is believed that there are networks within the PC matrix. Effects should then be focused on how to improve this kind of network and the network influence on PC/CNT properties. Mechanical testing results will be discussed in next chapter. Surface conductivity testing is also a good direction for future research. Futrue work also includes examining the composition of the network and junctions.

3.6 Mophorlogy comparison from different casting methods

In summary, different casting method yield different CNT/PC composite microstructures. The CNT network formed at what is the lowest concentration reported to date, and was examined under SEM.

It is believed that the entangled geometry of a CNT network is intrinsically more favourable to form than to align CNTs in this kind of PC/CNT composite and should lead to a higher strength, high electrical conductivity material through network.

Figure 3.20: SEM images of CNT/PC(with annealing) fractured at high temperature

Different casting procedures were used to form the network, and different fracture techniques were used to reveal this kind of network. The comparison results are showed in table 3.1.

It appears that high temperature casting always yields much better dispersed films than room temperature casting. The technique of high temperature casting is not without difficulties. In one aspect, it is not an easy process to control, high temperature is needed for quite long times to get good films, and it was difficult to obtain uniform thick films. Additionally, the solubility of CNTs is still quiet low (maximum weight percentage of CNT in PC remains below 1%).

Note that the fracture technique here is just for revealing the network. Even in room temperature fracture, the network should be there for the film from Tg casting, but the short break time and less flexibility of PC at room temperature make it hard to keep the network constant. Thus only isolated CNT were found most of time.

Even for Tg method with annealing, there is still a long way to go before really high concentrations of CNTs can be added and a well-dispersed CNT/PC composite can be formed. But appearing of CNT networks on a PC matrix does give some hopes for fabricating a really good composite material.

	Film quality / Cross-section structure	Thickness	Observation from RT fracture	Observation from Tg fracture	Remark
RT casting	Clear, uniform film Flat surface	Even thickness	Severe CNT aggregates	Severe CNT aggregates	
Tg casting with annealing	Pretty clear film Flat surface	Even thickness	Isolated CNTs	CNT Networks	
Tg casting without annealing	White film Rough surface	Uneven thickness		CNT Networks	with defects

Table 3.1: Morphology comparison from different casting methods.

Chapter 4

Property testing of carbon nanotube/polycarbonate composites

The high cost of CNTs needs to be addressed along with other scientific and engineering issues such as controlling CNT dispersion quality and improving CNT/polymer bonding. Pure CNTs cost up to 1,000 US\$/gram. Therefore using ASTM standard size samples of CNT/PC for mechanical testing become very expensive.

To reduce the whole study cost, tiny samples are used and hence some testing equipment adjustments are needed. Sometimes a new testing system has to be set up because of the small dimension of samples. Additionally small samples must be representative of the bulk samples.

In this chapter, Young's modulus results from TMA (Thermo-Mechanical Analyzer) and break strength from a built-in-house MTS system will be discussed. Also the thickness measurement will be introduced because it plays an important role in the strength calculation. There are also other attempts to measure other CNT/PC

properties.

4.1 Thickness issue in mechanical testing

The small size and large thickness variation of PC/CNT film samples make the thickness measurement one of the key issues in mechanical testing. To make mechanical testing results more accurate and the experiment much easier to handle, three different methods were tried.

Even a small error in thickness will have significant influence in stress testing. For example, a thickness error of two microns is large with respect to a film thickness of 10 to 30 microns. Even two microns will cause 10% error which is large compared to potential mechanical improvement obtained by a small concentration of CNTs.

4.1.1 Thickness measurement method

Three different methods were tried to measure the thickness of PC/CNT films. They are described below.

Weight method

It is quite simple and easy to use the weight method to calculate the average thickness of film. For films of uniform thickness, this average thickness should be very close to the real thickness values.

Since the density difference of PC and CNT is so small and there is never more than 1 % CNT in films, usually only the PC density is used to calculate the thickness of films. A square piece of sample of known area (Usually 20mm $\times$ 30mm) is used. A levelled digital balance was used to weigh this sample (Accuracy of weight is ± 0.1 mg).

