Chapter : 1 Introduction

Introduction

Polymer nanocomposites area has become an attractive field of research from both fundamental and industrial point of view. It is generally recognized that macroscopic properties of materials are determined, to a large extent by critical scale length, especially in the nanoscale, which defines the materials structure and organization. Thus, through the controlling of formation and dispersion of nanoparticles, properties of the resulting materials can be greatly improved.

Polymer systems are widely used because they are lightweight, posses design flexibility, and are easily processable [1-2]. These systems, however, generally posses inferior mechanical properties such as low strength and low elastic modulus as compared to metals and ceramics. One of the ways to improve mechanical properties of these systems while maintaining their desirable properties is by adding highmodulus reinforcing filler to make polymer composites [3]. Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites. In conventional polymer composites, many inorganic filers with dimensions in the micrometer range, e.g. calcium carbonate, glass beads and talc have been used extensively to enhance the mechanical properties of polymers. Such properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particles [4–5]. A further improvement of the mechanical properties can be achieved by using filler materials with a larger aspect ratio such as short glass fibers. It is logical to anticipate that the dispersion of fillers with dimensions in the nanometer level having very large aspect ratio and stiffness in a polymer matrix could lead to even higher mechanical performances. These fillers include layered silicates and carbon nanotubes. Carbon nanotubes (CNTs) have a substantially larger aspect ratio (1000) in comparison with layered silicates (200) [6-7]. Moreover, flexible CNTs also possess very high strain to failure. Rigid inorganic nanoparticles with a smaller aspect ratio are also promising reinforcing and/or toughening materials for the polymers. The dispersion of nanofillers in the polymers is rather poor due to their incompatibility with polymers and large surface-to-volume ratio. Therefore, organic surfactant and compatibilizer additions are needed in order to improve the dispersion of these nanofillers in polymeric matrices. For example, layered silicate surfaces are hydrophilic and proper modification of the clay surfaces through the use of organic surfactants is needed. The obtained product is known as 'organoclay'. In this context, organoclays can be readily delaminated into nanoscale platelets by the polymer

molecules, leading to the formation of polymer–clay nanocomposites. These nanocomposites belong to an emerging class of organic–inorganic hybrid materials that exhibit improved mechanical properties at very low loading levels compared with conventional microcomposites [8-9]. CNTs are recognized to agglomerate and entangle easily during processing of the nanocomposites, leading to poor mechanical properties. Several techniques such as ultrasonic activation, in situ polymerization and surfactant addition are commonly used to disperse CNTs in polymer matrices.

Carbon nanofibers (CNF) and nanotubes (CNT) have been used to modify several polymers including poly (propylene) [10 -11], poly- (methyl methacrylate) [12-13], and poly (ethylene terepthalate) [14], poly (styrene), High-density polyethylene [15] and poly (carbonate) [16-17]. Carbon nanofibers and carbon nanotubes have been blended into polymer matrices using conventional mixing methods such as use of twin-screw extruder [18-19], high shear mixer [20-21], as well as two-roll mill [22]. To improve CNF dispersion and nanofiber/polymer interfacial strength, carbon nanofibers have been functionalized [20], ball-milled [22], and surface treated with plasma [23].

The composites of engineering thermoplastics reinforced with thermoplastics liquid crystalline polymers (LCPs) have been extensively studied in recent years [24-25]. This is due to their favorable properties that include high stiffness and strength, better processability than short fiber reinforced composites. The remarkable mechanical properties of these blends arise from the nature of LCPs, which develop fibrillar structure in the melt state that are mostly maintained in solid state. The fibrillation of LCP in thermoplastic melts is influenced by several factors. These include miscibility between the LCP and thermoplastics, LCP concentration, and processing parameters such as the melt viscosity ratio of LCP to polymer matrix (V_r) melt temperature, flow mode and shear rate. Thermotropic liquid crystal polymers (LCP) may give anisotropic fibres, with very impressive mechanical properties, through conventional spinning operation [26-27]. These polymers can also be used as reinforcing agents for conventional thermoplastics materials since they form a diffused phase of particles which easily assume, during processing, a fibrilar geometry.

Background

The section briefly covers the theories, practices and literatures, which are important and related to this work.

1.1 Carbon nanotubes

Elemental carbon in the sp^2 hybridization can form a variety of amazing structures [28]. Apart from the well-known graphite, carbon can build closed and open cages with honeycomb atomic arrangement. The first such structure to be discovered was the C60 molecule by Kroto et al [29]. Although various carbon cages were studied, it was only in 1991, when Iijima observed for the first time tubular carbon structures [30].

Carbon nanotubes can be classified into single-walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs) and carbon nanofibers (CNFs). SWNT with a diameter of 1–2 nm consists of a single graphene layer wrapped into a cylindrical shape, and hemispherical caps seal both ends of the tube. SWNT can be further divided into three classes, i.e. armchair, zigzag and chiral depending on the arrangement of hexagons in their structures (Figure 1.1) [31]. In most cases, SWNTs tend to assemble into 'ropes' structure.



Figure 1.1: Single wall carbon nanotube

In contrast, MWNT comprises a number of graphene layers coaxially roll together to form a cylindrical tube. Each carbon atom within the atomic layer of a grapheme sheet is covalently bonded to three neighboring carbon atoms. Three sp² orbitals on

each carbon form s-bonds to three other carbon atoms. One 2p orbital remains unhybridized on each carbon; these orbitals perpendicular to the plane of the carbon ring combine to form the p-bonds. The atomic interactions between the neighboring layers are the van-derWaals forces. The outer diameter of MWNTs is about 3–10 nm (Figure 1.2) [32]. Vapor grown CNFs have a larger diameter ranging from 50 to 200 nm, and contain more defects han MWNTs. Compared to SWNTs and MWNTs, CNFs such as Pyrograf-III can be produced in higher volumes and at a lower cost by Applied Sciences, Inc. (ASI) [33].



Figure 1.2: TEM image showing the layered structure of multi-walled carbon nanotube

1.1.1 Carbon nanotube structure

The atomic structure of nanotubes is described in terms of the tube chirality, or helicity, which is defined by the chiral vector, C_h , and the chiral angle, θ . In Figure 1.3, we can visualize cutting the graphite sheet along the dotted lines and rolling the tube so that the tip of the chiral vector touches its tail. The chiral vector, often known as the roll-up vector, can be described by the following equation:

Where the integers (n, m) are the number of steps along the ziz-zag carbon bonds of the hexagonal lattice and a_1 and a_2 are unit vectors, shown in Figure 1.3. The chiral angle determines the amount of 'twist' in the tube. The two limiting cases exist where the chiral angle is at 0° and 30°. These limiting cases are referred to as ziz-zag (0°)

and armchair (30°) based on the geometry of the carbon bonds around the circumference of the nanotube. The difference in armchair and zig-zag nanotube structures is shown in Figure 1.4. In terms of the roll-up vector, the ziz-zag nanotube is (n, 0) and the armchair nanotube is (n, n). The roll-up vector of the nanotube also defines the nanotube diameter since the inter-atomic spacing of the carbon atoms is known.



