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Morphology and Mechanical Properties of PMMA/CNT composites.

by

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Abstract

Over the last decade, carbon nanotubes (CNTs) are regarded as promising candidate for mechanical reinforcement of polymers. This thesis is mainly focused on developing Polymer/CNT composites using Single-walled carbon nanotubes (SWCNTs) as an effective mechanical reinforcement agent in the host polymer, Poly(methyl methacrylate) (PMMA). PMMA/CNT composites were fabricated in the form of gels and transparent films. In PMMA/CNT films, an interconnecting network of CNTs was observed in the scanning electron microscope after stretching the films at high temperature. The films showed improved tensile properties and it was observed that CNTs in PMMA have added flexibility to the originally brittle polymer. The addition of CNTs in the PMMA gel can be used to control the pore size in the composite gels. It was observed that as we increased the CNT concentration in PMMA, the pores sizes on the polymer surface reduced in dimensions leading to improved mechanical properties of the polymers.

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To my parents

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Nomenclature

CNT	Carbon Nanotubes
CTE	Coefficient of Thermal Expansion
CVD	Chemical Vapor Deposition
HT	High Temperature
MTS	Materials Testing Systems
MWCNT	Multi-walled Carbon Nanotubes
PEEK	Poly(EtherEtherKetone)
PTFE	Polytetrafluoroethylene
PMMA	Poly(methyl methacrylate)
RT	Room Temperature
SEM	Scanning Electron Microscopy
SWCNT	Single-walled Carbon Nanotubes
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
S	Area of sample cross-section (mm^2)
L	Length of sample between the clips (mm)
Y_c	Young's modulus of composite (MPa)
Y	Young's Modulus

Chapter 1

Introduction

Carbon nanotubes have drawn great interest from many scientists and engineers worldwide since they were first synthesized in 1991 [1]. The tubes have wide scope in a variety of applications due to their unique mechanical and electronic properties. In the present thesis, an effort has been made to utilize their extraordinary properties.

1.1 Conventional Composite Materials

A composite material is a multi-phase (two or more components) material that is made artificially and exhibits a significant proportion of the properties of both constituent phases so that a better combination of properties is realized [2]. The main constituent phases are composed of reinforcement constituents (fibers, particles, flakes, and/or fillers) embedded in a matrix (polymers, metals, or ceramics). The matrix holds the reinforcement constituents to form the desired shape while the reinforcement improves the overall mechanical properties of the matrix [3].

The three main types of composite materials are: particle-reinforced composites, structural composites and fiber-reinforced composites. The dispersed phase for particle-reinforced composites is equiaxed (i.e., the particle dimensions are approximately the same in all directions). Particles used for reinforcing include ceramics and glasses such as small mineral particles, metal particles such as alu-

minum, and amorphous materials, including polymers and carbon black. Structural composites are combinations of composites and homogenous materials and the properties of these materials not only depend upon the constituent materials but also on the geometrical design of the various structural elements. Laminar composites and sandwich panels are the common structural composites. The fiber-reinforced composites are technologically the most important composites in which the dispersed phase is in the form of a fiber i.e., it has a large length-to-diameter ratio. The fiber-reinforced composites with exceptionally high specific strengths and specific modulus have been produced that utilize low-density fiber and matrix material. The fiber-reinforced composites are subclassified by fiber length and the fibers can be incorporated into the matrix either in continuous lengths or in discontinuous lengths.

The major function of the matrix is to transfer load between the fibers and hold the fibers in place. It also protects the fibers from environmental damage. There are different matrix materials that can be used when casting a composite material, such as thermoplastics, thermosets, metals and ceramics.

This thesis is focused on Poly(methyl methacrylate)/ Carbon nanotube (PMMA /CNT) composites which can be categorized as discontinuous fiber-reinforced composites.

Advantages of Composite Materials

Most composite materials are created to improve combinations of mechanical characteristics such as stiffness, toughness, and ambient high-temperature strength [4]. These are used mainly because they combine the properties of a light weight matrix and high strength/stiffness fibers. Hence, composite materials are light weight materials compared to conventional materials like metal alloys, ceramics and polymeric materials. Different materials have different strengths, therefore each type of material can take different amounts of loading for the same cross-

sectional area of material. Composite materials possess high specific strength (strength to density ratio) and good specific stiffness (modulus to density ratio). These materials are more fatigue resistant as compared with conventional materials. They have high stiffness and favorable “noise, vibration, and harshness” characteristics for particular industries, eg. car manufacturing. Composite materials can be designed to have zero thermal expansion as well. The design flexibility of composite materials due to their anisotropy and formability offer great design opportunities and flexibility for particular applications. They can be moulded into complex shapes for example, a surfboard or a boat hull.

Limitations of Composite Materials

Although composite materials have a great number of applications due to their versatility, they have major limitations as well.

Design complexity is one of the major hindrances for the advancement of composite materials as compared to other traditional materials like metals. Their fabrication technology is difficult to handle and sometimes it depends upon the skill of the manual labor, for example, weaving of the fibers. Moisture also affects some composite materials adversely. The manufacturing processes are more efficient when composites are used but the raw materials are expensive.

Newer and better composites materials are being researched to overcome these limitations and more engineering work is still required to resolve these limitations.

Applications of Composites materials

The applications of composite materials vary from spacecrafts to sporting goods to joint implants [5]. Each application using composite material is chosen due to its unique mechanical and physical characteristics.

Due to its advantage of being light weight over conventional materials, composite materials are widely used in the aircraft, aerospace and automobile industries. In the space shuttle and international space station, composite materials

like IM7/Poly(EtherEtherKetone) (IM7/PEEK), and carbon/epoxy are used virtually everywhere. Most of the sports goods like helmets, squash racquets, these days are made of Kevlar or carbon-fiber composites. This is due to their light weight, good strength and energy absorption properties. Kevlar is also used to make bullet-proof vests for the police.

1.2 Nano-composites

Nano-composites are composites where at least one of the constituent phases has a characteristic length in the range of $1 \sim 100$ nm, in the combination of two or more constituent phases [6].

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

The fabrication of homogeneous nanocomposites with carbon nanotubes remains a challenge in the current trends in developing novel composite materials. Because CNTs tend to form agglomerate structures, these are very difficult to disperse physically. Various methods and techniques are followed to overcome this problem.

1.2.1 Carbon Nanotubes

The carbon nanotubes discovered by Japanese scientist Iijima [1] have many interesting properties such as high mechanical strength, and remarkable electronic structure. This has inspired various scientists for a range of potential applications. The carbon nanotubes have two distinct forms, multi-walled nanotubes (MWCNTs) and single-walled nanotubes (SWCNTs).

Natural carbon exhibits distinct properties in two forms. Diamond which gives a strong mechanical strength and high electrical insulation; and graphite as a brittle material which conducts electricity at room temperature. The CNTs combine the mechanical strength of diamond with the electrical conductivity of graphite. However, the as-grown form of this new material is actually a mixture of semi-conducting and metallic tubes, in the approximate 2:1 ratio [10]. The mechanical properties of CNTs combined with their low density of $1.34 \text{ (gm/cm}^3\text{)}$ provides a wider scope for the development of the nanotube-reinforced composite materials.

1.2.2 CNT/Polymer Composite

For composite materials, a polymer is an ideal matrix consisting of a carbon backbone as a reinforcing material because of their structural compatibility. It is believed that incorporating carbon nanotubes (CNTs) in the polymer matrix will enhance the mechanical properties of the polymer and the composite will be a material with high strength and high Young's modulus and better electrical properties.

The study and design of the CNT/polymer composite emerged with an increased knowledge of the interactions of composites. CNT-based composites appear promising for applications in telecommunication [11], actuators [12] & [13], photovoltaic cells [14], light-emitting diodes (LEDs) [15], field emission [16] and radiation shielding [17]. The performance and lifetime of devices are enhanced through CNT composites. This also opens a venue for many nonconducting polymer applications with good structural stability and flexible processibility. Because mobility can be increased to avoid electrostatic effects, the composites can be used for passive electronic components as well as electromagnetic shielding [18]. By forming the CNT composites, we overcome the disadvantages pertinent to nonconducting polymers to improve their performance as a result of the superior

mechanical, thermal, and electric properties of CNT.

1.2.3 CNT/PMMA composites

The exceptional properties of nanotubes have motivated many researchers in different fields to experimentally investigate the mechanics of the nanotube-based composites. Uniform dispersion of CNTs within the polymer matrix and improved nanotube/wetting and wetting and adhesion are critical in the processing of these nanocomposites. For CNT/polymer composites, a water insoluble polymer PMMA was selected in this study as it is believed that it is a good solvent for nanotubes. It has high optical clarity and is a commodity polymer. SWNTs, have been chosen as filler in PMMA matrix. SWCNTs have very high modulus ~ 1 TPa and high strength ~ 100 GPa.

In this study, two approaches are used to investigate the morphology and mechanical properties of PMMA/CNT composites i.e., one is by casting PMMA/CNT film and other is by making PMMA/CNT gels.

1.3 Research Goals

For this research, the main focus was developing Polymer/CNT composites using scalable techniques i.e., laboratory-scale methods that can easily be developed on a large scale. It is believed that the dispersion and alignment of CNTs in polymers will improve the mechanical and electrical properties of the pure polymers. An understanding of the relationship between the microstructure of the materials and their properties is made and the production techniques are tailored to optimize the materials. The main goals of the present research were:

- Producing PMMA/CNT composite films
- Developing a novel technique for production of PMMA/CNT gels

- To investigate the morphological aspects of CNT/Polymer composites in films and gels
- To compare the mechanical properties of these newly-developed composites with the pure polymer

1.4 Thesis Outline

This thesis is divided into six chapters. This chapter provides a brief introduction. Chapter 2 presents the brief overview to the structure and manufacturing of CNTs. It outlines the background to several developments and directions in CNT research. Different casting methods and approaches made in developing nano-composites and the the knowledge of CNT composites regarding strengthening mechanisms are discussed.

Chapter 3 describes the starting materials used in our study. This chapter details the procedures applied for sample preparation and describes the different characterization methods used for the films and gels.

Chapter 4 presents the results of the morphological investigations made in PMMA/CNT films at different conditions and the effect of CNTs on the mechanical properties of PMMA/CNT films are discussed.