SEM method

Since the weight method is not a direct method to measure thickness, at least one direct method is needed to check the results from weight method. Optical microscopy and SEM methods are among the many options.

For SEM method, samples were cut and then fixed for viewing on a standard SEM puck. From the SEM image, the thickness can be easily measured at real positions along the cut edge of the film. The important factor affecting this thickness measurement is the shape of the cross section. Using a sharp blade and a relatively low temperature can lead to well defined edge. But at medium temperature with a blunt blade, some odd curved edges can also appear.

SEM parameters such as brightness, magnification and contrast are also critical in this method, see figure 4.1. The film the edge is quite clear, but sometimes it is not easy to find the edge.

Figure 4.1: Thickness measurement from SEM

The other problem of this method is that it can only be applied in quite limited

areas. The tilt angle between the sample and electron beam will add some errors on the final measurements.

Using this method, usually at one film edge, 4 or 5 experimental thickness were measured and an average thickness $T(\mu m)$ is calculated.

Optical microscope method

The optical method is almost the same as the SEM method and a Zeiss Axioplanz imaging microscope is used. The only difference from SEM is that the measured area is larger and after cutting, the sample is not fixed on a puck, but onto a glass slide. This glass can sit on the platform of optical microscope. By adjusting the focus of microscope several times, the focal surface could be adjusted to coincide with the cross-section of the cut edge. Thus, thickness can be measured at this place.

Optical pictures were used to get the average thickness for each part, see figure 4.2. The film edge is quite distinct from microscope and the magnification bar is much bigger than SEM method.

This method can be adopted to much bigger areas than SEM and it is also a direct method. The only handicap is finding the edge surface when focusing the optical microscope. This needs both patience and experience.

4.1.2 Method comparison

Different PC films were used to compare the different thickness measurement methods. The detailed results are showed in table 4.1

From the table it is obvious that there little difference among these three methods, especially between the weight method and the optical method. The biggest measured difference between these two methods is around $2.4 \mu m$, which is around 4 % of the whole thickness.

Figure 4.2: Thickness measurement from optical microscope: (a) film; (b) air between film and glass; (c) glass surface out of focus

Sample	Weight	SEM	Optical Microscope
Sample A	67.9	/	68(58,67,78,70)
Sample B	62.4	/	60(67,57,55,60)
Sample C	60.4	54.0(49.1,58.0,53.6,55.3)	58(60,63,57,53)

Table 4.1: Thickness of samples using different measurement methods (μm)

The weight method always yields the biggest thickness which is possibly due to the presence of some solvent. Also, the blade may compress the film a little bit when the samples were cut.

The optical method is simple and direct, but needs more time to adjust the microscope and set up. It is a destructive method. Once the sample is cut and mounted, it can not be used again for mechanical testing.

In the SEM method, it is difficult to control the tilt angle between the electron beam and sample. Since the sample tends to buckle (or curl) under the beam. These thickness numbers are less reliable. They are much different from the average thickness.

For an uniform film, the weight method is sufficient. For less uniform films, the optical microscope can help check the thickness at some localized places. SEM will be useful only for very thin films.

4.2 Young's modulus results from TMA

4.2.1 TMA set-up

A TMA: SSC5200 from Seiko Instruments Inc. was first used to test mechanical properties of PC/CNT composites. Due to its load limitation, only the Young's modulus results for these composites can be obtained.

TMA has many functions both in thermal and mechanical testing. SS (stress/strain) measurement is one of the frequently used functions. There are two modes for the SS function, force control and length control.

In force control mode, the force or stress can be controlled and the resulting length or strain change can be monitored. This mode is suitable for measuring CTE (coefficient of thermal expansion), storage and loss moduli, bulk expansion and even creep.

In length control mode, the length or strain can be controlled and the resulting force or stress change can be monitored. The applications for this mode are: measuring stress relaxation or establishing a stress-strain curve, etc.

