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Epoxy-based Carbon Nanotubes Reinforced Composites

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1. Introduction

Epoxy or polyepoxide is a thermosetting epoxide polymer that cures (polymerizes and cross-links) when mixed with a curing agent or "hardener". Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A. Figs. 1 and 2, respectively, show the molecular structure and 3-D model structure of bisphenol-A based epoxy resins. In 1936, bisphenol-A based epoxy resins were first jointly synthesized by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee in the United States. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, and Ciba went on to become one of the three major epoxy resin producers worldwide [May, 1987].

Epoxy resin is most commonly used as a matrix for advanced composites due to their superior thermal, mechanical and electrical properties; dimensional stability and chemical resistance. Epoxy surface coatings are among the most widely used industrial finishes and provide superior adhesion, flexibility and corrosion resistance when applied to metallic substrates [Jones, 1996]. Epoxy resins are also used with various curing agents, diluents and modifiers to create products with an almost unlimited range and variety of performance properties [The epoxy book, 2000].

Epoxy resins are widely used as high-grade synthetic resins, for example, in the electronics, aeronautics and astronautic industries [Morena, 1988; Njjuguna et al. 2007]. Depending upon the exact application, sufficient matrix conductivity is needed to provide electrostatic discharge or electromagnetic-radio interference shielding [Barrau et al., 2003]. However, epoxy resins are electrical insulators, and the widespread use of the epoxy resins for many high-performance applications is constrained because of their inherent brittleness, delamination and fracture toughness limitations. There were quite a few approaches to enhance the properties of epoxy resins which included: (i) chemical modification of epoxy backbone to make it more flexible, (ii) increasing the molecular weight of epoxy, (iii) lowering the cross-link density of the matrix and (iv) incorporation of a dispersed toughened phase in the cured polymer matrix [Dirlikov et al., 1996; Oh et al. 1996; Sue et al., 1996, Millhaupt & Buchholtz, 1996; Kinloch & Guild, 1996]. Though epoxy resins can be toughened effectively, such methods result in a decrease in other desirable mechanical and physical properties. In another approach, micro-sized filler materials have been used to modify the brittle polymers aiming at synergistic improvements in toughness and rigidity. The addition of filler, usually harder than the matrix, generally leads to an increase in

Young's modulus and a reduction in the ultimate elongation of the matrix [Sandler et al., 2003]. However, reports show that the toughening efficiency of these micro-sized particles is much lower, as the rigid particles cannot effectively stop crack propagation [Lee & Yee, 2000].

Fig. 1. (a) Molecular structure of bisphenol-A based epoxy resins. Reproduced with permission from Marcel Dekker Inc., USA.

Red=Oxygen, Ash=Hydrogen, Black=Carbon

Fig. 2. 3-D model structure of bisphenol-A based epoxy resins. Reproduced with permission from Marcel Dekker Inc., USA.

A newly developed strategy offering promising results is to reinforce epoxy matrices with nano-sized organic and inorganic particles such as carbon nanotubes (CNTs), carbon nanofibres (CNFs), nanoclays, metal oxide nanoparticles, etc. [Puglia et al., 2003; Al-Saleh & Sundararaj, 2009; Sinha Ray & Okomoto, 2003; Kim et al., 2008] and make new materials with enhanced properties. The unique properties of the nanoparticles such as nanometric size, high specific surface areas (up to 1000 m²/g) and the possibility of combining them with conventional reinforcements have caused intense research in the field of nanocomposites.

1.1 Carbon nanotubes

Of the various nanofillers used to modify polymer matrices, CNTs have attracted great interest recently as structural reinforcements because of their unique properties. CNTs are the stiffest known fibres which possess a tensile strength of 50–100 GPa and a measured modulus of 1.4 T Pa, which are by far the highest known [Zhu et al., 2003]. In addition, CNTs possess superior thermal and electrical conducting properties varying from metallic to moderate band-gap semi-conductive behaviors depending on their chirality, size and purity. Therefore, it is possible to improve the physical and mechanical properties and electrical conductivity by adding a certain amount of CNTs to the polymeric structures [Lau et al., 2003]. CNTs were first identified by M. Endo and his co-workers in the late 1970s [Oberlin et al., 1976] and caused tremendous interest when S. Iijima published his paper in *Nature* in 1991 [Iijima, 1991]. The synthetic methods for CNTs include the carbon arc-discharge method [Iijima, 1991; Kroto et al., 1985], laser vaporization of a graphite electrode [Thess et al., 1996] and the chemical vapour-deposition methods from various carbon precursors [Baker et al., 1972; Yacaman et al., 1993; Hsu et al., 1995; Pigney et al., 1997; Colomer et al., 1998]. CNTs have many structures, differing in length, thickness, spiral types and number of layers; although they are formed from essentially the same graphite sheet [Saito et al., 1992; Zhang et al., 1993; Bernholc et al., 1997; Rao et al., 1996; Iijima, 1992]. There are two main types of CNTs: single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs).

SWCNTs: The structure of a SWCNT can be conceptualized by wrapping a one-atom-thick layer of graphite (called graphene) into a seamless cylinder (see Fig. 3). Most SWCNTs have a diameter of close to 1 nm, with a tube length that can be many thousands of times larger. SWCNTs with lengths up to orders of centimetres have been produced [Journet et al., 1997].

MWCNTs: MWCNTs consist of multiple layers of graphite rolled on themselves to form a tube shape. There are two models which can be used to describe the structures of MWCNTs. In the Russian doll model, sheets of graphite are arranged in concentric cylinders. In the parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper (Fig. 4) [Dresselhaus, 1996].

Fig. 3. (a) Formation of SWCNT. Reproduced with permission from www.nanotech-now.com and (b) TEM image of SWCNTs.

There are also other two varieties of CNTs generally used for the preparation of composite materials with various polymer matrices. These are double-walled CNTs (DWCNTs) and cup-stacked CNTs (CSCNTs).

Fig. 4. (a) Computer generated MWCNT model. Reproduced with permission from www.nanotech-now.com and (b) TEM image of MWCNTs.

Fig. 5. (a) Computer generated image of DWCNT (www.nanotechweb.org) and (b) SEM images of DWCNTs. Reproduced from Endo et al., 2005.

DWCNTs: DWCNTs are considered as the simplest member of the family of MWCNTs, consisting of two coaxial SWCNTs [Saito et al., 2001; Endo et al., 2005]. DWCNTs have unique physical and mechanical properties due to their special double wall structure compared to those of SWCNTs and MWCNTs [Dai, 2002; Liu et al., 2001]. Figs. 5 (a) and (b), respectively, show the computer generated and SEM images of DWCNTs.

CSCNTs: CSCNT structure provides a hollow tubular morphology, composed of cup-shaped carbon units with diameters ranging from 50 to 150 nm and lengths of up to 200 μm , in contrast with conventional CNTs made up of seamless cylinders of hexagonal carbon network (see Fig. 6). In addition, the availability of reactive edges on the outer and inner surfaces of cup-shaped carbons to chemical functionalization or surface modification will open up new ways to utilize them in electronic, catalytic and photovoltaic applications. The ball milling processes are reported to result in a decrease in the average lengths of pristine CSCNTs (up to 200 μm) into 7 μm after 24 h milling [Endo et al., 2005; Endo et al., 2003; Kim et al., 2002; Iwahori et al., 2002]. However, individual cup-shaped carbons with the controlled diameter and size have yet to be obtained.

Fig. 6. (a) Computer generated model of CSCNTs and (b) SEM image of CSCNTs. Reproduced from Iwahori et al., 2002.

CNTs possess unique characteristics relative to the numerous available fillers: amazing mechanical properties, phenomenal electrical and thermal conductivity, nanoscopic size and

high aspect ratio make them the perfect choice in principle to use as reinforcement for polymer composites [Lu, 1997; Salvetat et al., 1999; Srivastava et al., 2003; Buryachenko et al., 2005; Thostenson et al., 2001; Ajayan et al., 2003; Thostenson et al., 2005; Sandler et al., 1999]. This combination of properties can also lead to electrical percolation at low concentrations and has naturally spurred considerable activity in producing value-added multifunctional polymer composites based on CNTs [Winey et al., 2007]. Although the CNT production cost is higher than that of conventional fillers, its low loading is advantageous because the effects on resin properties are minimal and the same processing equipment can be used with neat resins and nanocomposites. These polymer-based nanocomposites are expected to derive high properties at low filler volume fractions due to the high aspect ratio and high surface area to volume ratio of the nano-sized particles [Zhou et al., 2008; Hu et al., 2008; Santos et al., 2008].

In recent years, different types of polymer composites have been synthesized by incorporating CNTs into various polymer matrices such as polyamides [Zhao et al., 2005], polyimides [Cai et al., 2004; Ogasawara et al., 2004], epoxy [Winey et al., 2007; Hu et al., 2008; Liao et al., 2004], polyurethane [Koerner et al., 2005; Kuan et al., 2005], polypropylene [Seo et al., 2004; Li et al., 2004; Seo et al., 2005], polyethylene [Haggenmueller et al., 2006], polyethylene oxide [San et al., 2001], poly(vinyl alcohol) [Shaffer et al., 1999], poly(methyl methacrylate) [Jin et al., 2001], polycarbonate [Postscke et al., 2003], poly(butylene succinate) [Sinha Ray & Okamoto, 2003], polylactide [Chiu et al., 2008], polyaniline [Zing et al., 2008], polypyrrole [Sahoo et al., 2007], poly(N-vinylcarbazole) [Maity et al., 2007; Maity & Sinha Ray, 2008a; Maity & Sinha Ray, 2008b], poly(ethylene 2, 6-naphthalate) [Kim et al., 2008], poly(butylenes terephthalate) [Garcia-Gutierrez et al., 2008], poly(p-phenylene benzobisoxazole) [Kumar et al., 2002], glycopolymer [Gao et al., 2007] and others [Fragneaud et al., 2007]. However, the potential of using CNTs as reinforcements has not been realized mainly because of the difficulties in processing and the limitation on load transfer. The tiny size of the nanostructures intensifies their tendency to form agglomerates, and their large surface area per unit volume yields an augmented influence of the interfacial bonding on the effective properties of the composite. Because of the intrinsic van der Waals attraction of the CNTs to each other and high aspect ratio, tubes are held together as bundles and ropes having very low solubility in most solvents. When blended with the polymer, CNTs remain as entangled agglomerates which prevent homogeneous dispersion of the filler into the polymer matrix. Again, the smooth non-reactive CNT surface limits the load transfer from the matrix to nanotubes. Additional processing problem arises due to the increase in viscosity when the CNTs are added directly to the polymer [Zhu et al., 2003]. For CNT-composites, the problem is aggravated by the influence of tube morphology and content of amorphous carbon and metal impurities normally contained in the as-produced CNTs. These impurities, synthesized along with CNTs, are frequently removed (or at least reduced) by oxidative processes, which may lead to structural and morphological changes in the tubes [Martinez et al., 2003; Hiura et al., 1995; Xing et al., 2005]. Given the potential of the CNTs as reinforcement agents, several researchers have aggressively pursued their use in polymer nanocomposites: either thermoplastics or thermosettings [Liu et al., 2004; Andrews et al., 2002; Gryshchuk et al., 2006].

CNT-based epoxy composites are materials of high technological interest because of features such as their mechanical, thermal and electrical properties. A large number of recent works have dealt with CNT-reinforced epoxy. In spite of the aggressive work that has been lately dedicated to this topic, it is widely recognized that the experimental results are still not convergent and continuous research is needed in order to shed light on the development of

the composites of the future. Different processes and controversial results were reported on CNT-reinforced composites earlier concerning the improvement of their mechanical, thermal and electrical properties. Thus, the main objective of this article is to report, from the available literatures, the recent progress on the experimental research on CNT-based epoxy composites and their properties.

2. Epoxy-CNT composites-fabrication and characterization

2.1 MWCNTs-containing epoxy composites

MWCNTs consist of multiple rolled layers (concentric tubes) of graphite. They exhibit unique mechanical as well as electrical properties, which have caused them to be widely studied. This fantastic property of mechanical strength allows MWCNTs to be used as possible reinforcing materials. Just like current carbon fiber technology, MWCNTs reinforce would allow electrically conductive very strong and light materials to be produced. These properties of MWCNTs attracted the attention of scientists in all over the world to incorporate in epoxy matrix for the fabrication of advanced engineering materials. In this section, we reviewed various techniques used to prepare and characterize MWCNTs-containing epoxy composite materials.

2.1.1 Preparative methods and morphological study

Following the first report on the preparation of aligned arrays of MWCNTs by cutting epoxy-CNTs composites by Ajayan et al. [Ajayan et al., 1994], there have been continuous efforts to incorporate CNTs into various types of epoxy resins to fabricate functional composite materials with desirable electrical and mechanical properties. They reported a simple method to produce aligned arrays of CNTs into the epoxy matrix. MWCNTs produced by arc-discharge and purified nanotubes in ethanol were randomly dispersed in a liquid epoxy resin by mechanical mixing with a glass rod. The resin was prepared by mixing epoxy resin (Epon 812) with the curing agents dodecenyl succinic anhydride (DDSA: 12.4 ml) and methyl nadic anhydride (MNA: 9.4 ml) and the accelerating agent, 2,4,6-tris (diaminomethylaminomethyl) phenol (DMP 30: 0.7 ml) by magnetic stirring for 2 h. The composite after evacuation was hardened in capsular shaped blocks for 24 h at 60°C. Low and high magnification transmission electron microscopy (TEM) images of the thin slices cut from the composite showed that the thinner and longer nanotubes were preferentially oriented along the cutting direction, though the thicker tubes and nanoparticles had random orientation. Most of the tubes were adhered to the polymer matrix, and the directional cutting process created shear that induced flow of the tubes. The tubes on the surface were deformed during cutting (due to defect formation) and were oriented unidirectionally on the newly formed surface. The weak interfacial bond between tubes and the matrix was apparent from the unbroken and straightened CNTs after the cutting process which at the same time showed the extraordinary mechanical strength of the tubes.

In 1998, the same group studied the mechanical and load transfer behavior of MWCNT-epoxy composites in tension and compression [Schadler et al., 1998]. About 5 wt% of MWCNTs was ultrasonically dispersed in Epon 828 epoxy resin matrix. The composites were cured with triethylene tetraamine hardener by gelling overnight at room temperature (RT) and curing at 100°C for 2 h. The micro-structural analysis of the composite using scanning electron microscopy (SEM) revealed that while the CNTs were poorly distributed,

individual tubes were well dispersed in the matrix. Curved and interwoven tubes were observed in the composite showing extreme flexibility.

Sandler and co-workers [Sandler et al., 1999] dispersed untreated MWCNTs in an epoxy matrix using the process developed for carbon black [Schüler et al., 1997]. The matrix used in this study was an epoxy polymer based on bisphenol-A resin (Araldite LY 556) and an aromatic hardener (Araldite HY 932). Weight percentages ranging from 0.0225 to 0.15 wt% of the pristine CVD-grown [Tennent et al., 1992] MWCNTs (diameter 5–10 nm, length a few microns) were first dispersed in ethanol in an ultrasonic bath at RT for 1 h. The solution was then mixed with the resin and stirred for 1 h at 2000 rpm at 80°C. Ethanol was evaporated in a vacuum oven at 80°C for 1 h, and the mixtures were stirred again for 1 h at 2000 rpm. After adding the hardener, the mixtures were stirred at 2000 rpm for 15 min. The resulting epoxy nanocomposite was hardened in a vacuum oven at 140°C for 8 h.

Parts (a) and (b) of Fig. 7, respectively, show the SEM image of the CNT material and magnified transmission light micrograph of the composite sample containing 0.0225 wt% of CNTs. The images show a remarkable improvement in the dispersion of the CNTs in the epoxy resin due to the ultrasound exposure. At these low filler fractions, neither the processing behavior (viscosity) of the matrix nor the surface finish of the samples were adversely affected.

Fig. 7. (a) SEM image of CNT material, as-supplied and (b) magnified transmission light micrograph of the composite sample containing 0.0225 wt % CNTs. Reproduced from Sandler et al., 1999.

Gong et al. [Gong et al., 2000] used a non-ionic surfactant for dispersing CNTs in epoxy polymer matrix. The bisphenol-A epoxy resin with hydroxylated polyamine hardener H-91 and the surfactant polyoxyethylene 8-lauryl ($C_{12}EO_8$) were used for the composite preparation. In a typical procedure, 19.2 mg $C_{12}EO_8$ was dissolved in 0.5 g acetone in a small beaker to which 25.2 mg of MWCNTs was added and magnetically stirred for 15 min at room temperature. Then, 2.0 g epoxy and 0.5 g hardener were added. This produced a viscous suspension. The suspension was stirred for another 15 min until it appeared to be homogeneous. The mixture was poured into a mould and cured at RT overnight, followed by an elevated temperature cure at 80°C for 2 h and 120°C for 2 h. The control samples were made by using the same procedure without $C_{12}EO_8$ or CNTs.

Fig. 8. SEM photographs of CNTs on fracture surfaces of the composite samples: (a) without $C_{12}EO_8$ and (b) with $C_{12}EO_8$. Reproduced from Gong et al., 2000.

The morphology of the fractures surfaces of samples with and without the surfactant were analysed by SEM and results are presented in Fig. 8. CNTs in the composite without surfactant [Fig. 8(a)] appeared to be very long, wavy and lumped together, while the ones with the surfactant [Fig. 8(b)] were more evenly distributed and aligned along one direction. These observations indicated that the CNTs were better dispersed in the polymer matrix in the presence of the surfactant and the load was transferred to the tubes during the fracture process. The surfactant interacted with carbon through the hydrophobic segment, and at the same time, the hydrophilic segment could interact with the epoxy through hydrogen bonding which overcame the van der Waals attractive force between the carbon surfaces in a poor solvent [Everett et al., 1973; Israelachvili, 1992].

To study the deformation micromechanics of CNTs filled epoxy composites using Raman spectroscopy, Cooper et al. [Cooper et al., 2001] synthesized CNT-epoxy composites by adding CNT-ethanol mixture to uncured epoxy resin and then sonicated for 2 h. The solvent was evaporated in a vacuum oven overnight. The hardener was added, and the mixture was stirred well to distribute the nanotubes and again placed in a vacuum oven for about 30 min. The resin was moulded and cured at RT for seven days. The composite was formed by applying the epoxy resin-CNTs mix to the surface of the epoxy beam to give a layer of 0.1 mm thick and was cured at RT for seven days before testing. Unfortunately, authors did not report dispersion characteristics of CNTs in the epoxy matrix.

