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Polymer/Carbon Nanotube Nanocomposites
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1. Introduction
Polymer is a versatile material having many unique properties like low density, reasonable strength, flexibility, easy processibility, etc. However, the mechanical properties of these materials are inadequate for many engineering applications. Hence, there is a continuous search towards new polymeric materials with improved properties. Initially, blending of different class of polymer was used to fabricate new materials with unique properties. However, blending lead to only marginal improvement in physical properties which were still inadequate for engineering applications. So to improve the strength and stiffness of polymer materials different kinds of organic and inorganic fillers were used. It was observed that strength and stiffness of long fibers reinforced thermosetting polymer is comparable to metals at a fraction of their weight. As a result of which these material were used in aircraft and in sport equipment. However, processing of these materials is very difficult; therefore small fiber or particle reinforced composites were developed. The common particle fillers used were silica, carbon black, metal particles etc. But significantly high filler loading was required to achieve desired mechanical property, which thus increased cost and made processibility difficult. So to achieve high mechanical properties at lower filler loading, nanofillers were used. The nanofiller reinforced polymer matrix is known as polymer nanocomposite.

Polymer nanocomposites are a new class of composite materials, which is receiving significant attention both in academia and industry. As nano fillers are only a few nanometers (~10,000 times finer than a human hair) in dimension, it offers ultra-large interfacial area per volume between the nano-element and polymer matrix. As a result, the nanofiller reinforced composites exhibit enhanced toughness without sacrificing stiffness or optical clarity. It also possesses greater thermal and oxidative stability, better barrier, mechanical properties as well as unique properties like self-extinguishing behavior. Compared to different range of nanofillers, carbon nanotubes (CNTs) have emerged as the most promising nanofiller for polymer composites due to their remarkable mechanical and electrical properties (Ishikawa, 2001; Kracke & Damaschke, 2000). Currently, one of the most intriguing applications of CNTs is the CNT/polymer nanocomposites (Cai, 2000; Fiege, 1999; Gomes, 1999; Hersam, 1998; Ruiz, 1998). For the last two decades, a lot of research work has been done on evaluating the potential of CNTs as filler for polymer nanocomposites. In the present chapter, we will briefly discuss on CNTs and their properties, different fabrication methods of polymer nanocomposites and their mechanical, electrical and thermal properties.
Carbon Nanotubes – Polymer Nanocomposites

2. Carbon nanotubes (CNTs)

CNTs are long cylinders of covalently bonded carbon atoms which possess extraordinary electronic and mechanical properties. There are two basic types of CNTs: single-wall carbon nanotubes (SWCNTs) which are the fundamental cylindrical structure and multi-wall carbon nanotubes (MWCNTs) which are made of coaxial cylinders (Fig. 1), having interlayer spacing close to that of the interlayer distance in graphite (0.34 nm). These cylindrical structures are only few nanometre in diameter, but the cylinder can be tens of microns long, with most end capped with half of a fullerene molecule. It was first discovered by M. Endo in 1978, as part of his Ph.D. work at the University of Orleans in France, but real interest in CNTs started when Iijima (1991) first reported it in 1991. The field thrives after that and the first polymer composites using CNT as filler was reported by Ajayan et al (1994).

![Fig. 1. Schematic diagrams of single-wall carbon nanotube (SWCNT) and multi-wall carbon nanotube (MWCNT)](image)

2.1 Synthesis of carbon nanotubes

CNTs can be prepared using three methods which includes arc discharge, laser ablation and chemical vapor deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. High quality and large quantities of nanotubes can be synthesized by these methods.

i. Arc discharge

The carbon arc discharge method, initially used for producing C_{60} fullerenes, is the most common and perhaps easiest way to produce CNTs. But this technique produces graphitic impurities such as carbon soot containing amorphous carbon, anions and fullerenes. In this method an inert gas atmosphere is created in the reaction vessel by passing an inert gas at controlled pressure. Two graphitic rods constitute the electrodes, between which a potential difference is applied. As the rods are brought closer, a discharge occurs, resulting in formation of plasma (Fig. 2). The deposit, which contains CNTs, forms on the large negative electrode (cathode) while the smaller positive electrode (anode) is consumed. When a metal catalyst is used along with graphite, a hole is drilled in the carbon anode and it is filled with a mixture of metal and graphite powder. In this case, most nanotubes are found in soot deposited on the arc chamber wall.

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ii. Laser ablation
Laser ablation uses an intense laser pulse to vaporize a carbon target, which also contains small amount of metals such as nickel and cobalt and is placed in a tube furnace at 1200°C. As the target is ablated, inert gas is passed through the chamber carrying the grown nanotubes on a cold finger for collection (Fig. 3). This method mainly produces SWCNT in the form of ropes.

iii. Chemical vapor deposition
In this process a mixture of hydrocarbon, metal catalyst along with inert gas is introduced into the reaction chamber (Fig. 4a). During the reaction, nanotubes form on the substrate by the decomposition of hydrocarbon at temperatures 700–900°C and atmospheric pressure. The diameter of nanotubes that are to be grown are related to the size of the metal particles. This mechanism of CNT growth is still being studied. In Figure 4b two growth modes can be seen. The first ‘tip growth mode’ where, the catalyst particles can stay at the tips of the growing nanotube during the growth process and second ‘base growth mode’ where, catalyst particles remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate (Fig. 4b). This technique offers more control over the length and structure of the produced nanotubes compared to arc and laser methods. This process can also be scaled up to produce industrial quantities of CNTs. A number of reviews (Awasthi, 2005; Monthioux, 2002; Thostenson, 2001) are available which briefly discusses on these production techniques.