The basic specifications for TMA/SS function are:

- Load cell: 100 gram
- LVDT: 20 mm
- Optimum frequency: roughly 0.5 ~ 0.05 Hz
- Temperature: room temperature to 400°C

The Young's modulus of CNT/PC composite can be determined from the length change while applying a sinusoidal waveform load (the Force control mode) at a

constant temperature (usually room temperature). The steps involved with this procedure is listed at Appendix A.

4.2.2 Young's modulus results

Young's modulus of Tg annealed films were measured following the above procedures. Rectangular strips of the film were cut ($10\text{mm} \times 2\text{mm}$, thickness $0.010 \sim 0.06 \text{ mm}$) and mounted between two chucks. The parameters were set: offset load = 75g, load amplitude = 50g, initial pre-load = 5g and cycling frequency 0.01 or 0.05 Hz.

A sinusoidal waveform load/stress was applied and it made the displacement/strain follow the same waveform trend, shown in Figure 4.3. In Figure 4.3, the frequency was 0.01, and the CNT concentration was 0.063% w/w.

Figure 4.3: Displacement curve of TMA for Young's modulus measurement of CNT/PC = 0.063W/W%

Once the stress amplitude and corresponding strain amplitude are known, using the following equation, the complex Young's modulus Y^* (MPa) can be easily calculated:

$$Y^* = \frac{L \times F_0}{S \times L_0} \times (\cos \delta + i \sin \delta) \times 9.8 \quad (4.1)$$

Where:

L = sample length (mm)

S = sample cross-section area (mm^2)

F_0 = load amplitude (g)

L_0 = displacement amplitude (μm)

δ = phase difference (radian)

Y^* = complex Young's modulus (MPa)

In this research, CNT/PC films made with CNT concentration varying from 0.026% w/w to 0.26% w/w were tested, and their Young's Moduli were then calculated. The detailed Young's Modulus results are showed in Figure 4.4.

In Figure 4.4, it shows that as CNT concentration increases, there is a moderate (29%) increase in the Young's modulus for a loading of 0.06% w/w CNTs when compared to the pure 'wet annealed' PC.

Figure 4.4 also shows that Young's modulus decreases as the concentration of CNTs increases above 0.06%. This is the same trend with most filler reinforced polymer composites.

On the one hand, these results demonstrate a rather significant increase in Y (29%) given the small amount (0.06% w/w) of RCNT added. On the other hand, the decrease in modulus beyond this amount suggests that there is a limit to the stiffness increases that the RCNTs can impart on the PC matrix.

Figure 4.4: Young's modulus results

4.2.3 TMA Results discussion

For comparison, the theoretical Young's modulus for a PC matrix containing different w/w percentage CNT, based on a simple "rule of mixtures" estimate, is shown in Figure 4.5 using filled circles.

The rule of mixtures is a simple equation commonly used in composite study [2]. It describes the Young's modulus of a composite, Y_c , containing an aligned filler in a matrix. The rule of mixtures value is an upper bound expected in the ideal case of perfect dispersion and alignment of the fillers, and perfect bonding at the polymer/filler interface.

$$Y_c = Y_m \times V_m + Y_f \times V_f \quad (4.2)$$

Where:

Y_m = Young's modulus of matrix (MPa)

V_m = Volume fraction of matrix (%)

Y_f = Young's modulus of filler (MPa)

V_f = Volume fraction of filler (%)

Y_c = Young's modulus composite (MPa)

It is clearly shown in Figure 4.5 that in the 0.06% w/w composite, the RCNTs are providing 85% of this theoretical improvement to Y . As the concentration of CNTs increases, the difference between the theoretical value and real experiment value becomes bigger.

Interestingly, this very low CNT concentration approaches the minimum requirement in which a three dimensional network may occur within a given volume of PC, based on the average dry length and diameter of the RCNT starting material (see

Figure 4.5: Young's modulus results and the theoretical values

chapter 3). This percentage can also be compared to the percolation threshold for forming a CNT network.