On the other hand, Cui and co-workers [Cui et al., 2003] examined the influence of incorporation of surfactant during MWCNT-epoxy composite processing. In a typical experimental procedure, the epoxy resin Araldite D (diglycidyle ether of bisphenol) was mixed with an amine type hardener (HY 956) under the ratio 10:2 in weight. The MWCNTs prepared by CVD were purified by high temperature treatment and dispersed ultrasonically in acetone with 2 wt% of surfactant-Tergitol NP 7. The araldite D was added to the MWCNTs dispersed solution and ultrasonicated again for 15 min. The mixture was then mixed for 1 h, at 80°C by shear mixing with a rotating blade. The solvent was evaporated in a vacuum oven, and the mixture was cooled to RT. Polymerization of the mixture was done by stirring with a polymerizing agent at 120°C for 1 h. Two series of composites (with or without the surfactant) were prepared by varying the MWCNTs content from 0.26 to 12 wt%. Optical microscopy images showed a better dispersion of nanotubes in the presence of

the surfactant as reported by Gong et al. [Gong et al., 2000] However, at higher MWCNT content, agglomerates were observed in the matrix.

Other researchers investigated the effect of ultrasonication to disperse CNTs in the epoxy matrix. For example, Lau and co-workers [Lau et al., 2003] dispersed different weight fractions of MWCNTs, produced by arc-discharge method, into the epoxy resin (Araldite GY 251) by ultrasonication of resin with ethanol solution of CNTs for 2 h. The composites were dried in vacuum oven for two days to remove air bubbles and the solvent. Hardener (HY 956) was then added to the mixtures at a resin-to-hardener weight ratio of 1:0.23 and sonicated again for 1 h to get uniform nanotube distribution, and the samples were kept in vacuum at RT for 7 days before testing.

The SEM micrographs showed more micro-voids in composite samples at low CNT content when compared to the pure epoxy, which could be a possible reason for the decrease in composite hardness. However, the authors observed that with the continuous increase of the nanotube content, void size decreased (due to the formation of network structure) increasing the hardness property. Local deformation and pull out of CNTs were observed in the load direction.

Like previous authors, Park et al. [Park et al., 2003] also employed the sonication method to disperse CNTs in the epoxy matrix. In their experimental procedure, the MWCNTs (0.1, 0.5 and 2 vol.%) were first sonicated with methanol-based epoxy solution for 2 h, and the sonication was continued for 6 h at 35°C to remove the solvent. The samples were then dried in a vacuum oven at 50°C for 7 days. The morphological study by SEM clearly showed a significant increase in CNT-contact points or network in the polymer matrix with increase in CNT content. However, authors did not report details of morphological study by TEM.

In another report, Wong et al. [Wong et al., 2003] fabricated CNT-epoxy thin film by spin coating technique. Their main objective was to study the interfacial morphology of CNT/epoxy composite. A standard 4-in. silicon wafer was used to spin-coat the mixture of MWCNTs and epoxy resin (Epon SU-8). After curing the composite film system, the substrate was etched from the backside by deep reactive ion etching (DRIE) which left a circular thin film on the rigid substrate with a hole 8 mm in diameter. Extensive examination of the CNT-epoxy interface by TEM indicated that CNTs are in intimate contact with the polymer with no physical gap. No noticeable CNT pull out from the epoxy was observed in the CNT/epoxy slices after microtoming, and most of the CNTs remained in the epoxy, suggesting good adherence of the polymer to CNT. The authors tried to explain the observed CNT-polymer adhesion by proposing mechanical interlocking as a possible mechanism. However, the local non-uniformity along a CNT, such as varying diameter and bends (due to non-hexagonal defects), contribute to mechanical interlocking, and so, extra energy is needed to deform the polymer causing CNT-pull out. A molecular model of CNT with diameter variation embedded in an array of linear polyethylene illustrated this mechanism. (for better understanding refer Fig. 9).

The effect of processing conditions on the degree of dispersion of MWCNTs in epoxy matrix was studied by Sandler and co-workers [Sandler et al., 2003]. The aligned CVD-grown MWCNTs with loading of 0.001–1 wt% were used for composites preparation [Sandler et al., 1999]. For the preparation of composite, a required amount of CNTs were dispersed in a bisphenol-A resin (Araldite LY 556) by shear-intensive mechanical stirring using a dissolver disk. The mixture was then stirred at RT for 1 h at 2000 rpm. After reducing the resin temperature with dry ice in order to increase the viscosity (shear force) the mixture was again stirred for 1 h at 2000 rpm. Finally, the resin temperature was raised to 80°C and

Fig. 9. A molecular model of a CNT embedded in two layers of short linear polyethylene array. Extra energy is needed to pull the CNT through the 'interlock'. A is point of entry and B is near-pullout position. Reproduced from Wong et al., 2003

equilibrated for 10 min. After addition of the hardener at this temperature, the mixtures were stirred for 1 min at 500 rpm followed by 4 min at 50 rpm to allow for a homogeneous dispersion of the hardener and to enhance the nanotube agglomeration process. The moulded composites were cured at 140°C for 8 h.

SEM and optical microscopy images of the fractured composite surface revealed that though the procedure led to very good dispersion of low wt% of aligned CNTs in the polymer matrix, agglomeration occurs from 0.025 wt% onwards. The processing found to be much more difficult with entangled CNTs, as the densely packed tubes increased the viscosity of the resin even at low CNTs content.

In a subsequent work, Park et al. [Park et al., 2004] used oxyfluorinated MWCNTs (synthesized using the CVD process) to reinforce epoxy matrix. The objective was to study the effect of oxyfluorinated MWCNTs surfaces on the mechanical and interfacial properties of resulting composites. In a typical experimental procedure, MWCNTs outer surfaces were functionalized with F_2 , O_2 and N_2 gases in a batch reactor made of nickel at a pressure of 0.2 MPa with reaction time of 15 min. Surface analysis results with Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) showed fluorine/oxygen contents and -OH groups on MWCNT surfaces were maximized at 100°C. For the preparation of composite, the epoxy resin (diglycidyl ether of bisphenol A-DGEBA, YD-128) was mixed with 0.5 wt% of treated MWCNTs and sonicated for 3 h at 60°C. After adding the hardener diaminodiphenylmethane (DDM), the mixture was stirred thoroughly, degassed to remove bubbles and moulded. The samples were cured for 2 h at 120°C, 2 h at 150°C and finally, 1 h at 200°C. Results show that the mechanical and mechanical interfacial properties of the

resulting composites were improved with increasing F/O content. This indicates that polar groups such as fluorine and oxygen increases the wet-ability of CNTs surface with the epoxy matrix. However, authors did not do any morphological study of composites by electron microscopes.

The cure kinetics of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) [where 4,4'-diaminodiphenylsulfone (DDS) used as a curing agent] in presence of MWCNTs were studied by Xie and co-workers [Xie et al., 2004]. On the other hand, Martin and co-workers [Martin et al., 2004] studied the effect of processing conditions on the degree of dispersion of CNTs in the epoxy matrix. In a typical preparative method, the CNTs were mixed with 30 g of resin using a dissolver disk at 2000 rpm for 30 min at RT and for a further 30 min in a bed of dry ice. The samples were equilibrated at a new temperature and cured in a vacuum oven to remove excess air. In the first set of experiments, the temperature of the CNTs-epoxy resin mixture during addition of the hardener was varied as 25°C (sample A), 80°C (sample B) and 140°C (sample C). In the second set, stirring rates during the addition of the hardener were varied at 80°C at the last step to 0 rpm (sample D) and 200 rpm (sample E). For the third set of experiments, curing temperature was varied to 80°C (sample F) and 110°C (sample G).

Fig. 10. Transmission light micrographs of 0.01 wt% composites processed at different conditions (a) stirred at 50 rpm at RT, (b) stirred at 50 rpm at 80 °C, (c) stirred at 50 rpm 140 °C, (d) stirred at 0 rpm at 80 °C, (e) stirred at 200 rpm at 80 °C, (f) cured at 80 °C and (g) cured at 110 °C. Scale bar is in cm. Reproduced from Martin et al., 2004.

Transmission light microscopy was used to verify the quality of dispersion and micrographs are presented in parts (a-g) of Fig. 10. From the images it was observed that the CNTs remained well dispersed until the hardener was added. Local aggregation started with the addition of hardener. The good dispersion of CNTs without the hardener was explained with electrostatic stabilization and this theory is well known in the case of colloids [Hunter

et al., 1987]. The surface of the nanotubes was observed to be negatively charged [Prasse et al., 1987; Martin et al., 2004] which acted as a surface layer preventing aggregation. The addition of a hardener with an ionic strength different from that of the pure resin decreased the dispersion stability favouring cluster formation. Agglomeration at higher temperature led to finer and more evenly distributed tubes consistent with higher nucleation rate and lower barrier to aggregation [Fig. 10(a), (b) and (c)]. The nanotube network formation was also influenced by the curing temperature. Of different curing temperatures (80, 110 and 140°C) used, 110°C led to a more homogeneous dispersion.

In a subsequent report, the effect of amine functionalization of CVD-grown MWCNTs on different properties of epoxy resin was investigated by Gojny et al. [Gojny et al., 2004]. The epoxy resin Ruetapox LV 0164 was hardened with a poly-ether amine hardener Jeffamine T-403. Composites with non-functionalized and amino-functionalized nanotubes containing 0.05–0.75 wt% MWCNTs were prepared. For the synthesis of composites, the raw CNTs were first purified by oxidation and then surface modified by amine functionalization. These tubes were manually mixed into the hardener, sonicated for 20 min at 30% amplitude, mixed with the epoxy resin and again sonicated for 10 min. Finally, the composites were cured for 5 h at 80°C followed by 3 h at 130°C in vacuum for post curing.

Fig. 11. TEM-image of the dispersion of catalytically grown CNTs in an epoxy matrix. Reproduced from Gojny et al., 2004.

The TEM analysis of the sample (refer Fig.11) showed very good dispersion of functionalized nanotubes in the polymer matrix. The SEM images of the fractured surface of composites prepared in different methods revealed that suspending nanotubes in a curing agent like polyetheramine leads to homogeneous stable dispersion. The resulting composite neither showed agglomeration nor a fracture pattern. This indicates the presence of strong interfacial interactions between the CNTs surfaces with epoxy matrix.

Among the various methods, the effects of electric fields on CNTs dispersion in epoxy matrix during curing have also been investigated [Martin et al., 2005]. In a typical preparative method, 0.01 wt% CVD-grown MWCNTs (OD = 50 nm) were dispersed in about 15 g of bisphenol-A epoxy resin for 60 min at RT using a dissolver disk, rotating at 2000 rpm. The mixture was equilibrated at 60°C for a 10 min stirring at 2000 rpm, and then

the hardener (Araldite HY 932) was added (at 32/100 hardener/resin ratio). The mixture was stirred again for 1 min at 60°C at 500 rpm, and then left standing for 4 min to remove excess air. The composite was moulded and cured at 80°C for 4 h. Throughout the full curing cycle, D.C. and A.C. fields of 50, 100 and 200 V/cm were applied to induce the formation of aligned conductive nanotube networks between the electrodes.

The *in situ* transmission optical micrographs of composite showed that during the application of D.C. electric field, the CNTs moved towards the anode under electrophoresis due to the negative surface charges. The accumulation of nanotubes created high field strength, further adsorbing more and more tubes, forming dendritic agglomerates from 5 min curing time which increased with curing time. In A.C. fields, more uniformly aligned nanotube agglomeration was achieved with the same effect in bulk composites.

To study the effect of incorporation of surface oxidised MWCNTs on the glass transition temperature (T_g) of epoxy matrix, Barrau and co-workers [Barrau et al., 2005] prepared epoxy/MWCNTs composites by blending MWCNTs with epoxy resin. CVD-grown MWCNTs (<3 nm diameter) after acid treatment with HCl were used for composite preparation. CVD-grown MWCNTs containing trapped iron nanoparticles were also used for preparation of MWCNTs-containing epoxy composites [Zilli et al., 2005]. The main purpose of this work was to study the magnetic properties of resulting composites. The epoxy pre-polymer and the curing agent used were DGEBA LY 556 and isophorone-diamine (IPDA HY 2962), respectively. In a typical fabrication process, CNTs (0, 0.03, 0.1, 0.2, 0.4, 0.5 and 1 wt%) with diamine was sonicated in an ultrasonic bath for 30 min. The pre-polymer was then added to the compound, mixed at 700 rpm for 15 min and sonicated again for another 15 min (the amine/epoxy ratio was 1). The mixture was placed in a vacuum and dried for 120 min to eliminate air bubbles. The degassed composite was moulded and cured. The cure schedule was 60 min at 60°C, 60 min at 140°C and 360 min at 190°C. The SEM images of the fractured surfaces of the samples showed increased agglomeration of the CNTs above a threshold weight fraction of 0.4 wt%. Ganguli et al. [Ganguli et al., 2005] and Rajoria et al. [Rajoria et al., 2005] used the same method for the synthesis of MWCNTs containing epoxy composites.

In another article, Liu et al. [Liu et al., 2005] used rubbery and glassy epoxy matrices for dispersing CNTs. The MWCNTs with diameter 30–50 nm and length 1–5 μm were amine-treated with acid and SOCl_2 following the reported procedure [Li et al., 2005; Liu et al., 2003]. Two kinds of aliphatic amine curing agents— α,ω - polypropyleneoxide diamine (Jeffamine D-2000) and glycolitic polypropyleneoxide triamine (Jeffamine T-403)—were used to prepare composites the epoxy resin diglycidyl ether of bisphenol A (Epon 828). To prepare the CNT-epoxy composite, the required amount of functionalized CNTs (1 wt%) was first dispersed in chloroform. The curing agent was then added and sonicated for 1 h. After evaporating chloroform with continuous stirring, a stoichiometric amount of Epon 828 was added to the mixture and stirred for 1 h at 75°C. The mixture was degassed in vacuum for 1 h and moulded. Epon 828/D-2000 samples were cured at 75°C for 3 h and at 125°C for an additional 3 h. The Epon 828/T-403 system was stirred for 15 min at RT, followed by degassing in vacuum for 2 h. The curing was carried out at 80°C for 2 h and 125°C for 3 h.

Parts (a) and (b) of Fig. 12, respectively, show the SEM images of fractured surface of 1 wt % f-MWNTs-epoxy resin composites of Epon 828/D-2000 composite and Epon 828/T-403. It is clear from images that the MWCNTs were dispersed homogeneously in the rubbery Epon 828/D-2000 matrix. Strong interfacial bonding was inferred in this case, as the CNTs were of

Fig. 12. SEM images of fractured surface of 1 wt % f-MWNTs-epoxy resin composites: (a) Epon 828/D-2000 based and (b) Epon 828/T-403 based. Reproduced from Liu et al., 2005.

short free length with no pull out. On the other hand, the CNT dispersion was non-uniform in the glassy Epon 828/T-403 matrix, showing poor adhesion. The CNTs' ends were curved but still embedded in the matrix. The non-uniform dispersion of CNTs into the polymer matrix could be due to the high viscosity of the matrix. A different reinforcing effect of CNTs depending on nature of the polymer matrix is apparent from the images. Dong et al. [Dong et al., 2005] also used the same method for the preparation of MWCNTs-containing epoxy composites.

Fidelus et al. [Fidelus et al., 2005] used two different types of epoxy resins: (i) LY 564/hardener: HY 560 and (ii) Epon 815/hardener: Jeffamine T-403 polyetheramine for the fabrication of CNTs containing epoxy composites. In their experimental procedure, the surfactant sodium dodecyl sulphate (SDS) was first dissolved in tetrahydrofuran (THF) and MWCNTs were dispersed in the solution by ultrasonication for 1 h. Epoxy resin was then added under sonication for 4 min. To evaporate the solvent, the mixture was kept at 45°C overnight followed by 1 h in vacuum. The hardener was added (100:27 ratio for LY 564/HY 560 and 100: 43 ratio for Epon 815/T-403) and mechanically mixed with the epoxy/nanotube mixtures. The mixtures were vacuum dried (30–40 min for LY564/HY560 and 90–100 min for LY564/HY560) and moulded. The LY 564/HY 560 samples were cured at 80°C for 10 h or left at RT for 24 h and then cured at 80°C for 2 h. Epon 815/T-403 samples were cured at 125°C for 3 h.

The CNT dispersion was slightly less uniform in the Epon 815 resin when compared to LY 564 from the SEM images. The fracture surface for LY 564 appeared to be rougher, suggesting good wetting of the tubes in the matrix. These results also indicated that different polymer matrices have dissimilar reinforcing effect with CNTs.

To study the effect of MWCNTs aspect ratio on the properties of final composites, Pumera et al. [Pumera et al., 2006] fabricated MWCNTs/epoxy composites with two different types of MWCNTs. Both types of MWCNTs (CNT-200: length, 0.5–200 μm ; diameter, 30–50 nm; wall thickness, 12–18 nm and CNT-2: length 0.5–2 μm , diameter 20–30 nm, wall thickness 1–2 nm) were produced by the CVD technique. The purification was accomplished by stirring the CNTs in 2 M HNO_3 at 25°C for 24 h. Epoxy resin Epotek H77A and hardener Epotek H77B were mixed manually in the ratio 20:3 (w/w) using a spatula. CNT electrodes have been produced by loading the epoxy resin, before curing, with different amounts [i.e., 10, 12.5, 15, 17.5 and 20% (w/w)] of CNTs and mixed for 30 min. The composite was cured at 40°C for 1 week.