2.2 Properties of carbon nanotubes
The determination of physical properties of CNTs is relatively more difficult compared to other fillers due to very small size of CNTs. However a number of experimental studies
have been carried out on the direct determination of mechanical properties of individual CNTs (Yu et al., 2000a). The stiffness of CNTs was first determined by observing the amplitude of thermal vibrations in transmission electron microscopy (TEM) and the average stiffness values of 1.8 TPa and 1.25 TPa (Yu et al., 2000b) were reported for MWCNTs and SWCNTs, respectively. The in-situ tensile tests on individual MWCNTs and ropes of SWCNTs was performed by carrying out a stress-strain measurement using a “nanostressing stage” operating inside a scanning electron microscope (SEM). Experimental results showed that strength of outer shell of MWCNT ranged from 11 to 63 GPa at fracture strains of up to 12% and modulus values ranged from 270 to 950 GPa (Yu et al., 2000b). It was observed that strength of nanotubes depends on the number of defects, as well as interlayer interactions in MWCNTs and bundles of SWCNTs. Structural defects as well as bends or twists significantly affect mechanical strength of CNTs (Kane & Mele, 1997). Theoretical studies of the electronic properties of SWCNTs, suggest that nanotube shells can be either metallic or semiconducting, depend critically on helicity (Fig. 5) (Saito, 1992; Hamada, 1992; Mintmire, 1992). Tans et al. (1997) first, experimentally showed that there are indeed metallic and semiconducting SWCNTs, which verified the theoretical predictions. It was observed that due to poor control on synthesis, on average, approximately 1/3 of SWCNTs formed are metallic and 2/3 semiconductors (Odom et al., 1998). The room temperature conductivity of metallic SWCNT was found to be $10^5$ to $10^6$ S/m and for semiconducting tubes about $10^5$ S/m. The conductivity of SWCNT is close to the in-plane conductivity of graphite [$10^6$ S/m (Charlier & Issi 1996)]. Conductivities of individual MWCNTs have been reported in the range of $10^7$ to $10^8$ S/m (Ebbesen et al., 1996),
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depending on the helicities of the outermost shells or the presence of defects (Dai et al., 1996). The axial thermal conductivity of individual, perfect CNTs is reported to be as high as $3300 \text{ W/m/K}$ (Kim et al., 2001).

Fig. 5. A sheet of graphene rolled to show formation of different types of single walled carbon nanotube

3. Functionalization of carbon nanotubes

For a nanocomposite, a good dispersion of the filler within the host matrix is very important. At the same time it is also important to stabilize the dispersion to prevent re-aggregation of the filler. These tasks are particularly very challenging in case of nanofillers since the extremely large surface area lead to strong tendency to form agglomerates. CNTs are very well known to form aggregates during compounding and hence various techniques have been used to overcome this problem like use of sonication or mechanical mixing during the fabrication of nanocomposite which generally help in dispersing CNTs. But the most effective way to resolve this problem is surface functionalization of CNTs. Surface functionalization helps in stabilizing the dispersion, since it can prevent re-aggregation of nanotubes and also leads to coupling of CNT with polymeric matrix. Coupling between CNT and polymer matrix is also very important for efficient transfer of external stress to nanotube. In recent years, various methods have been developed for surface functionalization of CNT which includes functionalization of defect groups, covalent functionalization of sidewalls, non-covalent functionalization, e.g., formation of supramolecular adducts with surfactants or polymers (Fig. 6). Although surface functionalization leads to significant improvement in CNT dispersion and stress transfer but this method also causes deterioration of intrinsic properties of CNTs. Covalent functionalization often lead to tube fragmentation and the non-covalent functionalization results in poor exfoliation. Alteration of CNT properties lead to poor reinforcement and conductivity. Hence, it becomes obvious that dispersion and stabilization are not simple issues and compromises have to be made depending on the applications (Hirsch, 2002).

3.1 Covalent functionalization of sidewall

Local strain in CNTs, which arises from either pyramidalization or misalignment of $\pi$-orbitals of the $sp^2$-hybridized carbon atoms, makes nanotubes more reactive than a flat graphene sheet, thereby paving the path to covalently attach chemical species to nanotubes (Banerjee et al., 2005). Covalent functionalization of CNTs can be achieved by introducing
some functional groups on defect sites of CNTs (Fig. 7) by using oxidizing agents such as strong acids, which results in the formation of carboxylic or hydroxyl groups (-COOH, -OH) on the surface of nanotubes (Coleman, 2000, 2006, Singh, 2009). This type of functionalization is known as defect group functionalization. Such functionalization improves nanotube dispersion in solvents and polymers and imparts high stability in polar solvents. For example, Feng et al. (2008) reported that oxidation of MWCNTs with HNO$_3$/H$_2$O$_2$ and HNO$_3$/H$_2$SO$_4$ introduces some carboxylic groups on CNTs, which enhanced their stability in water at room temperature for more than 100 days. As a result, the water-stable nanotubes can easily be embedded in water soluble polymers such as poly(vinyl alcohol) (PVA), giving CNT/polymer nanocomposites with homogeneous dispersion of CNTs (Zhao et al., 2008). Oxidized nanotubes also show excellent stability in other solvents such as caprolactam, which is used in the production of polyamide (PA6) (Gao et al., 2005). Studies on acid functionalization of CNTs have shown significant improvement in interfacial bonding between CNTs and polymer matrices, which have been shown to give a stronger nanotube–polymer interaction, leading to improved Young’s modulus and mechanical strength (Gao, 2006; Sui, 2008; Yuen, 2008a, 2008b, 2008c; Luo, 2008; Rasheed, 2006a, 2006b; Sahoo, 2006; Wong, 2007).