There may be many reasons why the Young's modulus begins to decrease after only 0.06% CNT. It may be due to a limit in the solvability of CNTs in DCB, or it may be the results of poor interface bonding, or even because CNTs become aggregated again at a relatively high concentration.

Firstly, as the CNT loading increases, there is more chance for CNTs to aggregate. Since the procedure which was used in this research can only dissolve roughly 0.05% CNTs in DCB solution. (For example, in each sample, two grams PC and 10 ml DCB at different CNT concentrations was mixed. However what really dissolves in DCB is unchangeable: 95mg CNT per liter DCB. That is 0.05% CNT in PC solution.) The remaining non-dissolved CNTs are more difficult to respond to sonication and thus have more chance to aggregate.

Secondly, non-dissolved CNTs will not have the chance to get wetted by PC, which is the key factor in forming the bonding between PC and CNTs. Therefore the mechanical properties are not so effectively improved by non-dissolved CNTs.

4.3 Break strength results from built-in-house MTS

4.3.1 MTS fabrication and Calibration

The load limit for the Seiko TMA is 100 grams (roughly 1 Newton), and most Material Testing Systems (MTS) are designed to test the properties of metal at standard dimensions. Therefore, for most traditional mechanical MTS systems, the optimum

load is around hundreds to thousands of Newtons and their error is around tens of Newtons. For PC/CNT films, the small dimension of the sample make it difficult to get useful and accurate values from standard MTS equipment. Also, the Seiko and TMA does not have capacity to break these PC/CNT films. A new system is therefore necessary. The optimum load should be in the tens of Newtons and the error should be not bigger than 1 Newton. Based on these specifications, a new MTS system was designed and built.

The built-in-house MTS was designed, manufacture and assembled in the machinshop, in the Mechanical and Aerospace Department, Carleton University. In Figure 4.6, it shows the picture of MTS built-in-house. Basically, this MTS system has the following four sections:

1. Frame section

This includes a support structure, two aluminum clips for fastening the sample, two guide rods for obtaining a straight movement when applying the load, and a platform (mainly for fixing the motor subassembly), etc.

2. Stress-strain data acquisition section

A linear voltage difference transformer (LVDT) and load cell were used to monitor both the real time displacement and the real time load values. Thus the stress and strain were easily calculated.

3. Load adaptor section

A motor, a pulley, an O-ring, a big brass nut (with an outside groove for the O-ring) and a steel plate were combined to give the upper clip a straight movement at a constant speed.

4. Power supply section

Four different kinds power supplies were used in this system. LVDT : ± 15 volts, Load cell : 2 volts, motor: 12 volts, and power supply for computer.

The basic parameters for this MTS are:

- Load Cell: ~ 50 lb or 220N
- LVDT: ~ 4 inch or 100 mm
- Optimum load applying rate: ~ 0.15 to 0.5 mm/s
- Temperature: room temperature only

Besides the MTS system, to help analysis the data obtained from MTS, Data acquisition was used to transfer the data from MTS to a computer. In this research, the OMK-AD812 analog data acquisition module from Omega engineering Inc. was selected.

The OMK-AD812 has eight analog inputs and these inputs can be used single-ended or in odd/even pairs differentially ended. An internal reference voltage of $4.096\text{V} \pm 0.2\%$ yields a conversion of 1mv/LSB . There are also four digital input/output ports from the host printer port in AD812. The digital I/O lines can be set or cleared based on the analog inputs with the bundled software.

The module is connected to a PC compatible printer port and no external power supply is needed. The voltage signal outputs from LVDT and load cell were set to different analog.

After the MTS was set up and the data bench was connected (see Figure 4.7), four different lengths and five different weights were used to calibrate the LVDT and load cell. Straight lines were obtained for both components which means there are good

Figure 4.6: (a) Built-in-house MTS; (b) MTS mechanical part design model

linear relationships between the output numbers of the data bench and the real load and displacement values. See Figure 4.8 and Figure 4.9. The major testing procedure is listed in Appendix B.