Chapter 5 discusses the effect of the amount of CNTs on the morphology of PMMA/CNT gels in detail.

Chapter 6 discusses the conclusions on the basis of the results obtained from the present work and also gives the possible recommendations for the future work.

Chapter 2

Literature Review

2.1 Carbon Nanotubes

Carbon nanotubes were discovered in 1991 by the Japanese electron microscopist Sumio Iijima [1] accidentally while he was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes at NEC Laboratory in Tsukuba, Japan. He observed a variety of closed graphitic structures including nanoparticles and nanotubes, in the central core of the cathode. A short time later, Thomas Ebbesen and Pulickel Ajayan, from Iijima's lab, showed how nanotubes could be produced in bulk quantities by varying the arc-evaporation conditions. The nanotubes produced were multi-walled carbon nanotubes (MWCNTs) and then later in 1993, single-walled carbon nanotubes (SWCNTs) were discovered independently both by Iijima and Bethure *et al.* at IBM Almaden Research centre in California, U.S. [19]. In 1996, at Rice University in Texas, Smalley *et al.* first synthesized the SWCNTs [20]. This led the way to an explosion of research into the physical and chemical properties of carbon nanotubes in laboratories 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.

Figure 2.1: Allotropes of carbon (a) graphite, (b) diamond, (c) buckminster fullerene (C_{60}) and, (d) Buckytube, shown here with indeterminate length and each end capped with $\frac{1}{2}$ of a C_{60} .

2.1.1 Structure of CNTs

The known allotropes of carbon are diamond, graphite and buckminster fullerenes (C_{60}). Buckminster fullerenes, or buckyballs are the third most stable allotrope of carbon after graphite and diamond. These allotropes are shown in figure 2.1.

CNTs and nanofibers fall under the category of fullerenes. The structure of carbon nanotubes, in terms of bonding of carbon atoms and hybridization of orbitals, is essentially graphitic. The two main basic types of carbon nanotubes are MWCNTs and SWCNTs.

MWCNTs have multiple walls arranged as concentric cylinders around an inner tube. Figure 2.2(a) shows an oblique view of an uncapped, multi-wall carbon nanotube showing the inner walls with concentric cylinders. The diameter of a MWCNT is usually around $2 \sim 50$ nm, the length is between $0.2 \sim 2$ μm and distance between individual tubes is roughly ~ 0.34 nm.

In SWCNTs, as shown in figure 2.2(b), shows an oblique view of uncapped single-wall carbon nanotubes seen from the end. Single-wall tubes often clump together in bundles due to the van der waal forces between individual tubes. These bundles of SWCNTs are often referred to as nanotube ropes. The diameter of SWCNTs is usually around $1 \sim 10$ nm and the length is roughly several microns. Usually this type of CNTs contains carbon atoms together, with ~ 0.14 nm between neighboring atoms, rolled up in a seamless cylinder with a closed carbon cap on each end.

The intra-layer bonds are very strong in graphite, but between different layers only weak van der waal forces exist. The structure of carbon nanotubes have been explored by using high-resolution techniques. Experiments have confirmed that nanotubes are cylindrical structures based on the hexagonal lattice of carbon atoms that form crystalline graphite. There are three types of nanotubes possible, called armchair, zigzag and chiral nanotubes, depending on how the two-dimensional graphene sheet is “rolled-up”.

The atomic structure of nanotubes is described in terms of chirality or helicity of the tube, given by the vector, $\vec{C}_h$, and the chiral angle, θ [22] . In figure 2.3, it can visualize cutting the graphite sheet along the dotted lines and rolling the tubes so that the tip of the chiral vector touches its tail. The roll-up vector or chiral vector, can be expressed by the following equation:

$$\vec{C}_h = n \vec{a}_1 + m \vec{a}_2 \quad (2.1)$$

(a)

(b)

Figure 2.2: (a) Structure of uncapped multi-walled carbon nanotube, from an oblique view showing the inner walls [21] and, (b) Structure showing uncapped single-wall carbon nanotubes, from an oblique [21].

Figure 2.3: Definition of roll-up vectors as linear combinations of base vectors a_1 and a_2 [22].

Figure 2.4: Types of SWCNTs (a) armchair nanotube, (b) zigzag nanotube, and (c) chiral nanotube. The diameter of the nanotubes depends on the values of n and m . [23]

where the integers (n,m) are the number of steps along the zig-zag carbon bonds of the hexagonal lattice and $\vec{a}_1$ and $\vec{a}_2$ are unit vectors, shown in the figure 2.3. The amount of twist in the tube is given by chiral angle. The two limiting cases exist when the angle is at 0° (zig-zag) and 30° (armchair). The difference in the structure is shown in figure 2.4. In terms of role-up vector, the zig-zag nanotube is $(n,0)$ and armchair nanotube is (n,n) . Else, the structure falls in the chiral category. The properties of CNTs are mainly dependent on the CNTs dimension and chirality [23].

2.1.2 Production Methods

Carbon nanotubes are generally produced by three main techniques: arc discharge, laser ablation and chemical vapor deposition, each of which are briefly discussed here and a summarized comparison of these methods is made in table 2.1 [24].

Carbon Arc Method

The Carbon Arc Method is an excellent method for the production of both single-walled and multi-walled carbon nanotubes. This method produces nanotubes through the arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). Recent investigations have shown that it is also possible to produce nanotubes with the arc method in liquid nitrogen [25]. A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod. Nanotubes self-assemble from the resulting carbon vapor. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit forming on the carbon electrode [26]. The experiment setup of an arc discharge method is shown in figure 2.5.

Figure 2.5: Experimental setup of an arc discharge apparatus [24]

Research in the growth mechanism is increasing and measurements have shown that different diameter distributions have been found depending on the mixture of helium and argon. These mixtures have different diffusion coefficients and thermal conductivities. These properties affect the speed with which the carbon and catalyst molecules diffuse and cool affecting nanotube diameter in the arc process. This implies that single-layer tubules nucleate and grow on metal particles in different sizes, depending on the quenching rate in the plasma, and it suggests that temperature and carbon and metal catalyst densities affect the diameter distribution of nanotubes [26]. Depending on the exact technique used, it is possible to selectively grow SWNTs or MWNTs. The merits and demerits of this procedure are mentioned in table 2.1 and in this table this method is also compared with other main methods.

Pulsed Laser Vaporization

This technique was first reported by Smalley's group in 1995 at Rice University for the production of single-walled carbon nanotubes [28]. The merits of this method with respect to the other main methods are explained in table 2.1. In this method, a pulsed or continuous laser is used to vaporize a graphite target in an

Figure 2.6: Experimental setup of a laser ablation apparatus[24]

oven at 1200 °C. The oven is filled with helium or argon gas in order to keep the pressure at 500 Torr. A very hot vapour plume forms, then expands and cools rapidly. The schematic drawing of a laser ablation apparatus is shown in the figure 2.6. From these initial clusters, tubular molecules grow into single-wall carbon nanotubes until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become coated so heavily with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by van der waals forces [29].

Chemical Vapor Deposition method

This method is mainly used for mass production of CNTs and is promising for

Figure 2.7: Experimental setup of Chemical Vapor deposition [24]

producing CNTs commercially. This method is simple and can be scaled up to kilograms. This method is based on the theory of diffusion [30]. Under a certain pressure, a quartz tube is mounted across a flow furnace. A ceramic container with prepared catalyst is then seated inside the quartz tube. The reaction mixture i.e., 90% nitrogen and 10% acetylene is passed over the container for hours at a temperature ranging from 500–1000 °C and hence CNTs are produced. The main parameters in this process are the temperatures and catalysts.

Growth Mechanism

The way in which nanotubes are formed is not exactly known. The growth mechanism is still a subject of controversy, and more than one mechanism might

Main Methods	Arc discharge method	Chemical vapor deposition	Laser Ablation (vaporization)
Discovered by	Ebbesen and Ajayan, NEC, Japan 1992 [26].	Smalley, Rice, 1995 [25].	Endo, Shinshu University, Nagano, Japan [27].
Description	Connect two graphite rods to a power supply, place them a few millimeters apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs.	Place substrate in oven, heat to 600°C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs.
% Output	30 to 90%.	Up to 70%.	20 to 100%.
SWNT	Short tubes with diameters of 0.6 - 1.4 nm.	Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm.	Long tubes with diameters ranging from 0.6-4 nm.
MWNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm.	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.	Long tubes with diameter ranging from 10-240 nm.
Merits	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible.	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure.
Demerits	Tubes tend to be short with random sizes and directions; often needs a lot of purification.	Costly technique, because it requires expensive lasers and high power requirement, but is improving.	NTs are usually MWNTs and often riddled with defects.

Table 2.1: A summary of the major production methods and their efficiency [24]

be operative during the formation of CNTs. One of the mechanisms consists of three steps. A precursor to the formation of nanotubes and fullerenes, C_2 , is formed on the surface of the metal catalyst particle. From this metastable carbide particle, a rodlike carbon is formed rapidly. There is a slow graphitisation of its wall. This mechanism is based on in-situ TEM observations [31].

2.1.3 Unique Properties of CNTs

CNTs are stronger than steel, lighter than aluminium, and more conductive than copper. The main properties of CNTs are as follows:

Mechanical Properties

CNTs have remarkable mechanical properties and are considered as the toughest materials ever known. The Young's modulus of CNTs is $1 \sim 5$ TPa [32] and the tensile strength is known to be $50 \sim 200$ GPa [33] in comparison with graphitic carbon which is 650 GPa for Young's modulus and 4 GPa for tensile strength [5]. CNTs can be bent at large angles and re-straightened without damage whereas metals and carbon fibers fracture at grain boundaries.

Electronic and Electrical Properties

The electronic properties of CNTs mainly depends on the chirality and diameter. For example, the small diameter armchair CNTs are metallic, whereas the small diameter zigzag CNTs behave as semiconductors [34]. The electrons in CNTs move freely as in metals but they can pass currents 100 times higher than standard metals and can transport a high current upto 10^9 Acm^{-2} [35].

Thermal Properties

In the longitudinal direction, CNTs have very good thermal conductivity due to their high aspect ratio $\sim 10^6$ (i.e., length to diameter ratio) whereas in the perpendicular direction, the heat transport is very low. It is realized that CNTs can transmit heat better than diamond, which is highest thermal conductor presently

known [34]. The heat transmission predicted is 6,000 W/mK at room temperature whereas pure diamond transmits 3,320W/mK. CNTs are stable up to 2,800 °C in vacuum, 750 °C in air, whereas metal wires melt at 600 – 1000 °C.