Polymer molecules can also be grafted on the surface of CNTs in presence of these active functional groups (-COOH, -NH$_2$, -OH). Grafting of polymer chain on CNTs can be carried out either by ‘grafting from’ or ‘grafting to’ technique (Coleman, 2000, 2006; Liu, 2005). The grafting-from approach is based on the initial immobilization of initiators onto the nanotube surface, followed by in-situ polymerization with the formation of polymer molecules attached to CNTs. The advantage of this approach is that polymer-functionalized nanotubes with high grafting density can be prepared. However, this process needs a strict control of the amounts of initiator and substrate. The grafting from technique is widely used for the preparation of poly(methyl methacrylate) (PMMA) and related polymer grafted nanotubes. For example, Qin et al. (2004) reported the preparation of poly(n-butyl methacrylate) grafted SWCNTs by attaching n-butyl methacrylate (nBMA) to the ends and sidewalls of SWCNT via atom transfer radical polymerization (ATRP) using methyl 2-bromopropionate as the
Fig. 7. Covalent functionalization of carbon nanotubes on defects sites

free radical initiator. A similar approach was reported by Hwang et al. (2004) for the synthesis of PMMA grafted MWCNTs by potassium persulfate initiated emulsion polymerization reactions and use of the grafted nanotubes as a reinforcement for commercial PMMA by solution casting.

On the other hand, in case of grafting-to approach, attachment of already functionalized polymer molecules to functionalized nanotube surface takes place via appropriate chemical reactions. One of the first examples of ‘grafting to’ approach was published by Fu et al (2001). In this work carboxylic acid groups on the nanotube surface were converted to acyl chlorides by refluxing the samples with thionyl chloride. Then the acyl chloride functionalized CNTs were reacted with hydroxyl groups of dendritic poly(ethylene glycol) (PEG) polymers via the esterification reactions. The grafting-to method was applied for the preparation of epoxy-polyamidoamine–SWCNT composites (Sun et al., 2008). An advantage of this method is that, commercially available polymers containing reactive functional groups can be utilized.

3.2 Non-covalent functionalization with surfactant or polymer

The non-covalent functionalization has unique ability of preserving the intrinsic properties of nanotube which is very important for its electrical and thermal conductivity. Various studies have shown that surfactant or wrapping with polymer can lead to individualization of nanotube in aqueous or organic solvent. (Moore, 2003; Matarredona, 2003; Vigolo, 2000; Regev, 2004; Grossiord, 2005; Curran, 1998; Coleman, 2000; O’Connell, 2001). Moore et al. studied various anionic, cationic and non-ionic surfactants and polymers to determine their ability to disperse nanotube in aqueous media. They reported that size of the hydrophilic group of surfactant or polymer play a key role in nanotube dispersion. It was also observed that surfactant alone is not capable of suspending nanotubes effectively and vigorous sonication is required (Matarredona et al., 2003). Polymers such as poly(phenylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) can be used to wrap around nanotube in organic solvents such as CHCl₃ (Coleman et al., 2000). Polar side chain containing polymer, such as poly(vinyl pyrrolidone) [PVP] or poly(styrene sulfonate) [PSS] gave stable solutions of SWCNT/polymer complexes in water (O’Connell et al., 2001). The thermodynamic driving force for wrapping of polar polymer on nanotube is the need to avoid unfavorable
interactions between the non-polar tube walls and the polar solvent (water). To disperse the nanotube in non-polar polymer matrices, such as polyolefins, polymerization-filling technique (PFT) was used. In this process nanotube is first dispersed with catalyst and co-catalyst and followed by polymerization (Dubois & Alexandre, 2006). This technique leads to individualization of nanotube and allows the homogeneous dispersion of nanotubes upon melt blending.

4. CNT/polymer nanocomposites

In order to utilize CNTs and their extraordinary properties in real-world applications, CNT/polymer nanocomposites were developed. Currently, polymer composite is the biggest application area for CNTs. These nanocomposites are being utilized in different fields including transportation, automotive, aerospace, defense, sporting goods, energy and infrastructure sectors. Such wide range applications of such materials are due to their high durability, high strength, light weight, design and process flexibility. CNT/polymer nanocomposites are also used as electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding material because of high electrical conductivity of this material. However, the effective utilization of CNTs for fabricating nanocomposites strongly depends on the homogeneous dispersion of CNTs throughout the matrix without destroying their integrity. Furthermore, good interfacial bonding is also required to achieve significant load transfer across the CNT-matrix interface, a necessary condition for improving the mechanical properties of composites. So it is very important to achieve high degree of CNT dispersion during processing without affecting its property. In the following section we will discuss about the different processing techniques and properties of CNT/polymer nanocomposite.