Figure 4.7: Data bench connection

4.3.2 Strength results from MTS

After the built-in-house MTS was set up in the lab, the first tensile stretch experiment was tested on a pure PC film which was made in the lab. The result was compared with the results from encyclopedia of PC [50], see Figure 4.10. Figure 4.10 (a) is the stress-strain curve from encyclopedia of PC. Figure 4.10(b) is the stress-strain curve from built-in-house MTS.

Figure 4.8: Calibration for LVDT

Figure 4.9: Calibration for Load cell

Both sets of data have roughly the same yield strength (around 60 MPa), elongation (above 100%) and almost the same stress-strain profile after yield. Considering that the PC molecular weight and strain rate are not the same in these two tests, these results are quite good and prove that the MTS can give good results, despite the non-conventional specimen.

After testing pure PC, different concentration PC/CNT films were tested. The same CNT percentage films as in Young's modulus testing were used here (varying from 0.026% w/w to 0.26% w/w). Their in-process stress strain data can be obtained from the built-in-house MTS. The detailed strength-strain data, and how to transfer raw data to stress-strain curve are showed in Appendix D.

Figure 4.11 is a typical stress-strain curve obtained from built-in-house MTS. It is quite clear that the elongation of CNT/PC reduced sharply compared with the elongation of pure PC. The break strength of CNT/PC composite is almost the same level as the pure PC.

Since the CNT/PC composites are more brittle than the PC matrix, the break strength of PC/CNT films was the focus of this research. Figure 4.12 shows that as CNT concentration increases, there is not much change in the break strength, remaining in the vicinity of 50 MPa. This is almost the same level of strength as that of 'Wet annealing' PC. And due to the sample preparation time is quite long and not all the testing results from the samples can be used (some samples are failed not in the middle or have defects will not yield useful data we need), we only can have limited strength results. All these conclusions are based on the limited results we have.

Figure 4.12 also shows, in some cases as 0.146% and 0.178%, the break strength even decrease slightly. But this decrease is not so big, we still can conclude that our CNT/PC composite can at least keep the strength of pure PC. This decrease may also come from the imperfect film technique and not enough specimens tested. (We

Figure 4.10: Pure PC S/S curve comparison: (a) curve from literature(This curve was already shown in chapter 2, here just for comparison); (b) curve from built-in-house MTS

Figure 4.11: CNT/PC stress-strain curve

usually get 3 specimens for one weight percentage, but for some high concentration, we sometimes do not have 3 specimens).

It should be noticed that the strength of pure PC also decreases a little bit after go through sub T_g annealing. But this can be easily recovered by some chemical treatment, like adding some polymer modifiers [62].

Compared to other research results, for example CNT/PMMA composite samples, they retain slightly more than half the original break strength when blend the CNT in PMMA matrix, we can cast transparent well-dispersed CNT/PC films with CNT network. Even the strength is not improved, we at least not decrease it too much. And this method will help other researcher in their study to get well-dispersed CNT films. Beside CNT network may prove useful in other application, such as conductivity.

From Figure 4.13, we can see that elongation of CNT/PC composite decrease

Figure 4.12: Break strength results

sharply compared with pure PC. And as CNT concentration increases, it seems elongation do not change much. This is partially because of CNT, usually when adding filler, the elongation of composite will decrease some amount; partially because of sub Tg annealing, at most time annealing will embrittle the polymer composite[62].

Figure 4.13: Elongation results

Chapter 5

Conclusions

5.1 Results from CNT/PC composite

The properties of a nanocomposite material -carbon nanotube /polycarbonate composite, was studied in this research by using SEM, TMA and built-in-house MTS system.

The samples were made by a modified solution casting method at relatively high temperature. A large even and well dispersed CNT film was eventually obtained by following the experiment procedure. CNT/PC films with CNT concentration varying from 0.026% w/w to 0.26% w/w have been made by this method.