Figure 1. 3: Schematic diagram showing how a hexagonal sheet of graphite is rolled to form a carbon nanotube



Figure 1.4: Illustrations of the atomic structure of (a) an armchair and (b) a zig-zag nanotube

The chirality of the carbon nanotube has significant implications on the material properties. In particular, tube chirality is known to have a strong impact on the electronic properties of carbon nanotubes. Graphite is considered to be a semi-metal, but it has been shown that nanotubes can be either metallic or semiconducting,

depending on tube chirality [34]. All armchair SWNT are metallic with a band gap of 0 eV. SWNT with n - m = 3i (*i* being an integer and $\neq 0$) are semimetallic with a band gap on the order of a few meV, while SWNT with $n - m \neq 3i$ are semiconductors with a band gap of ca. 0.5-1 eV. Each MWNT contains a variety of tube chiralities, so their physical properties are more complicated to predict

Investigations on the influence of chirality on the mechanical properties have also been reported. The analytical work of Yakobson et al. [35, 36] examined the instability of carbon nanotubes beyond linear response. Their simulations show that carbon nanotubes are remarkably resilient, sustaining extreme strain with no signs of brittleness or plasticity. Although the chirality has a relatively small influence on the elastic stiffness, they concluded that the Stone-Wales transformation, a reversible diatomic interchange where the resulting structure is two pentagons and two heptagons in pairs, plays a key role in the nanotube plastic deformation under tension. The Stone-Wales transformation, shown in Figure 1.5, occurs when an armchair nanotube is stressed in the axial direction. Nardelli et al. [37] theorized that the Stone-Wales transformation results in ductile fracture for armchair nanotubes.



Figure 1.5: The stone wale transformation occurring in an armchair nanotube under axial tension

The classification schemes outlined above were combined to classify carbon nanostructures within the general hierarchy of carbon materials (Figure 1.6) [38]. The scheme is based on two major characteristics: the type of carbon atom hybridization and the characteristic sizes of nanostructures. Starting with a description of the bonding nature of carbon atoms, the idea is to analyse how different classes of carbon networks are formed with the increasing characteristic size of a carbon structure. Starting with small organic molecules (inner circle), the hierarchy of carbon materials can be described as an extension of organic molecular species to bulk inorganic all-carbon materials through a variety of carbon entities in the nanoscopic size range.



Figure 1.6: Classification of carbon nanostructures mark spⁿ correspondence of intermediate carbon forms with a noninteger degree of carbon bond hybridization

If we consider fullerenes, CNTs, graphene of finite size and the currently observed smallest nanodiamond clusters as basic structural units in the carbon nanoworld, prototype molecules can be assigned to these units at the scale of molecules (inner circle). It should be noted that this scheme does not mean that these molecules are involved in the synthesis of the units; rather we would emphasize topological similarities between organic species and inorganic materials. While the sizes of the representative members of sp² and spⁿ (2 < n < 3) families experimentally identified change rather smoothly from the molecular scale (few nanometres) to the scale of

nanostructures (tens of nanometres), for sp3 carbon forms there is currently a gap in sizes between the observed molecular forms of the highest diamondoids [39] (~1 nm in size, containing up to 50 carbon atoms) and the smallest nanodiamond particles $(\sim 2-3 \text{ nm in size}, \text{ few thousands carbon atoms})$. Recently, a hybrid form of an entity with a diamond core and fullerene-like outer shells called bucky diamond has been suggested and experimentally confirmed [40]. The next structural level in Figure 1.6, with a corresponding increase in the characteristic sizes, can be considered to consist of assemblies of the structural units, ranging from simple forms, such as multi-walled CNTs or carbon onions, to more complicated carbon architectures such as carbon black, schwarzites and ultrananocrystalline diamond films. Finally, at the upper micro/macroscopic scale there is diamond, graphite, carbolite, fullerite and the recently discovered single-walled CNT strands of macroscopic sizes [41]. While the described scheme corresponds to a bottom-up approach of molecular synthesis, it is also necessary to consider nanostructures obtained by top-down approaches using different nanopatterning techniques such as fabrication of diamond nanorods by reactive ion etching of diamond films [42]. Obviously, structural units from different families can be combined to form hybrid nanostructures [43].

1.1.2 Synthesis of carbon nanotubes

The MWNT were first discovered in the soot of the arc-discharge method by Iijima [30]. This method had been used long before in the production of carbon fibers and fullerenes. It took two more years for Iijima and Ichihashi [44], and Bethune et al. [45] to synthesize SWNT by use of metal catalysts in the arc-discharge method in 1993. Significant progress was achieved by laser-ablation synthesis of bundles of aligned SWNT with small diameter distribution by Smalley and co-workers [46]. Catalytic growth of nanotubes by the chemical vapor decomposition (CVD) method was first used by acaman et al. [47].

Arc- discharge

In 1991, Iijima reported the preparation of a new type of finite carbon structures consisting of needle-like tubes [28, 30]. The tubes were produced using an arc-discharge evaporation method similar to that used for the fullerene synthesis. The carbon needles, ranging from 4 to 30 nm in diameter and up to 1 mm in length, were



grown on the negative end of the carbon electrode used for the direct current (dc) arcdischarge evaporation of carbon in an argon-filled vessel (100 Torr) (Figure 1.7).

Figure 1.7: Arc- discharge scheme

Ebbesen and Ajayan [48] reported large-scale synthesis of MWNT by a variant of the standard arc-discharge technique. Iijima used an arc-discharge chamber filled with a gas mixture of 10 Torr methane and 40 Torr argon. Two vertical thin electrodes were installed in the center of the chamber. The lower electrode, the cathode, had a shallow dip to hold a small piece of iron during the evaporation. The arc-discharge was generated by running a dc current of 200 A at 20 V between the electrodes. The use of the three components—argon, iron and methane, was critical for the synthesis of SWNT. The nanotubes had diameters of 1 nm with a broad diameter distribution between 0.7 and 1.65 nm. In the arc-discharge synthesis of nanotubes, Bethune et al. used as anodes thin electrodes with bored holes, which were filled with a mixture of pure powdered metals (Fe, Ni or Co) and graphite [45]. The electrodes were vaporized with a current of 95–105 A in 100–500 Torr of He. The arc was generated between two graphite electrodes in a reactor under helium atmosphere (660 mbar)

Laser Ablation

In 1996, Smalley and coworkers produced high yields (>70%) of SWNT by laser ablation (vaporization) of graphite rods with small amounts [46] of Ni and Co at 1200 $^{\circ}$ C (Figure 1.8). The tube grows until too many catalyst atoms aggregate on the

end of the nanotube. The large particles either detach or become over-coated with sufficient carbon to poison the catalysis. This allows the tube to terminate with a fullerene-like tip or with a catalyst particle. Both arc-discharge and laser-ablation techniques have the advantage of high (>70%) yields of SWNT and the drawback that (1) they rely on evaporation of carbon atoms from solid targets at temperatures >3000 $^{\circ}$ C, and (2) the nanotubes are tangled which makes difficult the purification and application of the samples.



Figure 1.8: Laser- ablation scheme

Chemical Vapor Deposition (CVD)

Despite the described progress of synthetic techniques [49] for nanotubes, there still remained two major problems in their synthesis, i.e. large scale production and ordered synthesis. But, in 1996 a CVD method emerged as a new candidate for nanotube synthesis. This method is capable of controlling growth direction on a substrate and synthesizing [50] a large quantity of nanotubes. In this process a mixture of hydrocarbon gas, acetylene, methane or ethylene and nitrogen was introduced into the reaction chamber. During the reaction, nanotubes were formed on the substrate by the decomposition of the hydrocarbon at temperatures 700 to 900 °C and atmospheric [51] pressure. The process has two main advantages: the nanotubes are obtained at much lower temperature, although this is at the cost of lower quality, and the catalyst can be deposited on a substrate, which allows for the formation of novel structures.