Field Emission and other Properties

Measurements show that CNT emission current ranges up to 100 GAm and emission site density reaches 10^7cm^{-2} at 5V / μm field [36]. CNTs can activate field emission in phosphorus at 1-3 V with electrodes 1 micron apart. There are other promising properties of CNTs in the field of magnetic and hydrogen storage.

2.1.4 CNT Applications

The potential applications range from ultrathin, breathable, waterproof fabrics to bright, rugged flat-panel displays for televisions and computer monitors.

Energy Storage

Hydrogen and lithium can be electrochemically stored in CNTs. Hydrogen can also be stored in CNTs by gas phase intercalation [37]. Carbon nanotubes are replacing graphite, carbonaceous materials and carbon fibre electrodes in fuel cells, batteries and other electrochemical applications because of their small dimensions, smooth surface topology and perfect surface specificity. The electron transfer rate at the carbon electrodes is fastest on nanotubes [38]. Because of the cylindrical and hollow geometry and nanometer-scale diameters of SWNTs, it has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect.

Sensors and Nanoprobes

The flexibility of nanotubes is best utilized when using them in scanning probe instruments. As the tips of MWNT are conducting, they can be used in scanning tunnelling microscope (STM) and atomic force microscopy (AFM) instruments. Because of the high elasticity in comparison with the conventional Si or metal

tips the resolution is improved and also the tip does not crash easily because of very good elasticity. Due to the large length, nanotube vibration will remain an important issue, until shorter nanotubes can be grown controllably. Also, a pair of nanotubes can be used as tweezers to move nanoscale structures on surfaces [39]. Sheets of SWNTs have been suggested for use as electromechanical actuators, by copying the actuator mechanism present in natural muscles. SWNTs may be used as miniaturized chemical sensors.

Field emitting devices and Transistors

The nanotubes are used for field emitting applications because of the dependence of the conductivity and emission stability of the nanotubes on the fabrication process and synthesis conditions as the CNTs can emit electrons at a lower voltage while keeping a high current density and remaining stable. The main potential applications for nanotubes as field emitting devices are flat panel displays, gas-discharge tubes in telecom networks, electron guns for electron microscopes, AFM tips and microwave amplifiers. The field-effect transistor - a three-terminal switching device - can be constructed of only one semi-conducting SWNT. By applying a voltage to a gate electrode, the nanotube can be switched from a conducting to an insulating state [40].

Composite materials

The strength of carbon nanotubes makes them an ideal candidate for structural applications. For example, they may be used as reinforcements in high strength, low weight, and high performance composites. The another main advantage of using nanotubes for structural polymer composites is that nanotube reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behavior and better performance during compressive load. The low density of the nanotubes increases the electrical conductivity of the polymer composites.

In an example of non-structural application, the filling of photoactive polymers like PPV (Poly-p-phenylenevinylene) filled with MWNTs and SWNTs makes a composite [38] and these composites show a large increase in conductivity with only a little loss in photoluminescence and electro-luminescence yields. Another benefit is that the composite is more robust than the pure polymer. Nanotube-polymer composites could be used also in other areas, for example, they could be used in the biochemical field as membranes for molecular separations or for osteointegration (growth of bone cells). Other advantages are the low density of the nanotubes, an increased electrical conduction and better performance during compressive load.

2.2 Nanotube-Polymer Composites

The combination of carbon nanotubes with polymer matrices can be considered as a step forward in polymer and composite technology. An improvement of the mechanical properties of polymer nano-composites based on carbon nanotubes (CNTs), is dependent on a good dispersion and strong interactions between the matrix and filler. For this reason multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWNTs), produced by Arc-discharge or catalytic methods have been investigated as a filler by various groups ([1], [19], [20]).

2.2.1 Challenges in Polymer/CNT study

Various Setbacks

The main problem in polymer/CNT is to create a good interface between nanotubes and the polymer matrix, as the nanotubes are very smooth and have a small diameter of 1-20 nm, which is nearly the same as that of a polymer chain [41]. Secondly, CNTs do not readily suspend in polymers, thus the physics and chemistry of filler dispersion becomes a major issue. Thirdly, nanotube tend to

Figure 2.8: TEM image of partially exfoliated single-wall carbon nanotubes showing the rope-like structure [42]

form aggregates, due to strong attractive interactions, as shown in figure 2.8, are very difficult to disrupt [42]. These ropes, which are very common, behave differently under loads than individual nanotubes. The limiting factors for good load transfer could be sliding of cylinders in MWNTs and shearing of tubes in SWNT ropes. To solve this problem the aggregates need to be broken up and dispersed or cross-linked to prevent slippage.

Different Trials in the Polymer/CNT field

The CNT-polymer composites were initially reported by Ajayan et al. [43]. They mechanically mixed the purified MWNTs with epoxy resin. Since then, attention has been paid to composite materials with uniform and high loading of nanotubes. Carbon nanotube epoxy composites are most widely studied as non-conjugated polymer-based composites.

Sandler et al. [44] has also done similar work and reported that untreated carbon nanotubes were dispersed in an epoxy matrix. The use of carbon nanotubes

Figure 2.9: Optical micrographs of epoxy-nanotube composites; (a) pure epoxy, (b) 0.001 wt%, (c) 0.005 wt%, and (d) 0.005 wt%. Scale bar is 1 cm and the sample thickness is about 2.2 mm. The formation of small local nanotube aggregates at a loading fraction of 0.0025 wt% can be seen, which then leads to the macroscopic network of nanotubes at higher filler contents.

not only reduces the percolation threshold to below 0.04 wt%, but also increases the overall conductivity. Although ultrasound in ethanol and the intense stirring process improves the dispersion of the nanotubes, it is not impossible to break up all the entanglements of the carbon nanotubes.

Similar work was done by Gong et al [45] reporting that using surfactants as welding agents might improve dispersion and thermo-mechanical properties of carbon nanotubes/polymer(epoxy) composites, but even with the addition of the surfactant, complete homogeneous dispersion of the nanotubes was not obtained.

Epoxy-nanotube composite films were made and as shown in the figure 2.9, the films were cloudy and opaque even with very small concentration of CNTs.

2.3 Gels and Gel Characteristics

The soft, resilient and sometimes wobbly materials known as jellies are usually made from fruit juices cooked with sugar or from cooked-down meat juices, and have been used in households for several centuries. In the 1860s, Thomas Graham

Figure 2.10: Schematic illustration of (a) covalent(chemical) cross-linking and (b) physical (non-covalent) cross-linking in polymer gels. Examples of physical cross-linking are (c) helix formation by hydrogen bonding and (d) chelation of cations(•) [52]

took interest in this kind of material and reported unusual diffusion properties of jellies [48]. Later, he also introduced the term hydrogel for hydrates of silicic acid with gelatinous properties [49]. In 1974, Flory pointed out one essential feature of the gel which is universally identified as an essential characteristic of a gel, i.e., its solid-like behavior [50].

In 1993, one gross definition was proposed by Almdal et al [51], stating that a gel is soft, solid or solid-like material which consists of at least two components, one of which is a liquid present in abundance. The elastic and resilient character should be observable by the human eye and a gel should not flow under the influence of its own weight.

Polymer gels are produced through the cross-linking of polymer chains, by the formation of either covalent bonds (chemical cross-linking) or non-covalent bonds (physical cross-linking) as shown in figure 2.10 [52]. In polymer gels the system is characterized by an elastic cross-linked network and by a fluid filling the interstitial spaces.

2.3.1 Application of Polymer Gels

The key industries using gels including pharmaceuticals, photographic, paper and food industries. These industries utilize gels and gelling processes in order to fulfill many functions from control release, surface coatings and consumer products.

The major type of polymer gels are hydrogels, which swell extensively in water. The most common hydrogels are polyelectrolyte gels. However, gels based on polyacrylamide or poly(ethylene oxide) are called neutral gels because their affinity to water is much lower than of charged gels. These hydrogels are extensively used as super absorbents because of their high swelling capacity. The hydrogels are used as functional materials e.g., carriers for controlled drug release, membranes with regulated permeability, sensor devices and artificial muscles. These purposes also require high cooperativity of response to change in external conditions and develop internal microstructure of the gels.

Gels are well used for medical applications and the first use of gels for medical applications was presented by Wichterle and Lim in 1960 [53]. It involved the manufacturing of soft contact lenses and implant materials from hydroxyethyl methacrylate polymers. Since these early uses, gels have been used as vehicles for the delivery of drugs for both local treatment and systemic effects, as reviewed in [54]. Many different administration routes have been explored [[55] - [63]]. Energy gels [64] are an example of gels used to provide a compact energy source to athletes.

2.3.2 PMMA Gels

PMMA is a synthetic polymer and it forms gels in a large variety of solvents [65]. Like biopolymers, stereoregular PMMA possesses the ability to form double helices [66]. The mixtures of syndiotactic PMMA (sPMMA) and isotactic PMMA (iPMMA) can form a double-helical structure, called a stereocomplex, in which the syndiotactic chain wraps around isotactic filament. Some interesting features are

shown by the thermoreversible gelation of PMMA and it makes this system hybrid between synthetic polymers and biopolymers [67]. The weak interactions like hydrogen bonds, van der Waals and electrostatic forces can be disrupted by heating. These gels fall in the category of physical gels which are usually thermoreversible. In chemical gels the network connections occur through covalent bonds.

The Shull *et al.* in Northwestern university is working on PMMA thermoreversible gels [68]. These gels are based on triblock copolymers with poly(methyl methacrylate) end blocks and a poly(n-butyl acrylate midblock). The work approach is to enhance the mechanical properties of PMMA gels. The mechanical properties of these gels are determined by a thermally reversible aggregation of the syndiotactic PMMA end blocks of an acrylic triblock copolymer, which is diluted with a selective solvent for the center block. The adhesive and mechanical properties of these gels are related to their structural features, which are quantified by small angle X-ray scattering experiments. The gels are significantly strengthened by the addition of low molecular weight isotactic PMMA homopolymers. Acrylic acid moieties increase the adhesive performance of these materials without affecting their structure. By employing a unique gel casting process, a network structure with the desired properties can be formed, giving materials that are ideally suited for use as pressure sensitive adhesives.