Fig. 13 shows SEM images for: (A) long-carbon nanotube-based CNT-200-EC electrode, (B) short-carbon nanotube-based CNT-2-EC electrode, and (C) the conventional GEC electrode. Results showed good dispersion of CNTs in the polymer matrix in general when compared to the conventional graphite-epoxy composite (GEC). CNT-2-EC showed more uniform dispersion in the epoxy matrix, while CNT-200-EC revealed sponge-like topography. In another work, Ganguli et al. [Ganguli et al., 2006] investigated the effect of loading and surface modification of MWCNTs on the fracture behavior of epoxy composites. The epoxy resin was a two-phase SC-15 epoxy resin system, and the MWCNTs were CVD-grown with 10–50 nm diameter and 1–10 μm length, and each had 10–70 graphene layers. The MWCNTs were surface modified both physically and chemically, the details of which are given in Table 1. The chemical modifications of the MWCNTs were done by a method developed by Xie and Wong i.e., acid refluxing with a nitric-sulphuric acid mixture [Xie et al., 2003]. The bifunctional epoxy resin, SC-15 was mixed with MWCNTs (0.05, 0.1, 0.15 and 0.25 wt%) using a high speed-mixing arm at 3500 rpm in the opposite direction of the mixture. The composite samples were cured and moulded in stainless steel moulds.

Fig. 13. SEM images for: (a) long-carbon nanotube-based CNT-200-EC electrode, (b) short-carbon nanotube-based CNT-2-EC electrode, and (c) conventional GEC electrode. Reproduced from Pumera et al., 2006.

Specimen	Milling	Annealing	Functionalization
MWCNT1	Milled	None	Chem treatment
MWCNT 2	Milled	None	None
MWCNT 3	Raw	None	Chem treatment
MWCNT 4	Raw	None	None

Table 1. Samples used in the study. Reproduced from Ganguli et al., 2006.

The fractured surface morphology of the notched samples from SEM analysis showed ridge formation on all the samples with more fracture for the acid-treated than for the ball-milled sample. The AFM image of the neat resin showed uniform circular indentations formed from the incompatibility of the prepolymer with the hardener during curing. A rougher surface with well dispersed dense MWCNTs was observed for acid-treated composite when compared to the ball-milled sample. Acid treatment was hence found to be advantageous over physical treatment to get better dispersion.

On the other hand, the effect of MWCNT dispersion on the light transmittancy of MWCNT-epoxy composites was investigated by Wang et al. [Wang et al., 2006]. The CVD-grown MWCNTs with outer diameters of 20–80 nm were used for composite preparation. The MWCNTs were first acid-treated and followed by refluxed with SOCl_2 in DMF. Triethylenetetramine (TETA) was then used for surface functionalization. The modified and unmodified MWCNTs were added to molten epoxy resin (bisphenol A-epichlorohydrin epoxy resin, E-44) under magnetic agitation at 80°C for 20 min. The suspensions of MWCNTs in epoxy resin were then sonicated at 80°C for 2 h. The black mixture thus obtained was further added to triethanolamine (TTA) hardener and agitated for 3 min. After degassing in a vacuum oven, the mixture was moulded and cured at 100°C for 2 h, followed by post curing at 120°C for 16 h.

Optical microscopy and TEM were used to study the morphology of the composites. The results showed poor dispersion of unmodified CNTs in the epoxy matrix while the modified CNTs showed relatively uniform dispersion with conglomerations in the nm range.

Kim et al. [Kim et al., 2006] modified MWCNTs by acid, amine treatment or plasma oxidation to improve interfacial bonding and dispersion of nanotubes in the epoxy matrix. CVD-grown MWCNTs with average diameter of 13 nm and length of 10 μm , epoxy resin (YD 128) and hardener (TH 432) were used in the study. The CNTs were purified in a 3:1 65% $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture at 100°C for 30 min. The acid-treated CNTs were functionalized with octadecyl amine (ODA) at 120°C for 5 days or irradiated with Ar plasma containing 1% of O_2 for 1 min. Suspensions of untreated CNTs in ethanol or of chemically modified CNTs in ethanol were sonicated for 2 h and slowly dispersed in heated epoxy resin for 1 h. The mixture was kept under vacuum at 80°C for 5 days to evaporate the ethanol. The plasma-treated CNTs were directly mixed with the epoxy resin.

The SEM images of various samples showed poor dispersion of untreated CNTs in the epoxy. The acid- and plasma-treated tubes showed relatively good dispersion when compared to amine-treated CNTs.

Yaping et al. [Yaping et al., 2006] proposed a new method to disperse MWCNTs homogeneously in an epoxy matrix. CVD-grown MWCNTs (diameter 30–100 nm) were first heated with an excess 2.5 and 20 wt% of diethylenetetramine (DETA) ethanol solution for 30 min, washed with ethanol and dried. MWCNTs and MWCNTs- NH_2 (0.2, 0.4, 0.6 and 1.0%) were added to the epoxy resin at 120°C (CYD-128) and dispersed in a high-speed homogenizer of 20,000 rpm for 20 min. The mixtures were degassed at 90°C for 30 min, and an appropriate amount of hardener (amine 593#) was then added at 50°C. After degasification, the mixture was moulded and cured at 60°C for 1 h. The TEM images showed that the modified CNTs were evenly distributed in the substrate of epoxy resin.

In another recent report, Chen et al. [Chen et al., 2006] proposed a two-step acid-epoxy functionalization of MWCNTs coupled with anionic homopolymerization chemistry to build up the epoxy network. CVD synthesized MWCNTs (length 5–15 μm , diameter 40–60 nm) were acid-treated by refluxing MWCNTs with 250 ml of concentrated 3:1 $\text{H}_2\text{SO}_4/\text{HNO}_3$ (70%) [Liu et al., 1998] followed by HCl addition [Chen et al., 1998] to obtain COOH -MWCNTs. The esterification of $-\text{COOH}$ groups with epoxy monomers phenyl glycidyl ether (PGE) or DGEBA (Epon 828) was carried out in a DMF solution, using triphenylphosphine (TPP) as a catalyst (0.1 mole TPP per mole of epoxy groups). The reaction was performed by refluxing at 150°C under nitrogen for 36 h. After the treatment, PGE-MWCNTs and DGEBA-MWCNTs were thoroughly washed with ethanol, collected with the PTFE membrane and dried in a vacuum oven for 24 h. Various CNT samples (0.5, 1 and 3 wt%)

were dispersed in THF under sonication for 5 min. DGEBA was dissolved in THF (1:1 by volume) in a dual axis high-speed mixer. Both mixtures were blended in the mixer and sonicated for another 5 min. Finally, THF was evaporated in a vacuum chamber at 100°C overnight. 4-dimethylamino pyridine (DMAP) was added to the mixture in a molar ratio of 0.08 mole DMAP per mole of epoxy groups and mixed further 10 min. The final blend was moulded and cured. The curing cycle employed was 3 h at 80°C, 3 h at 120°C and 30 min at 160°C [dell'Erba et al., 2004].

The examination of the composite surface by SEM showed isolated CNT agglomerations with unmodified and acid-treated MWCNTs. PEG and DGEBA modified MWCNTs were dispersed uniformly in the matrix.

Zhang et al. [Zhang et al., 2006] used MWCNTs produced by CVD (10–25 nm diameter, 10–25 µm length) to prepare nanocomposite with epoxy resin. CNTs were ultrasonicated for 1 h in acetone (0.1 mg/ml) and then for another hour after the addition of epoxy. The acetone was then removed by heating the mixture to 70°C while stirring, followed by evaporation under high vacuum at 50°C for 24 h.

The surface analysed by SEM and TEM confirmed a good adhesion between the CNTs and the epoxy matrix without CNT bending or cracking. Capless CNTs were in the bulk debris with deformed walls. This preparation method seems to align the CNTs in the sliding direction.

Thostenson and co-workers [Thostenson et al., 2006] utilized a calendering approach similar to that developed by Gojny et al. [Gojny et al., 2004] to disperse CVD-grown MWCNTs (15–20 nm diameter, length over 10 µm) in an epoxy matrix and studied the evolution of the composite structure during processing. MWCNTs were added to the bisphenol-f epichlorohydrin epoxy resin (Epon 862) by hand mixing. The mixture was processed in the three-roll mill consisting of three chrome-plated hardened steel rolls that are 80 mm in diameter, where the speed of the apron roll was set to 250 rpm. The nanotube/epoxy suspension was processed until there was no material left in the feed area between the feed and centre rolls to ensure shear mixing at progressively smaller gap settings of 50, 30, 20, 10 and 5 µm. The mixture was heated to 50°C in an oven to reduce the viscosity. Curing agent (Epicure W) at a ratio of 26.4/100 was added and mechanically stirred at 500 rpm for 5 min. The resin was then degassed in a vacuum oven for 15 min at 50°C, molded and cured for 6 h at 130°C. Smaller gap settings of 10 and 5 µm produced highly dispersed CNTs with less agglomeration.

The composite morphology and CNT dispersion were investigated by SEM. Composites processed at 10 µm showed CNT pull out along the fracture path with tail like CNT structure in comparison with that processed at 5 µm.

To get a clear understanding of the influence of CNTs incorporation on the performance of epoxy matrix, Zhuang et al. [Zhuang et al., 2006] prepared a series of composites by incorporating MWCNTs (20 µm length, 80 nm diameter) into an epoxy resin. In their study, a low-viscosity epoxy system was used. MWCNTs (0.05%, 0.075%, 0.1%, 0.3%, 0.5% or 1.0%) were dispersed in about 30 ml of acetone by sonication for 10 min. The mixture was poured into the prepared mixture of a novolac epoxy resin (F-51), methyl hexahydrophthalic anhydride (MHHPA) hardener with 4, 6-tris (dimethylaminomethyl) phenol (DMP-30) as accelerator and then processed for 2 h by ultrasonication along with mechanical stirring at about 100 rpm at 60–70°C for 10 min. The prepared mixture was molded, degassed in a vacuum oven at 80°C for 30 min and then heated according to the specified curing schedule. The curing conditions for the prepared composites are given in Table 2.

No.	Cure Process
1	24 h at 80°C
2	3 h at 80°C+24 h at 100°C
3	3 h at 80°C+24 h at 120°C
4	3 h at 80°C+3 h at 120°C +3 h at 150°C
5	3 h at 80°C+3 h at 120°C +3 h at 150°C+3 h at 180°C

Table 2. Different cure conditions for neat epoxy and MWCNT-epoxy composites..
Reproduced from Zhuang et al., 2006.

CNT concentration from 0.5 wt% produced agglomerations, and according to the authors, the CNT content should be smaller to ensure the stable dispersion of the tubes. 0.1 wt% of CNTs was found to be the critical tube content giving homogenous distribution. The fracture surface analysed by SEM of the samples with 0.1 wt% CNTs cured at different temperatures showed different adhesive nature for the CNTs in the matrix. 100–120°C was found to be the optimum. At lower temperature, curing was insufficient, while at higher temperature, bonding was poor due to the difference in thermal expansion coefficient of the epoxy and CNTs.

Sham et al. [Sham et al., 2006] studied the influences of UV/O₃ as well as TETA treatments for the surface functionalization of MWCNTs and dispersion in an epoxy matrix. The MWCNTs (diameter 10–20 nm, length 10–50 µm, surface area 420 m²/g) were dispersed in acetone via ultrasonication, washed with de-ionized water and dried at 80°C. The MWCNTs were then subjected to UV/O₃ treatment (in a Jelight 144AX-220 UV/ O₃ cleaning system) at varying exposure durations from 2 min to 1 h. The UV/O₃ treated MWCNTs were mixed with a TETA solution and sonicated at 60°C for 1 h. The mixture was then rinsed using excess acetone and filtered. The treated MWCNTs were sonicated with DGEBA (Epon 828) for 5 h followed by out gassing in a vacuum oven at 80°C overnight. A stoichiometric amount of curing agent, metaphenylenediamine (mPDA), was added into the mixture and carefully stirred for 3 min. The mixture was moulded and cured at 80°C for 2 h, followed by post curing at 150°C for 2 h.

The dispersion of CNTs in the polymer matrix was studied by optical microscopy. The CNT surface became more hydrophilic after UV/O₃ treatment and amine functional groups increased the dispersion of CNTs in the matrix. This method gives an alternative approach to oxidize CNTs through damaging process like concentrated acid treatment.

Ci et al. [Ci et al., 2006] evaluated the different reinforcement roles of CNTs in those composites with different matrix stiffness while the curing process is controlled. To understand that, MWCNTs (diameter 20–60 nm) produced by a floating catalyst method [Andrews et al., 1999] were dispersed in acetone by ultrasonication for 1 h, filtered and dried. To prepare CNT-epoxy composite, the 0.5 wt% CNT powder was directly added into a liquid epoxy (bisphenol A-epichlorhydrine), and the solution was mechanically stirred for 5 min to form a homogeneous suspension. 10.7 wt% of an epoxy hardener (triethylenetetramine) was mixed into the suspension and softly stirred for about 2 min. The mixture was placed in a vacuum chamber for about 30 min. Finally, the suspension was moulded and cured for 48–72 h. A series of matrices with different stiffness were prepared by changing the epoxy/hardener ratio and the curing time. High magnification SEM images of soft and stiff matrices showed CNT pull out from the fracture surface. In the soft matrix, good interfacial bonding was observed between the CNTs and the matrix. The results indicated that CNTs have different reinforcing roles for the same polymer depending on the stiffness of the matrix.

Moisala and co-workers [Moisala et al., 2006] reported the use of 80 μm long CVD-grown MWCNTs [Singh et al., 2003] (0.005-0.5 wt%) in an epoxy system consisting of a bisphenol-A resin (Araldite LY 556) and an aromatic amine hardener (Araldite XB 3473). The composites were made by the high-shear mixing procedure published by Sandler et al [Sandler et al., 2003].

Vacuum-assisted resin transfer moulding (VARTM) process was also used to fabricate epoxy-based composites [Qui et al., 2007]. In a typical processing, pristine and functionalized MWCNTs were infused through and between glass-fibre (A1010 uni-warp knitting glass fibre) tows along the through-thickness direction (refer Fig. 14). MWCNTs were refluxed with a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ for 30 min, washed with distilled water and filtered. Functionalized MWCNTs were dispersed ultrasonically in the curing agent Epicure W followed by addition of Epon 862. CNT-dispersed resin fluid was infused into the layers of fabric, and the impregnated fibre cloth (pre-preg) was laid up to fabricate composite parts through conventional VARTM.

Fig. 14. Illustration of through-thickness reinforcement by CNTs: (a) one ply fabric and (b) one ply fabric impregnated by MWCNT-resin. Reproduced from Qiu et al., 2007

The wetting and dispersion effects of the MWCNT-resin fluid in the glass fabrics examined by optical microscopy showed successful impregnation in the layered fabrics with CNTs (acid-treated CNTs gave better results) both in inter- and intra-tow arrears. Similar method was also used by Lee et al. [135] for the fabrication of epoxy composites.

CNTs-containing epoxy composites were fabricated by using four different processing conditions, as listed in Table 3 [Li et al., 2007; Ma et al., 2007]. SEM images showed large agglomerated from Conditions A and B whereas these agglomerates were almost completely absent for the composites produced by Conditions C and D. Silane functionalized CNTs (condition D) were dispersed more uniformly, confirming much better dispersion of CNT in epoxy matrix. The optical microscope images showed CNT agglomerates within small localized area for Condition A. For Condition B, the CNT agglomerates covered a larger area. Though the disentanglement was satisfactory for Condition C, the dispersion was poor. The surface treatment provided in Condition D reduced the re-agglomeration and gave a good dispersion state for the CNTs. TEM images showed that there was a systematic reduction in the packing density or “degree of entanglement” that occurred in the order of Conditions A-D, and the corresponding aspect

ratios decreased because of the gradual breakage of CNTs. This article highlighted the importance of silane treatment for improved interfacial interactions and CNT dispersion in epoxy matrix.

Condition	Dispersion Method
A	As received CNT+ epoxy shear mixing for 30 min at 3000 rpm
B	CNTs dispersed by ultrasonication for 1 h in acetone + epoxy Ultrasonication for 2 hat 60°C
C	UV/O ₃ treatment of CNT for 1h and ultrasonication for 2h in acetone+ epoxy Shear mixing for 30 min at 3000 rpm
D	CNTs were ball milled for 2h ultrasonicated in toluene for 1h UV/O ₃ treatment for 2h, followed by Silane treatment [202] + epoxy Ultrasonicated for 2 hat 60°C

Table 3. Processing conditions used to disperse CNTs. Reproduced from Li et al., 2007.

In a similar type of work, Chen et al. [Chen et al., 2007] described the influence of different dispersion methods of CNTs in epoxy resin. The MWCNTs (diameter 10–30 nm, length 5–15 μm, surface area 40–300 m²/g) were dried at 100°C for 2 h and were crushed with a mortar for 10 min before mixing (untreated). The dried CNTs were mixed with a HNO₃ solution (4 mol/l) was boiled at 100°C for 1–2 h while stirring at 300 rpm, washed and dried (acid-treated). The acid-treated CNTs were sonicated in a solution of the coupling agent 3-glycidyloxypropyltrimethoxsilane (GLYMO) in acetone (13.6 mol/L) (the weight ratio of coupling agent to CNTs was 1:10 until all the solution was completely evaporated (functionalized). A dual asymmetric centrifuge (speed mixer) was used to mix the CNTs into the hardener or the resin (the resin to hardener ratio was 1:4). The other dispersion methods used were sonication and hand mixing. The mixture was then moulded and cured by heating from 20 to 60°C in 2 h, heating from 60 to 80°C in 2 h and holding at 80°C for 4 h. Zhou et al. [Zhou et al., 2007; Zhou et al., 2008] used a high intensity ultrasonication to process the MWCNT-epoxy composite. Pre-calculated amounts (0–0.4 wt%) of MWCNTs (length 3–10μm, diameter 30–50 nm) and Epon 862 resin were mixed together under high intensity ultrasonication for 1 h on pulse mode, 50 s on/ 25 s off along with ice-cooling. Epicure W (100:26 resin: hardener) was added to the modified resin and mixed using a high-speed mechanical stirrer for about 10 min. The liquid was preheated to 80°C in a vacuum oven for 30 min to reduce its viscosity, molded and cured for 4 h at 120°C. The SEM images showed that ultrasonic cavitation is an efficient method of infusing CNTs into epoxy resin when CNT weight fractions are lower than 0.3 wt%. CNTs uniformly dispersed in the matrix prevented crack propagation and increased surface roughness. Above the 0.3 wt%, CNTs agglomerated.