1.1.3 Properties of CNT

Electrical properties

The Unique Electrical Properties of carbon nanotubes are to a large extent derived from their 1-D character and the peculiar electronic structure of graphite. They have extremely low electrical resistance. Resistance occurs when an electron collides with some defect in the crystal structure of the material through which it is passing. The defect could be an impurity atom, a defect in the crystal structure, or an atom vibrating about its position in the crystal. Such collisions deflect the electron from its path. But the electrons inside a carbon nanotube are not so easily scattered. Because of their very small diameter and huge ratio of length to diameter-a ratio that can be up in the millions or even higher. In a 3-D conductor, electrons have plenty of opportunity to scatter, since they can do so at any angle. Any scattering gives rise to electrical resistance. In a 1-D conductor, however, electrons can travel only forward or backward. Under these circumstances, only backscattering (the change in electron motion from forward to backward) can lead to electrical resistance. But backscattering requires very strong collisions and is thus less likely to happen. So the electrons have fewer possibilities to scatter. This reduced scattering gives carbon nanotubes their very low resistance. In addition, they can carry the highest current density of any known material, measured as high as 10^9 A/cm² [52, 53]. One use for nanotubes that has already been developed is as extremely fine electron guns, which could be used as miniature cathode ray tubes (CRTs) in thin high-brightness low-energy low-weight displays. This type of display would consist of a group of many tiny CRTs, each providing the electrons to hit the phosphor of one pixel, instead of having one giant CRT whose electrons are aimed using electric and magnetic fields. These displays are known as Field Emission Displays (FEDs). A nanotube formed by joining nanotubes of two different diameters end to end can act as a diode, suggesting the possibility of constructing electronic computer circuits entirely out of nanotubes. Nanotubes have been shown to be superconducting at low temperatures.

Mechanical properties

The carbon nanotubes are expected to have high stiffness and axial strength as a result of the carbon–carbon sp^2 bonding [54]. The practical application of the nanotubes requires the study of the elastic response, the inelastic behavior and buckling, yield strength and fracture. Efforts have been applied to the experimental

[55, 56] and theoretical investigation of these properties. Nanotubes are the stiffest known fiber, with a measured Young's modulus of 1.4 TPa [57]. They have an expected elongation to failure of 20-30%, which combined with the stiffness, projects to a tensile strength well above 100 GPa (possibly higher), by far the highest known. For comparison, the Young's modulus of high-strength steel is around 200 GPa, and its tensile strength is 1-2 GPa.

Thermal Properties

Prior to CNT, diamond was the best thermal conductor. CNT have now been shown to have a thermal conductivity at least twice that of diamond [58]. CNT have the unique property of feeling cold to the touch, like metal, on the sides with the tube ends exposed, but similar to wood on the other sides. The specific heat and thermal conductivity of carbon nanotube systems are determined primarily by phonons. The measurements yield linear specific heat and thermal conductivity above 1 K and below room temperature [59-60]. The linear temperature dependence can be explained with the linear k-vector dependence of the frequency of the longitudinal and twist acoustic phonons [61]. The specific behavior of the specific heat below 1 K can be attributed to the transverse acoustic phonons with quadratic k dependence [62]. The measurements of the thermoelectric power (TEP) of nanotube systems give direct information for the type of carriers and conductivity mechanisms.

1.2 Carbon nanofibers (CNFs)

Carbon nanofibers CNFs are a form of vapor –grown carbon fiber which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis of hydrocarbons. With regard to properties of physical size, performance improvement, and product cost, CNFs complete a continuum bounded by carbon black, fullerenes, singlewall to multiwall carbon nanotubes on one end and continuous carbon fiber on the other, as illustrated in Figure 1.9.



Figure 1.9: Sizes from single-wall carbon nanotubes to conventional carbon fibers

Carbon nanofibers are able to combine many of the advantages of these other forms of carbon for reinforcement in commodity and high performance engineering polymers. Carbon nanofibers have transport and mechanical properties that approached the theoretical values of single crystal graphite, similar to fullerenes, but they can be made in high volume at low cost- ultimately lower than that of conventional carbon fibers. In equivalent production volumes, CNFs are projected to have cost comparable to E-glass on per pound basis, yet they possess properties that are far exceed those of glass and are equal to, or exceed, those of much more costly commercial carbon fiber. Maruyama et al. an excellent review of carbon nanotubes and nanofibers in composite materials [63].

1.2.1 Manufacturing

Carbon nanofibers are manufactured by Applied Sciences, Inc. /Pyrograf Products (ASI) located in Cedarville, Ohio (Website: <u>http://www.apsci.com</u>), by pyrolytic decomposition of methane in presence of iron based catalysts particles at temperatures above 900 °C. Figure 1.10 shows how pyrograf carbon nanofibers are produced at ASI.



Figure 1.10: Schematic showing the production of raw Pyrograf carbon nanofibers

Typically about 100 mg of powdered catalyst is placed in a ceramic boat, which is positioned in a quartz tube located in a horizontal tube furnace. The catalyst is reduced in a dilute hydrogen-helium stream at 600 °C and quickly brought to the desired reaction temperature. Following this step, a mixture of hydrocarbon, hydrogen, and inert is introduced into the system, and the reaction is allowed to proceed for about two hours. This method produces about 20 g of carbon fibers from the more active catalyst system.

1.2.2 Properties

Pyrograf-I, an early product, possessed a diameter in micrometers and was the first generation of the applied sciences. Pyrograph-III is a patented, very fine, highly graphitic. Pyrograph –III is available in diameters ranging from 50 to 200 nm and lengths of 50 to 100 μ m, as shown in a TEM micrograph in Figure 1.11.



Figure 1.11: TEM micrograph of Pyrograf- I VGCF

Therefore, CNFs are much smaller than conventional continuous or milled carbon fibers (5 to 10 μ m) but significantly larger than carbon nanotubes (1 to 10 nm). Compared to PAN and pitch based carbon fiber, the morphology of CNFs is unique in that there are far few impurities in the filament, providing for graphitic and turbostatic graphite structures , and the graphene planes are more preferentially oriented around the axis of the fiber. Consequences of the circumferential orientation of high- purity graphene planes are lack of active sites on the fiber surface, making CNFs more resistant to oxidation and less reactive for bonding to matrix materials. Also, in contrast to carbon fiber derived from PAN or pitch precursors, CNFs are produced only in a discontinuous form where the length of fiber can be varied from about 100 μ m to several centimeters , and the diameter is on the order of 100 nm. As a result, CNFs possess an aspect ratio of about 1,000.

Carbon nanofibers exhibit exceptional mechanical and transport properties, thus demonstrating their excellent potential as an attractive component for engineering materials.

Property (units)	As grown	Heat treated
Tensile strength (GPa)	2.7	7.0
Tensile modulus (GPa)	400	600
Ultimate strain (%)	1.5	0.5
Density (g/cc)	1.8	2.1
Electrical resistivity ($\mu\Omega$ -cm)	1000	55
Thermal Conductivity (W/m-K)	20	1950

Table 1.1: Properties of carbon nanofibers (CNFs).