2.4 PMMA/CNT composites

Carbon nanotube/polymer composites are fabricated by direct mixing or in-situ polymerization. In-situ polymerization is a better way for homogenous dispersions because nanotubes are more likely to disperse in a precursor monomer than in the polymer.

Thin films of PMMA/SWNT composite have been fabricated by spin coating [46]. It was found that the polymers intercalated between nanotubes into bundles.

At low nanotubes concentration, amorphous carbon was dispersed well, thus more uniform films were prepared. A combination of solvent casting and melt mixing has been used to fabricate SWNT/PMMA composites [47]. Melt mixing produced compositionally uniform films on the micrometer scale, while the films prepared by solvent casting were heterogeneous. Mechanical properties and electrical conductivity of the aligned nanocomposite fibers were improved by melt spinning. Drawback of this method is that melt spinning described by the authors is too complex and time-consuming.

Since the work in CNT field is not older than a decade, there are still many things to be looked at in CNT manufacture and its characterization. In this present thesis, an effort is made to overcome the problem of dispersion of CNTs in polymer films. Also, an effort is made to have different way of casting polymer/CNT composites in the form of polymer gels.

Chapter 3

Materials and Methods

This chapter includes the starting materials used in this study and the various methods used to characterize the results.

3.1 Starting Materials

3.1.1 PMMA

PMMA is used as a host polymer in this study. The chemical structure of PMMA is shown in figure 3.1. It is a vinyl polymer and is synthesized from free radical vinyl polymerization from the monomer methyl methacrylate.

PMMA is a clear thermoplastic material with unique combination of properties including crystal clarity, resistance to light and weathering, breakage resistance,

Figure 3.1: PMMA structure.

and mechanical strength, making them at advantage over plastics. The best known commercial product of PMMA is plexiglas. The hardness of PMMA makes it suitable for substitute for glass, metals and wood in many applications.

In the beginning, two different molecular weights (M_w) were considered for the experiments. Initially the experiments were started with lower M_w of 120,000 and then further the experiments were done with higher increasing M_w of 350,000. The PMMA sample used in this study has M_w of 350,000. The PMMA was purchased from Aldrich and is 59.2% syndiotactic, 36.6% atactic and 4.2% isotactic. The reduced viscosity is between 150-160 gm/cm³ and specific gravity is 1.17 gm/cm³ at 20°C. The density of the PMMA is 1.170 gm/cm³. This homopolymer has polydispersity between 4-5, based on the proton NMR. The softening point is 120°C. For the M_w of the glass transition temperature (at mid point) is 122°C and is measured by Differential Scanning Calorimetry (DSC) as shown in the figure 3.2. From figure 3.2, it can be observed that there is one sharply changed slope of heat flow which is corresponding to the T_g of PMMA. This T_g matches the value with the manufacturer's claimed value.

3.1.2 Carbon nanotubes

Carbon nanotubes are a very expensive material and their cost depends upon their purity. SWCNTs are used in this study. To make our research cost-effective, we purchased manufactured SWCNTs from Carbolex Inc. with the purity range from 50 to 70 vol % (Carbolex AP-grade). For using SWCNTs as our starting material, we purified the Carbolex SWCNTs in-house. Carbolex SWNTs consist of single-walled, closed-ended, carbon nanotubes, which are made by the arc method. They have diameters around 1.4 nm, and form rope-like bundles with an average final diameter of 30 nm as measured from Scanning Electron Microscope (SEM) images. The measured lengths of these entwined rope-like bundles (RCNTs) range from

Figure 3.2: DSC of pure PMMA

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. To purify CNTs (carbolex), we use procedures previously reported [69] for small scale batches of CNTs. These RCNTs were oxidatively purified using nitric acid (HNO_3), repetitively washed with water then centrifuged ($15,000 \times g$ 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 recovered a very low yield of pure CNTs, approximately 11 mg trapped in a filtration membrane and 6 mg in “loose flakes”. SEM showed that all supernatant solutions also contain a high concentration of CNTs, as shown in figure 3.3. The final neutral supernatant solution is used in our composite formation. The figure shows the supernatants from 1 to 4. A lot of tiny ropes exist especially among supernatants 2 to 4 as observed from the SEM graphs. In supernatant 1, only isolated ropes can be found. Figure 3.5 shows the SEM pictures of the final supernatant used in this study. The CNT/water supernatant suspension shows no sedimentation or aggregation after a year, see Figure 3.3.

The pure SWCNTs do not suspend in water and they are in the form of ropes. These ropes are held together by van der waals and the final diameter does not change after the purification steps, as shown in figure 3.4(a) and figure 3.4(b). The RCNT diameters are estimated from SEM images as follows. By measuring the diameters of several (around 50) CNT ropes in the SEM image, the average diameter can be calculated. By calculation, we are 95 % statistically confident that with a sample size of 50, the average diameter is of the two samples in figure 3.4(a) and figure 3.4(b) is nearly same [70]. Therefore, we can conclude that

¹supernatant: the clear fluid above a sediment or precipitate

Figure 3.3: Supernatant vial after 3 months (a) acid and impurities; (b) supernatant 1 to 4; (c) washed water solution

purification has no effects on diameters of CNTs. Before and after purification, the diameters of CNTs are the same value: around 30nm. From the literature, purification usually shortens the CNTs. But due to the limitations 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 more than 5 to 10 μm .

3.2 Film Preparation

The PMMA/CNT composite films are cast both at room temperature and at high temperature with appropriate solvents. First, a solvent was set which is compatible with both PMMA and CNTs. There are many solvents that dissolve PMMA, but dispersion of CNTs was a problem. The purified CNTs are in the form of supernatant solution as explained in section 3.1.2. The detailed procedure of casting the films at room temperature and at high temperature are explained as follows:

(a)

(b)

Figure 3.4: Diameter distribution of (a)CNI and Carbolex CNTs before purification, (b)Carbolex after purification.

Figure 3.5: SEMs of purified supernatant

3.2.1 Film Casting at Room Temperature

First, we chose acetone as an appropriate solvent and we used the following procedure to make our CNT/PMMA films. We selected acetone as a solvent, mainly because of easy processing of PMMA and the experience from the literature. The procedure is as follows:

- Dissolve PMMA in acetone (Caledon, laboratory grade)
- Stir CNTs that have already been dissolved in H₂O in a sonicator (1510 Branson Ultrasonic Cleaner, output power is 70W) for 5 minutes
- Add CNT/H₂O supernatant solution to PMMA/Acetone
- Dissolve the mixture of PMMA, CNT and acetone for approximately 3 hrs with the magnetic stirrer
- Cast onto polytetrafluoroethylene (PTFE) (non-stick) surface using the solution casting apparatus, see Figure 3.6. Solution Casting apparatus ². The drag speed is around 60 mm/minute
- Cure at room temperature for another 30 minutes with cover
- Vacuum dry 48h at room temperature
- DSC examination to make sure that all solvent has been removed

3.2.2 Film casting at High Temperature by Wet Annealing Method

To improve the CNT dispersion and quality, the films were cast at high temperature using toluene as a solvent. At room temperature, PMMA is hard to dissolve

²It is an equipment that casts the films automatically at a constant speed/uniform thickness. There is a platform with two guided rods where a desired surface (like glass, PTFE etc.) can be put on and films can be made above that. Below the platform, there is a motor and other parts which can provide constant speed in one direction. The transformer is provided to select the known speed. This apparatus was made and donated by Xerox Research Center of Canada

Figure 3.6: Picture of solution casting apparatus and spreader.

in toluene and is not able to give clear solution with the addition of CNTs. The detailed procedure is as follows:

- Dissolve PMMA in toluene (Caledon, laboratory grade) at $60 - 70^{\circ}\text{C}$ using digital hot plate and covered with aluminum (Al) foil to maintain an even temperature.
- Stir the mixture of PMMA, toluene and supernatant (CNTs + water) for approximately 3-4 hrs. upon hot plate
- Cast onto silicon (Si) coated glass plate at 60°C by hand using the same spreading tools as room temperature (RT) casting method
- Cure at 60°C for 10 minutes
- Vacuum dry at 40°C for 24hrs.
- DSC is taken to make sure that solvent is completely removed

These films made by this method are highly transparent even with high percentage of CNTs and are used for doing Materials Testing Systems (MTS), high temperature (HT) stretching and SEM analysis.

3.2.3 Gel Preparation

We have also developed a technique to disperse CNTs in PMMA gels. The method that we followed to make gels is as follows:

- Dissolve PMMA in acetone by magnetic stirring
- Add CNT/H₂O supernatant solution to PMMA/acetone
- Dissolve the mixture of PMMA, CNT and acetone for approximately 3 hrs with the magnetic stirrer
- Quench the solution at -80°C for 10 minutes
- Keep at RT to let solvent evaporate

3.3 Characterization Methods

This section explains the various methods used to characterize the morphological and mechanical properties of the composite material in comparison with the pure material.

3.3.1 Film Thickness Measurement

During mechanical testing, thickness of the films plays a major role. Even a small error in the calculation of the thickness will have significant influence on the measured stress. Even two microns will cause 10% error, which is large compared to the potential mechanical improvement obtained by a small concentrations of CNTs.

To make mechanical testing results more accurate and the experiments more reliable and easy, three different methods were tried.

Weight Method

This is the easiest method to calculate the average thickness of the film. As the films are uniform, the calculated average thickness should be very close to the real thickness of the films.

The density difference of PMMA and CNT is very small and the maximum amount of CNTs in a film never exceeds 1%, hence only the density of PMMA is used to calculate the thickness of films. A levelled digital balance (accuracy of weight is ± 0.1 mg) was used to weigh the sample of known area (usually 20mm X 30mm).

SEM Method

Among many other options, SEM and optical microscope are direct methods to measure the thickness of the films. In SEM, sample preparation is the major factor. Even in thickness measurement, the shape of the cross section plays a vital role. 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 several positions along the cut edge of the film. Using a sharp blade and at room temperature during cutting can lead to a well defined edge, but higher temperature or a blunt blade will create some curved edges. Also, while mounting the sample in the SEM the free height of the sample should be minimal, or the sample can roll-over and can give a false image.