In another report, García and co-workers [García et al., 2007] manufactured epoxy nanocomposites by wetting as-grown arrays of vertically grown CNTs (synthesized by CVD) by the submersion method. Two grades of SU-8 UV-curing thermoset epoxy (Microchem 2000.1 and 2025) were selected to prepare the composites. The substrate with CNT pillars was inverted on a stage above a reservoir containing the SU-8 resin. The substrate was then lowered until the pillars contacted the surface of the reservoir. The CNT pillars were soaked for 2 min, and subsequently the SU-8 was cured by the standard process: pre-baking at 65°C for 2 min and at 95°C for 5 min, UV curing for 90 s, post-baking

for 1 min at 65°C and 3 min at 95°C and a final post-baking step at 135°C for 24 h. The regularity of the contraction and the vertical alignment of the CNTs following wetting and curing were revealed by the SEM images. The wetting results showed that the capillarity effect wets CNTs with polymers having viscosities similar to resins used as matrices for traditional composite materials.

On the other hand, Tseng et al. [Tseng et al., 2007] proposed a novel method for the preparation of epoxy composite through the use of functionalization of MWCNTs by plasma treatment and maleic anhydride (MA). CVD-grown MWCNTs were purified by HCl refluxing and oxidation at 600°C. Then the MWCNTs were subjected to plasma treatment [Tseng et al., 2006a, Tseng et al., 2006b]. MA with a concentration of 0.1 M dissolved in toluene was injected into the reactor to graft onto the MWCNTs surfaces at 50°C for 3 h (CNTs-MA). The CNTs-MA were washed by toluene, centrifuged and dried at 70°C overnight. For the preparation of the CNTs-MA-epoxy composites, first, CNTs-MA were added into the diamine curing agent, *N,N'*-bis (2-aminopropyl) polypropylene glycol, and the mixture was shear mixed for 2 h and sonicated for another 15 min. Subsequently, Epon 828 resin was added and further shear mixed at 80°C for 30 min. Finally, the resulting mixture was outgassed in a vacuum oven for 2 h and then moulded and cured. The curing cycle was 80°C for 2 h, 120°C for 2 h and 140°C for 4 h.

The SEM and TEM images of fractured surfaces of the un-functionalized CNTs (u-CNTs) based epoxy composites showed non-uniform dispersion and formation of agglomerates for untreated CNTs (u-CNTs), while the CNTs-MA system showed good homogeneity and dispersion with CNTs tightly held to the matrix.

Bekyarova et al. [Bekyarova et al., 2007] used electrophoresis for the selective deposition of MWCNTs on woven carbon fabric. The CNT-coated carbon fibers (CF) panels were subsequently infiltrated with epoxy resin using VARTM to fabricate multiscale hybrid composites. CVD-produced MWCNTs (length 2–6 µm) were refluxed with nitric acid to functionalize them with –COOH groups and were dispersed in water by ultrasonication to obtain dispersions of 0.05 mg/mL. For the electrophoretic deposition, carbon fabric IM7 was fixed in a stainless steel frame, and two stainless steel plates were positioned on both sides as counter electrodes. The carbon fabric was immersed in the nanotube dispersion, and a positive potential of 10 V/cm was applied to the CF. The CNT-CF preforms were infiltrated with epoxy (Epon 862) mixed with the curing agent (Epikure W) using VARTM. After the infiltration of epoxy, the composites were cured for 6 h at 130°C.

From the SEM images, the MWCNTs were found to be deposited as individual tubes with some tubes protruding from the CF surface. The examination of the interface between the CF matrix and the CNTs showed that the CNTs were strongly attached to both the CF and the epoxy matrix.

Sandoval et al. [Sandoval et al., 2007] dispersed controlled amounts of MWCNTs in stereolithography layered (SL) epoxy-based resins. Commercially available epoxy-based SL resins – DSM Somos® WaterClear™ and WaterShed™ – were used as the composite's matrix materials. MWCNTs prepared by CVD (diameter 15–45 nm, length 5–20 µm, surface area ~220 m²/g) were purified by means of acid etching and directly seeded in the SL resins to the desired concentrations by means of shear and ultrasonic dispersion for 1 h. The nanocomposite was poured into a vat to manufacture sample parts by selectively curing it to a prescribed geometry using standard SL manufacturing in the multi-material SL machine.

The SEM image taken from the down-face of the sample showed a “winkling effect” which never existed in the pure SL resins, whereas the upper surface was smooth. TEM results

showed affinity between the composite's constituents and strong interfacial bonding effects (buckled nanotubes).

Yuen et al. [Yuen et al., 2007] prepared MWCNT-epoxy composites with CVD-grown MWCNTs (diameter 40–60 nm, length 0.5–40 μm , surface area 40–300 m^2/g). A DGEBA type epoxy resin was dissolved in acetone. The CNTs were also dispersed in acetone. The two solutions were mixed, 4,4'-diaminodiphenyl sulfone solution (curing agent) was added, and the blend was stirred thoroughly. Solvent was removed completely at 40°C. The composite was cured at 150°C for 4 h, followed by post curing at 180°C for 1 h. SEM images showed that the CNTs were mostly buried inside the epoxy matrix with aggregation of some of the CNTs.

Camponeschi et al. [Camponeschi et al., 2007] investigated the effect of orientation and alignment of MWCNTs embedded in different epoxy polymer matrices [Aeropoly (AP) and Coldfix] under an external magnetic field. The CNTs were dispersed in the resin through ultrasonication. TEM images revealed that CNTs are aligned in the direction of applied magnetic field in the case of AP systems whereas CNTs in the CF system showed various regions of local alignment not necessarily in the field direction.

For the preparation of MWCNTs containing epoxy composites, Abdalla et al. [148] and Shen et al. [Shen et al., 2007] used different amino-functionalized MWCNTs, whereas Kovacs et al. [Kovacs et al., 2007] employed a master batch approach. In a typical preparative method, a master batch of epoxy resin containing a high nanotube concentration was prepared with a dissolver disk rotating at 2000 rpm for 2 h at RT. An appropriate amount of hardener (mixing ratio of 23:100 parts per weight of hardener versus resin) was added and subsequently processed in three different ways. The first sample set was stirred at 500 rpm for 10 min at 80°C then poured into aluminium moulds and further stirred at 50 rpm for 5 min at 80°C (referred to as slow stirring, SS). The second and third sets of samples were stirred at 500 rpm for 10 min at 80°C (medium stirring, MS) and 2000 rpm 15 min at room temperature (fast stirring, FS). The filler concentration in the remaining master batch was then lowered by adding pure resin and again stirred for 30 min at 2000 rpm. All samples were cured in an oven at 120°C overnight.

Fig. 15 shows light microscopy images (7.5 mm width and 5.5 mm height) of 0.5 mm thick samples from each preparation method (rows) and with different nanotube concentrations (columns). The microscopy images of various samples showed gradual development of CNT network to a superstructure in all the processing conditions. Above 0.2 wt% of CNTs, all samples showed homogeneous CNT dispersion.

Yaglioglu et al. [Yaglioglu et al., 2008] presented a process for transfer-printing films and arrays of patterned microstructures by incorporating vertically aligned CNTs (VA-CNTs) in a layer of conductive epoxy. VA-CNTs were deposited on a substrate coated with patterned catalyst by the CVD method. A copper substrate was coated with a thin layer of two parts of isotropic conductive epoxy (Loctite 3888) consisting of silver paste and a hardener. The substrate was brought in contact with the CNT column, a gentle vertical pressure was applied and the assembly was cured at 150°C for 30 min. The copper substrate was then manually separated from the silicon substrate, and the CNT columns were transferred to the copper substrate, owing to the relatively strong adhesion with the epoxy compared to the weak adhesion to the growth substrate.

Fig. 15. Light microscopy images (7.5 mm width and 5.5 mm height) of 0.5 mm thick samples from each preparation method (rows) and with different nanotube concentrations (columns). Reproduced from Kovacs et al., 2007.

Sample	Sequence of addition of constituents	Mixing speed (rpm)	Mixing time	Curing temperature and time	Mixer
A	(1) Epoxy+MWCNT (2) (1)+hardener	(1) 720 (2) 80	(1) 1 h (2) 10 min	(2) 80°C, 2 h	Stirrer
B	(1) Epoxy+ethanol+MWCNT (2) (1)+hardener	(1) 720 (2) 80	(1) 1 h (2) 10 min	(1) 80°C, 2 h (2) RT, 48h	Stirrer
C	(1) Epoxy+ethanol+MWCNT (2) (1)+hardener	(1) 720 (2) 80	(1) 1 h (2) 10 min	(1) 80°C, 2 h (2) 80°C, 3 h	Stirrer
D	(1) Epoxy+MWCNT (2) (1)+hardener	(1) 2000 (2) 2000	(1) 1 min (2) 1 min	(2) 80°C, 3 h	Planetary mixer
E	(1) MWCNT + Epoxy (2) (1)+hardener	(1) 2000 (2) 2000	(1) 4 min (2) 1 min	(2) 80°C, 3 h	Planetary mixer
F	(1) MWCNT + Epoxy (2) (1)+hardener	(1) 2000 (2) 2000	(1) 4 min (2) 1 min	(2) 80°C, 3 h	Planetary mixer
G	(1) Epoxy+hardner (2) (1)+MWCNT	(1) 2000 (2) 2000	(1) 20 s (2) 1 min	(2) 80°C, 3 h	Planetary mixer
H	(1)Epoxy+hardner (2)+MWCNT	(1) 2000 (2) 800	(1) 20 s (2) 1 min	(2) 80°C, 3 h	Planetary mixer

Table 4. Processing conditions for various samples. Reproduced from Hu et al., 2008. studies by SEM showed no noticeable difference for fractured surfaces of various samples indicated that processing methods had no effect on morphology.

An in situ polymerization process was used by Hu et al. [Hu et al., 2008] for the fabrication of CNT-epoxy composites. In this study, an insulating bisphenol-F epoxy resin (jER806) with an amine hardener (Tomaïdo 245-LP) was used. Two kinds of mixing machines—a 4-bladed propeller stirrer with the highest rotation speed of 720 rpm and another planetary mixer with two rotation axes—were used in experiments. Eight samples with 2 wt% MWCNTs loading were prepared under different conditions. For all samples, the ratio of epoxy resin to the hardener was 5:3. The processing conditions are summarised in Table 4.

Fig. 16. SEM images of: (a) CSD/epoxy and (b) CMW/epoxy composites showing tube dispersion. Reproduced from Perez et al., 2008.

Like Pumera et al. [Pumera et al., 2006], Pèrez and co-workers [Pèrez et al., 2008] also studied the effect of aspect ratio (length/diameter) of MWCNTs on epoxy matrix reinforcement. CVD-grown CNTs of two different morphologies were used for the preparation: CSD (diameter 3–170 nm, length 5–9 μm) and CMW (diameter up to 45 nm, length 30 μm). The aspect ratio (L/d) of the CMW nanotubes was approximately 17 times larger than that of the CSD ones. First, the desired amount of tubes was dispersed in ethanol for 2 h at RT using an ultrasonic bath. The ethanol/tubes solution was then mechanically mixed with the epoxy resin (Epon 828) at 80°C for 2 h using a magnetic stirrer. The ethanol was then fully evaporated in a vacuum oven at 80°C. The resin/tubes mixture was again stirred for 1 h at 75°C under mechanical agitation. The curing agent *m*-phenylenediamine (mPDA) was then added into the resin under agitation at 75°C, moulded and cured for 2 h at 75°C followed by 2 h at 125°C.

SEM images [refer Fig. 16 (a) and (b)] showed relatively good dispersion for CSD tubes. The shorter length CMW tubes appeared to be agglomerated. Authors believe the high viscosity of the CMW/ethanol mixture which is unfavourable for the composite processing and dispersion.

Yeh et al. [Yeh et al., 2008] reported the fabrication and mechanical properties of MWCNT-epoxy composites by the hot press method. MWCNTs (diameter 20–40 nm, length 5–15 μm) were used as the reinforcement in the epoxy E120-H100. The epoxy was first mixed with the hardener completely, and the mixed compound was put in an oven at 60°C for 5 min. Different weight percentages (0–5 wt%) of MWCNTs were added to the epoxy compound and mixed by a magnetic stirrer for 10 min at 60°C. The composite was kept in the oven at 60°C for another 5 min to increase its viscosity and then hot-pressed at 80°C under pressure (150 psi) for 2 h. Topographical results from SEM revealed good adhesion between the CNTs and the epoxy matrix.

Li and co-workers [Li et al., 2008] used both CNTs and graphite nanoplatelets (GNPs) for the fabrication of epoxy based composites. GNPs with average thickness and diameter of 4.5 and 46 μm , respectively were produced from graphite-intercalated compound and MWCNTs (diameter 10–20 nm, length 10–50 μm) were prepared by CVD. The CNTs and GNPs were exposed to ultraviolet (UV) light for 20 min and an ozone environment for 5 min to introduce oxygen-containing functional groups on their surfaces. Treated CNTs were sonicated in acetone for 4 h. Epon 828 epoxy was added and mixed via sonication for 2 h. The treated GNPs were subsequently added and mixed using a high shear mixer for 30 min at 3000 rpm. Ultrasonication for 1 h at 80°C followed to further break the agglomerates. The mixture was out-gassed at 80°C for 2 h, and a curing agent (1,3-phenylenediamine) was added to the mixture in the ratio of 14.5/100 by weight. The composite was moulded and cured at 80°C for 2 h, followed by post-cure at 150°C for 3 h. Several different combinations of CNT/GNP hybrid nanoreinforcement contents were added into the epoxy matrix, with the CNT contents ranging 0–1.0 wt% while the total filler content was maintained at 2 wt% loading.

Santos et al. [Santos et al., 2008] investigated the nanocomposite prepared from CVD-grown MWCNTs (diameter 10–40 nm, length 5–20 μm , surface area 136 m^2/g), XR1555 epoxy resin and HY-951 Aradur hardener. MWCNTs were suspended in a 1 wt% SDS solution [Connel et al., 2002], and the mixture was ultrasonicated for 90 min. The suspension was centrifuged, and acetone was added to the supernatant to flocculate and remove nanotubes from the suspension. The CNTs were dispersed in the epoxy resin with simultaneous low mechanical stirring and strong sonication for series 1. Next, the hardener was added to the nanotube-epoxy mixture. For series 2, CNTs were dispersed in acetone and then in epoxy. The mixture was maintained in a vacuum oven at 60°C for 15 h for solvent evaporation, and in sequence, the hardener was added with low mechanical agitation and strong sonication. The samples were moulded and cured as follows: (i) temperature ramp of 1°C/min up to 40°C and kept isothermal for 2 h at 40°C and (ii) temperature ramp of 1°C/min up to 60°C and kept isothermal for 8 h at 60°C. The reaction was completed in a vacuum stove for 7 days at 30°C. The successful enhancement of CNT dispersion by using the solvent similar to other reports [Liao et al., 2004; Park et al., 2003; Barrau et al., 2005; Yuen et al., 2007] was revealed by infrared optical microscopy and SEM analyses. The SEM images showed that the unidirectional cleavage and smooth fracture surfaces of the neat epoxy matrices became isotropic and rough after the introduction of the fillers for both the series. However, the MWCNT aggregates (series 1) were concentrated in small areas whereas in composites (series 2), the nanotube bundle distribution seems more homogeneous throughout the entire surface.

2.1.2 Thermal and mechanical properties

Composite materials consisting of a polymer and CNTs frequently exhibit improved thermal and mechanical properties when compared to those of pristine polymers containing a small amount of CNTs. Improvements include higher modulus, increased strength, thermal and thermo-mechanical stability. However, the degree of improvement of thermal and mechanical properties of epoxy-based composites materials directly depends on the nature of MWCNTs and matrix, and also the method used to fabricate composites.

Schadler et al. [Schadler et al., 1998] studied the mechanical behaviour of the epoxy composite with CVD-grown CNTs under compression and tension by measuring the shift for the sensitive second order CNT-Raman peak at 2700 cm^{-1} [Rao et al., 1997]. The analysis showed a larger Raman peak shift in compression (7 cm^{-1} negative) compared to tension,

showing effective load transfer. The composite modulus increased significantly in compression mode with respect to pure resin. The similar types of results also reported by Cooper et al. [Cooper et al., 2001] by observing the stress-induced Raman shift, the modulus of MWCNT composite was calculated as 0.3 TPa.

Table 5 shows the effect of surfactant on the thermo-mechanical properties of CNT-epoxy composites [Gong et al., 2000]. From the results it is obvious that while the addition of CNTs alone increases the storage modulus and glass transition temperature (T_g) moderately (surfactant by itself has little effect), both properties increase significantly with the addition of CNTs in the presence of the surfactant. Addition of 1 wt% CNTs gave more than 30% improvement in storage modulus.

On the other hand, Cui and co-workers [Cui et al., 2003] found that a higher amount of the surfactant decreased T_g because of the plasticizer effect, although MWCNTs were homogeneously dispersed in the epoxy matrix. A regular increase of T_g with tube content was observed for the samples without surfactant, which could be associated with increasing interface area with a rather good anchoring [Keddie et al., 1994; Long et al., 2001]. There was no significant change of T_g with the series prepared with surfactant, which contradicts the results from Gong et al. [Gong et al., 2000]

Samples	G' (GPa)			T _g (°C)	
	-60 (°C)	-20 (°C)	20 (°C)	tanδ	G''
(a) epoxy	1.90	1.65	1.43	63	50
(b) epoxy + C ₁₂ EO ₈	1.53	1.38	1.20	62	47
(c) epoxy + 1 % tube	2.12	1.90	1.60	72	53
(d) epoxy + C ₁₂ EO ₈ +1 % tube	2.54	2.18	1.80	88	64

Table 5. Storage moduli and glass transition temperatures (T_g) of pure epoxy and composite samples. Reproduced from Gong et al.,2000.

The hardness and flexural properties of epoxy composite containing varying amount of CNTs were studied by Lau and colleagues [Lau et al., 2003]. The hardness of the CNT-composites was superior to that the pure epoxy and the hardness increased with CNT content. However, the bending strength of pure epoxy decreased with the introduction of CNTs, revealing that the load was not transferred effectively to the CNTs due to poor interfacial interaction. Park et al. [Park et al., 2003] also used sonication to prepare the composites. The tensile strength and modulus of composite increased with increase in CNT content (0.5 to 2 vol%), whereas elongation at break decreased systematically. A 50% improvement in tensile strength was observed with 2 vol% of CNTs, and the modulus increased two times compared to the pure resin.