Table1.1 lists the properties of vapor- grown carbon fibers, both as grown and after a graphitizing heat treatment to 3000 °C. Note that, due to the difficulty of direct measurement of nanofibers, the values in the Table1.1 are measured on vapor- grown carbon nanofibers that has been thickened to several micrometers in diameter. Such fibers consist of almost exclusively of chemical vapor deposition (CVD) carbon, which is less graphitic and more defective than the catalytically grown carbon core that constitutes the CNFs. Thus, the properties listed in the table represent an estimate for the properties of CNFs.

One of the goals for the broad utility of CNFs is to provide mechanical reinforcement comparable to that achieved with continuous tow carbon fiber at a price that approached that of glass fiber reinforcement, and low cost composite fabrication methods such as injection molding. Theoretical models suggest that reinforcement by discontinuous fibers such as CNFs can be closely approach that of continuous fibers, as long as the aspect ratio of the fibers is high and the alignment is good [64]. Work is going on to improve mechanical benefits of CNFs through fiber surface modification to provide physical and chemical bonding to the polymer matrix. Such modifications resulted in strength and modulus improvements of four to six times the values of neat resin; however, these values are still a modest fraction of what may be anticipated from idealized fiber-matrix interface and alignment of the fibers within the matrix. The more immediate opportunities for use in structural composites lie in prospect of modifying the properties of the matrix material. For example, use of small volume loading of CNFs in epoxy may allow for improvement of interlaminar shear strength of PAN or pitch- based composites. The CNFs additives to fiberglass composites could provide benefits to a suite of properties, including thermal and electrical conductivity, coefficient of thermal expansion, and mechanical properties, as suggested by the data in Table 1.2 [64]. Figure 1.12 shows a close –up of Pyrograf- III CNF, respectively. Figure 1.13 shows the TEM micrograph of an individual CNF with the hollow core in two distinct regions, catalytic and deposited [64].

Fiber content	Tensile	Tensile	Electrical resistivity		
(wt%)	strength (MPa)	modulus (GPa)	(ohm·cm)		
17% PR-19	51.5	4.55	3.2		
17% PR-19, OX	47.4	4.65	7.1		
5% PR-19 in	44.1	11.52	5.0		
10% ¼" glass					
5% PR-19, OX	33.8	8.92	7.0		
in10% ¼" glass					

Table 1.2: Thermoset Polyester	[/] Pyrograf-III	Composite	Properties.
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Figure 1.12: TEM micrograph showing the single Pyrograf –III carbon nanofibers



Figure 1.13: TEM micrograph showing carbon nanofibers have a hollow core and two distinct regions, catalytic and deposited

Pyrograf –III is available as PR-19 and PR-24 in three different grades. They are AG (as grown CNF), PS (pyrolytically stripped CNF), and HT (heat treated CNF) grades.

PR-19 CNF has fiber diameters of 100 to 200 nm and fiber lengths of 30 to 100 micron. PR-24 CNF has fiber diameters of 60 to 150 nm and fiber length of 30 to 100 micron.

Carbon nanofiber nanocomposites can offer multifunctional performance for several potential aerospace and other commercial applications, as follows:

- 1. EMI shielding, electrostatic painting, antistatic
- 2. Thermal conductivity of spacecraft, batteries, and electronics
- 3. Improved mechanical properties in polymers (composite structure injection molded parts, tires)

4. Reduced coefficient of thermal expansion (CTE) for spacecraft resin systems Applied Sciences, Inc. has suggested that CNFs can be used for the following applications: (a) for improving strength and modulus, as shown in Table 1.3 ; (b) for lowering resistance, as shown in Table 1. 4; (c) for CTE control, as shown in Table 1. 5; and (d) as strain -compliant conductors, as shown in Table 1.6.

Generic area	Military	Civilian	
Synthetic rubber	Tank tracks, aircraft	Automotive tires, aircraft	
	tires, ship structures	tires, ship structures,	
		sporting goods	
Thermoplastic structures	Aircraft, satellite	Auto body structures,	
	structures, ship	sporting goods, optical	
	structures, optical	components	
	components		
Thermoset structures	Aircraft, satellite	Auto body structures,	
	structure, ship	sporting goods, optical	
	structures, optical	components	
	components		
Carbon/epoxy structures	Airframes, especially Z-	Sporting goods,	
	direction enhancement	automotives, aerospace	
		structures	

Generic area	Military	Civilian	
Static dissipation	Satellite charge control,	Fuel hoses and tubing for	
	fuel lines, hoses, tubing,	automobiles, electronics	
	ordnance	assembly	
Electrostatic paint spray	Aircraft, ground vehicles,	Auto body components,	
	ships, other structures	aircraft, other vehicles	
Electromagnetic	Plane crash reduction,	High speed computing,	
interference mitigation	avionics, RF, secure	communications	
	facilities		
Lightning strike	Aircraft (especially	Aircraft, ground structures	
mitigation	composite airframe),		
	ships, radomes, ordnance		
	bunkers		
Compliant contacts	Solar cells, electronics,	Electronics	
	scanning electron		
	microscopy		

Table 1.4: CNFs for	Applications for	Lower Resistance.
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Table 1.5: CNFs for applications for CTE Control.

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Generic area	Military	Civilian	
Optics	Low cost injection	Low cost injection	
	moldable mirrors, laser	moldable optics	
Structures	Satellite structures	Auto body	
	(especially where stability	components(match	
	in orbit is important),	aluminum or steel) and	
	aircraft, ground vehicles,	for aerospace and ships	
	ships		
Electronics	MCT devices, electronic	Electronic boards,	
	boards, high power	computers, cooling	
	electronics	components	

Table 1.6: CNFs for applications for Strain-Compliant Conductors.

Generic area	Military	Civilian
Compliant Contacts	Solar cell contacts for	Electronic boards, solar
	spacecrafts, electronics	cell contacts, high
	boards	temperature lead free
		solder alternative
Thermal control		Temperature actuators,
devices		temperature
		measurement devices

Recent studies showed that the achievement of significant mechanical reinforcement in CNF composites requires high fiber loading and is somewhat depended on generating an appropriate interphase between the CNF and the matrix. Novel surface treatments under development have yielded good improvements in the tensile modulus and strength of CNF-reinforced polypropylene. Adding surface functional groups, particularly oxygen groups, has also demonstrated benefits for interphase development. Carboxyl and phenolic groups contributing to a total surface oxygen concentration in the range of 5 to 20 atom percent have been added to CNF and have been used to fabricate epoxy polymer matrix composites to provide improved flexural strength and modulus. The effect of similarly functionalized CNF in bismaleimide (BMI) polymer matrix composites also shows promise. Data for propylene, epoxy, and BMI/CNF- reinforced composites indicate the higher fiber volume loading will find a role in structural composite markets as price and availability improve.

1.3 Carbon Nanotube/Nanofibre-reinforced Polymer Composites

There are at least three general experimental methods to produce polymer nanocomposites: mixing in the liquid state, solution-mediated processes and in-situ polymerization techniques. The direct melt-blending approach is much more commercially attractive than the latter two methods, as both solvent processing and in-situ polymerization are less versatile and more environmentally contentious.