SEM parameters such as brightness, magnification and contrast are also critical in this method. The film edge is quite clear, but sometimes it is not easy to find the edge. The tilt angle between the sample and electron beam will add some errors on the final measurements and will influence the results and limit the accuracy. Using this method, usually at one film edge, 4 or 5 experimental thickness was measured by using Northern Eclipse (version 6.0) image processing software and an average thickness in (μm) is calculated.

Optical Microscope

An optical microscope is very similar to measuring the thickness with the SEM method and a Zeiss Axioplanz imaging microscope is used. The only difference from SEM is that the measured area is larger and the sample is cut and fixed on a glass slide. This glass slide can sit on the platform of the optical microscope. By adjusting the focus of microscope several times, the focal surface could be adjusted to coincide with the cross-section of the edge.

Optical microscope is a direct method and the larger areas can be considered for sample making as compared to SEM. But to get the proper focus of the edge surface in optical microscope requires both patience and experience.

3.3.2 Thermo-mechanical Analyzer (TMA)

TMA set

TMA: SSC5200 from Seiko Instruments Inc. is used to test the Young's modulus of PMMA/CNT composites.

TMA has many functions both in thermal and mechanical testing. SS (Stress/Strain) measurement is one of its most commonly used function. There are two modes for the SS function, length control and force control.

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

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

The basic specifications for TMA/SS functions are:

- Load Cell: 100 gram
- LVDT: 20 mm

Figure 3.7: TMA Set-up

- Optimum frequency: roughly $0.5 \sim 0.05$ Hz
- Temperature: room temperature to 400°C

TMA testing procedure for Young's modulus

The Young's modulus of the PMMA/CNT composite film can be determined from the length change by applying a sinusoidal waveform load at room temperature.

Samples were of width 2 mm, and if the thickness of the sample was less than $20\ (\mu\text{m})$, the width is increased to 3 mm. The system was balanced to zero. The upper chuck of the sample holder was placed in the calibration tray, and the system was set to perform an automatic balance operation. Care should be taken while fastening the sample to the chucks. The TMA instrument has its own operating software whose parameters are to be set to appropriate values before starting the experimentation. Typical parameters include mode selection, frequency, preload, load amplitude and temperature control. It is important that

the strain remains in the elastic range over the entire load cycle. Hence it is pre-requisite that offset distance should be enough to keep the samples stretched during the whole operation. TMA typically takes 10 to 20 minutes to finish the testing and output the test results data. The data is then analyzed using Matlab.

3.3.3 Material Testing Systems (MTS)

Generally, Material Testing Systems (MTS) are designed to test the properties of metals at high loads and with standard dimensions. In traditional mechanical systems, the optimum load is hundreds to thousands of Newton and their errors range in tens of Newton. But for the PMMA/CNT films, this is a huge load as the amount of load required is typically in tens of Newton with the maximum error of 1 Newton. Also, the load limit for the Seiko TMA is 100 grams (~ 1 Newton) and it does not have the capacity to break the PMMA/CNT films. This necessitates the design and assembly of an in-house MTS system. Thus a MTS was built in-house by Yiquen Pei and is available in Mechanical and Aerospace department laboratory at Carleton University [71]. Figure 3.8 shows the picture of MTS built-in house. It has four main sections as follows:

1. Frame section

This part includes a support structure, LVDT, two aluminum clips for fastening the sample, load cell which is fixed on the top of upper plate on the aluminum clip, two guide rods for obtaining straight movement when applying the load, and a platform for fixing the motor subassembly etc.

2. Stress-strain data acquisition section

A linear variable differential transformer (LVDT) and load cell were used to monitor the real time displacement and the real time load values. Thus the stress and strain were calculated by using the equations 3.1 and 3.2.

3. Load adapter section

It is required to give the straight movement to the upper clip at a constant speed to avoid any discrepancy in the data. It is provided by the assembly consisting of a motor, a pulley, an O-ring, a brass nut having an outside groove for the O-ring and a steel plate.

4. Power supply section

It is integrated with four different kinds of power supplies. The systems and their supplied voltages are namely, LVDT: ± 15 Volts, Load cell: 2 Volts, Motor: 12 Volts and power supply for computer.

The basic parameters for this MTS are:

- Load cell: $\sim 50\text{lb}$ or 220N
- LVDT: ~ 4 inch or 100mm
- Optimum load applying rate: ~ 0.15 to 0.5 mm/s
- Temperature: room temperature

Once the MTS was set up and the data bench was connected, four different lengths and five different weights were used to calibrate the LVDT and load cell. Straight line plots were obtained for both components which means there are good linear relationships between the outputs members of the data bench and the real load and displacement values.

3.3.4 Strength results from MTS

In the built-in-house MTS, the first tensile strength stretch test experiment was on a pure PMMA film which was made in the lab. The results were compared with the results from the literature. [72].

Figure 3.8: MTS apparatus

3.3.5 MTS testing procedure for break strength

MTS testing requires samples in the rectangular piece approximately 15 to 20 mm wide and 30 to 40 mm in length. Before starting the testing procedure, the MTS apparatus was run without fastening the samples in it to get the friction values of the guided bar. Since the ambient temperatures and lubrication affect this value, at least three empty runs are needed before each experiment to get an average offset value for the load cell.

Then the sample was plugged between the upper and lower aluminum clips. Proper care was taken to align the samples straight and in the center of the clips with proper tightness with the help of screws as shown in the figure 3.8.

Once these basic adjustments are done, we needed to start the attached Omega data bench software. Various parameters such as data display parameters, data acquisition frequency and data plot parameters, data format, scale and offset values for the LVDT and load cell were set to appropriate values. The data Acquisition frequency was chosen to be 40ms, i.e., at every 40 ms, a group of data is transferred to the computer. The motor speed was adjusted so as to obtain the required strain rate. At the end of testing, the software provides detailed stress-strain data. The data can also to transferred to stress-strain curve by using following formulation as in equations 3.1 and 3.2.

$$Strain = \frac{N5 \times 100}{L \times C_{LVDT}} \quad (3.1)$$

$$Stress = \frac{N3}{S \times C_{cell}} \quad (3.2)$$

Stress = Stress of the composite(MPa)

Strain = Strain of the composite(%)

C_{cell} = calibration coefficient of load cell (13/N)

Figure 3.9: High temperature Mechanical stretching.

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

N3 = number from data bench output channel 3

N5 = number from data bench output channel

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

L = Length of sample between the clips (mm)

3.3.6 High Temperature stretching

Procedure

In order to view the micro-structure of the films, a high temperature technique was used. The stretching procedure also involves samples in the rectangular piece approximately 10 to 20 mm wide and 30 to 40 mm in length. Temperature of the oven is set to 60 °C. At temperatures above 60 °C - 65 °C, the films shrink or come out of the clamp. This can be due to the low value of the (T_g) of PMMA. The cut film sample is clamped in the mechanical stretcher with the help of screws and proper care has been taken to align the sample straight and in the center of the clips as shown in the figure 3.9. The stretcher is then placed in the oven at the set temperature. Once the sample attains the required temperature, the knob at the end of the stretcher is rotated to stretch the sample. This is repeated several times depending upon the ductility of the sample. The number of rotations required by the sample during the stretching of the sample is taken into consideration and the

strain is computed. The change in length (δL) per turn is calculated and is equal to 0.11 mm.

3.3.7 Scanning Electron Microscopy (SEM)

The SEM is an extremely versatile instrument capable of providing information on surface topography, composition, crystallography and magnetic properties of solid objects. All SEM's operate by irradiating a target specimen with a finely focused beam of electrons. This results in a number of electron-specimen interactions which are responsible for a variety of emission signals. Although the magnitude of each signal depends variously on specimen morphology, composition and crystallography, ultimately it is the amount of current (I_b) in the electron beam which determines signal strength. The maximum resolution possible is in theory determined by the diameter of the electron beam (d_b). Consequently, the electron optical system of any SEM is designed to produce maximum I_b for minimum (d_b) and consists of an electron gun and two or more electron lenses.

3.3.8 Pore Size Measurement

Calculation of average pore size

As we shall discuss in section 5.3, the polymer gel surface consists of large number of pores which can be observed from the SEM images of the gel surface. A typical SEM image is as shown in the figure 3.10 (a). The pores appear as dark holes in the image. Since the number of pores in the image is very large, manual measurement of the pore sizes becomes extremely difficult and prone to errors. Alternatively, the images are analyzed using image processing techniques as described here.

The method used for the analysis can be divided into four main stages. In the first stage, the image is enhanced. The range of gray scales present in the image is adjusted by stretching them to fit the full range of 0 to 255. This improves

the image contrast and the information in the image becomes more visible. This is followed by edge enhancement in order to clearly distinguish the pores edges. Then the enhanced image is converted into binary image by setting up a certain threshold. All gray scales below this threshold are converted into zero and all other scales are treated as 255. This converts all dark holes in the image representing pores into black with remaining background as white. The binary image is then inverted to make the pores white on black background for simplicity of calculations. The neighborhood pixels representing pores are grouped together in the binary image. Small groups such as 4 or 8-neighborhood are ignored as they may represent the artifacts in the image. These groups of bounded pixels are numbered and labelled for further calculations. Finally, the area of each pore is calculated in terms of pixels. The area is converted into usable units by multiplying by a scaling factor. Final statistics are calculated such as number of pores in the image, size of largest pore, size of smallest pore and average size of pores for the given image. Further analysis of the results is given in section 5.5. Figure 3.11 is a self-explanatory figure showing that how the above method is implemented.

A sample analysis of an image is presented in figure 3.10 (a). A SEM image of 1.095 wt.% CNTs in PMMA gel is considered.

3.3.9 Differential Scanning Calorimetry

Differential scanning calorimetry is a technique used to study the behavior of polymers when they are heated. It is the most widely used of all thermo-analytical techniques used to characterize phase transitions of materials caused by thermal energy and is applicable to several types of materials such as polymers, organic materials, metals, ceramics and composites. The DSC technique measures the amount of energy (or heat) absorbed or released by a material as it is either heated or cooled or maintained at a constant temperature. The DSC instrument monitors

(a)

(b)

Figure 3.10: (a) SEM image of a PMMA gel surface with CNT concentration of 1.095 wt.%, (b) The binary image obtained from the image processing algorithm which is used for pore sizes calculations.