Wan et al. measured the mechanical properties of CNT-epoxy thin film prepared by spin coating using a shaft-loaded blister method [Wan et al., 1999]. The results showed that 0.1 wt% of CNTs loading can enhance the elastic modulus of the pure epoxy thin film by 20%, however, the failure strain of composite was lower than neat resin. This is due to strong interfacial bonding between CNTs and the matrix.

The effect of oxyfluorination of CNTs on the surface fracture properties of epoxy matrix was also reported [Park et al., 2004]. Impact strength and fracture toughness showed maximum values for the composite prepared using CNTs with highest surface oxygen and fluorine groups. Oxyfluorination contributed to the enhancement of adhesive forces between the filler and epoxy by changing the surface polarity and activity of CNTs.

In another report, Xie et al. [Xie et al., 2000] analysed the cure kinetics of an industrially used epoxy polymer TGDDM/DDS blended with MWCNTs using differential scanning calorimetry (DSC). Previous studies showed autocatalytic mechanism for TGDDM/DDS composite curing [Cole et al., 1991; Nam et al., 1993; Barral et al., 1998]. The present study revealed the accelerating effect of MWCNTs on the epoxy curing reaction during the initial stage (autocatalytic nature), which decreased with increasing amounts of CNTs. The catalytic effect of MWCNTs in the initial stage was attributed to the surface -OH groups which help in opening the epoxide rings. The reaction becomes diffusion controlled at higher CNT content. The authors used the autocatalytic model by Sourour and Kamal [Sourour & Kamal, 1976] with modification through diffusion control function to explain the entire curing process.

Fig. 17. The effect of MWCNTs and MWCNTs-NH₂ content on: (a) impact strength and (b) bending modulus of MWCNTs-containing epoxy composites. Reproduced from Yaping et al., 2006.

Compound	Structure
Ethylenediamine (e-MWCNT)	$H_2NH_2CCH_2NH_2$
1,6-Hexanediamine (h-MWCNT)	$H_2NH_2CCH_2CH_2CH_2CH_2CH_2NH_2$
4,4'-Diaminodiphenylmethane (p-MWCNT)	$H_2N-C_6H_4-CH_2-C_6H_4-NH_2$
4,4'-Diamino-dicyclohexyl methane (c-MWCNT)	$H_2N-C_6H_{10}-CH_2-C_6H_{10}-NH_2$

Table 6. Exact compounds for different functionalization. Reproduced from Shen et al., 2007

Epoxy composites prepared with amine functionalized MWCNTs were used to investigate the thermo-mechanical properties [Gojny et al., 2004]. The results from dynamic-mechanical thermal analysis (DMTA) showed a strong increase in storage modulus around T_g below which there was no noticeable effect. The loss modulus also increased from 0.05 wt% CNTs

but decreased at higher CNT-content probably due to agglomeration. The addition of CNTs (nonfunctionalized and amine-functionalized) showed distinctive increase in T_g for the composites. Stronger increase in T_g was observed for amine-functionalized CNTs with linear dependence on CNT-content. Yaping et al. [Yaping et al., 2006] used multi-functional amine (DETA) for the functionalization of CNTs before adding them to epoxy matrix. They also found that with amine functionalization the CNTs can be better dispersed in the matrix, leading to enhancement in mechanical properties (refer Fig. 17). A significant increase in bending strength and flexural modulus (100% and 58%) could be obtained with very small amount of CNTs (0.6 wt%). Shen et al. [Shen et al., 2007] investigated the reinforcing role of different amine-functionalized MWCNTs in epoxy composites. The thermal decomposition temperature for all the amine-modified CNT-epoxy was higher than that of the pure resin. A maximum increase of 35°C was observed for 0.25 wt% p-MWCNTs (pure MWCNTs) whereas h-MWCNTs (amine functionalized MWCNTs) had the least effect (refer Table 6). Higher amounts of CNTs decreased the decomposition temperature. Introduction of CNTs to the matrix increased the flexural strength and modulus where p-MWCNTs gave the best results. However, they observed a decrease in T_g with amine-functionalized CNTs. Barrau et al. [Barrau et al., 2005] also reported T_g depression of 5°C for the epoxy composite when the CNT content was in the range 0-0.04 wt%. The glassy storage modulus increased below T_g with the addition of the filler though the increase was not linear over the CNT range.

The increase in T_g with the addition of MWCNTs was also reported by Ganguli et al. [Ganguli et al., 2005] MWCNTs significantly increased the ultimate strength and strain to failure of epoxy resin. In comparison to OLS fillers (17% increase), CNTs showed increased fracture toughness (170% increase) when mixed with neat epoxy.

The stiffness and damping properties of the CNT-epoxy composite were examined by Rajoria et al. [Rajoria et al., 2005] with free and forced vibration tests. A 700% increase in damping ratio was observed with an optimum 5 wt% CNTs. Though storage modulus was not affected by CNT addition, loss modulus increased with CNT content and showed a maximum at 7.5 wt%. The stick and slip mechanism was used to explain the increase in damping ratio with no change in stiffness, which implies poor adhesion with no significant load transfer between the filler and epoxy.

Liu et al. [Liu et al., 2005] compared the effect of amine-functionalized CNT rubbery (Epon 828/D-2000) and glassy (Epon 828/ T-403) epoxy polymers. With 1 wt% of CNTs, the rubbery matrix showed significant improvement in tensile modulus (28%), tensile strength and breaking strain, whereas the glassy matrix showed no marginal increase in properties except for the impact toughness. From these observations it is clear that low viscosity epoxy matrix is advantageous for CNT fillers in composite processing. The reinforcing effect of MWCNTs in two different epoxy polymers (Epon 815 and LY 564) has been investigated by Fidelus et al. [Fidelus et al., 2005]. The nanotubes were dispersed using SDS as the surfactant. A large reduction in T_g was observed for LY 564 with 0.5 wt% of CNTs. By contrast Epon 815 showed no change. A moderate increase in Young's modulus was observed for all the composites. LY 564 showed substantial improvement in the tensile strength (70% with 0.5 wt% and 50% with 0.05 wt% MWCNTs loading) while for Epon 815 there was no noticeable change. The reinforcing effect of CNTs was found to be different for different polymer matrices. Ci et al. [Ci et al., 2006] prepared epoxy matrices with different stiffness by controlling the curing step and investigated the reinforcing effect of MWCNTs. According to the results, CNTs have a more significant role in the soft matrix than in the hard matrix. 0.5 wt% of CNTs was found to be enough to produce a 200% increase in

Young's modulus and up to 140% increase in tensile strength, and these values decreased with increasing hardness of the matrix. Camponeschi et al. [Camponeschi et al., 2007] examined the alignment effect of MWCNTs under magnetic field on the mechanical properties of two different epoxy matrices. The AP system showed an increase in tensile modulus and Young's modulus when compared to the coldfix system. When compared to the pure epoxy, the CF-based system showed a detrimental effect on all the properties. The results showed that the alignment of CNTs under magnetic field that leads to improvement in properties depends on the polymer matrices.

The influence of MWCNTs on the friction and wear behaviours of epoxy composites was studied by Dong et al. [Dong et al., 2005] and results are summarized in Fig. 18. The increase in microhardness and reduction in friction coefficient were optimum at 1.5 wt% of MWCNTs. The composite showed lower wear rate compared to pure epoxy polymer. The mechanical reinforcing and self-lubricating properties of MWCNTs help to improve the tribological behaviors of the composite. Zhang et al. [Zhang et al., 2006] also reported the wear properties of CNT-epoxy composites prepared by the ultrasonication method. Addition of only 0.1 wt% of CNTs dramatically reduced the wear rate when compared to the pure epoxy matrix. However, the contact sliding in the wear test is reported to deform the CNTs leading to its fragmentation. Chen et al. [Chen et al., 2007] proposed sonication as a better CNT dispersion method to decrease wear rate for the composites.

Fig. 18. Variation of the (a) microhardness and (b) friction coefficient of MWCNTs-epoxy composites with MWCNTs content. Reproduced from Dong et al., 2005.

Ganguli et al. [Ganguli et al., 2006] in another work used MWCNTs surface modified by different methods to reinforce the epoxy matrix. About 10% increase in the onset point of thermal degradation and a 30-40% decrease in the coefficient of thermal expansion (CTE) were observed for all the nanocomposites. Ball-milled and acid-treated samples exhibited better mechanical properties with 0.1 wt% CNTs. 0.15 wt% gave better results where the fracture toughness increased by 40% and 80%, respectively for ball-milled and acid-treated MWCNT composites. Qiu et al. [Qiu et al., 2007] also used acid-treated MWCNTs dispersed in epoxy to fabricate composites with glass fibre by the VARTM method. With 1 wt% loading of acid-treated MWCNTs, noticeable enhancement in tensile strength, Young's modulus (14% and 20% respectively) and toughness were observed. They also reported a decrease in CTE (25.2%) with the introduction of CNTs to the polymer matrix. Bekyarova et al. [Bekyarova et al., 2007] also used the VARTM technique to produce a CNT-carbon fibre-

epoxy composite. The addition of 0.25% of CNTs resulted in an enhancement of interlaminar shear strength by 27%. Santos et al. [Santos et al., 2008] reported no change in CTE for composites prepared with CNTs dispersed with the help of SDS and acetone.

Fillers	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
No filler (epoxy)	26	1.21	2.33
Untreated CNTs	42	1.38	3.83
Acid treated CNTs	44	1.22	4.94
Amine treated CNTs	47	1.23	4.72
Plasma treated CNTs	58	1.61	5.22

Table 7. Mechanical properties of pure epoxy and CNT-epoxy composites . Reproduced from Kim et al., 2006.

The mechanical properties of composites prepared using MWCNTs functionalized through different methods are summarized in Table 7 [Kim et al., 2006]. Tensile strength, elongation at break and Young’s modulus of the surface modified CNT-epoxy composite were higher when compared to the neat resin. The results were very good, with plasma-treated CNT sample showing the effectiveness of this surface modification. Tseng et al. [Tseng et al., 2007] functionalized MWCNTs by plasma treatment followed MA grafting and prepared a CNT-epoxy composite. Just 0–1 wt% CNTs produced elongation upto 43% (380% increased as compared to the pristine epoxy) and more than 100% improvement in tensile modulus. The T_g also increased significantly with the addition of CNTs (increase was greater for MA-CNTs-epoxy system). Chen and colleagues [Chen et al., 2006] tried two-step acid epoxy functionalization of MWCNTs to improve the dispersibility and flexural strength of the composite. Functionalization with two different epoxides polyethylene glycol (PEG) and DGEBA led to stable and uniform dispersion of CNTs in epoxy. PEG functionalization (monoepoxide) was more efficient in enhancing flexural strength and elastic modulus of the composite. The higher efficiency of PEG was attributed to the presence of more surfaces – OH groups on MWCNTs available for chemical bond formation with epoxy matrix. Abdalla and co-workers [Abdalla et al., 2007] used carboxylated and fluorinated CNTs to reinforce the epoxy matrix. Both functionalizations showed positive results on the mechanical properties, though fluorinated CNTs showed the highest values. T_g and shear moduli were higher for the composites with 1 wt% CNTs.

Thostenson and co-workers [Thostenson et al., 2006] studied the effect of processing conditions on the mechanical properties of composites prepared through intense shear mixing by the calendering method. Though the CNTs were more dispersed with a processing gap setting of 5 μ m, the fracture toughness was higher for composites processed at 10 μ m. The thermal conductivity showed a linear relationship with CNT content; with the highest concentration of 5 wt%, about 60% increase in thermal conductivity was measured. Increase in thermal conductivity with CNT-content was also reported by Moisala et al. [Moisala et al., 2006] On the other hand; Yuen et al. [Yuen et al., 2007] reported no significant improvement in thermal conductivity by adding CNTs to the epoxy matrix, though T_g increased rapidly when the CNT content was below 0.1 wt%. Chen et al. [Chen et al., 2007] tried different CNT treatments and mixing methods to prepare CNT-epoxy matrices and investigated the thermo-mechanical properties. The results indicated that only in the absence of effective dispersion methods like speed mixing or sonication, is pre-

treatment of CNTs (with acid or coupling agent) necessary. The sample produced by the combination of sonication and speed mixing (untreated) showed the highest values for storage modulus and T_g , and the values were very close to those prepared using pre-treated CNTs. Sonication was found to be disadvantageous for acid-treated CNTs as it leads to fracture of pre-damaged CNTs.

While analysing the effect of CNT content and curing temperature on the flexural properties of epoxy matrix, Zhuang et al. [Zhuang et al., 2006] found that the composites possess higher strength at MWCNT content in the range of 0.05–0.1 wt%. A maximum of 9% increase with respect to pure epoxy was observed with 0.075 wt% CNTs. Composites with the same CNT content cured at different temperatures indicated a reinforcing effect between 100 and 120°C. The stiffening effect disappeared at higher temperatures.

An instrumented indentation technique to measure the elastic modulus and hardness of CNT array-epoxy composites was employed by Lee et al. [Lee et al., 2007]. A steady increase in elastic modulus of the composite up to 75% was observed when compared to the neat resin over the entire range of indentation test.

On the other hand, Zhou and co-workers showed that during processing, there is a strong effect of sonication intensity on the thermal and mechanical properties of CNT-epoxy composites [Zhou et al., 2003]. Studies revealed a steady increase in storage modulus with CNT content (93% with 0.4 wt% of CNTs) and about 22°C increase in T_g . However, the decomposition temperature of the composite decreased for composites with higher amounts of CNTs. The modulus also showed gradual increase (11.7% with 0.4 wt% CNTs), but the tensile strength reached a maximum at 0.3 wt% filler content (28.3% improvement). However, Sandoval et al. [Sandoval et al., 2007] used non-localized ultrasonic dispersion to introduce MWCNTs to epoxy matrix. CNTs at a concentration of 0.05% (w/v) in WaterShed™ resulted in an increase of the ultimate tensile strength, fracture strength and hardness at temperatures beyond ~200°C. A 51.8% increase in Young's modulus was noticed with the introduction of 5 wt% CNTs when compared to the pure epoxy specimen [153]. Composites were prepared by hot press. The tensile strength showed a 17.5% increase with 3 wt% of MWCNTs. The properties decreased at higher amount of CNTs.

Fig. 19. DMA results of neat epoxy, CSD/epoxy, and CMW/epoxy composites: (a) storage modulus (E') and (b) loss factor ($\tan \delta$). Reproduced from Perez et al., 2008

Garcia and co-workers [García et al., 2007] used dimensions measured from SEM images to predict the Young's modulus of a vertically aligned (VA) CNT array-epoxy composite. The Young's modulus increased from 3.7 to 12 GPa, and the reinforcement for the CNT pillars was 220%, showing effective reinforcement. On the other hand, Yaglioglu et al. [Yaglioglu et al., 2008] proposed a novel technique to transfer VA-CNTs to copper substrate using epoxy polymer. The Young's modulus of CNT-epoxy composite pillars was calculated to be 1.2 GPa when compared to the as-grown CNT columns (2.2 MPa).

Pérez and co-workers [Pérez et al., 2008] investigated the effect of aspect ratio of MWCNTs on the mechanical properties of the epoxy system. The introduction of nanotubes (CSD or CMW) made the epoxy resin slightly more flexible and tougher with no noticeable increase in strength and a decrease in elastic modulus. These properties were similar for different types of CNTs. However, the impact strength of the epoxy resin improved by 84% when 1 wt% of higher aspect ratio tubes (CMW) were mixed with the resin, and by 63% when the same amount of CSD tubes were used. The storage modulus of CSD epoxy, which was lower than that of neat resin below 97°C, increased between 97 and 135°C. For CMW composites storage modulus was much higher. Both the composites showed an increase in T_g values (refer Fig. 19). Li and co-workers [Li et al., 2008] used a CNT/GNP hybrid to reinforce epoxy matrix. The flexural modulus of the composite was 21% higher than that of the pure epoxy matrix while the flexural strength was not affected. The fracture toughness showed 21% improvement compared to 2 wt% GNP alone and 57% compared to neat epoxy.

2.1.3 Electrical properties

Over the last few years, the potential use MWCNTs as conducting fillers to improve the electrical conductivity of epoxy matrix has been established. Several authors have reported significant enhancement in electrical conductivity with a very small loading of MWCNTs in the epoxy matrix, while maintaining the mechanical performance of composites. Sandler et al. [Sandler et al., 1999] reported the electrical conductivity of an epoxy matrix containing untreated CNTs around 10^{-2} Sm^{-1} at a filler content of 0.1 vol% which is much higher compared to the composite containing conventional carbon black filler. The conductivity showed gradual increase with CNT content. The percolation threshold was found to be in between 0.0225 and 0.04 vol% of CNTs. Park et al. [Park et al., 2003] also found that the resistivity of composite decreased with CNT content, and the threshold concentration reached 0.5 vol.% of CNTs. However, Cui et al. [Cui et al., 2003] reported a relatively high percolation threshold around 8 wt% of CNTs for two series of epoxy composites prepared with and without surfactant from D.C. resistivity measurements. The wrapping of the CNT surface by the surfactant prevents particle-particle interaction and contributes to the high critical wt% of the filler to attain percolation network.

On the other hand, Sandler and co-workers [Sandler et al., 2003] suggested the used of aligned MWCNTs to get a uniquely low percolation threshold. CNT concentration of about 0.0025 wt% was found to be enough to produce the conducting network within the epoxy matrix in this case. Martin et al. [Martin et al., 2004] reported similar results in another work. The bulk conductivity values varied from dielectric nature to 10^{-3} depending on the nanotube aggregation and dispersion levels obtained under various processing conditions. According to them, the processing parameters should be carefully adjusted to achieve very low percolation threshold. Moisala et al. [Moisala et al., 2006] also prepared conductive epoxy composite with MWCNTs with a percolation threshold of 0.0025 wt% using high shear mixing procedure proposed by Sandler et al. [Sandler et al., 2003]. Li and co-workers [Li et al.,

2007] investigated the electrical properties of composites prepared using four different processing conditions. The D.C. conductivity was different for different composites. The results suggested that the formation of conductive CNT network requires a moderate aspect ratio of CNTs and this phenomenon is independent of CNT dispersion state.

Martin et al. [Martin et al., 2005] in another work used A.C. and D.C. electric fields to align a conductive CNT network in epoxy matrix. The network formed under the A.C. field was more uniform and aligned in comparison to that formed under the D.C. field, and hence, the maximum current density was higher for composite formed in the A.C. field. Increase in current density was observed in both the cases with CNT content (0.005–0.02 wt%).