1.3.1 Solution processing of composites

Perhaps the most common method for preparing polymer– nanotube composites has been to mix the nanotubes and polymer in a suitable solvent before evaporating the solvent to form a composite film [65]. One of the benefits of this method is that agitation of the nanotubes powder in a solvent facilitates nanotube deaggregation and dispersion. Almost all solution-processing methods are variations on a general theme that can be summarized as: 1) dispersion of nanotubes in either a solvent or polymer solution by energetic agitation; 2) mixing of nanotubes and polymer in solution by energetic agitation; 3) controlled evaporation of solvent, leaving a composite film.

In general, agitation is provided by magnetic stirring, shear mixing, reflux, or, most commonly, ultrasonication. Sonication can be provided in two forms: mild sonication in a bath or high-power sonication using a tip or horn.

1.3.2 Melt processing

While solution processing is a valuable technique for both nanotube dispersion and composite formation, it is completely unsuitable for the many polymer types that are insoluble. Melt processing is a common alternative that is particularly useful for dealing with thermoplastic polymers [66]. This range of techniques makes use of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening. The advantages of this technique are its speed and simplicity, not to mention its compatibility with standard industrial techniques [67]. Melt processing can be used for production of both bulk polymer composites and composite fibers. In general, melt processing involves the melting of polymer pellets to form a viscous liquid. Any additives, such as carbon nanotubes, can be mixed into the melt by shear mixing. Bulk samples can then be fabricated by techniques such as compression molding, injection molding, or extrusion. However, it is important that processing conditions are optimized, not just for different nanotube types, but for the whole range of polymernanotube combinations. This is because nanotubes can affect melt properties such as viscosity, resulting in unexpected polymer degradation under conditions of high shear rates [68]. For many applications, fibers are more suitable than bulk materials. In addition, fiber-production techniques tend to be suited to the alignment of nanotubes within the fiber. A number of studies have focused on production of composite fibers by melt processing. Fiber processing is generally similar to melt processing, but usually involves a process such as extrusion to produce an elongated sample which can then be drawn into a fiber [69].

1.3.3 In situ Polymerization processing

Over the last five years, in-situ polymerization in the presence of carbon nanotubes has been intensively explored for the preparation of polymer-grafted nanotubes and processing of the corresponding polymer-composite materials. The main advantage of this method is that it enables grafting of polymer macromolecules onto the convex walls of carbon nanotubes. This then provides a better nanotube dispersion and formation of a strong interface between the nanotube and the polymer matrix. In addition, in-situ polymerization is a very convenient processing technique that allows the preparation of composites with high nanotube loading and provides very good miscibility with almost any polymer type. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which can not be processed by solution or melt processing.

Initially, in-situ radical polymerization was applied for the synthesis of poly (methyl methacrylate) (PMMA)–MWNT composites by Jia et al. [70]. In this work, in-situ polymerization was performed using the radical initiator 2,2' azobisisobutyronitrile (AIBN). The authors believed that p-bonds in carbon nanotubes were initiated by AIBN, and therefore nanotubes could participate in PMMA polymerization to form a strong interface between the MWNTs and the PMMA matrix. Since then, Velasco-Santos et al. [71] and Putz et al.[72] have also used AIBN as an initiator of in-situ radical polymerization to incorporate functionalized MWNTs and SWNTs into PMMA matrices.

In-situ polymerization was also very useful for the preparation of polyamide– carbon-nanotube composites. For instance, polyamide 6 (PA-6)–MWNT composites have been prepared by in-situ hydrolytic polymerization of e-caprolactam in the presence of pristine and carboxylated MWNTs [73]. E-Caprolactam monomer was found to form an electron-transfer complex with MWNTs, giving a homogeneous, polymerizable master solution, which facilitated the formation of composites with homogenously dispersed nanotubes. In another work, Gao et al. [74] reported a new and improved chemical-processing technology that allows the continuous spinning of SWNT– PA-6 fibers by the in-situ ring-opening polymerization of caprolactam in the presence of nanotubes. This process results in a new hybrid material with characteristics of both the fiber and the matrix, and with excellent compatibility between the SWNTs and nylon 6.

In-situ epoxidation has also been used for the preparation and processing of epoxy-polymer composites. For instance, carboxyl and fluorine-functionalized SWNTs have been integrated into epoxy polymers via the formation of covalent bonds by in-situ epoxy ring-opening esterification and amine-curing chemical reactions [75]. The same group has further developed a fully integrated nanotube– epoxy composite material with direct covalent bonding between the matrix and SWNTs. This uses functionalized SWNTs prepared via diamine reactions with alkylcarboxyl groups directly attached to the SWNT sidewalls [76]. In-situ polymerization reactions have also been applied for the preparation of other polymer–nanotube composites. For example, Kumar et al. have synthesized new ultra-strong poly (*p*-phenylene benzobisoxazole) (PBO) composites in the presence of SWNTs in poly (phosphoric acid) (PPA) by in-situ PBO polymerization [77]. After the polymerization, PBO/ SWNT composite fibers have been spun from the liquid-crystalline solutions using dry-jet spinning.

In general, in-situ polymerization can be used for the preparation of almost any polymer composite containing carbon nanotubes that can be non-covalently or covalently bound to the polymer matrix.

1.4 Relevant literature on carbon nanotube/carbon nanofiber composites

Since the documented discovery of carbon nanotubes (CNT) in 1991 by Iijima [30] and the realization of their unique physical properties, including mechanical, thermal, and electrical, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of these properties. The CNT can be thought of as the ultimate carbon fiber with break strengths reported as high as 200 GPa, and elastic moduli in the 1TPa range [78]. This, coupled with approximately 500 times more surface area per gram (based on equivalent volume fraction of typical carbon fiber) and aspect ratios of around 103, has spurred a great deal of interest in using CNT as a reinforcing phase for polymer matrices. Increasing attention is being focused on the CNT surface, namely the interface between the CNT and surrounding polymer matrix. From micromechanics, it is through shear stress build-up at this interface that stress is transferred from the matrix to the CNT. Numerous researchers have attributed lower-than-predicted CNT-polymer composite properties to a lack of interfacial bonding [79]. If one considers the surface of a CNT, essentially an exposed graphene sheet, it is not surprising that interfacial interaction is a concern. It is the weak inter-planar interaction of graphite that provides its solid lubricant quality, and resistance to matrix adhesion. This is exaggerated by the chemically inert nature of graphene structures. Significant toughening of polymer matrices through the incorporation of CNT has been reported [80]. A loading of 1 wt% MWNT, randomly distributed in an ultra-high molecular weight polyethylene was reported to increase the strain energy density by 150% and increase the ductility by 140%. Secondary crystallites, which nucleated from the MWNT, were attributed a higher mobility and

hence the increase in strain energy [81]. A similar effect was found in aligned MWNT/polyacrylonitrile. Fibers containing 1.8 vol% MWNT with an approximately 80% increase in energy to yield and energy to break [79]. A process of spinning 60 wt% SWNT/polyvinyl alcohol fibers with pre-drawn energy absorbing capacity nearly 3.5 times spider silk (165 J/g) was reported. Slippage between SWNT bundles was suggested as the mechanism responsible for the enhancement in the toughness. The addition of 1 wt% MWNT to isotactic polypropylene (iPP) was shown to affect crystal nucleation from differential scanning calorimetry and X-ray diffraction measurements [82]. Compared with neat iPP, there was an increase in crystallization rate for the composite material with evidence of fibrillar crystal growth rather than spherulite growth. These modifications in the morphology of a polymer matrix combined with the energy required for CNT debonding and pull-out suggest CNT may augment the energy absorption or toughness characteristics of the composite. A twofold increase in the tension-tension fatigue strength for an aligned SWNT/epoxy composite was found in comparison to typical carbon fiber/epoxy composites. Embedded CNT [83] may effectively prolong the formation of and/or bridge micro cracking/ crazing that can propagate and lead to fatigue failure. CNT reinforced polymer composites are seen as a potentially fruitful area for new, tougher or fatigue resistant materials. Further investigations into the toughness and fatigue properties of these composites are needed to understand the reinforcing mechanism at work.