4.1 Processing of CNT/polymer nanocomposites

From the above discussion, it is very clear that CNTs have strong tendency to form aggregates due to their large surface area. These aggregates persist unless high shear forces are applied e.g., vigorous mixing of the polymer. But such mixing often damages nanotube structures, compromising their properties. Therefore, the biggest challenge is to fully disperse individual nanotubes in the matrices to realize full potential of CNTs. Surface modification of CNTs have somewhat helped in dispersing CNT but long term stability is still a real challenge. Nevertheless, several approaches have been successfully adopted to obtain intimate mixing of nanotubes with polymer matrices, including dry powder mixing, solution blending, melt mixing, in-situ polymerization and surfactant-assisted mixing.

i. Solution processing

The most common method for preparing CNT/polymer nanocomposites involves mixing of CNT and polymer in a suitable solvent. The benefit of solution blending is rigorous mixing of CNTs with polymer in a solvent which facilitates nanotube de-aggregation and dispersion. This method consists of three steps: dispersion of nanotubes in a suitable solvent, mixing with the polymer (at room temperature or elevated temperature) and recovery of the nanocomposite by precipitating or casting a film. Both organic and aqueous medium have been used to produce CNT/polymer nanocomposites [Bandyopadhyaya, 2002; Pei, 2008; Wu, 2007; Cheng, 2008]. In this method dispersion of nanotube can be achieved 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. The use of high-power ultrasonication for a long period of time can shorten the nanotube length, i.e. reduces the aspect ratio, which is detrimental to the composite properties (Badaire et al., 2004).

To minimize this problem, surfactants have been used to disperse higher loadings of nanotubes (Islam, 2003; Barrau, 2003; Bryning, 2005a). Islam et al. (2003) reported that SWCNT (20 mg/mL) can be dispersed in water by using 1% sodium dodecylbenzene sulfonate as surfactant and low power, high-frequency (12 W, 55 kHz) sonication for 16-24 h. However, it has a major drawback of retaining surfactant in the nanocomposites which deteriorate the transport properties of nanocomposites. Bryning et al. (2005a) prepared SWCNT/epoxy nanocomposites and showed that the thermal conductivity of composite is much lower if surfactant is used for SWCNT dispersion.

In solvent blending, slow evaporation step often lead to CNT aggregation. To overcome this problem, CNT/polymer suspension can be kept on a rotating substrate [spin-casting (Lamy de la Chapelle et al., 1999)] or can be dropped on a hot substrate [drop-casting (Benoit, et al., 2001)] to expedite the evaporation step. Coagulation [developed by Du et al. (Du et al., 2003)] is another method, which involves pouring of a CNT/polymer suspension into an excess of non-solvent. This lead to entrapment of SWCNT by precipitating polymer chains which turn prevents the SWCNT from bundling. The method is very successful in case of PMMA and polyethylene [PE] nanocomposites (Haggenmueller et al., 2006).

ii. Melt blending

While solution processing is a valuable technique for both nanotube dispersion and nanocomposite formation, it is less suitable for industrial scale processes. For industrial applications, melt processing is a preferred choice because of its low cost and simplicity to facilitate large scale production for commercial applications. In general, melt processing involves the melting of polymer pellets to form a viscous liquid and application of high shear force to disperse the nanofillers such as CNTs. Successful examples of melt blending include MWCNT/polycarbonate (Poetschke et al., 2003) MWCNT/ nylon-6, (Liu, 2004; Zhang, 2004) SWCNT/polypropylene, (Bhattacharya et al., 2003) and SWCNT/polyimide (Siochi et al., 2004) nanocomposites. Although melt blending is very simple, but high shear force and high temperature can deteriorate nanocomposite property, as high shear force which is required to achieve CNT dispersion can also lead to CNT fragmentation. So an optimum shear stress is required to achieve desired dispersion at lowest possible damage of CNTs.

The use of high temperature is also very critical, as high temperature enhances CNT dispersion by lowering the viscosity but too high temperature can degrade the polymer intrinsic properties. So optimization of temperature is also very important. To overcome these challenges many modification in melt compounding has been made like : Haggenmueller et al. (2000) combined the solution and melt blending by subjecting a solvent cast SWCNT/polymer film to several cycles of melt pressing. An approach developed by Jin et al (2002) introduces polymer-coated MWCNT (rather than pristine MWCNT) into the polymer melt to promote compatibilization. However optimization of processing conditions is an important issue, not just for different nanotube types, but for the whole range of polymer–nanotube combinations (Dubois & Alexandre, 2006).

iii. In-situ polymerization

In recent years, in-situ polymerization has been extensively explored for the preparation of polymer grafted nanotubes and processing of corresponding polymer composite materials. The main advantage of this method is that it enables grafting of polymer macromolecules
onto the walls of CNTs. In addition, it is a very convenient processing technique, which allows the preparation of nanocomposites with high nanotube loading and very good miscibility with almost each polymer matrix. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution or melt processing. Depending on required molecular weight and molecular weight distribution of polymers, chain transfer, radical, anionic, and ring-opening metathesis polymerizations can be used for in-situ polymerization processing. Initially, in-situ radical polymerization was applied for the synthesis of PMMA/MWCNT nanocomposites (Jia, 1999; Velasco-Santos, 2003; Putz, 2004). More recently (Wu, 2009) studied the mechanical and thermal properties of hydroxyl functionalized MWCNTs/acrylic acid grafted PTT nanocomposites and showed a significant enhancement in thermal and mechanical properties of PTT matrix due to the formation of ester bonds between –COOH groups of acrylic acid grafted PTT and –OH groups of MWCNTs.

