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PM REVIEW

Review on Thermoset-carbon Nanotube Nanocomposites

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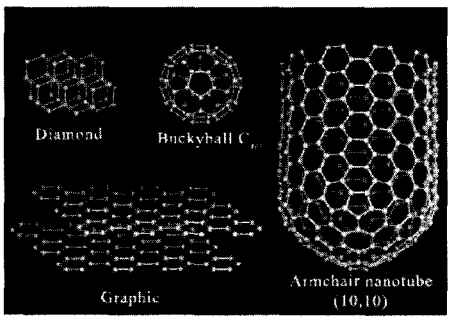
1. Introduction

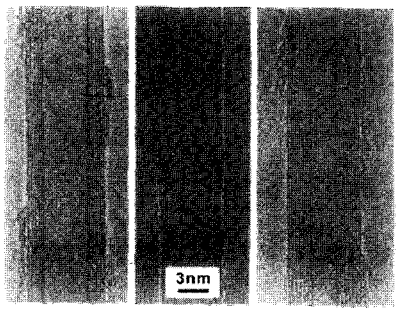
Fullerenes were discovered in 1985 at Rice University by Richard Smalley, Robert Curl and Harold Kroto, who were awarded the Nobel Prize in chemistry in 1996. The most basic fullerene is comprised of 60 carbon atoms arranged in a geodesic pattern, named the buckyball (inset above) in honor of Buckminster Fuller. Carbon nanotube (CNT) is an elongated buckyball about 0.5-2 nanometer in diameter (about 1/100,000th the diameter of a human hair).

CNTs have two distinct forms: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs are composed of a graphene sheet rolled into a cylinder[1] (Fig. 1) while MWNTs consist of multiple concentric graphene cylinders[2] (Fig. 2). Compared with MWNTs, SWNTs are expensive and difficult to obtain and clean, but they have been of great interest owing to their expected novel electronic, mechanical, and gas adsorption properties[3].

CNTs have unique atomic structure, very high aspect ratio, and extraordinary mechanical properties (strength and flexibility). The use of CNTs in polymer nanocomposites has attracted a wide attention[4-9]. CNT nanocomposites have been proved to be potential for flame-retardant performance[10], improved electrical conductivity and electrostatic



(a)



(b)

Fig. 1. (a) Different forms of carbon-based materials (Photo courtesy of Rice University) and (b) electron micrographs of nanotubes with different numbers of graphene layers. The outer diameters of the nanotubes are 6.7 nm (left), 5.5 nm (middle) and 6.5 nm (right)[1].

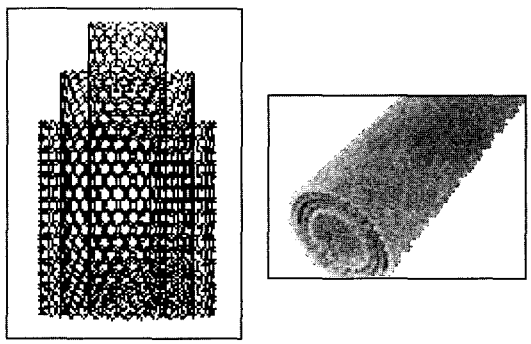


Fig. 2. MWNT[2].

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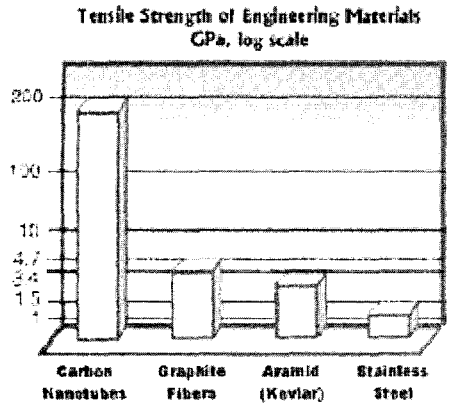


Fig. 3. Tensile strength of carbon nanotube in compared with conventional fibers[13].