The influence of carbon nanotube (CNT) contents on electrical and rheologicalm properties of CNT-reinforced polypropylene (PP) composites was studied. As a result, the volume resistivity of the composites was decreased with [84] increasing the CNT content and the electrical percolation threshold was formed between 1 and 2 wt% CNT, which were caused by the formation of conductive chains in the composites (Figure 1.14). And the viscosity of the composites was increased with the addition of CNT, which was accompanied by an increase in elastic melt properties (Figure 1.15). This could be explained by the higher aspect ratio of the CNT. And the composites containing more than 2 wt% CNT exhibited non-Newtonian curves at low frequency.



Figure 1.14: Electrical Volume resistivity of MWNTs/PP composites as a function of carbon nanotube content [84]



Figure 1.15: Viscosity of MWNT/ PP composites measured at 170 °C [84]

Polyimide/carbon nanotube (PI/CNT) nanocomposites [85] with different proportions of CNT were fabricated by in situ process. The bending strength and microhardness of the PI/CNT nanocomposites were measured. The friction and wear behavior of the nanocomposites was evaluated on an M-2000 friction and wear tester. The results showed that the bending strength and microhardness of the PI/CNT nanocomposites increased with increasing CNT content and reached stable values at a certain content of CNT. CNT could effectively enhance the friction-reduction and antiwear capacity

of the nanocomposite because it increased the load capacity and mechanical strength of the CNT/PI. The variables such as applied load and sliding speed had a significant influence on friction and wear performance.

Composites of high molecular weight polyaniline (PANI) [86] and various weight percentages of single-walled carbon nanotubes (SWNT) were fabricated using solution processing. Electrical characteristics of metal–semiconductor (MS) devices fabricated from the PANI/SWNT composites were studied. Current– voltage (I–V) characteristics of these devices indicate a significant increase in current with an increase in carbon nanotube concentration in the composite.

Emilie et al. [87] found that the tensile modulus and yield strength increased with the addition of SWNT loading in a polyimide SWNT composite. The increase was much higher than that observed for film samples (which were cast without preferred SWCNT orientation), but much less than what was expected from an oriented discontinuous fiber reinforced polymer composite. This low level of improvement was likely due to inefficient and incomplete dispersion. With the aid of improved dispersion, significant reinforcing effects of the aligned fibers on the mechanical properties are anticipated. Improvements in mechanical reinforcement may also be realized with a matrix designed to promote uniform dispersion by capitalizing on physical interaction with SWCNT inclusions to improve the nanotube/matrix interface so as to maximize load transfer across the interface.

In a study by Pötschke et al. a masterbatch of PC– MWNT [88] (15 wt%) was diluted with different amounts of PC in a small scale conical twin screw extruder (DACA Micro Compounder) to obtain different compositions of MWNT. In this system, electrical measurements indicated percolation of MWNT between 1.0 and 1.5 wt %(Figure 1.16).



Figure 1.16: Electrical conductivity vs. MWNT contents for PC-MWNT composites [84]

A novel polyacrylamide–carbon nanotubes [89] (PAM–CNT) copolymer has been prepared by ultraviolet radiation initiated polymerization. The PAM–CNT copolymer was characterized by the instruments of Fourier transform infrared spectroscopy, UV–visible absorbance spectra, fluorescence spectra and transmission electron microscope. The morphology and micro-tribological properties of PAM– CNT thin films on mica were investigated by atomic force microscopy/friction force microscopy (AFM/FFM). The friction of the films was stable with the change of applied load and the friction coefficient decreased significantly as the CNT addition. The results show that the rigid rod-like CNT in polymer would enhance load-bearing and anti-wear properties of the thin films.

SMA encapsulated SWNT [90] are melt mixed with PA12 matrix in a conical twin-screw extruder. The process of encapsulation by SMA copolymer leads to a finer dispersion of SWNT and enhanced interfacial adhesion between PA12 and SMA modified SWNT. This leads to enhanced mechanical properties, which is manifested by tensile and dynamic mechanical properties. Formation of network structure (Figure 1.17) has been identified in unmodified SWNT composites by electrical conductivity measurements and morphological investigations by scanning electron microscopy.



Figure 1.17: SEM of composite PA12+ 6 wt% SWNT after tensile testing, area near fracture surface [90]

Zou et al. showed that for the dispersion of MWNT in a polymer [91] matrix by screw extruder, there is a critical MWNT concentration of 1.0 wt% where a fine network of filler is formed; therefore the composites possess improved mechanical properties.

Shuying et al. found from DSC analysis that the introduction of SWNT [92] increases the glass transition temperature of the composites and low concentration of SWNT act as nucleating agents to the crystallization of ABS as small melting peaks were observed at 0.5 wt% and 1 wt% of SWNT.

Nanocomposites consisting of double-wall carbon nanotubes [93] (DWCNT) and an epoxy matrix were produced by a standard calandering technique. A very good dispersion of both DWCNT and carbon black (CB) in an epoxy resin could be observed. The investigation of the (fracture-) mechanical properties resulted in an increase of strength, Young's modulus and strain to failure at a nanotube content of only 0.1 wt%. The correlation of the experimentally obtained Young's moduli showed a good agreement with a modified Halpin-Tsai theory. Poly (methyl methacrylate) (PMMA) nanocomposites have been processed [94] by melt blending. The amount of nanofibers used was 5 and 10 wt%, respectively. The PMMA/CNF composites were processed into 4 mm diameter rods and 60 mm diameter fibers using small-scale melt spinning equipment. At 5 wt% CNF, composite rods as well as fibers show over 50% improvement in axial tensile modulus as compared to the control PMMA rod and fibers, respectively. The reinforcement efficiency decreased at 10 wt% CNF. The PMMA/CNF nanocomposites fibers also show enhanced thermal stability,

significantly reduced shrinkage and enhanced modulus retention with temperature, as well as improved compressive strength.

Significant improvements in the Mechanical properties [95] of the epoxy/SWNT nanocomposites were illustrated by a 50.8% increase in the storage modulus by Liao et al. (Figure 1.18). The significant improvements of nanotube dispersion and mechanical performance were attributed to the combined use of tip sonication and acetone as dispersion aids during sample processing.



Figure 1.18: Storage modulus of the nanocomposites [95]

1.4.1 Mechanical Properties of Polymer-Nanotube Composites

Owing to their unique mechanical properties, carbon nanotubes are considered to be ideal candidates for polymer reinforcement. However, a large amount of work must be done in order to realize their full potential. The exemplary results of the mechanical properties of various nanotube–polymer composites prepared by different techniques are summarized in Table 1.7.