In-situ polymerization was also very useful for the preparation of polyamide/CNT polymer nanocomposites. Park et al. (2002) also reported the synthesis of SWCNT reinforced polyimide nanocomposites by in-situ polymerization of diamine and dianhydride under sonication. Epoxy nanocomposites comprise the majority of reports using in-situ polymerization methods, (Schadler, 1998; Zhu, 2003, 2004; Gong, 2000; Ajayan, 2000; Moniruzzaman, 2006a) where the nanotubes are first dispersed in the resin followed by curing the resin with the hardener. Zhu et al. (2003) prepared epoxy nanocomposites by this technique using carboxylated end-cap SWCNT and an esterification reaction to produce a composite with improved tensile modulus. It is important to note that as polymerization progresses and the viscosity of the reaction medium increases, the extent of in-situ polymerization reactions might be limited.

In general, in-situ polymerization can be applied for the preparation of almost any polymer nanocomposites containing CNTs which can be non-covalently or covalently bound to polymer matrix. Non-covalent binding between polymer and nanotube involves physical adsorption and wrapping of polymer molecules through van der Waals and H–H interactions. The role of covalently functionalized and polymer grafted nanotubes will be considered in more detail below.

5. Alignment of carbon nanotubes in nanocomposites

The superior properties of CNTs offer exciting opportunities for new nanocomposites, but the important limitation for some potential applications of CNTs come from the fact that randomly oriented nanotubes embedded in polymer matrices have exhibited substantially lower electrical and thermal conductivities than expected (Fischer, 1997; Hone, 1999). Nanotube alignment can be obtained prior to composite fabrication or during composite fabrication or after composite fabrication by in-situ polymerization (Raravikar, 2005; Feng, 2003), mechanical stretching (Jin et al., 1998), melt fiber spinning (Haggenmueller, 2000, 2003), electrospinning (Gao, 2004; Hou, 2005; Ko, 2003) and application of magnetic or electric field (Ma, 2008; Componeschi, 2007). Haggenmueller et al. (2000) have tried a combination of solvent casting and melt mixing methods to disperse single-walled CNTs in PMMA films and subsequently melt spun into fibers. However, only the melt mixing method was found to be successful in forming continuous fibers. Ma et al. (2008) studied alignment and dispersion of functionalized nanotube composites of PMMA induced by electric field and obtained significant enhancement in dispersion quality and alignment

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stability for oxidized MWCNTs as compared to pristine MWCNTs. Camponeschi et al. (2007) found that orientation and alignment of CNTs embedded in the epoxy under a magnetic field increased and showed improvement in mechanical properties of the resulting nanocomposites. Gao et al. (2004) prepared SWCNT/poly(vinyl pyrrolidone) fibres by electrospinning using electrostatic forces and found SWCNT exhibit good alignment and dispersion. Xie et al. (2005) showed that enhanced dispersion and alignment of CNTs in polymer matrices greatly improve mechanical, electrical, thermal, electrochemical, optical and super-hydrophobic properties of CNT/polymer nanocomposites. Safadi et al. (2002) prepared PS/MWCNT nanocomposite films by spin casting at high speed (2200 rpm) and found that MWCNTs were aligned in specific angles relative to the radial direction: 45° and 135° on average. The presence of ~2.5 vol.% MWCNTs doubles the tensile modulus and transforms the film from insulating to conducting. Thostenson & Chou (2002) found that tensile strength and modulus of melt drawn PS/MWCNT composite films increased by 137 and 49% respectively, compared to the undrawn PS film.

6. Properties of CNT/polymer nanocomposites

Incorporation of CNT in polymer matrix resulted in a significant change in mechanical, electrical and thermal properties of polymer matrices. Various factors that influence property modification are processing techniques, type of CNT, aspect ratio and CNT content. It is generally observed that a particular processing method which is good for one property may not be good for another. One such example is surface modification of CNT which generally enhances the mechanical properties but deteriorates the electronic properties. So it is very important to optimize the various conditions to obtain the nanocomposite with desired properties. A number of studies have been aimed at evaluating the mechanical, electrical and thermal properties of CNT/polymer nanocomposite under different conditions and filler loading.

6.1 Mechanical properties of CNT/polymer nanocomposites

The excellent mechanical properties of CNTs, as discussed above, suggest that incorporation of very small amount of CNTs into a polymer matrix can lead to structural materials with significantly high modulus and strength. Significant advancement has been made in improving the mechanical properties of polymer matrix by mixing small fraction of CNTs. Qian et al. (2000) reported that adding 1 wt.% MWCNTs in the PS by solution-evaporation method, results in 36–42 and ~25% improvements in tensile modulus and tensile strength, respectively. Biercuk et al. (2002) have also reported increase of indentation resistance (Vickers hardness) by 3.5 times on adding 2 wt. % SWCNTs in epoxy resin. Cadek et al. (2002) also found significant improvement in the modulus and hardness (1.8 times and 1.6 times) on addition of 1 wt% MWCNTs in PVA matrix. Homogeneous dispersion and alignment of CNTs in polymer matrix had a significant effect on the properties of resulting composites. Velasco-Santos et al. (2003) reported that by enhancing the dispersion of CNT by using an in-situ polymerization, the storage modulus of PMMA/MWCNT nanocomposites at 1 wt.% of MWCNTs at 90°C increased by 1135%.