A micro scale network of CNTs was revealed by stretching the CNT/PC sample around Tg and then examining by SEM. This network is obtained from purified CarboLex CNT supernatant and at the CNT concentration of 0.026%.

Thermo-Mechanical Analyzer (TMA) was used first to test mechanical properties of PC/CNT composites. It shows that as CNT concentration increases, there is a moderate (29%) increase in the Young's modulus for a loading of 0.06% w/w CNTs when compared to the pure 'wet annealed' PC. Interestingly, this very low CNT

concentration, provides 85% of the theoretical aligned CNTs improvement to Young's modulus. This percentage is also near the percolation threshold for forming a CNT network.

TMA also demonstrated there was a limit to the stiffness increases that the RCNTs can impart on the PC matrix. Young's modulus of CNT/PC composite decreases as the concentration of CNTs increases above 0.06%.

To test the strength-strain properties of films, a built-in-house MTS system which was most suitable for the medium load application, was manufactured. By installing the LVDT, Load cell, Data acquisition hardware and software, the stress-strain curve of films can be obtained.

But unfortunately when tested, the CNT/PC samples show that as CNT concentration increases, there is not too much change in the break strength, remaining in the vicinity of 50 MPa, This is almost the same level of strength as that of 'Wet annealing' PC.

5.2 Future work

The mechanical properties of CNT/PC composite which were tested in-house were the Young's modulus and break strength. However, it is also desirable to characterize the properties of the network in CNT/PC composites in terms of electrical conductivity, hardness and even fatigue. The limitation as to the dimensions of these samples and special equipment need to be considered to finish these experiments.

5.2.1 Conductivity testing

The CNT concentration in this research can be as high as 0.26 % (four times of the percolation limit), and there is a connected network in this CNT/PC composite.

Therefore, another property improvement is anticipated, good electrical conductivity.

In recent years, dispersing conducting fillers (such as carbon black) in insulating polymer matrices have been widely studied because of their importance both in basic science and engineering applications (for example, lithium-polymer batteries.). For good applications, conductive polymer composites need to fulfill the following requirements: low filler content (this will keep the flexibility of matrix), low resistance and low conductivity variation under mechanical or thermal loading[63].

The low filler concentration needed for an increase in the macroscopic conductivity is also best described by the percolation transition theory. For electric conductivity of most polymer composites filled with powdery materials, the percolation threshold is between 5 and 20 Vol%.

The percolation threshold will decrease significantly as the aspect ratio of the fillers increases. Since CNT has the highest aspect ratio among carbon black fillers (see chapter 2), it is believed that CNT/polymer composites will have a great application in conducting polymers. Already some literature calculations and experiments [64], showing that the percolation for CNT conductivity is no more than 0.04%, due to their high aspect ratio.

In general, both DC (direct current) and AC (alternating current) conductivities can be measured. For the actual measurement, two probe or four probe tests are the most common ASTM methods. This test method, extremely sensitive to samples with and without a conductive filler.

Due to the limited equipment availability, we can not test the PC/CNT composite conductivity in-house. Therefore, we are pursuing a commercial testing company, Bodycote material testing Canada Inc, to obtain these results. The sample size requirement is quite large 50×50 mm compared to other mechanical tests. We already finished the sample preparation for this.

5.2.2 Hardness testing on nanoindentation

The nanoindentation technique enables testing materials at a submicron scale. An indenter is pushed into a sample's surface, such as a polymer composite film, and the ultra-low load indentation system provides continuous record of hardness, stress and strain, etc. The mechanical properties can be evaluated at very small localized areas.

For CNT/PC composite, the hardness testing in local areas will help the characterization of CNT network dimension and dispersion. It is also a good way to get stress-strain curves. Further contact with outside labs using nanoindentation is under way to try to test the present CNT/PC composite.