CNT type	Polymer	r Preparation method	E _p [GPa]	σ _{Tp} [MPa]	E _c [GPa]	σ _{Tc} [MPa]	CNT content	Ref.
MWNT	PS	Solution processing	1.19	12.8	1.69	16	1 wt%	[96]
MWNT	PS	Solution processing	1.53	19.5	3.4	30.6	5 wt%	[97]
MWNT	HDPE	Solution processing	0.98	20	1.35	25	1 wt%	[98]
MWNT	PVA	Solution processing	1.9	81	7.4	348	0.6 vol%	[99]
MWNT	PMMA	melt processed	2.7	64	3.7	80	10 wt%	[100]
MWNT	PA 6	melt processed	2.6		4.2	_	12 wt%	[101]
MWNT	Nylon	melt processed	0.4	28	1.24	58	2 wt%	[102]
MWNT	PA 12	melt processed fibers	0.8		1.6		10 wt%	[103]
MWNT	Nylon 610	in-situ polymerization	0.9	35.9	2.4	51.4	1.5 wt%	[104]
SWNT	PVA	solution processing	2.4	74	4.3	107	0.8 wt%	[105]
SWNT	РР	melt processed	0.85	30.8	0.93	33.7	0.75 wt%	[106]
SWNT	PP N	melt Melt processed fibers	6.3	709	9.8	1032	1 wt%	[107]
SWNT	PA6	in-situ polymerization	0.44	40.9	1.2	75.1	1.5 wt%	5 [108]
SWNT	РВО	in-situ Polymerization	138	2600	167	4200	10 wt%	. [77]

 Table 1.7: Mechanical properties of various CNT/polymer composites.

1.4.2 Influence of Functionalization on Polymer/ CNT composites

The effect of functionalization to achieve bonding between the matrix and the nanotubes was shown by Frankland et al. [109] via molecular dynamics simulation. They have shown that an improvement in mechanical properties can already be achieved if less than 1% of the carbon atoms of the carbon nanotubes form reactive bridges to the matrix. A breakthrough in the development of carbon nanotube-reinforced epoxies could be made via chemical functionalization of CNTs with multifunctional amines. The improvement of the bonding to the matrix as well as a better dispersion of the CNTs could be observed [75, 76]. A schematic representation of functionalization process is shown in Figure 1.19 [110].



Figure 1.19: Functionalization process for CNTs showing the step from oxidation to the composite manufacturing

In the first step, an oxidative treatment of the nanotubes was used to develop carboxylic groups. This leads to an opening of the CNT cap (Figure 1.20), which would enable a direct bonding of the tube ends to the matrix via the carboxylic groups. In the second step, the carboxylic groups would react with multifunctional amines and form bonds (either ionic or under the given conditions, covalent) to these amines via an acid-base reaction. In the third step, with the addition of the epoxy resin, the free amino functions on the surface of CNTs will react with the epoxy molecules forming equivalent bonds, which lead to an improved nanotube matrix bonding.



Figure 1.20: Opening of the caps of oxidized arc grown MWNTs

Shaffer and coworkers have demonstrated that acid treatment enables stable aqueous solution of catalytically produced MWNTs to be prepared [111]. Solution based methods have also been used to produce nanotube/polystyrene composites. Both SWNTs and MWNTs were solubilized by functionalizing with a polystyrene copolymer [112]. This was achieved by first acid treating the tubes and then carrying out esterification of the surface bound carboxylic acid. The polymer modified carbon nanotubes were shown to be soluble in common organic solvent. To prepare composites, polystyrene was dissolved in the nanotube solution and nanotube polystyrene thin films prepared using wet casting.

Another common method to assimilate the polarity of CNT and matrix is the use of surfactants. The advantage of this procedure is the physical adhesion, which does not reduce the structural quality of CNTs, whereas a covalent integration of functional groups is always related to structural changes of graphitic layers. Similar to surfactants, conjugated polymers (e.g. PmPV) can also physically bond to CNTs and be utilized to improve the compatibility of CNTs and matrix [113]. Influence of a non-ionic surfactant (Tertigol NP 7) in the nanocomposite processing has been analysed by Cui et al. [114]. These results demonstrated that the glass transition

temperature is increasing with the nanotube content, and on the other hand, the percolation threshold is found for a rather high critical volumic concentration.

1.4.3 Potential applications of CNTs and their composites

Carbon nanotubes are being wildly considered for the use as energy storage materials (fuel cells), advanced aerospace composites, co-axial cable, field emitting devices, transistors, EMI shielding in electronic devices, nanoprobes and sensors, composite materials, to name a few. The potential applications of carbon nanotubes and their composites are listed below:

- Field emitters: Carbon nanotubes have been shown to have excellent emission characteristics: emission has been observed at fields lower than 1 V/µm, and high current densities of over 1 A/cm² have been obtained [115].
- Energy storage: The advantages of considering CNTs to store energy are their cylindrical and hollow geometry, nanometer scale diameter, and perfect surface specificity. Energy carriers such as hydrogen can be stored in an adsorbed form on CNTs, which are capable of absorbing and releasing large quantities of this element easily and reliably [116].
- Sensors: Strong dependence of the properties of CNTs on surface modification, mechanical deformation, doping, coating, etc. make them a very attractive material for chemical, biological, and physical sensors. Small changes in the environment of the CNT can cause drastic changes to its electrical properties [117].
- High strength composites: The outstanding properties of CNTs have enabled the development of composite systems with improved mechanical performance [118, 119].
- Conducting polymer composites: A high aspect ratio of CNTs allows for lower percolation than other fillers [120].

- Heat dissipation coatings: Extraordinary thermal properties make CNTs promising filler for heat dissipating materials [121, 122].
- EMI shielding materials: CNTs act as an absorber/scatterer of radar and microwave radiation.

1.5 Liquid Crystalline Polymer

A liquid crystal, or mesophase, is a state of matter between the liquid and crystal states. Liquid crystals are ordered like crystals but flow like liquids. The responsible anisotropic entities are known as mesogens. Liquid crystals are either thermotropic, which means that they are liquid crystalline in the temperature range between melt and solid states, or lyotropic, which means that they form liquid crystals in concentrated solutions. The temperature at which phase transition from liquid crystal to melt state occurs is called the isotropization (T_i) or clearing temperature (T_c).

Liquid crystals are classified according to the shape of the mesogens and the structure and appearance of the mesophases. Mesogens are either rod-like or disk-like and they are divided into three main classes: nematic, smectic, and cholesteric. The main classes are further divided into subgroups.

The mesogenic units in a liquid crystalline polymer may be in the main chain or the side chain of the polymer. Polymeric liquid crystals are also classified according to their chemical structure and the conditions under which the LC state is formed. Main-chain LCPs may be either fully aromatic or built up of rigid mesogens and flexible spacers. In side-chain LCPs, the rigid mesogenic units usually are present in pendant side chains (Figure 1.21) [123].



Figure 1.21: Model structure of smectic and nematic rigid and semi-flexible main chain LCPs and nematic side- chain LCPs where mesogens occurs in pendant side chains

The main-chain LCPs are generally synthesized by polycondensation methods. Nematic structures are easy to produce since only large mesogens are required. Short mesogens connected by short flexible spacers are also possible. Smectic structures are usually obtained if rigid rod-like mesogens are present in periodic sequences or if mesogens of equal length are connected by large flexible spacers.

Radical polymerization of vinyl monomers is the most frequently used method for the synthesis of side-chain LCPs. The polymerization of suitable monomers and the reactions between mesogenic oligomers and flexible chains have also been utilized in the synthesis of side-chain LCPs [124].