charging behavior, optical emitting devices[11,12], and in lightweight, high strength composites[10]. NASA shares the growing interest in SWNTs because of their extraordinary mechanical, electrical and optical properties, which are superior compared to MWNTs. In the axial direction, they exhibit electrical conductivity as high as copper, thermal conductivity as high as diamond and strength approximately 100 times greater than steel at $1/6^{th}$ the weight and they are strongest fiber obtained so far (Fig. 3). Thus it is believed that developments in nanotechnology will lead to stronger and lighter composite materials for next generation spacecrafts and satellites (Fig. 4).

However, the application of CNTs is facing with many different challenges as follows. There are several methods for preparation of CNTs. Arc-discharge and laser ablation methods have been widely used in the earlier period of time. However, the large-scale production of SWCNTs with controlled conformation still remains challenging. In the past few years, chemical vapour deposition (CVD) has been used as a promising solution. The process is simpler and has a higher productivity than the arc-charge process. However, the CNTs produced by the catalytic process are usually thicker than those by the arc-discharge process and often consist of large aggregates[3-5]. In addition, the growth mechanisms of SWCNTs are not well understood. This has limited the development of production of methods to produce large quantities of SWCNTs, including the laser ablation/oven technique, the arc vaporization process, and chemical reaction methods such as the high-pressure carbon monoxide disproportionation (HiPco) and combustion techniques.

Secondly, CNTs do not spontaneously suspend in polymers, thus the chemistry and physics of filler dispersion become a major issue. The research challenge is particularly tremendous due to the unique character of these unusual materials. Due to strong attractive interaction, NTs tend to form bundles or "ropes" (Fig. 5) (most likely 10-200 nm in diameter) that are very difficult to disrupt[14]. Furthermore, ropes are tangled with one another like spaghetti of polymers. With high shear, these ropes can be

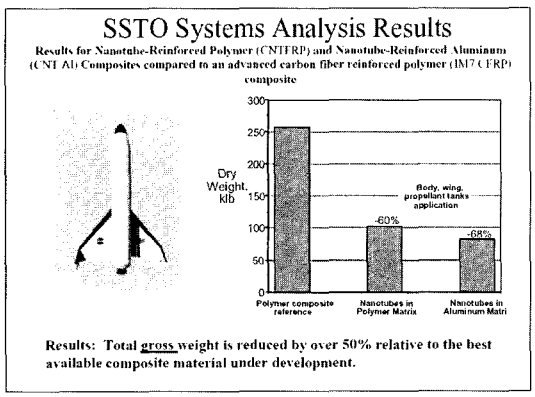


Fig. 4. Weight saving factor of carbon nanotube composites in space application[13].

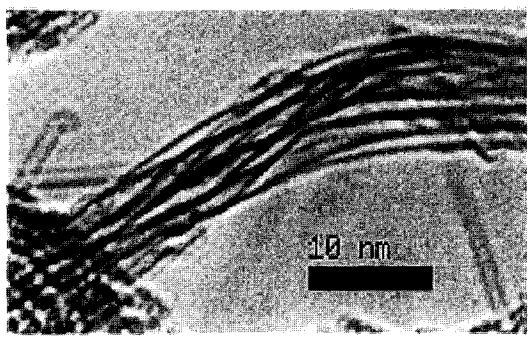


Fig. 5. TEM image of partially exfoliated SWNT showing the rope-like structure[14].

untangled, but it is extremely difficult to further disperse at the single tube level. On the other words, dispersion of nanotubes in polymers has tremendously problem in terms of thermodynamics.

On the other hand, the poor interface interaction between the carbon nanotubes and most of polymer matrix, such as epoxy, polyamide, polycarbonate, polyester, etc. Thus, the reinforcing effect of the nanotubes is limited, especially when combined with a poor dispersion.

Several methods have been reported to solve the problem, through functionalization of carbon nanotubes or strong acids, certain solvents and surfactants, which will be discussed later.