Although, addition of CNTs lead to enhancement of mechanical properties of the polymer matrix but the improvement is still well below the expected value. At current stage, the extraordinary properties of CNTs are still not fully utilized in polymer composites. Many
Research works have indicated that poor adhesion between the matrix and nanotube is the limiting factor in imparting the excellent mechanical properties of nanotubes in composites. As load transfer from matrix to CNTs play a key role in mechanical properties of the nanocomposite, good interfacial bonding is very important. Load transfer between the matrix and filler depends on the interfacial shear stress between the two (Schadler et al., 1998). A high interfacial shear stress will transfer the applied load to the filler over a short distance and a low interfacial shear stress will require a long distance. There are three main load transfer mechanisms operating between a matrix and filler.

a. **Micro-mechanical interlocking**
This is the amount of load transfer due to mechanical interlocking which is very poor in nanotube composites because of the atomically smooth surface of nanotubes. As CNTs has some surface defects like varying diameter and bends/twist due to non-hexagonal defects, along a CNT, mechanical interlocking do play a role in CNT-polymer adhesion.

b. **Chemical bonding between filler and matrix**
A chemical bond either ionic or covalent significantly improves the interfacial interaction between matrix and filler that enables a stress transfer.

c. **Weak van der Waals bonding between filler and matrix**
The van der Waals interaction arises from the molecular proximity and is the only mode of interaction between CNTs and the matrix in absence of chemical bonding. Hence, formation of chemical bonding between CNT and polymer can significantly improve the mechanical properties of nanocomposites. Recently, Blake et al. (2004) developed butyl-lithium-functionalized MWCNTs which can be covalently bonded to chlorinated polypropylene (CPP). The CPP/MWCNT was then compounded with CPP/tetrahydrofuran (THF) solution to obtain CPP/MWCNT nanocomposites. They showed that on addition of 0.6 vol% MWCNT, the modulus increased by three times and both tensile strength and toughness (measured by the area under the stress–strain curve) increased by 3.8 times (from 13 to 49 MPa) and 4 times (from 27 to 108 J/g), respectively. Bal & Samal (2007) showed that the amine functionalized CNTs get completely dispersed in polymer matrix in comparison to unmodified CNTs. Telescopic pull-out was also observed in case of functionalized MWCNTs (Gojny et al., 2005). It was observed that although CNTs get pulled out from the matrix the outer wall still remained in the matrix. This is possible because only weak van der Waals forces are present between the various concentric tubes of the MWCNT where as the outer tube is covalently bonded to the matrix. Such a pull-out process suggests that efficient load transfer occurs from matrix to the outer tube, due to strong covalent bonding between epoxy matrix and CNT. These observations suggest that the efficiency of property improvement depends on the type of CNT, processing techniques and the compatibility between CNT and host matrix. Although chemical functionalization of CNT can improve the compatibility between CNT and polymer which inturn improves the mechanical properties but it has a deteriorating effect on the other properties of nanocomposites such as electrical and thermal conductivity. However, the rapid growth of this field suggests the solution to these problems are not very far and in coming few years’ desire of obtaining super strong polymer material will be realized.

### 6.2 Electrical properties of CNT/polymer nanocomposites
With exceptional mechanical properties, CNTs also possess very high intrinsic electrical conductivity. The electrical conductivity of individual CNTs ranged between $10^7$ to $10^8$ S/m that is comparable to metals (Ebbesen et al., 1996). Very high electrical conductivity of CNTs...
have helped to impart conductivity in highly insulating material like polymer by fabricating polymer nanocomposites. The enhancement in electrical conductivity of insulating polymer by several orders of magnitude has been achieved with a very small loading (0.021 wt %) of nanotubes in the polymer matrices, which helped in preserving other performance aspects of the polymers such as optical clarity, mechanical properties, low melt flow viscosities, etc. As a result, these conducting materials are in growing demand in different application areas such as transparent conductive coatings, electrostatic dissipation, electrostatic painting and electromagnetic interference shielding applications.