Figure 3.11: Explanation of Pore Measurement

Figure 3.12: Schematic representation of DSC cell.

the quantitative heat flow as a direct function of the sample temperature. This heat flow/temperature data provides valuable information of physical/chemical properties of the materials, for example the glass transition temperature (T_g), the crystalline melting temperature (T_m), the crystallization temperature (T_c) and the specific heat capacities (C_p). Polymorphic transitions are also detectable [73].

In this research, a DuPont 990 DSC was used. The schematic representation of DSC cell is given in figure 3.12. Glass transition temperatures were obtained using 7~10 mg sample and heating rate of 10 °C/min to 250 – 300 °C under nitrogen flow (50~70 mL/min). The parameters of DSC are as follows: isothermal for 10 °C/minutes at room temperature, then ramp 10.0 °C/min to 250 °C and then cool down the DSC by 30 °C/min to 30 °C.

Chapter 4

PMMA/CNT Films

This chapter deals with the effect of CNTs on the morphological and mechanical properties of PMMA films. The films were cast with the appropriate solvent and were characterized by using different techniques. The effect of CNTs in the films on the glass transition temperature was studied by using DSC, the fractured surfaces of the films were investigated at by using SEM. The effect of CNTs on the mechanical properties were also investigated by using MTS and TMA.

4.1 Preparation of PMMA/CNT films

4.1.1 Film casting at room temperature

The preparation of a composite film began with selection trials of a suitable solvent. Precursor solutions were prepared by dissolving PMMA in various solvents like $CHCl_3$ and CH_2Cl_2 . The films cast with these solvents were highly brittle and were very difficult to peel off from the glass substrate. Then the amount of concentration of CNTs in the solution is varied. Initially, the PMMA used in this study had an average M_w of 120,000. A Silicon coated substrate was used to cast the films but did not serve the purpose as films were stuck on the substrate. A final test using PTFE (teflon-coated) substrate was found suitable for these films. These low M_w films were brittle as well as were full of static charge. Hence, handling these films was very difficult even for the simple jobs like making samples

for the DSC test. Addition of CNTs in these films were also tried. Films were cloudy and not uniform. Aggregation of CNTs was seen and was noticeable with the naked eyes. Hence, it was concluded that though $CHCl_3$ and CH_2Cl_2 are good solvents for PMMA but they do not solve the purpose for this study. It led to the search for a more appropriate solvent. Acetone was chosen, for it is a good solvent of PMMA [74] because of the stronger interaction of PMMA-acetone.

Acetone was used as a solvent to cast films with PMMA at room temperature. The cast films were clear and transparent. PMMA is a brittle polymer and, therefore the cast films were highly brittle. As we use CNTs in the form of supernatant solution as mentioned in section 3.1.2 containing a small amount H_2O , another trial of film casting was made by adding a known small amount of H_2O in the PMMA/acetone solution. The film was cloudy, totally opaque, brittle and hard to peel off from the substrate. PMMA is totally insoluble in water but due to the presence of acetone, it dissolves into the solution. Though the presence of water in the solution was very little, it led to cloudy film. Then the known amount of CNT supernatant was added. The cast film was still cloudy but was very flexible as compared to the pure film. Here, it became obvious that CNTs were adding the flexural strength to the brittle films of pure PMMA. The example is shown in figure 4.1.

Then a higher M_w , 350,000 of PMMA was tried as it was assumed that with the higher molecular weight the films will be less brittle. The pure films of PMMA and PMMA/CNT were cast and it was observed that films with higher molecular weights with same thickness were easier to handle. This method was chosen as the most promising technique. The general procedure for casting PMMA/CNT film at room temperature by using acetone as a solvent is explained in the section 3.2.1. The films cast with acetone were clear and transparent and there was not aggregation of CNTs in the films as shown in figure 4.2 (b). But the need for

(a)

(b)

(c)

Figure 4.1: Films cast at room temperature (a) clear PMMA / acetone film (b) cloudy PMMA / acetone/ H_2O and, (c) cloudy PMMA/ acetone/ CNTs

Figure 4.2: Figure shows (a) HT film cast with 1.095 wt.% of CNTs in PMMA/CNT composite film and, (b) RT film cast with 0.73 wt.% of CNTs in PMMA/CNT composite film.

casting the films at high temperature was felt because the room temperature films were not able to give much information in SEM about behavior of CNTs in the film.

4.1.2 Film casting at high temperature

The films cast at the room temperature were clear and transparent but to improve the CNT concentration, quality and the better mobility of CNTs in the film, the casting of films at a higher temperature was used. Since acetone has a flash point of 18° C and a boiling point of 56° C, another solvent was required that can be used to cast films at high temperature. Toluene was chosen as it is good solvent for PMMA and is compatible with CNTs. The films were cast at high temperature by following the procedure as explained in section 3.2.2. An example of the cast film with 1.095 wt.% CNTs in PMMA/CNT composite film is shown in figure 4.2 (a). The film is transparent and clear even with this very high wt.% of CNTs in it. This method is able to produce transparent films even at very high concentration

of CNTs whereas in figure 2.9, it is clearly observed that small quantities of CNTs forms aggregation in the films.

The films cast were transparent and the thickness of these films were between 30-60 μm . The dispersion of CNTs were much better than the RT cast films as there was no aggregation of CNTs visible in the film. These films could be used for high temperature stretching and SEM analysis. After setting the experiment parameters PMMA/CNT films were cast with varying wt.% of CNTs in the films. These films were utilized for the characterization.

4.2 Results and Discussions for PMMA/CNT films

The films cast at room temperature as well as at high temperature were clear and transparent and were used to characterize different methods as explained in chapter 3.

4.2.1 Thickness Method Comparison

The thickness of the films was measured by using the three methods as explained in section 3.3.1 for comparison. It was observed that there was very little difference among the obtained values of thickness from each of the methods. The biggest difference that was observed among the methods was between the optical microscope and the weight method which was 2.2 μm . This is equivalent to $\sim 4\%$ of the whole thickness.

In the weight method, due to the presence of some solvent the maximum thickness was observed. As for other methods, samples were cut by using blade which may compress the original thickness of the film.

4.2.2 SEM

SEM is mainly used to examine the morphology of PMMA/CNT films i.e., after blending the CNTs with PMMA, this technique is used to investigate how the CNTs reinforce PMMA matrices.

The PMMA films cast by using acetone as a solvent were fractured at room temperature. The films were between 30-50 μm thick. As shown in the figure 4.3, fracturing the films at room temperature, the SEM images did not give much useful information. SEM is mainly a surface microscope technique. When the films were fractured at room temperature, the fracture was very brittle and hence there was no chance for CNTs to carry the load and be pulled out. At higher temperatures, as shown in the figure 4.4, CNTs can be easily seen in the SEM images.

4.2.3 Stretching of Films at High Temperature

The need for stretching the films at high temperature was to give more information about the internal morphology of the PMMA/CNT films. The idea behind stretching the films at high temperature was to cause the films to thin and hence give enough time for CNTs to bear the load and be pulled out. The films were stretched by following the procedure explained in section 3.3.6.

While stretching the films at high temperature $\sim 60^{\circ} C$, the pure films were brittle and there was no necking seen during the fracture. But for the PMMA/CNT films it was observed that at high temperature, the films showed a little necking and there was noticeable elongation in the film. In high temperature stretch, the pure PMMA film breaks with 83.8 % elongation whereas the PMMA/CNT film with 0.73 wt.% of CNTs elongates with little necking and breaks with 240 % elongation. An example showing the necking formed in PMMA/CNT film with 0.73 wt. % of CNTs is shown in figure 4.5.

(a)

(b)

Figure 4.3: SEM image showing the fracture in 0.73 wt.% CNTs in RT cast PMMA/CNT film during room temperature stretching.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4.4: SEM images of high temperature cast PMMA/CNT films and stretched at cast at 60° C (a), (b), (c), (d), (e) and, (f).

Figure 4.5: SEM image representing the necking formed in HT cast 0.73 wt.% CNT PMMA/CNT film during HT stretching

The high temperature stretching of the samples was done by following the procedure explained in section 3.3.6. In this method the samples were stretched at a slow strain rate at a known temperature in order to examine these films. SEM was used to look at the fractured surfaces.

Network found in CNT/PMMA composites

The CNT entanglements were observed as shown in the figure (4.6, 4.7, 4.8), and shows the CNT networks observed in PMMA/CNT films. The similar CNT network was observed in PC/CNT films after stretching the films at high temperature [75]. The CNTs network observed in these pictures shows that the CNTs are present in the films in the form of ropes. The purified SWCNTs purchased from Carbolex have a diameter of 30 nm as described in section 3.1.2. When the cast films were stretched at high temperature, the thickness of the film sample is reduced to approximately 1 μm . From the figures (4.7, 4.8), the measured diameter of the fibrils in the stretched films is between 90 ~ 150 nm and the diameter of nodulus is between 200 ~ 250 nm. The measured diameter of the networked

Figure 4.6: CNTs entanglements in PMMA/CNT films (a), (b), (c) and (d).

fibrils is 3-4 times than that of pure RCNTs, suggesting a thick adsorbed layer (coating) of PMMA. Along with the network formation, the presence of nodules and complete curvature of CNT ropes as shown in figures 4.4(c) and 4.4(d) respectively, is also of interest. These nodules or curved CNTs may connect to these CNT fibrils. It is believed that these nodules are the junction points where RCNTs have bundled or crossed each other. The tensile strength of composite material may be affected by the PMMA/RCNT at these points. This behavior of adhesion between PMMA and the RCNT is difficult to characterize.

4.2.4 Glass Transition Temperature (T_g)

A key parameter for characterizing a polymer is the glass transition temperature, T_g . The T_g of the films were obtained by using a DSC instrument as explained in section 3.3.9.

The multi-walled nanotubes have shown 10% increase in the glass transition of PMMA irrespective of the amount of CNTs added, when the composite films were cast with different concentrations of CNTs added into PMMA [76].

The T_g obtained from DSC for PMMA film samples and PMMA/CNT composite films with different concentrations of CNTs are shown in figure 4.9. The T_g for pure PMMA powder as received from the supplier is 122 °C and is shown in the figure. On the graph 4.9 (a), the mid point T_g for the pure PMMA powder is 122.19 °C. The PMMA film cast with toluene as a solvent has T_g of 114.64 °C and is shown by curve (b) and similarly the % amount of CNTs is increasing from (c) to (f) in the figure. It is clearly observed that there is no significant change in the T_g of the composite films with the addition/increase of CNTs. For curves 4.9 (c) and (d) small blobs have been observed and the origin of these are unknown.