2. Dispersion of Carbon nanotube[15]

Several factors make the dispersion of nanophase carbon particularly troublesome. These factors are dominated by strong attraction between carbon species of both enthalpy and entropy origin. In addition, the nano-scale dimensionality of carbon nanotubes leads to an enhancement of these attractive forces.

The origin of the attractive forces between graphilitic structures is well known. Due to the extended π-electron system, these systems are highly polarizable, and thus subject to large attractive van der Waals forces. These forces are responsible for the secondary bonding that holds graphitic layers together. In the case of CNTs, these forces lead to so called "ropes". Extended structures are formed by side-by-side aggregation of the nanotube ropes.

When suspended in a polymer, an attractive force between filler particles also arises due to pure entropy factors[16,17]. Polymer chains in the corona region of the colloidal filler suffer an entropy penalty since roughly half of their configurations are precluded. Therefore there is a depletion of polymer in the corona, thus results in an osmotic pressure forcing the filler particles together. This effective attraction is intrinsic to colloids dispersed in polymers.

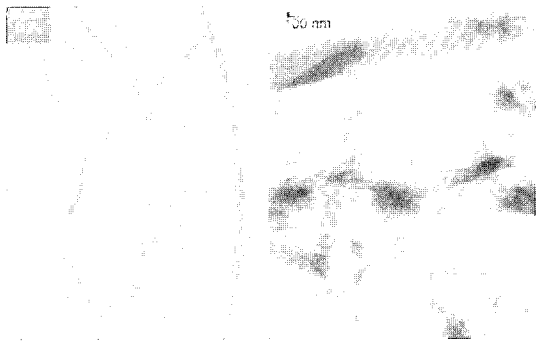


Fig. 6. Transmission electronic micrographs of CNTs[18].

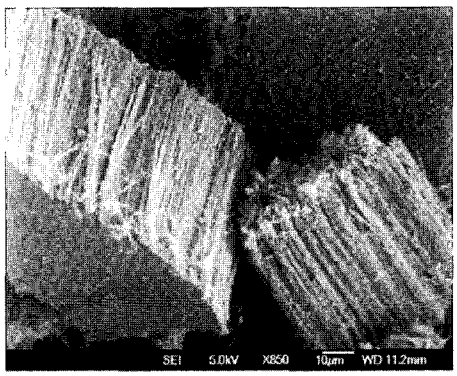


Fig. 7. Bundles of aligned nanotubes- as produced[19].

Sometime the linear structure of carbon nanotubes leads to cooperatively enhanced forces because rods interact along a line. Sometime, beside the entanglement between nanotube, the twist at the end of the tubes is also observed in some cases, depending on the fabrication method as shown in Figure 6.

It is also observed that there are types of nanotubes that are produced as bundles (Fig. 7). In order to have an optimal load transfer from the matrix to the nanotubes, they must be separated. The nanotubes are attached to each other by Van-der-Waals forces, but they interact along their whole length. Therefore, the overall attraction forces are relatively high.

Dispersion of CNTs is particularly intractable because the forces described above are especially large. The advantages of carbon nanotube fillers

have not been fully realized because of the difficulty of obtaining fully dispersed nanotubes. Also the lack of interface between the nanotubes and polymer matrix inhibits load transfer from the matrix to nanotubes[20].

The situation is improved, since strategies have been devised to overcome barriers to dispersion. A lot of methods have been reported to solve the problem of dispersion, through functionalization of carbon nanotubes or strong acids, certain solvents and surfactants.

2.1. Dispersion in solvents and surfactants

Solution-phase handling would be exceptionally useful for many of CNT applications. To date, the best solvents reported for generating SWNT dispersions are amides, particularly N,N-dimethylformamide (DMF) and N-methylpyrrolidone (NMP)[21,22]. However, the dispersions re-aggregate on a time-scale of days. Ausman et al investigated the room-temperature solubility of SWNTs in a variety of solvents. It was found that a class of non-hydrogen-bonding Lewis bases could provide better solubility [23]. The problem that pristine SWNTs are fully soluble is still not overcome.