The electrical conductivity of CNT reinforced polymer nanocomposites depends on many factors including type of CNTs, aspect ratio, surface functionalization and CNT content. The electrical conductivity of nanocomposite increases with increasing CNT loading till a critical filler concentration where a dramatic increase in conductivity is observed. This critical filler concentration is called electrical percolation threshold concentration. At percolation threshold concentration, filler forms a three-dimensional conductive network within the matrix, hence electron can tunnel from one filler to another, and in doing so it overcomes the high resistance offered by insulating polymer matrix. The percolation threshold is typically determined by plotting the electrical conductivity as a function of the reduced mass fraction of filler and fitting with a power law function (Fig. 8). As formation of percolating networks depends on both intrinsic conductivity and aspect ratio of the filler, the nanotube/polymer nanocomposites exhibit very low percolation threshold because of high conductivity and high aspect ratio of CNTs. Brining et al. (2005b) studied the effect of aspect ratio on percolation threshold concentration by preparing SWCNT/epoxy nanocomposites with nanotubes from two different sources, HiPco and laser oven, having aspect ratios of ~150 and ~380 respectively. They reported a smaller percolation threshold with the higher aspect ratio nanotubes. Similar observation was also made by Bai & Allaoui (2003); they found more than 8-fold decrease in threshold concentration in MWCNT/epoxy composites when the MWCNT length was increased from 1 to 50 μm. In general, the minimum percolation threshold concentration for SWCNT/polymer nanocomposite is 0.0021 wt % in epoxy matrix (Martin et al., 2004). For different polymer systems it ranged from 0.0021 to 15 wt% CNT loading (Bauhofer & Kovacs, 2009). These studies show that the percolation threshold concentration and nanocomposite conductivity also depends on polymer type, synthesis method, aspect ratio of CNTs, disentanglement of CNT agglomerates, uniform spatial distribution of individual CNTs and degree of alignment [Bryning, 2005b; Moniruzzaman, 2006b; Du, 2005].

Another factor which significantly affects the electrical conductivity of nanocomposite is the chemical functionalization of CNTs because it disrupts the extended π-conjugation of nanotubes and thereby reduces the electrical conductivity of isolated nanotubes. Sulong et al. (2009) showed that incorporation of acid and octadecylated functionalized MWCNT in epoxy matrix decreased the electrical conductivity of nanocomposites. Similar results have also been reported by Park et al (2009). Hence, it is important to optimize the modification condition or reagent to achieve minimum deterioration of electronic properties of CNTs. Nevertheless, significant improvement in electrical conductivity of polymer on CNT addition lead to the development of CNT/polymer conductive nanocomposites for electronics, automotive and aerospace applications with uses such as electrostatic dissipation, electromagnetic interference (EMI) shielding, multilayer printed circuits, and...
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Fig. 8. Plot of dc electrical conductivity ($\sigma$) vs weight fraction of MWCNT in PTT/MWCNT composites [inset shows the log-log plot of $\sigma$ vs $[(\rho - \rho_c)/\rho_c]$]

Conductive coatings (Baughman, 2002; Dresselhaus, 2004; Holt, 2006; Martel, 1998; Minoux, 2005; Zhang, 2005). The rapid development of electrical industry, demands fabrication of light weight and effective EMI shielding material for the protection of workspace and environment from radiation coming from computers and telecommunication equipment as well as for protection of sensitive circuits. Thus electrically conducting polymer nanocomposites have received much attention recently compared to conventional metal-based EMI shielding materials (Chung, 2001; Joo & Epstein, 1994; Kim, 2003; Yang, 2005a), because of their light weight, resistance to corrosion, flexibility and processing advantages. The use of CNT have significantly reduced the filler loading required to achieve desired EMI SE, thus reduced the cost and weight of the material (Chung, 2001; Micheli, 2009; Sundararaj & Al-Saleh, 2009; Yang, 2005b).

The effect of aspect ratio on EMI SE was shown by Sundararaj & Al-Saleh. They reported that SE of 1 mm thick shielding plate made of 7.5 vol% MWCNT/polypropylene (PP) nanocomposite was much higher (35 dB) than 7.5 vol% (HS-CB)/PP composite (18 dB) in the X-band frequency range. Yang et al. (2005b) studied the EMI shielding behavior of MWCNT/PS nanocomposites and achieved SE of ~20 dB at 7 wt % MWCNT loading. Although, lower value of SE of CNT composites have also been reported, e.g., Liu et al. (2007) achieved only ~17 dB at 20 wt% MWCNTs loading in polyurethane (PU) whereas Kim et al. (2004) reported ~27 dB SE at 40 wt% CNT loading for MWCNT/PMMA films. These observations suggest that SE of CNT filled polymer nanocomposite depends on many factors including fabrication techniques, purity of CNT, dispersion etc. Recently significant efforts have been made in understanding the EMI shielding mechanisms of polymer nanocomposite as it is very important for the best utilization of shielding capabilities of material and for designing nanocomposite at lowest possible filler loading and cost. Three types of EMI shielding mechanisms have been proposed, namely: reflection, absorption and multiple reflections [Sundararaj & Al-Saleh, 2009; Chung, 2001; Liu, 2007]. Some previous studies have shown that in MWCNT/polymer nanocomposites, SE is mainly absorption dominated where as SWCNT/polymer nanocomposites are mainly reflection dominated.
material. The application area of EMI shielding materials depends on the dominant shielding mechanism like absorption based EMI shielding materials are used in radar, microwave communication technology, stealth (self concealing) technology, microwave darkroom and anti-EMI coating application.