In a very interesting work, Thostenson and co-workers [Thostenson et al., 2006] prepared composites using the calendaring approach and optimized the processing conditions. As seen in Fig. 20, composite with higher CNT dispersion obtained with a 5 μm gap setting showed lower electrical resistivity than that with agglomerated structure especially at lower CNT-content. The effect of processing conditions on electrical conductivity was also investigated by Hu et al. [Hu et al., 2008]. Electrical conductivity of various samples are presented in Fig. 21. It can be seen from figure that the conductivity of the samples prepared with the solvent (B and C) are lower than that of A (without solvent). Higher curing temperature is found to be effective (C) in establishing conducting network in the matrix. The lower conductivity value for sample E revealed that long mixing time has a detrimental effect on conductivity. The procedure in which CNTs were added to the pre-prepared epoxy/hardener increased the conductivity (E). Comparison of samples G and H indicated that slower mixing speed increased the conductivity significantly (see Table 4 for the fabrication conditions).

Fig. 20. DC volume resistivity of the as-processed composites showing percolation thresholds occurring below 0.1%. Reproduced from Thostenson et al., 2006.

Fig. 21. Electrical conductivities of various samples (note that the electrical conductivity of Sample B is lower than 10^{-6} S/m). Reproduced from Hu et al., 2008.

Fig. 22. Comparative plot of the ac conductivity of the CNT-epoxy nanocomposite as a function of the CNT content. Reproduced from Tseng et al., 2007.

The A.C. conductivity of epoxy composite containing plasma-treated MA-modified CNTs was measured by Tseng et al. [Tseng et al., 2007] and corresponding values are presented in Fig. 22. The results showed an increase in conductivity with the introduction of CNTs to the epoxy system, which improved with CNT content. However, the epoxy with

functionalized CNTs showed a lower percolation threshold (0.1–0.2 wt%) than the one with untreated CNTs (0.5–0.6 wt%). Improved conductivity could be attributed to better dispersion of CNTs, which lowers the amount of CNTs required for the formation of conductive network, which contradicts the results by Li et al [Li et al., 2007].

Bekyarova et al. [Bekyarova et al., 2007] demonstrated the enhancement of out-of-plane conductivity by depositing a small amount of MWCNTs on CF and using it as filler in epoxy matrix. A remarkable increase in electrical conductivity by using CNT/GNP filler in epoxy was demonstrated by Li et al. [Li et al., 2008]. Sandoval et al. [Sandoval et al., 2007] also reported a decrease in electrical resistivity in CNT-epoxy composite with percolation threshold around 0.6 wt%. Santos and co-workers [Santos et al., 2008] proposed 0.5 wt% of CNTs as the critical concentration to get improved electrical conductivity for the CNT-epoxy composite prepared by using a surfactant and acetone solvent.

Fig. 23. Comparative plot of the composite conductivity as a function of nanotube weight fraction for the three different sample preparation methods. Reproduced from Kovacs et al., 2007.

On the other hand, for the first time, the possibility of the co-existence of two percolation thresholds was proposed by Kovacs et al. [Kovacs et al., 2007]. Fig. 23 shows the comparative plot of the composite conductivity as a function of nanotube weight fraction for the three different sample prepared using three different methods. Results showed that the percolation concentrations of 0.011, 0.024 and 0.08 wt% for composites prepared by slow, medium and fast stirring, respectively, in the kinetic region (below 0.1 wt% CNT content) due to the emergence of networks between dispersed immobile CNT particles. A plateau was observed thereafter in all the cases similar to that reported by Sandler et al. [Sandler et al., 2003], where the flocculation cannot further improve conductivity through the network. As the concentration increases above 0.1 wt% additional conducting channels establish increasing conductivity.

Pérez and co-workers [Pérez et al., 2008] used MWCNTs of different aspect ratios (CSD and CMW) in the epoxy matrix and studied the electrical properties of the resulting composites.

Measurement of D.C. electrical conductivity indicated that introduction of CSD CNTs has no effect on the conductivity of the epoxy matrix, whereas the high aspect ratio CMW CNTs increased the conductivity of pure resin by 10 orders of magnitude. The percolation threshold was found to be 1 wt% for these composites.

2.2 SWCNT containing epoxy composites

SWCNTs consist of a single sheet of graphene rolled seamlessly to form a cylinder with diameter of order of 1 nm and length up to centimetres. Some SWCNTs are stronger than steel, lighter than aluminium, and more conductive than copper. For example, theoretical and experimental results on individual SWCNTs show extremely high tensile modulus (640 GPa to 1 TPa) and tensile strength (150-180 GPa). Not only that depending on their structural parameters, SWCNT can be metallic or semiconducting. Because of these extraordinary properties of single SWCNT, there is a great enthusiasm to incorporate SWCNTs into the epoxy matrix to fabricate electrically conductive materials with balance of mechanical properties. Over the last few years, researchers are using different techniques to disperse SWCNTs in epoxy matrix. The section below reviews the preparation and physicochemical characterization of various types SWCNTs-containing epoxy composites.

2.2.1 Preparative methods and morphological study

In 2001, Cooper et al. [Cooper et al., 2001] first used SWCNTs as reinforcement for epoxy polymer matrix. The used SWCNTs were synthesized by two different methods such as pulsed-laser SWCNT-P and arc-discharge SWCNT-A. The composites were fabricated by the same procedure used for the preparation of MWCNTs-containing epoxy composites (see section 2.1.1). Ultrasonication was used to incorporate SWCNTs into epoxy resin by Puglia and co-workers [Puglia et al., 2003 a; Puglia et al., 2003 b]. 5 and 10 wt% of SWCNTs (diameter 1.2–2 nm, length several μm) were ultrasonically dispersed for 2 h in the liquid epoxy resin (DGEBA). All samples were then cured with DETA hardener (DETA/DGEBA = 1:7.25) using a cure schedule with a temperature ramp from 30 to 150°C at a heating rate of 10°C/min. The SEM images of the composite with 5 wt% SWCNTs loading showed good interaction between the filler and the epoxy matrix that helps in opening CNT bundles and dispersing the tubes. The same technique was also used by Barrau et al. [Barrau et al., 2003b] for the synthesis of CNT-composite with bisphenol-A epoxy polymer (LY5641) and an amine hardener (HY2954 at resin/curing agent ratio 100/35) by sonication. Purified SWCNTs synthesized by the CVD method (0.04 to 2.5 wt%) were dispersed in ethanol using ultrasonication at RT for 2 h. The liquid epoxy resin was added to the dilute suspension of nanotubes, and the mixture was again sonicated for 1 h. The solvent was removed in a vacuum oven at 80°C, and the mixture was stirred at 2000 rpm for 1 h. The hardener was then added and mixed mechanically at 2000 rpm for 15 min. The mixture was molded and then returned to vacuum for 20 min for degassing. The epoxy matrix was cured in the oven at 120°C for 20 min and then at 145°C for 4 h.

In another work, Barrau et al. [Barrau et al., 2003 a] used palmitic acid ($\text{C}_{16}\text{H}_{32}\text{O}_2$) as a surfactant for the dispersion of CNTs in epoxy polymer solution used in the previous study [Barrau et al., 2003 b]. Acid-purified SWCNTs (content varied between 0.05 and 0.8 wt%) were not dried after acid purification to prevent their agglomeration in bundles. Epoxy resin was added to the CNT solution in water, and the mixture was sonicated for 1 h and dried in a vacuum oven at 100°C for 1 h. Palmitic acid was then added, and the mixture was sonicated

for 1 h at RT. The ratio of nanotubes to palmitic acid varied from 1:2 to 2:1 by weight. Hardener was added subsequently and mechanically mixed. The final mixture was moulded and cured in an oven at 120°C for 20 min and 145°C for 4 h. The SEM images of composite fractured surfaces are given in Fig. 24. The SEM images showed good dispersion of CNTs in the samples prepared with the surfactant. Individual CNTs covered with the surfactant were homogeneously dispersed in the matrix.

Fig. 24. Field emission SEM images of: (a) CNT-C₁₆H₃₂O₂- epoxy composite for 0.8 wt % CNTs and 1:1 CNTs to C₁₆H₃₂O₂ weight ratio. The arrows indicate (A) individual CNTs and (B) CNTs covered with palmitic acid. (b) CNT-epoxy composite for 0.8 wt % CNTs without palmitic acid. The scale bar corresponds to 200 nm. Reproduced from Barrau et al., 2003a.

Significant improvement in the dispersion of SWCNTs was obtained by Zhu and co-workers [Zhu et al., 2003] through acid treatment and subsequent fluorination. HiPco produced SWCNTs were sonicated for 1 h in a 3:1 mixture of H₂SO₄/HNO₃ (70%), washed with NaOH and dried at 70°C overnight. Acid-treated nanotubes were fluorinated [Mickelson et al., 1998] in a Monel reactor heated to 150°C for 12 h with a gas-flow ratio for F₂ and He was 1:10. The functionalized nanotubes (F-SWCNTs) were dispersed in DMF (2 mg/mL) by sonication for 5 min and then for 1 h in an ultrasonic bath. The epoxy resin (Epon 862) was then added, and the solution was stirred for 30 min. DMF was evaporated at 100°C in a vacuum chamber, and the blend was stirred for 5 min with a high-shear mixer. Further stirring was done after adding the curing agent, Epicure W. The blend was degassed for 5 h in a vacuum oven, moulded and cured at 100°C under a pressure of 0.3 MPa for 2 h followed by another cycle of 2 h at 160°C. Optical micrographs and SEM images revealed noticeable enhancement in dispersion of F-SWCNTs throughout the epoxy matrix in comparison with that of the pristine SWCNTs.

Ren and co-workers [Ren et al., 2003] used aligned SWCNTs produced by the arc-discharge [Liu et al., 2000] method for the preparation of reinforced epoxy composite. To fabricate the composite sample, a thin layer of epoxy resin (Epicote 1006) was evenly brushed onto a hard surface. 20 mm-long SWCNT ropes (0.1–0.9 vol. %) were then aligned by a slight tension and laid onto the epoxy layer. More epoxy was then applied to cover the SWCNT ropes, and the composite was cured for 72 h at RT. The SEM image of the fatigue fracture surface, showed good wetting of CNT ropes in epoxy, which indicated strong interfacial adhesion. The long pull out length of CNTs suggested high shear stress between the phases.

In another work, Gou et al. [Gou et al., 2004] fabricated epoxy composites with HiPco bucky paper containing SWCNTs. Epon 862 epoxy resin and Epicure W curing agent were mixed at a weight ratio of 100:26.4 and diluted with acetone. The composite was prepared by the infiltration of resin solution through the bucky paper followed by hot pressing. The sample was cured for 2.5 h at 177°C under pressure, cooled to RT, post-cured at 177°C for 2 h and finally, cooled to RT inside the oven. The SEM analysis showed the presence of curved and interwoven SWCNTs on the composite surface indicating good wetting between the CNTs and epoxy.

The arc discharge-produced SWCNTs were also used for reinforcing epoxy polymer [Valentini et al., 2004]. SWCNTs were purified by selective oxidation and acid refluxing followed by vacuum annealing. SWCNTs (5 and 10 wt%) were sonically dispersed for 2 h in the liquid epoxy resin (DGEBA). All samples were then cured after adding DETA hardener (DETA: DGEBA 1:7.25) with a temperature ramp from 30 to 150°C at a heating rate of 10°C/min. SWCNT-epoxy composites were prepared using an ultrasonication procedure by Zhou et al. [Zhu et al., 2004].

Sample no.	Tip sonication (h)	Bath sonication (h)	Surfactant	Acetone
1	0	0	Yes	Yes
2	6	6	0	0
3	6	0	0	Yes
4	0	6	Yes	0
5	6	0	Yes	0
6	6	6	Yes	Yes

Table 8. Processing parameters of nanocomposite samples. Reproduced from Liao et al., 2004.

Liao et al. [Liao et al., 2004] investigated the various dispersion processes of SWCNT in SC-15 epoxy matrix. BYK-9076 surfactant was added into SC-15 resin solution in acetone. SWCNTs (0.5 wt%) were added to this solution and manually stirred for 10 min. Tip and bath sonication were used to further disperse the nanotubes. The mixture was vacuum dried

Fig. 25. SEM images of (a) SC-15 neat resin, (b) and (c) nanocomposite (sample 3). Reproduced from Liao et al., 2004

at 75°C for 1 h and then cooled to RT. Finally, the mixture was molded and cured in an oven at 60°C for 2 h followed by post-curing at 93.3°C for another 4 h. The composite processing conditions are given in Table 8. The neat resin showed a smooth surface which can propagate cracks easily in the SEM images [see Fig. 25 (a)]. However, the higher degree of surface roughness with highly curved crack propagation pattern was observed for the nanocomposite [see Fig. 25 (b)].

To study the effect of incorporation of SWCNTs on the nanomechanical properties of epoxy matrix, Li and co-workers [Li et al., 2004] prepared a series of composites with varying SWCNTs loading. In a typical procedure, Epoxy monomer [1,1-bis (4-cyanatophenyl) ethane] pre-polymerized at 80°C for 48 h was also dissolved in THF. 2 g of SWCNTs were purified by acid refluxing, functionalized with methyl-4-aminobenzoate [Bahr et al., 2001, Dyke et al., 2003], dispersed in THF and added to the pre-polymer solution. After removing the solvent, the composite was dried in a vacuum oven at 60°C for 12 h. The final mixture was then molded and cured at 170°C for 12 h. Investigations on the surface morphology of the composite by SEM indicated better dispersion of tubes at lower concentration. Wrapping of tubes with the polymer showed good adhesion between the two components. However, at higher CNT content, CNT agglomerates were found.

On the other hand, Wang et al. [Wang et al., 2004] used the infiltration method as reported by Gou et al. [Gou et al., 2004] to fabricate SWCNT-reinforced epoxy composites. The SWCNTs (diameter 0.8–1.2 nm, length 10–1000 nm) were first dispersed into water with the aid of Triton X-100 surfactant and then sonicated to form a well-dispersed and stable suspension. The SWCNTs suspension was filtrated to form buckypapers which were composed of uniform SWCNT rope networks. The low viscosity resin solution (Epon 862 and the curing agent was Epicure W mixed at a weight ratio of 100:26.4) was allowed to infiltrate the buckypapers to impregnate the SWCNT rope networks. The composites (up to 39 wt%) were moulded in a hot press and cured at 177°C for 2.5 h under pressure, cooled to RT and post-cured in the oven for another 2 h. The AFM and SEM examinations of the composite fracture surface revealed uniform impregnation of epoxy throughout the buckypaper. In another publication Lucas et al. [Lucas et al., 2004] used SWCNTs from HiPco method [Nikolaev et al., 1999] to disperse in Araldite epoxy resin LY5052. Fluorinated SWCNTs (FSWCNTs) were employed by Miyagawa et al. [Miyagawa et al., 2004] to improve the properties of epoxy polymer. Use of FSWCNTs was previously reported by Zhu et al [Zhu et al., 2003]. FSWCNTs (up to 0.5 wt%) were sonicated in acetone for more than 5 h (1 g/1000 ml). Epon 862 epoxy resin was processed with curing agent methyltetrahydrophthalic-anhydride (MTHPA), aradure HY 917 and an accelerator 1-methylimidazole DY 070 at the ratio 100:92.7:1 and added to the FSWCNT solution under magnetic stirring for 1 h. The acetone was removed by vacuum extraction at approximately 100°C for 24 h, and then MTHPA and 1-methylimidazole were blended into the solution. The specimens were cured at 80°C for 4 h followed by 160°C for 2 h. In a subsequent work, the same group synthesized composites using FSWCNTs and bio-based epoxy polymer [a mixture of Epon 862 and epoxidized linseed oil (ELO)] following the same procedure [Miyagawa et al., 2005].

Yun et al. [Yun et al., 2005] demonstrated a simple method for the fabrication of a novel SWCNT-epoxy composite material. The purified SWCNTs were dispersed in DMF by mixing for 5 h and low level ultrasonication for 2 h. This solution was molded and dried at

180°C for 5 h under vacuum to produce a nanotube paper. Epoxy (Epon 862) and a curing agent (Epicure W) were mixed well without any solvent and then applied on the surface of the nanotube paper. This layered composite was cured in an oven for 4 h at 120°C.

Brown et al. [Brown et al., 2005] obtained improved dispersion of HiPco synthesized SWCNTs in an epoxy matrix by the sonication method. In a typical synthetic method, 0.01 g SWCNTs were first purified [Strong et al., 2003] and added to 7.25 g of Jeffamine D2000 (curing agent), and the mixture was sonicated for 3 min. 2.75 g of Epon 828 heated at 75°C was added to the SWCNTs/D2000 mixture. One formulation was made with conventional mixing with epoxy. Other formulations were sonicated for 1 h at 75°C after adding the epoxy. The samples were molded and cured for 2 h at 75°C followed by 2 h at 125°C. SEM analysis showed good wetting of highly dispersed CNTs by epoxy without any CNT pull out. The TEM image revealed a well distributed network of SWCNT ropes with no individual SWCNTs. To study the effect of dispersion state of SWCNTs on rheological, mechanical and thermal properties of epoxy composites, Song et al. [Song et al., 2005] prepared a series of SWCNTs-containing epoxy composites.

The solvent effect for SWCNTs dispersion was also demonstrated by Lau and co-workers [Lau et al., 2005] SWCNTs (0.5 wt%) were dispersed into one of the solvents (acetone, ethanol or DMF) with strong sonication for 1 h. Epoxy resin (Araldite GY 251) was added into the CNT suspension and sonicated for another hour. The mixture was then placed on a hot plate at 60, 80 and 140°C for 45, 70 and 110 min for acetone, ethanol and DMF, respectively, to completely evaporate the solvent. All the samples were degassed for 4 h, molded and cured after the amine hardener (CIBA HY 956) was added. The samples were pre-cured on a hot plate at 50°C for 10 min with stirring and then cured at RT for 24 h. The samples were designated as S1 (no solvent), S2 (acetone), S3 (ethanol) and S4 (DMF). SEM images of the fracture surfaces of various samples showed no significant difference in the state of dispersion. However, the diameters of the SWCNTs varied from sample to sample. The number of SWNT bundles pulled out from the epoxy matrix was on the order of $S2 > S3 > S4$, showing ethanol and DMF to be better choices for CNT dispersion.