With aid of surfactants, CNTs have been dispersed in water. Surfactants can deposit on the surface of nanotubes[24] and help form stable colloidal dispersion[25,26]. The surfactant acts as a coupling agent and may introduce a steric repulsive force between the CNTs. The repulsive force overcomes the van der Waals attractive force between the CNT surfaces. A polyelectrolyte-surfactant-MWNT complex can help MWCNTs dissolve in organic solvents by forming a lamellar structure[27]. However, removing the surfactant afterward is problematic although the instinct structure of nanotube is not destructed.

SWNTs have been solubilized by functionalization of nanotubes. For example, nanotubes could be solubilized well by functionalizing the end-caps with long aliphatic amines[28]. Further, it has been reported that SWNTs have been solubilized by functionalizing their sidewalls with fluorine[29] and with alkanes[21]. However, the above reactions caused the opening of the nanotubes tips or detrimental damage to their sidewalls owing to the harsh conditions[30,31].

2.3. Surface functionalization of CNTs

In the untreated nanotubes may be dispersed using ultrasound, but do not remain in quiescent suspension at high concentration. The use of ultrasound has been shown to cause defects at nanotubes[32]. Appropriate chemical oxidation of their surfaces, with the mixture of concentric acid and sulfuric acid, can introduce oxygen-containing functional groups onto surface. During this process, open ends are formed in the oxidizing environment. After such treatment, the nanotubes form a well-dispersed electrostatically stabilized colloid in water and ethanol[33].

It has been indicated that through chemical reaction, SWNT bundles form intercalation compounds with HNO_3 after they are immersed in nitric acid solution for a short period of time. The inter-nanotube spacing within the bundles is expanded due to intercalation. Individual SWNTs can be exfoliated from the bundles after longer exposure to HNO_3. It is demonstrated that nanotubes consisting of aggregates can be easily dispersed to individual fibers by treatment with strong acids[14].

More important is that the presence of oxidizing groups helps the attachment of organic or inorganic materials to the surface that is important to soluble nanotubes, self-assembly on surfaces and chemical sensor, although destruction of structure of nanotubes makes them less intriguing for some applications.

The intrinsic polarity of graphitic structures can be overcome by chemical means. That is, if the π-system were disrupted through defects, the polarizability and resulting van der Waals forces would be reduced. Surface functionalization might achieve this goal. However, the chemical modification of

SWNTs at the molecular level has been little studied to date. This is largely limited because it is difficult to obtain pure SWNTs, and SWNTs do not dissolve in solvents.

Several studies of chemical modification of carbon nanotubes have been reported. Chen *et al.* reported on the derivatization of SWNTs dissolved in organic solutions with thioylchroride and octadecylamine[28]. Reaction of soluble SWNTs with dichlorocarbene led to functionalization of the nanotubes. They found that by solution-phase near-infrared spectroscopy, the band gaps of some types of SWNTs could be investigated directly. This type of near–infrared spectroscopy allows the study of the effects of chemical modifications on the band gaps of SWNTs. This is very important to the molecular design of new SWNT-based materials.

Wong *et al*[34] reported modification of MWNT via amide bond. The amide bond forms between amine and carboxyl functional groups bonded to the open ends of MWNTs. With the use of these modified nanotubes as AFM tips, the binding force between single protein-ligands pairs can be measured, based on molecular interaction.

The polymer-bound carbon nanotubes can be formed by covalently attaching nanatubes to highly soluble linear polymers, such as poly(propionylethylenimine-co-ethylenimine) (PPEI-EI) via amide linkages or poly(vinyl acetate-co-vinyl alcohol) (PVA-VA) via ester linkages. The samples of polymer bound nanotubes are soluble in both organic solvents and water, and highly colored homogenous solutions are formed[35,36].