The T_g reported on the graph for each particular sample in the figure 4.9 is within the range of ± 2 °C because of the uncertainty in the measurement from the

(a)

(b)

Figure 4.7: CNTs entanglements in PMMA/CNT films (a) SEM image representing the stretching of the films in PMMA/CNT, zoomed part shows the network of CNTs, (b) SEM image representing the network of CNTs at high temperature stretching.

(a)

(b)

Figure 4.8: CNTs entanglements in PMMA/CNT films (a) CNT network with nodulus, and (b) The SEM image similar to SWCNT picture.

Figure 4.9: Glass transition curves for (a) PMMA powder as received, (b) pure PMMA film (c) PMMA/CNT film with 0.1825wt. % CNTs (d) PMMA/CNT film with 0.365 wt. % CNTs (e) PMMA/CNT film with 0.73 wt. % CNTs (f) PMMA/CNT film with 1.095 wt. % CNTs

instrument. The graph shown in figure 4.10 shows the standard deviation in the measurement of T_g in the DSC instrument. This graph considered the variation in the readings for 3-4 different samples for the same wt.% of CNTs.

Figure 4.10: Graph showing the variation in T_g verses Wt.% of CNTs.

4.2.5 MTS

The main focus of the mechanical measurements of nano-composites has been on the transfer of stress from the polymer matrix to carbon nanotubes. The samples with different concentration of CNTs in PMMA matrix were tested in the MTS machine. The concentrations vary from pure PMMA film to an addition of 1.095 wt.% CNTs. Their in-process data can be obtained from the built in house MTS. Even though the wt.% of CNTs e.g., 1.095 wt.% in the films is very high, the films are clear and is shown in figure 4.2.

The literature value for the tensile modulus of pure PMMA varies between 60-80 MPa [72].

In figure 4.11, curve (a) shows the Stress-Strain curve for pure PMMA. According to the curve the break strength for pure PMMA film is 81.07 MPa which is very close to 80 MPa at 1.27% strain. This curve shows that PMMA has brittle behavior. For the 0.365 wt.% CNTs, curve (b) shows that the film breaks at 78.2 MPa at a higher elongation with strain value at 2.36%. This is 1.09 strain (%)

more than the pure PMMA film. Similarly, with the increase in the % CNTs as shown in the figure, the increase in elongation(% strain) is observed. It is clearly observed in figure 4.11 that for curve (d) the elongation of PMMA/CNT is sharply increased as compared with the elongation of pure PMMA. The sample breaks at the strain (%) value of 5.53. Note that the poor resolution of the LVDT makes it difficult to find Youngs modulus from this apparatus. In section 4.2.6, we will use TMA for this purpose.

The maximum break strength is obtained for 0.73 wt.%, CNTs which can be clearly seen in table 4.1. The reason is not clear but it shows that there is limit to the strength increase that RCNTs can impart on the PMMA matrix. Similar observations were also made in PC/CNT composites [75], there an optimal CNT concentration for the strength increase in PC/CNT composites was observed, after which further addition of CNTs decrease the strength. The break strength is almost the same for the pure PMMA, 0.365 wt.% and for 1.095 wt.% CNTs. It can be clearly seen that the elongation in the films in comparison with the pure PMMA film has significantly increased. In the PMMA/CNT films with 1.095 wt.% CNTs, the elongation is at a maximum but the break strength falls back to pure PMMA break strength levels. On comparing the Strain(%) values in the curve, from curve (a) to (c), the samples break at the maximum break strength without the presence of any necking in the sample. With the increase in the wt.% of CNTs further to 1.095 wt.%, the maximum break strength of sample observed is at 3.86 strain (%) but the sample breaks at a value of 5.53 strain (%). This shows a little bit of necking in the sample before it breaks. Thus CNT seems to induce greater ductility in the PMMA films.

These results are concluded with the average sample testing of four films per concentration of CNTs in the film. The results show that there is no significant increase in the break strength with the addition of CNTs except for the 0.73 wt. %

Figure 4.11: Stress-Strain Characteristics of PMMA/CNT films with varying wt.% of CNTs (a) Pure PMMA film, (b) 0.365 wt. % CNTs (c) 0.73 wt. % CNTs (d) 1.095 wt. % CNTs.

Amount of (% wt.) CNTs	Stress(MPa)	Strain (%)
0.0	81.07	1.27
0.365	78.2	2.36
0.73	96.50	3.97
1.095	78.03	3.86

Table 4.1: Comparison of results obtained from MTS machine for different wt. % CNTs in PMMA films.

CNTs but there is significant increase in elongation and we can even see formation of necking in the films at higher concentration at room temperature from the graph 4.11 and figure 4.5.

Figure 4.12: Comparison of TMA results for Pure PMMA and 0.72 wt. % CNTs in PMMA/CNT composite.

4.2.6 TMA

The Young's modulus of PMMA films were observed by following the procedure as explained in section 3.3.2. A sinusoidal waveform load/stress was applied and it made the displacement/strain follow the same waveform trend, shown in figure 4.12. From these curves, the Young's modulus is calculated by the procedure mentioned in section 3.3.2.

In the figure 4.12, the comparison is made between the pure PMMA film and 0.73 wt. % CNTs in PMMA/CNT composite. It is clearly shown in the figure that with the increase in the concentration of CNTs in the film the Young's modulus is increased. In the example shown in the figure it is clear that there is moderate increase of 16.7 % in the Young's modulus for the loading of 0.73 wt. % CNTs as compared to the pure PMMA film cast at the room temperature.

4.3 Conclusions

A method has been developed to prepare a highly transparent polymer film, with uniformly dispersed CNT. This has been applied to polycarbonates [71] and PMMA in this present study. Here, in this study, even 1.095 wt.% of CNTs has given a very clear film. This technique proves to be applicable to a range of polymers and is scalable. A network structure develops when this method is used for preparation of the composite. A moderate increase in Youngs modulus is observed. The break strength does not change significantly but the % increase in elongation is about 5.53% as compared to the pure PMMA film. At high temperature, this increase is even observed at low concentration of CNTs. But there is no major change is observed in glass transition temperature.

Chapter 5

PMMA/CNT Gels

This chapter reports the preparation of the of the Polymer/CNT gels preparation with the polymer matrix being PMMA. In recent years, lots of work has been done to utilize the properties of CNTs in various ways with polymers. Here, in this chapter, a new approach is made by which CNTs are used within a polymer gel.

5.1 Preparation of Gels

The PMMA gels were prepared by dissolving 0.5 gm of PMMA in 4 ml acetone. The vial containing this solution was quenched at -80°C for 10 minutes in a dry ice/acetone bath. The detailed procedure of gel formation is explained in section 3.2.3. Each gel formed was left in RT to dry. By removing the solvent at RT, the underlying structure of gel is preserved. The PMMA/CNT gels are formed by dissolving 0.5 gm of PMMA in 4 ml amount of acetone and then adding a known amount of purified CNTs suspended in an aqueous solution. An example of PMMA/CNT gel with 0.73 wt.% concentration of CNTs is as shown in figure 5.1.

The gel shows that the carbon nanotubes are well dispersed in the gel solution and after the quenching of the solution, we observed that there was no phase separation between the polymer and carbon nanotubes. In contrast, phase sep-

Figure 5.1: Example of PMMA/CNT gel

aration (i.e., the dried gel showing two phases, one cloudy and one clear part) was observed when the solution was not adequately stirred and the supernatant solution was not well-dispersed. The gel samples dried over the time after leaving them at RT and shrunk in size. Figure 5.2 shows the dried pure PMMA gel and PMMA/CNT gel with 0.73 wt.%. The gels become brittle after getting dried at RT. These gels are made by using acetone as a solvent and it has boiling point of 56°C . It was observed to evaporate very easily at RT.

5.2 Flexibility of gels

Stretching of gels

The mechanical properties of the polymer gels were investigated. As the carbon nanotubes are well dispersed in the gel solution it was believed that CNTs will improve the gel properties. A typical example of PMMA/CNT gel with 0.73 wt.%

Figure 5.2: Example of (a) pure PMMA gel and, (b) PMMA/CNT with 0.73 wt.% after the gels gets dried

of CNTs is as shown in figure 5.1. The PMMA/CNT gels formed are flexible and can be stretched. The figure 5.3(a) shows the gel sample of 0.73 wt.% of CNTs in PMMA gel being stretched. The approximate initial length of gel is 2.5 cm as can be observed from the figure. The gel is stretched with the help of tweezers and it is observed that the gel is very flexible and can be stretched easily, as seen in figure 5.3(b). In figure 5.3(c) the stretched length is increased to 5 cm which is almost double of the original length.

Twisting of gels

The other way to show flexibility of the gel is by twisting it. The example of twisting the gel is shown in figure 5.4. The gel sample is easy to twist.

5.2.1 Creep test

Creep is the deformation that occurs over a period of time when a material is subjected to constant stress at constant temperature. In metals, a creep test is done at high temperature but in plastic materials creep is common at room temperature and is called cold flow or deformation under load. In our gel samples, the tensile

(a)

(b)

(c)

Figure 5.3: Images of the gel during stretching (a) before stretch (b) while stretching and (c) after the stretch

(a)

(b)

Figure 5.4: Images of the gel during twisting (a) and, (b)

creep test aims to measure the deformation of gel samples. The deformation in the pure PMMA gel and the PMMA/CNT gel was compared. The gel samples were made as explained in section 3.2.3. It was presumed that gel samples with CNTs should have better creep strength as compared to pure PMMA gel because of the mechanical properties of CNTs. To quantify this presumption, a standard test method was devised. Due to the sample size and uniformity limitation of the gel, a desiccator was used. We choose a desiccator to maintain a closed atmosphere for the test. The small beaker was put in the desiccator and samples were hung in this beaker from a support. Both the samples were cut of same initial length (1 cm) and width (2 cm) and thickness (1.5 mm). The gel samples were hung in the presence of acetone vapors at room temperature in order to prevent the drying of the gels. The samples were clamped with equal weights of 4 gm. We tied very small weights around the gel samples. It was made sure that the visible length of the gel samples in between the clamp and the weights should be the same. The samples were under observation for 60 hrs i.e., 2.5 days. The change in length for PMMA gel was 1.2 cm and the change in length for PMMA/CNT gel was 1.03 cm which was 17% less than the pure gel sample. The creep test apparatus is as shown in the figure 5.5.