Rajoria and co-workers [Rajoria et al., 2005] prepared the fabrication of epoxy composites with SWCNTs and MWCNTs following the same method. Poor adhesion between SWCNTs and matrix was observed from the SEM image in this case. Fidelus et al. [Fidelus et al., 2005] used randomly oriented SWCNTs (HiPco, diameter 0.8–1 nm) for the preparation of epoxy composites employing procedure similar to that used for MWCNTs. Moisala et al. [Moisala et al., 2006] also reported the fabrication of SWCNT- and MWCNT-based epoxy composites using the same procedure.

Bryning et al. [Bryning et al., 2005] used two types of SWCNTs: (a) laser synthesized (length 230–802 nm, diameter 1.2–1.5 nm) and (b) HiPco (length 79–257 nm, diameter 0.8–1.4 nm) with different aspect ratios in epoxy polymer employing two different processing methods. 0.004 wt% pure SWCNTs were ultrasonically dispersed in DMF. SWCNT/DMF suspension was added to epoxy resin (Epon 828), and the mixture was sonicated for 4 h at 80°C. Epikure 3234 curing agent was then added, and the mixture was sonically stirred for 2 min. The samples were divided into two batches and one batch was cured at 90°C for 30 min in a water bath without sonication (non-sonicured) while the other batch was cured at 80°C in a sonicator bath (sonicured). The cured samples were annealed at 120°C for 2 h. The SEM of the non-sonicured samples showed re-aggregation of SWCNTs, while the sonicured samples showed that the SWCNT dispersion was quite homogeneous.

In another work, Hadjiev et al. [Hadjiev et al., 2006] reported the use of ODA-functionalized SWCNTs for the synthesis of epoxy-SWCNTs composites. SWCNTs produced by the laser ablation technique [Arepalli et al., 2004] were purified [Chaiang et al., 2001] and treated with concentrated H_2SO_4 , 30% H_2O_2 mixture at 70°C for 20 min. The SWCNTs were refluxed with ODA at 110°C for 40 h. Excess amine was removed by sonication and washing with ethanol and THF. The suspension of ODA-SWCNTs in 70% acetone/30% toluene was mixed with epoxy resin Epikote 862. After removing acetone, Epikure W was added, and the mixture was stirred well. The composite was vacuum dried for 2 h at 60°C and molded. This was followed by annealing at 80°C for 30 min in a vacuum oven. The curing cycle involved an annealing at 121°C for 1 h and at 175°C for 2 h. TEM images showed the presence of SWCNTs with physisorbed ODA molecules in the epoxy matrix. The embedded tubes appeared to have a bent structure.

Wang and co-workers [Wang et al., 2006] proposed an effective amino functionalization through diazotisation of SWCNTs for reinforcing epoxy polymer composites. About 50 mg of pristine SWCNTs was dispersed with 50 ml DMF under sonication to which 7.366 g Epikure-W curing agent was added followed by 2.7 ml isoamyl nitrite. The mixture was heated to 80°C for several hours, diluted with DMF, filtered and washed with DMF. The DMF was removed with ether, and the CNT membrane was vacuum dried at 65°C for 10 h. The CNT membrane was made into a paste with acetone. The excess acetone was removed, and the required amount of EPI-W was added. The mixture was transferred to the epoxy resin diluted with acetone, which was sonicated for 10 h under ice-cooling. The composite was dried under vacuum and cured in a hot press at 177°C for 2.5 h. The subsequent post-cure was done at 177°C for another 2 h. Fig. 26 shows the AFM image of grafted SWCNT-epoxy composite section under tapping mode. The AFM image of the composite section showed high embedding and uniform dispersion of functionalized SWCNTs throughout the epoxy matrix.

Fig. 26. AFM image of grafted SWCNT-epoxy composite section under tapping mode. Reproduced from Wang et al., 2006.

Tao et al. [Tao et al., 2006] demonstrated a simple method to fabricate epoxy composites. Three different grades of SWCNTs; short SWCNTs (S-SWCNT with diameter 0.8–1.6 nm, length 500 nm), HiPco-SWCNTs (diameter 3–5 nm) and XD-grade CNTs (XD-CNT), which was a mixture of single, double and triple-walled CNTs were used in the study. About 1 g of Epikote 862 and 0.264 g of Epikure W were mixed with 1 wt% of CNTs in a mortar and pestle for 30 min. Surface morphology analyzed by SEM showed good dispersion and distribution of CNTs. The nanotube wetting was relatively better with HiPco SWCNTs.

In another work, Li and his group [Li et al., 2006, Huang et al., 2007] used SWCNTs with different aspect ratios for fabricating SWCNT-epoxy composites. Arc discharge-produced SWCNT-long, SWCNT-short and annealed SWCNT-short were used in this study. A commercially available bisphenol A-type epoxy resin (618 type) and an amine-type hardener [$C_{17}H_{31}CONH(C_2H_4NH)_2H$]₂, were used to prepare the polymer matrix at the ratio 2:1. SWCNTs were first dispersed in acetone by ultrasonication at RT for 2 h, and to this suspension epoxy resin/acetone solution was added. The mixture was again sonicated for 2 h, and hardener was added during mechanical stirring. The mixture was further sonicated for 15 min, molded and cured at RT overnight. SEM showed nice dispersion of SWCNTs in the matrix.

Lau et al. [Lau et al., 2006], in another work, compared the reinforcing effect of CVD-synthesized SWCNTs [Li et al., 2006 b] with coiled CNTs [Lu et al., 2004] in an epoxy matrix. Nanotubes were initially dispersed into ethanol with strong sonication for 1 h. The desired amount of epoxy resin (Araldite GY 251) was added, and the mixture was sonicated again for 1 h. Solvent was removed, and the mixture was degassed in vacuum for 4 h. After adding the hardener (CIBA HY 956), the mixture was molded and cured with stirring at RT for 24 h. Comparison of the SEM images of the composites indicated good anchoring of coiled nanotubes to the matrix, while poor adhesion leading to large holes in the matrix was observed for SWCNTs.

On the other hand, Liu et al. [Liu et al., 2007] reported, for the first time, the clay-assisted dispersion of SWCNTs in epoxy polymer. In a typical preparative method, HiPco-produced SWCNTs and unmodified natural montmorillonite clay (Cloisite[®]Na⁺, CEC = 92.6 meq/100 g) were first suspended in 40 ml acetone with sonication for 20 min. Epoxy resin (D.E.R. 354), curing agent (ECA-100) and amine catalyst (N,N-Dimethylbenzylamine) were then dissolved in acetone and mixed with the SWCNT-clay suspension. This mixture was mechanically stirred for 5 min at 1720 rpm and then for 30 min at 3100 rpm followed by sonication in a water bath for 1 h. The acetone was removed, and the mixture was cured for 1 h at 95°C followed by 3 h at 150°C. Significant improvement in SWCNT dispersion was observed for samples containing clay from optical microscopy and SEM images.

Wang et al. [Wang et al., 2007] modified and integrated SWCNTs into the epoxy matrix through covalent and non-covalent functionalization. Selected methods, including oxidation, polymer wrapping, and mechanical chopping were used to functionalize HiPco-produced SWCNTs (diameter 0.8–1.2 nm, length 100–1000 nm). Oxidation (o-SWCNTs) involved stirring SWCNTs with concentrated H₂SO₄ acid for 1 h, washing and drying. In polymer wrapping, SWCNTs were magnetically and ultrasonically stirred with gum arabic, filtered and dried (GA-SWCNTs). In mechanical chopping, SWCNTs (c-SWCNTs) were dispersed in Triton-X 100, washed with isopropanol and chopped with a diamond knife. Functionalized SWCNTs were made into a paste with acetone. The curing agent DETDA was added to the functionalized SWCNT paste and sonicated for 30 min under ice cooling. The solution was mixed with epoxy resin (Epon 862) diluted with

acetone using sonication for 3.5 h under ice cooling along with magnetic stirring. The mixture was dried in vacuum for 10 h, molded and cured in a hot press at 177°C for 2.5 h. The subsequent post cure was conducted at 177°C for another 2 h. SEM characterization showed a smooth surface for the neat resin. The raw SWCNTs gave non-uniform distribution in the matrix. All the functionalized SWCNT-epoxy composites revealed rougher surfaces due to better dispersion of CNT network.

Lucas et al. [Lucas et al., 2007] in another work used 0.05 wt% of HiPco SWCNTs to reinforce the epoxy matrix. A mixture of SWCNTs hardener HY5052 was first sonicated for an hour and then magnetically stirred for 30 min. After the addition of epoxy resin LY5052, the mixture was manually stirred for 5 min, molded and degassed in vacuum for 30 min. The cold-cured sample was prepared by leaving the composite to cure at RT in air for 7 days, while the hot-cured samples were prepared by leaving the mould in an oven overnight at a fixed temperature (40–150°C).

Bekyarova et al. [Bekyarova et al., 2007b] demonstrated the fabrication of hybrid epoxy composites with acid-functionalized SWCNTs (arc-discharge) by the infiltration method reported with MWCNTs [Bekyarova et al., 2007a]. 0.2 and 0.5 wt% of acid-functionalized SWCNTs (SWCNT-COOH) were mixed with Epon 862 and the curing agent Epikure W. This solution was infused with carbon fibre using VARTM technique for 1 min. After the infiltration, the specimens were cured for 6 h at 130°C under vacuum. SEM images showed rougher surfaces for SWCNT containing samples.

Wang and co-workers [Wang et al., 2008] used an *in situ* functionalization method to graft epoxide onto SWCNTs' outer surfaces and improve the integration of SWCNTs into the epoxy matrix. HiPco SWCNTs were ground with three drops of benzene and dispersed into glycidyl methacrylate (GMA) by sonication. The mixture was then stirred with benzoyl peroxide (BPO) and heated to 75°C for 24 h under strong stirring. The mixture was diluted with benzene and filtered, washed with acetone (repeated three times) and annealed at 60°C for 10 h. The resultant epoxy-grafted SWCNT (g-SWCNTs) membrane was ground to a paste with chloroform. The curing agent was added to the g-SWCNT paste and mixed with chloroform. The epoxy resin was diluted and added to the SWCNT suspension, which was sonicated for 3 h. Finally, the mixture was placed under high-speed shearing at 2000 rpm for 3 h. The resultant composite mixture was vacuum dried for 12 h, molded and cured in hot press at 177°C for 2.5 h. The subsequent post-cure was conducted at 177°C for another 2 h. Composite samples were prepared with 0.5 and 1 wt% SWCNT loading.

The fracture cross section of the samples examined by SEM showed very good dispersion of g-SWCNTs in the epoxy matrix with no apparent agglomeration. However, pristine SWCNTs formed large agglomerates in the composite.

Valentini et al. [Valentini et al., 2008] demonstrated how the grafting of butylamine onto CF₄ plasma-treated SWCNTs is used to obtain a cross-linked epoxy composite. SWCNTs (length 50 nm–1 µm, diameter 0.8–2 nm) were subjected to plasma-assisted fluorination [274] to get F-SWCNTs. F-SWCNTs were ultrasonically dispersed in liquid butylamine for 30 min using a thermostatic bath at 5°C. The F-SWCNT grafted with butylamine (BAM-SWCNTs), were then added to epoxy resin DGEBA. The same procedure was adopted to prepare a composite with un-modified SWCNTs (BAM-u-SWCNTs). SEM images in this case also showed better dispersion with amine functionalized nanotubes.

Wang et al. [Wang et al., 2008] produced an SWCNT-epoxy composite using the solution casting technique. SWCNTs from arc-discharge (diameter 1.2–1.5 nm, length >2 µm) were purified by treating with concentrated HNO₃ at 80°C for 1 h to eliminate impurities. Acid-

treated SWCNTs were dispersed in ethanol and sonicated for 30 min. Different SWCNT weight fractions were then mixed with epoxy resin (E-51) under sonication for 2 h. Hardener *N,N*-benzyl dimethyl amine (BDMA) was added into the mixtures in two steps: Half of the BDMA was added into the nanotube/epoxy mixtures before stretching, and the mixture was sonicated and stirred at 1500 rpm simultaneously again for 1 h. The other half of the BDMA was added after a repeated stretching process. The SWCNT-epoxy composite was then stretched along one direction at a draw-ratio of 50 and then folded along the same direction and stretched repeatedly 100 times at ambient atmosphere manually at a speed of 0.5 m/s for 30 min. The film samples were compressed under a pressure of about 10 MPa for 5 min using a hydraulic press. All samples were kept in vacuum at RT for 7 days. SEM micrographs demonstrated that SWCNTs were well aligned along the stretching direction.

2.2.2 Thermal and mechanical properties

Using Raman spectroscopy, the deformation of SWCNTs produced by different methods in the epoxy matrix was studied by Cooper et al. [Cooper et al., 2001]. The second order Raman peak at 2640 cm^{-1} which is a measure of load transfer was shifted significantly to a lower wavenumber ($\sim 13\text{ cm}^{-1}/\%$ strain) for composite with SWCNT-P when compared to the one SWCNT-A. This demonstrated better reinforcing ability of laser produced SWCNTs. Based on the strain-induced Raman shift, the modulus of SWCNTs was calculated as 1 T Pa, which was higher than that for MWCNTs. Puglia et al. [Puglia et al., 2003a, Puglia et al., 2003b] observed up-shifted Raman peaks for composites containing 5 wt% of SWCNTs.

The peak shift was significant for the radial breathing mode (RBM), which is dependant on the tube diameters [Rao et al., 1997, Eklund et al., 1995]. The shift represented intercalation of resin with CNTs during the curing reaction, which exerts pressure on the dispersed nanotubes and changes the vibrational frequencies. The rate of the cure reaction and thermal degradation increased with SWCNT content up to 5 wt% above which there was no pronounced effect. Individual nanotubes were well dispersed in the matrix, which contributed to the higher surface for heat propagation. Similar results were reported by Valentini et al [Valentini et al., 2004]. Hadjiev et al. [Hadjiev et al., 2006] also reported an up-shift of Raman bands for composite containing ODA-functionalized SWCNTs. RBM intensities of SWCNTs in epoxy matrix with applied strain has been investigated by Lucas et al [Lucas et al., 2004]. The intensity measurements on the composite with 0.025 wt% SWCNTs (strain between -0.6 and 0.65) showed that some peaks increased the intensity while others decreased depending on the chirality and diameter. In another work, the same group [Lucas et al., 2007] demonstrated the up-shift of RBM bands for epoxy composites as a function of curing temperature.

Zhu and co-workers [Zhu et al., 2003] reported improved mechanical properties for composites prepared with fluorinated SWCNTs. Epoxy composites with 1 wt% functionalized nanotubes showed 18 and 24% improvement in tensile strength and modulus respectively when compared to the resin with unmodified SWCNTs. Over the neat resin, the modulus of these specimens showed a 30% increase. Fluorinated nanotubes were well dispersed in the matrix, showing good interaction with the epoxy matrix thereby reinforcing the polymer. Miyagawa et al. [Miyagawa et al., 2004; Miyagawa et al., 2005] also reported dramatic improvement in storage modulus for epoxy composites with a very small amount of fluorinated SWCNTs. The modulus increased by 1.1 GPa with the addition of only 0.3 wt% of FSWCNTs, representing a 33% improvement. Brown et al. [Brown et al., 2005] also

reported 30–40% improvement in storage modulus with very low CNT content of 0.1 wt%. The reinforcing effect of small SWCNT content (0.05–0.1 wt%) was observed by Liu et al. [Liu et al., 2007] as well.

Ren et al. [Ren et al., 2003] demonstrated the good potential of SWCNTs as reinforcing filler and evaluated the fatigue strength of SWCNTs in epoxy as twice as that of CF-based composites. Gou et al. [Gou et al., 2004] studied the mechanical properties of HiPco SWCNT-reinforced epoxy matrix. The DMA results (refer Fig. 27) showed an increase in composite storage modulus with the introduction of CNTs. A 250–300% increase in storage modulus was observed with the addition of 20–30 wt% nanotubes below T_g .

The damping characteristic of SWCNT-epoxy composites prepared by ultrasonication was investigated by Zhou et al. [Zhou et al., 2004]. For samples with SWCNTs, damping

Fig. 27. Storage moduli of SWCNT-epoxy composites. Reproduced from Gou et al., 2004.

Fig. 28. (a) Storage modulus and (b) T_g 's of the composites. Reproduced from Liao et al., 2004.

increased with strain up to 1 wt% CNTs and then decreased. The concept of “stick and slip” frictional motion could effectively explain the observations. Rajoria et al. [Rajoria et al., 2005] reported similar results on the damping properties of MWCNT-epoxy composites. Higher damping for SWCNT-epoxy composite was also observed by Wang et al [Wang et al., 2004]. The effect of various SWCNT dispersion process (Table 8) on the mechanical properties of epoxy was reported by Liao et al [Liao et al., 2004]. DMA results of SWCNT/SC-15 composites thus obtained are summarized in Fig. 28. From the results, only tip sonication was found to consistently improve nanotube dispersion and mechanical properties. The highest storage modulus was observed for Sample 3 (50.8% when compared to the neat resin) which was fabricated by using tip sonication in the presence of acetone and with only 0.5 wt% of CNTs. All the samples with nanotubes except sample 2, showed lower T_g than that of pure epoxy. Sample 2 and the neat resin were prepared without using surfactant or solvent, so the decrease in T_g for the other samples was attributed to the surfactant or solvent effect. Linear decrease in T_g with increase in fluorinated SWCNT content was also reported by Miyagawa et al [Miyagawa et al., 2004]. A detrimental effect of clay on T_g of SWCNT-epoxy was demonstrated by Liu et al. [Liu et al., 2007] where the samples without clay showed increase in T_g values when compared to neat resin. Wang et al. [Wang et al., 2004] observed no obvious change in T_g for composites with varying SWCNT content prepared by the infiltration method. Brown et al. [Brown et al., 2005] also reported unchanged T_g values for the composites.