5.2.3 Fatigue testing

The toughness of PC is quite high among engineering polymers, and the CNT network should facilitate absorption of the fracture energy. Thus the fatigue properties of this PC/CNT composite should show an improvement over the pure polymer. However, the film sample thickness is too small and requires more elegant equipment to test this property.

Appendix A

TMA testing procedure for Young's modulus

The Young's modulus of CNT/PC composite can be determined from the length change while applying a sinusoidal waveform load (the Force control mode) at room temperature. The detailed procedure is list below.

- Cut the samples

A square piece with exact dimension measurement is required. The thickness of PC/CNT films used in these tests was measured as in section 2.1.1. For most film samples, the width was 2 mm, unless their thickness was less than 20 μm . In this case, the width was increased to 3mm. The length of the samples need to be sufficient to clamp securely in the tension probe, usually 50mm.

- Balance the system

This step is performed to balance the system for zero. The upper chuck of the sample holder is placed in the calibration tray, and the system is set to perform an automatic balance operation.

- Fasten the samples

Using a setting plate of desire length (5,10 or 20 mm), place the upper and lower chuck. Be careful about the alignment of samples, and use screws to tighten the film sample onto the chucks.

- Set the software parameters

Set the mode to SS, select frequency, set preload, set load amplitude, and input the sample information including file name and turn off temperature control.

- Offset the sample displacement distance

It is important that the strain remains in the elastic range over the entire load cycle. Offset enough distance is prerequisite to keep the samples stretched during the whole operation.

- Start to run TMA

The last step is to start the experiment. In 10 to 20 minutes, TMA will finish its testing and stop automatically. At last all these data can be can be transferred to hard disc.

Appendix B

Calibration of Load cell

After the MTS was manufactured, assembled and the data bench was connected to MTS system, calibrations of the LVDT and load cell became a must. Otherwise all the numbers outputted from data bench were meaningless.

Since both LVDT and Load cell have liner relationships with load or displacement, the calibrations of them are simple and easy to finish. The calibration procedure of Load cell is listed below:

- Disconnection of the power supply

This mainly include the power supplies for LVDT and motor.

- Selection of different weight for calibration

Usually 4 to 5 weights are used and the overall weights should be within the scope of Load cell capacity.

- Disconnection of the load adaptor section

Loose the O-ring and unfasten the big brass nut to take off the cover steel plate above the pulley.

- Disassembly the guided rods

This could be completed easily by unfastening the screws on both ends of two guided rods. After disassembly the guided rods, the load cell could be moved freely.

- Apply different loads upon Load cell

By fastening the big brass nut again and by adding different weights in the upper clip, the corresponding numbers for different weights are outputted from data bench.

- Data recording and analysis

After getting the data of weights and numbers in data bench, using Excels or other software, a straight line can be obtained which yield the calibration coefficient of Load cell.

Since the calibration for LVDT is much easier than the calibration of Load cell, so the calibration of LVDT is not discussed here.

Appendix C

Data bench connection with Stress/strain data output

After calibration of LVDT and Load cell, the stress/strain data (force/displacement) were outputted as voltage values and can be transferred to computer through data bench, like the module **OMK-AD812** used in this study.

The **OMK-AD812** analog data acquisition module has eight analog inputs with twelve-bit resolution. The inputs can be used single ended or in pairs differentially. An internal reference voltage of $4.096\text{V} \pm 0.2\text{V}\%$, yields a conversion of $1\text{mV} / \text{LSB}$, see Figure C.1.

The analog inputs can be configured for single ended input or in odd/even pairs for differential input. Any combination of single ended and differential configurations may be used. When using the inputs in differential mode, only the designated plus (+) input supports the sample/hold feature. Therefore, changes in the minus (-) input during sampling may cause a conversion accuracy error. The input frequency and amplitude on the minus input should be limited to reduce errors.

In this study, single ended input is used, see Figure C.2. The positive output of

Figure C.1: OMK-AD812 data bench

Load cell is connected to pin **7**, which is corresponded to analog **3** and the positive output of LVDT is connected to pin **11**, which is corresponded to analog **1**. The negative outputs of LVDT and Load cell are ground to pin **20** and **21**.