5.3 Morphology of Different Concentration of CNTs in PMMA Gels

5.3.1 SEM pictures for different concentrations of CNT gels at same magnification

For future development of new polymer materials, there is a need for understanding their micro-structures. Electron microscopy is a fundamental tool for helping to meet this need. The SEM pictures of the gels showed well-defined change in the morphology for changes in the concentration of CNTs. Specifically, the pore size

Figure 5.5: Apparatus set-up for creep test

within the gel is inversely related to the CNT concentration. To investigate the effect of CNTs on PMMA gel formation, different amount of weight percentage of CNTs were added. Figure 5.6 shows the surface morphology of PMMA gels with varied amount of CNTs at the same scale on the SEM micrographs. These images were taken at 1000x magnification. Figure 5.6 (a) shows the image of PMMA gel with no CNTs. It can be clearly observed from the figure that pores are not well-defined and the surface is uneven. Similarly, figure 5.6 (b) to (e) demonstrates the trend that with the increase in the wt.% of CNTs the number of pore increases. With the increase in the pores it is also very obvious that these pores are more uniform pores, and the size of these pores decreases as the amount of wt.% of CNTs is increased. Figure 5.6(e) shows the surface of the PMMA gel with 1.095 wt.% of CNTs in gel sample. It is clearly seen that the pores are very uniform and form foam like structure. The pore size of PMMA gels with varying wt.% of CNTs are quantified and explained in section 5.5.

Figure 5.6: SEM images of PMMA gel (a) with no CNTs, (b) 0.1825 wt.% CNTs, (c) 0.365 wt.% CNTs, (d) 0.73 wt.% CNTs and (e) 1.095 wt.% CNTs. taken at 1000x magnification.

Figure 5.7: SEM images of PMMA gel with no CNTs. (a) and (b) shows the general overview of the gel surface.

From Figure 5.7 to figure 5.11 more SEM images are shown for the different CNT concentrations to show the trend for the decrease in the pore size with the increase in the CNT concentration.

Figure 5.12 and 5.13 shows the SEM images of 0.73 wt.% and 1.095 wt.% CNTs in PMMA/CNT gels showing the nanotubes coming out of the pores.

The CNT network observed in PMMA/CNT gels are shown in figure 5.14. Figure 5.14(a), shows the network observed with 1.095 wt% CNTs in PMMA/CNT gel. Figure 5.14(b) and 5.14(c) shows the network observed in 0.73 wt% CNTs in PMMA/CNT gel.

5.4 3-D orientation

The gel samples are made in order to look into the micro-structures using SEM. It was observed in the SEM, that the gel samples have different microstructure in different directions. Figure 5.15 shows a 3-D schematic representation of the cross sections of a gel with 0.73 wt.% CNTs. Figure 5.15 (a) shows the top surface of the gel during formation. The pore openings can be clearly observed in this image. Figure (b) and (c) shows the vertical cross-section of the same sample.

Figure 5.8: SEM images of PMMA gel with 0.1825 wt.% CNTs (a) shows the general overview, and (b) shows the zoomed part on the gel surface

Figure 5.9: SEM images of PMMA gel with 0.365 wt.% CNTs (a) shows the general overview, and (b) shows the zoomed part on the gel surface

Figure 5.10: SEM images of PMMA gel with 0.73 wt.% CNTs (a) shows the general overview, and (b) shows the zoomed part on the gel surface

Figure 5.11: SEM images of PMMA gel with 1.095 wt.% CNTs (a) shows the general overview, and (b) shows the zoomed part on gel surface

Figure 5.12: In SEM images of PMMA gel with 0.73 wt.% CNTs (a) and, (b) showing the CNTs inside the pores.

These edges are perpendicular to each other. The anisotropic shape of the pores can be observed from these vertical sections. Clearly, the pores are not through holes parallel to the vertical edges of the cross section but they appear as random and blocked in the midway.

This type of structure was observed in all the concentration of CNTs. The pore starts in one direction and from the surface it appears as the pore are through but when pores are looked in from the other direction it appears that they are walls and can be observed as boundaries.

5.5 Pore Size Measurement

In section 5.3, SEM images with different concentration of CNTs have shown different pore sizes. The gel preparation was repeated and samples were looked in SEM at different angles and in different directions. The measurement of pore size was now carried out. Various trial methods were implemented, such as measuring pores of each picture by hand or using Northern Eclipse Software to measure the pixels. But these methods were prone to errors and a standard and unbiased measurement method was needed to be developed. To follow a standard and un-

(a)

(b)

Figure 5.13: SEM images of PMMA gel with 1.095 wt.% CNTs (a) and, (b) showing the CNTs inside the pores.

Figure 5.14: Network formation by CNTs in gel (a) shows CNT network formation with 1.095 wt.% CNTs, (b) and, (c) shows the CNT network formation with 0.73 wt.% CNTs

Figure 5.15: 3-D schematic describing anisotropic nature of the pores in the gel with 0.73 wt.% of CNTs in PMMA gel, (a) top surface of the gel showing the pores, (b) and (c) vertical cross-sections of the gel in two perpendicular directions showing that the pores are anisotropic.

Amount of (% wt.) CNTs	Average Pore Size (Sq. μm)
0.0	no pores
0.1825	140.03
0.365	136.87
0.73	124.14
1.095	93.22

Table 5.1: Comparison of % amount of CNTs and average pore area

biased measurement, the pore measurement was done by the method as explained in section 3.3.8.

The image processing based method explained in section 3.3.8 is employed for calculation of average pore sizes for each sample. As described earlier, the SEM images are converted into binary images using digital image processing technique such as thresholding. These binary images are then used for further analysis. Typically 4- or 8- neighborhood is used to calculate the connected pixels representing pores in the binary image. Any group of white pixels which is connected among each other is represented as a hole in the binary image. In 4 neighborhood approach, we look for white pixels which are connected to all its 4 neighboring white pixels and mark the group as a hole. Whereas in 8-neighborhood, pixels are marked which are connected to its 8 neighboring white pixels. The later approach is more robust which eliminates the possibility of false marking of the holes. Pore areas are then calculated in terms of pixels. A statistical analysis of pore sizes and number of pores having that size is carried out. A typical plot is as shown in figure 5.16 . Figure 5.16 shows the zoomed up portion of the same plot. Once all pores and their sizes are calculated, the average pore size for that particular image is calculated. The sizes are then converted into appropriate usable units by multiplying them by corresponding scaling factors.

The algorithm was applied to various samples having different CNT concentrations. It is observed that as we increase the concentration of CNTs in PMMA

(a)

(b)

Figure 5.16: Histograms of SEM image of 1.095 wt% CNTs in PMMA/CNT gel after analysis showing variation of number of pores with their size. (a) overall histogram and, (b) zoomed up plot showing distribution for smaller pore sizes. The pore areas are calculated in pixels. They are then converted into square micrometer units by multiplying by corresponding scaling factors.

Figure 5.17: Variation of average pore size with wt. % of CNTs

gels, the average pore size tends to reduce in dimensions. Figure 5.17 shows the variation of average pore size with concentration of CNTs. Table 5.1 gives the exact average pore sizes in sq. micrometers for different concentrations of CNTs.

This section clearly illustrates the variations of pore sizes with change in concentration. The pore sizes becomes smaller as we increase the CNT concentration in the PMMA gel.

Chapter 6

Conclusions and Future Recommendations

6.1 Conclusions

The purpose of this thesis was to study the morphological and mechanical properties of the PMMA/CNT composites. This thesis presents brief summary of CNTs and their casting methods along with different procedures for gel and film preparation. The main emphasis of the research is laid on morphological investigations on PMMA/CNT films and gels and effects of CNTs on their mechanical properties.

Due to the diverse and promising properties of CNTs, the PMMA matrix was used to make composite materials. The properties of PMMA/CNT composites were studied and compared by using SEM, DSC, built in-house MTS, pore measurement, high temperature stretching and TMA.

The film samples were made both at the room temperature and at the high temperature with the varying wt.% of CNTs from 0.1825% to 1.095 wt.%. The films made were transparent and clear by following the experimental procedure.

The cast films were investigated in SEM and for the high temperature films showed the formation of micro-scale network in the films. The network was revealed for the purified Carbolex CNT supernatant.

The addition of CNTs add flexibility to the brittle PMMA films. In MTS,

PMMA/CNT films showed an increase in the elongation in the films and even formation of necking with the addition of CNTs at 1.095 wt. % of films. Even in TMA, there is an increase of 16.7% in Young's modulus for the 0.73 wt.% of CNTs as compared with the pure PMMA films.

This thesis also presents a novel experimental set up for Polymer/CNT gel preparation with polymer matrix being PMMA. The morphology of different concentrations of CNTs in gels is analyzed. It is observed that as we increase the CNT wt.% in PMMA gel, the pore sizes tend to shrink in dimensions.

This research work thus opens up a new direction in the polymer composites by proposing newer techniques to improve the Polymer/CNT composites by exploring in its novel way.

6.2 Recommendations for Future Work

Though the scope of this thesis is limited to morphological analysis and testing the mechanical properties, it can be extended to analyzing electrical properties of polymer composites. It is expected that PMMA/CNT composites will improve the electrical properties of polymers due to the observed entangled network of CNTs in the composite films.

Since PMMA is an insulator but the CNTs are good conducting material, the electric conduction of PMMA/CNT composite should be measured and it could be utilized in place of the materials where intermediate conduction is required.

For PMMA/CNT composite, the hardness testing in local areas will help the characterization of CNT network dimension and dispersion. Nanoindentation technique which enables testing materials at sub-micron scale can be used for this purpose. Fatigue properties of PMMA/CNT composite should be tested.

In the present study, pore size of the gels was measured from the SEM images. The pore volume of these gels should be measured using a porosimeter. Different

solvent system should be investigated to see the effect of CNTs in PMMA gel. Mechanical properties of these gels should be tested. This work can be extended to other polymer gel system to see the effect of CNTs on the pore size and the pore volume.

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