On the other hand, Li et al. [Li et al., 2004] used AFM to study the hardness, elastic modulus and scratch resistance of SWCNT-epoxy composites. Epoxy with 5 wt% SWCNTs loading showed an increase in the elastic modulus by 75% and hardness by 30% in comparison to the pure epoxy matrix. The storage modulus and the loss modulus also increased with increasing CNT-content. However, composites with 3 and 5 wt% SWCNT showed debris particles and cracks inside or around the scratch tracks for the scratch tests due to the presence of CNT agglomerates. Wang et al. [Wang et al., 2004] noticed an increased storage moduli for the SWCNT-epoxy composites which was less than that predicted due to poor load transfer as a result of dispersion effects. They observed no regular trend in mechanical properties with CNT-content.

The influence of SWCNT dispersion on mechanical properties of epoxy was studied by Song et al [Song et al., 2005]. Epoxy composites with poorly dispersed CNTs showed higher storage and loss modulus due the presence of larger agglomerates that can trap polymer in the void reducing volume fraction of polymer matrix. However, improved tensile strength and elongation at break were observed in the case of composite with good CNT dispersion. Thermal conductivity was higher for samples with well-dispersed CNTs which showed an increasing trend with nanotube amount. Moisala et al. [Moisala et al., 2006] in contrast observed a decrease in thermal conductivity for epoxy composites with SWCNT addition.

Lau and co-workers [Lau et al., 2005] dispersed SWCNTs in an epoxy matrix using various solvents and studied the thermal and mechanical properties of the resulting composites. In comparison with the pure epoxy sample S1, the hardness value of acetone-dispersed sample S2 increased slightly, while the hardness values of the ethanol-dispersed sample S3 and the DMF-dispersed sample S4 decreased (more pronounced decrease for DMF sample of about 56% with neat resin). A relatively higher amount of residual solvent resulted in poor mechanical properties of S3 and S4.

Fidelus et al. [Fidelus et al., 2005] used two different epoxy polymers (Epon 815 and LY 564) and randomly oriented SWCNTs (0.01 to 0.5 wt%) for the preparation of epoxy composites.

Below 50°C, only moderate increase in storage modulus and decrease in T_g were observed for both series with respect to the pure matrix. On the other hand, a substantial increase in impact strength (18 and 35%, respectively, for LY 564 and Epon 815) was measured with the loading range. MWCNTs showed better reinforcing effect than SWCNTs.

Wang and co-workers [Wang et al., 2006] demonstrated reinforcement of epoxy polymer by amine-functionalized SWCNTs. Fig. 29 shows typical DMA results of SWNT-epoxy composites. Composite containing amine-functionalized SWCNTs showed a noticeable increase in storage modulus compared to those with pristine SWCNTs and neat resin. The storage modulus of the epoxy increased from 2.44 to 3.04 GPa with 0.5 wt% of functionalized CNTs (24.6% improvement). At the same time, introduction of the same amount of pristine CNTs could produce only a 3.2% improvement in modulus. T_g values were 170, 164 and 158°C for pure epoxy, pristine SWCNT-epoxy and functionalized SWCNT-epoxy, respectively. In another work [Wang et al., 2008], they used epoxide-grafted SWCNTs (x-SWCNTs) in strengthening the epoxy matrix. Similar trends in storage modulus and T_g were reported. Valentini et al. [Valentini et al., 2008] proposed plasma fluorination followed by amine treatment as an effective functionalization procedure for SWCNTs to obtain better dispersion in epoxy. However, the tensile strength and elongation at break were lower for BAM-u-SWCNTs-epoxy composite with respect to the pure resin. At the same time, incorporation of CNTs (both functionalised and pristine) showed a positive effect on elastic modulus.

Fig. 29. Typical DMA results of SWNT-epoxy composite. Reproduced from Wang et al. 2008

Lau et al. [Lau et al., 2006] compared the mechanical properties of composites reinforced with SWCNTs and coiled CNTs at the same nanotube concentration of 2 wt%. Coiled CNTs were found to be superior to SWCNTs in hardening the matrix by about 3 times. Flexural strength of composite with coiled tubes was also higher due to the good mechanical locking between coiled tubes and the polymer.

The promising role of SWCNTs functionalized by different methods in reducing CTE of epoxy composite was demonstrated by Wang et al. [Wang et al., 2007]. CTE values of the

neat epoxy resin and nanocomposites below the T_g range are presented in Fig. 30. All the composites showed lower T_g than the pure polymer. The reduction in CTE value for p-SWCNT-epoxy was not that significant when compared to those with functionalized SWCNTs. From the results, it is clear that the reduction in CTE values depends on the functionalization method. Substantial decreases in CTE values 52.4, 42.4 and 13.9% were observed for c-SWCNT (chopped SWCNTs)-epoxy, o-SWCNT (oxidized SWCNTs)-epoxy and w-SWCNT (polymer-wrapped SWCNTs)-epoxy, respectively.

Fig. 30. CTE values of the neat epoxy resin and composites below the T_g range. Reproduced from Wang et al., 2007.

The mechanical performance of hybrid epoxy composite containing acid-functionalized SWCNTs was reported by Bekyarova et al. [Bekyarova et al., 2007b]. The flexural strength of the composite showed no significant improvement with the introduction of SWCNTs. However, the shear strength showed 20 and 40% increases with the incorporation of 0.2 and 0.5 wt% SWCNT-COOH.

Wang et al. [Wang et al., 2008] reported significant improvement in mechanical properties for composites with aligned SWCNTs. 3 wt% loading of SWCNTs showed significant improvement in the tensile strength (8–21.1 MPa) and Young's modulus (415–843 MPa). Tensile strength decreased at higher CNT weight fractions larger than 6 wt%.

2.2.3 Electrical properties

The conducting properties of SWCNT-epoxy composites have been investigated by Barrau et al [Barrau et al., 2003 b]. According to the observations, the D.C. conductivity increased as a function of CNT weight fraction (0–2.5 wt%). A dramatic increase in conductivity was observed between 0.2 and 0.4 wt% of CNTs, and the percolation threshold was calculated as 0.3 wt%. The conductivity increased with temperature below the percolation threshold, and above the threshold it was independent of temperature for all the CNT contents. The effect of palmitic acid on the conductivity for the same epoxy system was studied in another work [Barrau et al., 2003 a]. Fig. 31 shows the comparative plot of the dc conductivity dependence

on the CNTs content at RT(■) with palmitic acid at 1:1 CNTs to $C_{16}H_{32}O_2$ weight ratio and (○) without palmitic acid. Higher conductivity was measured for composites with palmitic acid in comparison to pure resin and the composite without palmitic acid, and the conductivity was observed to be dependant of the surfactant concentration. The composite with 1:1 CNT/palmitic acid ratio showed the highest conductivity, which is attributed to better CNT dispersion. The percolation threshold was between 0.05 and 0.1 wt% of CNTs.

Fig. 31. Comparative plot of the dc conductivity dependence on the CNTs content at RT(■) with palmitic acid at 1:1 CNTs to $C_{16}H_{32}O_2$ weight ratio and (○) without palmitic acid.

Reproduced from Barrau et al., 2003a.

Valentini et al. [Valentini et al., 2004] reported an increase in dielectrical properties of SWCNT-epoxy composites with the incorporation of SWCNTs as conductive fillers.

Brown et al. [Brown et al., 2005] measured the A.C. conductivity for SWCNT-epoxy matrix. According to the results, the composite showed very low conductivity at 0.01 wt% of CNTs very similar to that of pure epoxy polymer. As the CNT content was increased to 0.1 wt%, the composite became more conductive. A jump in conductivity value was observed between 0.01 and 0.05 wt% of CNTs (percolation threshold). These results were consistent with the work of Barrau et al. [Barrau et al., 2003 a]

Song et al. [Song et al., 2005] reported the electrical conductivity of composites with different degrees of dispersion of SWCNTs. Introduction of CNTs to the matrix increased the conductivity up to 1.5 wt% of CNTs. The conductivities of composites with well-dispersed SWCNTs were slightly higher than those with poor dispersion. A percolation threshold less than 0.5 wt% was observed for both series of composites.

Very low threshold concentration [$5.2 (+1.9/-0.5) \times 10^{-5}$] for non-sonicated laser oven SWCNT-containing epoxy composite was proposed by Bryning et al. [Bryning et al., 2005] This was 2-fold lower than the corresponding HiPco SWCNT-epoxy composite. The sample without sonication showed aggregation of CNTs which contributed the rapid percolation. Li et al. [Li et al., 2006, Huang et al., 2007] reported a percolation threshold of 0.062 wt% for composites with SWCNTs with high aspect ratio. With short-SWCNTs and annealed-short-SWCNTs, the threshold concentrations were 0.318 and 0.342 wt%, respectively.

In another work, Moisala et al. [Moisala et al., 2006] measured the percolation threshold for SWCNT-epoxy composites as 0.05–0.23 wt%, which was higher than that observed for MWCNTs (0.005 wt%). An increase in electrical conductivity for epoxy composites was also observed by Liu and co-workers [Liu et al., 2007]. Addition of 0.2 wt% of clay to the system containing 0.05 wt% of SWCNTs dramatically increased the conductivity. Furthermore, the percolation threshold of the epoxy composites was reduced 0.05 wt% SWCNTs to 0.01 wt% SWCNTs with the introduction of clay.

Valentini et al. [Valentini et al., 2008] demonstrated an increase in electrical conductivity for composites with amine-functionalized SWCNTs. Wang et al. [Wang et al., 2008] showed the effect of CNT alignment on electrical conductivity. The conductivity measurements with CNT content showed that very small amounts of aligned SWCNTs are enough to obtain significant enhancement in electrical conductivity. The percolation threshold along the stretching direction was observed to be lower than the value perpendicular to the SWCNT orientation.

2.3 DWCNT-containing epoxy composites

Gojny et al. [Gijny et al., 2004] fabricated epoxy composites with increased mechanical properties with amine-functionalized DWCNTs by the calendering technique. The matrix was epoxy resin (MGS L135i) together with the amine-curing agent H 137i. Pure or amine-functionalized DWCNTs (0.1 wt%) were used to reinforce the epoxy resin. CNTs were manually mixed into the resin, and in the following step, a three roll calander was used. The dwell time of the CNT-EP suspension on the rolls was approximately 2 min while nanotubes were dispersed in the resin by the enormous shear forces. The suspension was collected, mixed with the hardener for 10 min by stirring, cured for 24 h at RT and finally post-cured at 60°C for 24 h. For comparison, samples containing the DWCNTs (as-received and amino-functionalized) were mixed with the amine-curing agent, sonicated for 10 min and cooled to RT. The resin was added under stirring, and the mixture was sonicated again under the given conditions but cooled in a water bath to avoid an untimely curing. Finally, the composite was cured for 24 h at RT followed by a 24 h at 60°C post-curing.

TEM and SEM images of the achieved distribution of DWCNTs and amine-functionalized DWCNTs in the epoxy matrix by the use of a calander showed homogenous distribution and exfoliation of CNTs over the composites prepared by sonication method. The Young's modulus of the composites increased with the introduction of nanotubes. Composite with amine-functionalized DWCNTs showed higher modulus when compared to the non-functionalized DWCNTs. All composites had a significantly higher fracture toughness compared to the neat epoxy.

Li et al. [Li et al., 2006] also prepared epoxy composites with well aligned DWCNT strands by the solution mixing method. The aligned DWCNTs were prepared by the CVD method [Li et al., 2005]. The epoxy resin (E-44) and polyamide hardener (volume ratio 2:1) were successively dissolved in acetone. DWCNT strands were then immersed into the solutions for 1 min. The composite fibres were dried and cured completely for 7 days at RT.

Good interfacial bonding between the polymer and filler was revealed by TEM analysis. Compared to DWCNTs, the composite showed significant improvement in tensile strength and Young's modulus (25% and 75% respectively). The second-order Raman peak was down-shifted for the composite showing effective load transfer.

An epoxy system containing carboxy DWCNTs (C-DWCNTs) functionalized with N-methyldiethanolamine (MDEA) has been investigated by Terenzi and co-workers [Terezeni et al., 2008]. The polymeric matrix of the composite was obtained from a DGEBA epoxy resin and a solid MDEA. The C-DWCNTs were stirred in the MDEA at the melting temperature of the amine (i.e., 100°C for 45 min). 1 wt% of MDEA/C-DWCNTs, were added to epoxy. Another preparation method of first mixing the C-DWCNTs with epoxy and then adding the MDEA moiety was also used.

The SEM analysis of the fracture surface indicated very good nanotube dispersion and homogeneity for the sample with MDEA-functionalized DWCNTs. The calorimetric results showed that addition of CNTs increased the curing rate, and this effect was maximum for functionalized DWCNTs.

Gojny et al. [Gojny et al., 2005], in another work, studied the mechanical and electrical properties of epoxy matrix reinforced with DWCNTs and amine-modified DWCNTs. The composites were manufactured via the resin transfer molding (RTM) process. The CNTs were manually added to the resin (L135i) system. This was further mixed with a shear mixer at a gap setting of 5 μm at speeds of 20, 60 and 80 rpm for the first, second and third rolls, respectively, with a dwell time of 2 min. The suspension was then stirred for 10 min with the hardener H137i and cured at RT for 24 h followed by a post cure at 60°C for another 24 h. The mixture was then infused with the glass fibre by RTM and cured as described previously. The post curing was done at 80°C for another 24 h.

The interlaminar shear strength of the glass fibre-reinforced polymer showed noticeable increase by 20%, whereas the tensile properties remained unaffected. The electrical properties were anisotropic in nature. The conductivity measured in plane was much higher than that obtained for out of plane, which was attributed to the conduction paths by CNTs located between the matrix channels of glass fibre. attributed to the conduction paths by CNTs located between the matrix channels of glass fibre.

2.4 CSCNT-containing epoxy composites

The effect of the dispersion, ozone treatment, and loading of CSCNTs on mechanical, electrical and thermal properties of the epoxy-CSCNT composites were investigated by Choi et al [Choi et al., 2005]. CSCNTs (diameter 60–100 nm, length 20–40 nm) were prepared by floating catalyst [Tibbetts et al., 1993]. CSCNTs were oxidized with ozone at RT for 1 h and dried at 100°C for 12 h. To prepare the composites, the CSCNTs (0, 5, 10 and 20 wt%) were dispersed in acetone by sonication, added to the epoxy resin and stirred at RT at 600 rpm for 15 min. After evaporating the acetone, the mixture was vacuum dried at 80°C for 30 min. The hardener was then blended into the mixture at RT for 10 min. The mixture was kept under vacuum at RT again for 10 min. Samples were cured at RT for 16 h followed by 120°C for 3 h.

SEM images of the fractured cross section of the composites containing untreated and ozone-treated CSCNTs showed no difference in the dispersion states except for the presence of more voids in the composites with untreated CSCNTs. TEM observation under low magnification revealed nanotube aggregates in both the untreated and treated composites. The ozone-treated CSCNTs showed better wetting in the epoxy matrix. The electrical conductivity increased with increasing CSCNT content. No significant effect of ozone treatment was observed on electrical conductivity. Tensile strength and Yong's modulus for both series of composites were almost similar. The coefficient of friction was lower for the

composites when compared to the pure epoxy where the ozone-treated CSCNT sample gave the lowest value. Measurement of thermal properties indicated that the heat resistance of the composites increased with CSCNT loading regardless of ozone treatment. Composites with untreated and ozone-treated CSCNTs showed an increase in T_g (drastic increase with ozone treated CNTs), and the magnitude decreased with CNT-content.

Yokozeki et al. [Yokozeki et al., 2007] investigated the matrix cracking behaviors in carbon fibre-epoxy laminates filled with CSCNTs. The CSCNTs used in this study were synthesised by a floating reactant method [Liu et al., 2001] with aspect ratio 10. A two-step mixing procedure was employed; EP827 epoxy and CSCNTs (0, 5 and 12 wt%) were combined using the planetary mixer at 70°C, and then, CSCNTs were dispersed using the wet mill at 70°C for 45 min. The blended CSCNT-dispersed epoxy was diluted with EP827, and the dicyandiamide curing agent was added to the compounds. A wet coater was used to impregnate the carbon fibres with the resin.

The introduction of CSCNTs resulted in stiffness and tensile strength improvement in the 90° direction. The highest values were obtained for the sample with 5 wt% CSCNT content. Retardation of matrix crack formation was clearly observed in CSCNT-dispersed resin laminates with 40% improvement in fracture toughness. SEM images showed rougher surfaces for composites.

3. Conclusions

Recently, much attention has been paid to the fabrication of reinforced composites where the reinforcement filler size has reduced to nanometer range. These engineering materials are expected to have high strength-weight and modulus-weight ratios when compared to the normal commercial polymer composites where microscale particles are incorporated. Among various nanoreinforcements used today, CNTs are considered as potential fillers for the composites to improve mechanical, electrical and thermal transport due to their remarkable structure dependent properties. However, two issues concerning the effective improvement of composite properties are the interfacial bonding and uniform dispersion of the tubes in the polymer matrix. In addition, the conventional mechanisms and theories explaining the effect of filler on structural, mechanical and physical properties may not applicable to CNTs and other nano-fillers.

From the existing literature, considerable effort has been given to the synthesis and processing of CNT-reinforced epoxy composites. The modification of epoxy resins with CNTs could endow the materials with some superior properties such as broadening of T_g , significant increases in mechanical properties and substantial improvement in thermal and electrical conductivity. The reports published so far on these materials focus on investigating whether a CNT-modified epoxy matrix yields improved properties with neat epoxy as the matrix material. Except a few reports, most of the published work advocates surface functionalization of CNTs and use of a surfactant as possible routes to enhance the dispersion and interfacial adhesion between CNTs and epoxy matrix. Various types of CNTs with or without physical and chemical modifications were utilized to fabricate the composites to make them effective fillers regarding mechanical properties—especially toughness—and the properties of the resulting composites were also analyzed.

However, the extent of homogeneous dispersion is found to be dependant on the aspect ratio, volume fraction, CNT entanglement, matrix viscosity and inter-tubular interactions. Different methods including sonication, stirring and calendering have been proposed for the

preparation of composites where some of the reports contradict each other in the effectiveness to get uniform CNT distribution. Though the CNT-reinforced epoxy has been shown to be a possibility, realising the properties of individual CNTs in assemblies of CNTs is a formidable challenge. An efficient exploitation of CNTs as structural elements is generally related to the degree of dispersion, impregnation with matrix and the interfacial adhesion. Much work remains to be performed in order to understand how the nano-reinforcement results in major changes in material properties.

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