6.3 Thermal properties
Thermal properties of a composite are equally important as its mechanical and electrical properties because it gives more freedom in selecting processing conditions and also application area. It is observed that incorporation of CNTs in polymer matrices results in increase of glass transition, melting and thermal decomposition temperatures due to hindered chain and segmental mobility of the polymers. To improve the thermal endurance of CNT/polymer nanocomposites, surfactant as the wetting agent were also incorporated. Gong (2000) and Velasco-Santos et al. (2003) reported that addition of 1 wt.% CNTs with a surfactant in epoxy and PMMA matrix increased the glass transition temperature by ~25 and ~40 °C respectively. Incorporation of CNTs in polymer matrices also enhances the rate of crystallization by acting as nucleating sites [Deshpande & Jape, 2009; Zhang, 2008] which in-turn reduces the processing time and enhances mechanical strength. There are reports according to which addition of CNTs in polymer matrix can hinder the crystallization of polymer matrices (Jin, 2007; Diez-Pascual, 2009). Our recent study on MWCNT/PTT nanocomposite suggested that presence of MWCNTs in PTT matrix delays the crystallization and lead to formation of bigger crystallites (Gupta & Choudhary, 2010). Thermal stability and melting temperature of polymer matrices were improved in presence of CNTs. Kashiwagi et al. (2000) found that the thermal decomposition temperature of polypropylene in nitrogen increases by ~12 °C on 2 vol. % MWCNTs loading. Because of the excellent thermal conductivity of CNTs, incorporation of CNTs significantly improves the thermal transport properties of polymer nanocomposites which lead to its usage as printed circuit boards, connectors, thermal interface materials, heat sinks, and other high-performance thermal management systems. Choi et al. (2003) reported 300% increase in thermal conductivity of epoxy matrix at room temperature on 3 wt % SWCNT loading and an additional increase (10%) when aligned magnetically. Biercuk et al. (2002) prepared an epoxy nanocomposite with 1 wt % raw (not purified) laser-oven SWCNT and showed a 125% increase in thermal conductivity at room temperature. Alignment of CNTs also plays an important role in improving the transport properties of a material. Choi et al. (2003) found 10% increase in thermal conductivity of epoxy composite with aligned MWCNTs in comparison to non-aligned MWCNTs.

7. Application of CNT/polymer nanocomposites
With their excellent range of properties, CNTs have opened up a new age of advanced multifunctional materials. Incorporation of CNTs in polymer matrices provides materials that could be used for many high performance engineering applications. Currently, the most widespread use of CNT nanocomposites is in electronics. These nanocomposites could be used to shield electromagnetic interference and as electrostatic-discharge components. The microwave-absorbing capability of nanotubes could be exploited to heat temporary housing structures and may have applications in space exploration. Thin layers of nanotubes on plastics might also be used in transparent conducting composites. High mechanical strength
of these nanocomposites could be utilized to make some high-end sporting goods such as tennis rackets, baseball bat etc, and thus delivering superior performance. In short, the biggest market for CNT nanocomposites will undoubtedly be for high-value applications that can absorb the added costs, which includes commercial sectors such as electronics especially aerospace (which requires lightweight, high-strength, high-temperature-resistant composites) and energy (for example, in nanotube-reinforced rubber seals for large oil recovery platforms). Once the cost of nanotubes becomes comparable to that of carbon fibre (or even to that of the much cheaper reinforcing agent, carbon black), commodities such as nanotube-filled rubber tyres could become a reality.

8. Conclusion and future scope

Studies on CNT/polymer nanocomposite suggests that CNT has great potential in altering the properties of polymer matrices. The quality of CNT/polymer nanocomposites depends on many factors including type of CNTs, chirality, purity, defect density, aspect ratio, % loading, dispersion, alignment and interfacial adhesion between the nanotube and polymer matrix. A lot of research work has been carried out to improve the quality of CNTs and processing techniques. The biggest challenge in realizing the full potential of CNTs is to achieve homogeneous dispersion of CNTs so that maximum filler surface area will be available for load-transfer between filler and matrix. The functionalization of nanotubes provides a convenient route to improve dispersion and stress transfer between CNT and polymer matrix, but more improvement in this field is required to preserve the intrinsic properties of CNTs. It is important to focus on different methods of noncovalent functionalization of nanotubes and discover a route which can improve the dispersion and compatibility without negatively affecting the composite properties. The actual task of dispersing the CNTs in polymer matrix is performed during its manufacturing. The three major processing techniques namely, solution, melt and in-situ polymerization have their unique advantages in fabricating CNT/polymer nanocomposite. Although solution blending produces high quality composite but melt compounding is much simpler and provide option for large scale production. Recently, in-situ polymerization is also showing great potential in fabricating CNT/polymer nanocomposite. The success of processing technique is directly related to performance of composite. The maximum improvement in mechanical properties of polymer matrix is observed in case of in-situ polymerization which produces covalent bond between CNT and polymer matrix. However it negatively influences the electronic properties of the composite. The increase in electrical conductivity of polymer material on CNT addition is the biggest advantage of fabricating CNT/polymer nanocomposite. As significant improvement in electrical conductivity is observed at very low CNT loading, CNT/polymer nanocomposite is finding application as light weight, low cost and highly effective ESD and EMI shielding material. The thermal properties of the polymer matrix also modified by CNT addition like CNT increases the glass transition, melting and thermal decomposition temperatures. CNT also influences the crystallization rate and percentage crystallinity by acting as nucleating agent. Improvement in both crystallization rate and percentage crystallinity enhances its mechanical and processing properties. So finally we can conclude that CNT is ideal filler for fabricating polymer composite but some serious challenges need to be addressed before fully realizing the extraordinary properties of CNT in polymer nanocomposite.
9. References


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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This book focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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