Common liquid crystalline polymers are elongated cylinder-like molecules. Their anisometry can be determined by the aspect ratio x = L/D, where L is the length and D the diameter of the molecule. The larger the aspect ratio, the greater is the tendency of the molecule to maintain a preferred orientation at temperatures higher than the melting point and, therefore, the wider is the temperature range of stability of the mesophase. Molecular rigidity is another important feature of LCPs. The molecules should not have a bent conformation [125].

Most commercial LCPs are copolyesters, copolyamides, or polyester-amides. LCP structures range from wholly aromatic to partially aliphatic and they have widely varying melting points. There are currently two major families of wholly aromatic thermotropic LCPs on the market: Vectra from Celanese and Xydar from Amoco Chemical Company [126]. One of the most common commercially available lyotropic LCPs is Kevlar which contains terephthaloyl and para-phenylene diamide parts (Figure 1. 22) [127].



Figure 1.22: Structures of commercial available LCPs: Vectra, Xydar, Kevlar

In recent years, many area of research relating to the development of new and improved commercial products made from liquid crystal polymers (LCPs) and LCP blends have been engineered. The use of liquid crystalline polymers in blends with commercial thermoplastics for the modification of rheological and mechanical properties is a promising way for the development of a new generation of composite polymeric materials. It is because of two reasons. First, the LCPs have very low melt viscosity allowing good flow properties, hence the addition of a small amount of LCPs to thermoplastics can result in a considerable reduction in the blend melt viscosity thereby improving the process-ability of engineering plastics. Second, the LCPs have a more rigid molecular structure and they generally exhibit a high degree of order in the melt under the conditions of shear and extension during processing. Therefore, the LCP phase can deform into fibril domains and these fibrils than act as the reinforcing element in the in situ composite as a result of the inherent high strength and stiffness of the LCPs. It is generally considered that the viscosity of the additive components must be considerably lower then the host matrix for fibril formation to occur [128]. This condition is valid for most of the LCP polymer blends so the formation of fibrils in-situ is regarded as straightforward. The in-situ reinforcement of conventional thermoplastics, using minor LCP component additions

often results in highly elongated fibrous structure. These not only improve blend properties, but also reduce equipment wear and fiber breakage, as experienced with conventional short fiber composites. Reinforcement through the addition of LCPs to thermoplastics has been investigated over the last few years with encouraging results.

Current research on TLCP/thermoplastic blends is, indeed, heavily directed toward the addition of a compatibilizer (or coupler) as a means of improving the interaction between blend components. Typically, these compatibilizers are functional/reactive polymers or monomers (reactive blending), block or graft copolymers, or polymers with liquid crystalline properties. Most are low molecular weight compounds or oligomers possessing low melting temperature, but also some monomeric multi-functional compounds are highly effective couplers in polymer blends [129]. Compatibilization may influence the final blend properties in complex ways. One effect of compatibilization is to reduce the interfacial tension between the blend components, causing an emulsifying effect and leading to an extremely fine dispersion of one phase in the other. Another major effect is the increased adhesion at phase boundaries, which gives improved stress transfer. Chiou et al. [130] recently studied in situ compatibilized PP/LCP (Vectra A900) blends, using ethylene–glycidyl methacrylate (EGMA) copolymer as the reactive compatibilizer. The polyethylene segments of EGMA are miscible with PP, while the epoxy functional groups can react with the carboxylic acid or hydroxyl end-groups of the TLCP to form an EGMA-g-LCP copolymer. The in situ formed EGMA-g-LCP copolymer resides along the interface and reduces the interfacial tension between the base polymers.

Recently, Li et al. and Xie et al. have studied the PBT-LCP and PBT-PA-66-LCP blends, and observed that the melting temperature of the PBT and PA-6, 6 phases tends to decrease with increasing LCP addition and mechanical properties of this blend were improved by LCP presence [131,132]. Chang and coworkers used tetra-functional epoxy and bisphenol-A type solid-state epoxy resin as a reactive compatibilizer in PBT-PA6 and PBT-PA6, 6 blends, respectively. From the Changs works [133], mechanical properties and processability of polyamide and polyester blends were improved by the reactive compitibilizer, which could caused the reaction between the components. The compatibilization in in-situ composites can be achieved by incorporation of physical and/or chemical interactions between the two phases. These techniques for compatibilization in in-situ composites can be classified into three types: (1) the addition of a third component as a compatibilizer; (2) transesterification between matrix and TLCP; (3) the addition of a third polymer into binary polymer blends. The differences between the first and third types are that in the former, usually the third component is a pre-made compound (or polymer) and its fraction in compatibilized blends is often less than 10 wt%. While the third polymer used in ternary blends is an as-received commercial product and its content in ternary blends can be changed in a wide range for tailoring the properties of blends [134].

It is expected that the compatibilizer concentrates at the interfacial region and reduces the interfacial tension like an emulsifier. Adhesion may be enhanced through interpenetration and entanglements. This approach is also successfully utilized for the compatibilization in in-situ composites. Generally, the third components include functionalized polymers, ionomer and graft or block copolymer consisting of segments whose chemical structure and solubility parameters are similar to those of the polymers being blended. A great number of papers focused on the compatibilization of functionalized polymers for in situ composites. A fiber or filler can act as a nucleating agent for crystallization, and can reduce the mobility of the polymer chains close to it due to interaction with the surface of the fiber. The presence of either micro or nanofiller can also lead to compatibilization in polymer blends due to an increase either in viscosity or through their presence at the interface.

1.6 Main objectives of the thesis work

The main objectives of the present work are as follows:

- 1. Comprehensive characterization and successful development of CNF/CNT/LCP reinforced composites
- 2. Improvement in the Mechanical, thermal and electrical properties of polymers
- 3. Compare the properties of Polyetherimide (PEI) composites reinforced with as-received and functionalized CNFs.
- 4. Development of carbon nanofiber/syndiotactic polystyrene composites in the presence and absence of LCPs.
- Preparation and properties of Polyetherimide (PEI)/ multiwalled carbon nanotubes (MWNTs) composites in presence of polyacrylic elastomers (ACM).

- Study on mechanical, thermal, morphological and electrical behaviour of synthesized Poly (methyl methacrylate)/MWNT composites as affected by manufacturing process.
- 7. Development of SiC coated MWNTs reinforced PES nanocomposites with improved dispersion.
- 8. In-situ Reinforcement of Poly (butylene terephthalate) and Butyl rubber by liquid crystalline polymer (LCP).
- Self-reinforcing composites based on ethylene acrylic elastomers (Vamac B124/ liquid crystalline polymer (LCP)

1.7 Specific Objectives

The specific objective of the present work deals with the effective use of CNT/CNF as a reinforcing material for polymers, so that the concerns about the mechanical, thermal and electrical properties of polymers can be solved. Keeping this objective in mind, surface modifications of CNT/CNF (e.g. acid modification) and various fabrication processes were use to improve the dispersion and adhesion at interface between polymer and nanofiller. Also the use of liquid crystalline polymers in blends with commercial elastomers and thermoplastics for the modification of mechanical, thermal, and dynamic properties because LCP phase can deform into fibril domains and these fibrils than act as the reinforcing element in the in situ composite as a result of the inherent high strength and stiffness of the LCPs.

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