The module is hosted and powered by a PC compatible printer port and no external power supply is required. The Module is compatible with SPP, BPP, EPP and ECP type printer ports.

The module passes through four bi-directional digital input/output ports from the host printer port. The digital I/O lines can be set or cleared based on the analog inputs with the bundled software. This function was not used in this study.

Figure C.2: Pin configuration of OMK-AD812

Appendix D

MTS testing procedure for break strength

- Cut the samples

Roughly, samples were cut into a square piece approximately 15 to 20 mm wide and 50 mm in length. Thickness should be measured as described in section 2.1.1.

- Run system without samples

This is mainly to get the friction values of guide bar. Since different ambient temperatures and lubrication will effect this value. Before each experiment at last 3 empty runs are needed to get a average offset value for the load cell.

- Fasten the samples

Upper and lower Aluminum clips were used to fasten the samples. Care was taken to align the samples with the proper tightness, and screws were used to tighten the samples.

- Set the software

To start Omega data bench software: select data display parameters, data acquisition frequency and data plot parameters; set the data format, scale and offset values for the LVDT and load cell. Input the sample information including file name and sample dimensions.

Data acquisition frequency: 40 ms was chosen as the data acquisition frequency, meaning that every 40 ms, a group of datum is transferred to the computer.

- Start to run MTS

Before starting to run MTS system, the motor speed (strain rate) needs to be pre-determined. Usually 1% /s to 2 % /s is used here.

- Output the detailed stress-strain data

Table D.1 shows part of original data from data bench.

- Transfer data to stress-strain curve

According to the following equation, the data in above table can be then transferred to stress and strain. Stress-strain curves of CNT/PC composites then can be easily obtained, like shows in Figure D.1.

$$\text{Stress} = \frac{N3}{S \times C_{CELL}} \quad (\text{D.1})$$

$$\text{Strain} = \frac{N5 \times 100}{L \times C_{LVDT}} \quad (\text{D.2})$$

Where:

Sample	Output 1	Output 3	Output 5
pure PC/48.9-1-March21/03	11:33:43	500	50
pure PC/48.9-1-March21/03	11:33:43	502	56
pure PC/48.9-1-March21/03			
pure PC/48.9-1-March21/03	11:33:44	508	78
pure PC/48.9-1-March21/03	11:33:44	509	86
pure PC/48.9-1-March21/03	11:33:44	510	91
pure PC/48.9-1-March21/03	11:33:44	510	94
pure PC/48.9-1-March21/03	11:33:44	511	100
pure PC/48.9-1-March21/03	11:33:44	512	103
pure PC/48.9-1-March21/03			
pure PC/48.9-1-March21/03	11:35:16	1529	766
pure PC/48.9-1-March21/03	11:35:16	1534	770
pure PC/48.9-1-March21/03			

Table D.1: The actual data of LVDT and load cell

Stress= stress of composite (MPa)

Strain= strain of composites (%)

C_{CELL} = calibration coefficient of load cell (11.17/N)

C_{LVDT} = calibration coefficient of LVDT (39.3/mm)

N3= number from data bench output channel 3

N5= number from data bench output channel 5

S= area of sample cross-section (mm^2)

L= length of sample between the clips (mm)

Figure D.1: Young's modulus results

Appendix E

MTS testing results for strength

Table E.1 shows all the useful original strength data from MTS.

CNT (%)	thickness (mm)	strength (MPa)	average (MPa)
0.0	45.7	54.1	51.9
0.0	35.0	49.7	
0.063	39.2	52.9	
0.063	39.2	51.5	
0.063	32.4	48.2	
0.063	32.4	61.1	53.43
0.146	38.1	47.6	47.6
0.178	42.7	50.2	50.9
0.178	42.7	51.6	
0.255	56.89	55.82	55.82

Table E.1: The original strength data from MTS

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