However, the above several approaches have the drawback that acid-treated end-caps, the most convenient chemical "handles" for further modification, are tied-up.

It has been demonstrated that carbon nanotubes can be covalently fluorinated within the temperature range from 250°C to 400°C[29]. And fluorine can be effectively removed from the SWNTs using anhydrous hydrazine. Boul et al reported that sidewall-alkylated nanotubes can be obtained by reacting sidewall-fluorinated nanotubes with alkyl magnesium synthesis or by reaction with alkyllithium precursors[21].

When Koshio et al investigated the purification of SWNTs by utrasonication of SWNTs in a monochlorobenzene (MCB) solution of poly(methyl methacrylate) (PMMA)[37], they found that SWNTs reacted with the organic liquid during ultrasonic process. They explained that ultrasound forms hot spots in the mixture of SWNTs and organic liquids. At the hot spots, Organic molecules, such as MCB and PMMA, are decomposed. Meantime, reactive species form and then the sidewalls of the SWNTs are damaged. Carbon-dangling bonds form under high temperature and pressure. The reactive organic species react with the dangling bonds of SWNTs. They believed that this simple ultrasonication technique should achieve surface functionalization of SWNTs in various ways[38]. In these latter cases, the sidewall functionalization coverage is high, resulting naturally in a modification of the intrinsic SWNT properties.

For applications requiring the high conductivity of carbon nanotubes, all the above methods are not attractive. Another strategy that scientists have begun to explore is to attach organic molecules to these tubular nanostructures in a noncovalent way in order to preserve the nanotubes π networks- and thus their electronic characteristics.

Dai and coworkers have found a "simple and general approach for noncovalently anchoring aromatic molecules to sidewalls of SWNTs" (Fig. 7). They used a molecule containing a planar pyreny group. The pyreny group irreversibly absorbs to the surface of a SWNT with π-stacking forces. The molecule's tail is tipped with a succinimidyl ester group. While an amine group attacks the ester function, the ester group is readily displaced and an amide bond forms[39]. This may be very useful not only for immobilizing proteins or DNA, but also for solubilizing carbon nanotubes.

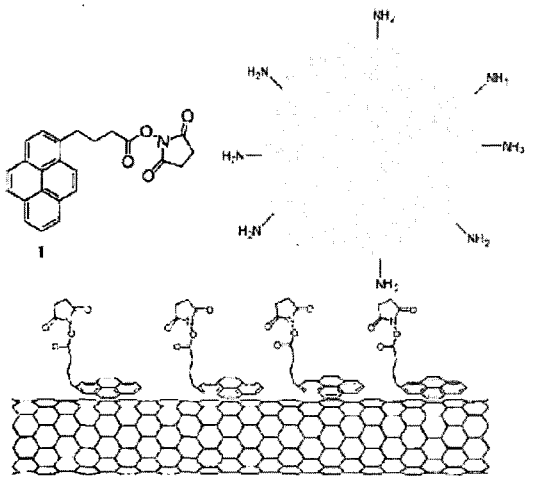


Fig. 7. Pyrenebutanoic Acid, Succinimidyl Ester 1 irreversibly adsorbing onto the sidewall of a SWNT via p-stacking[39].

Staddart et al produced bundles of SWNTs that have a conjugated polymer helically wrapped around. The polymer is a poly(m-phenylenevinylene) with octyloxy chains. After SWNTs were added to a solution of this polymer and then the mixture was sonicated, a stable suspension of nanotubes was produced. They believe that "the polymer wraps itself around the SWNT bundles, with the phenylene rings and vinyl units of the polymer backbone". The polymer hugs the nanotube surfaces, as a result of π-π interactions[40]. Since the suspension can be considered as a polymer-nanotube composite, it is mentioned in more detail on next section together with other polymer solutions that have similar behaviors. Actually, due to some analogies between polymer solution and carbon nanotube dispersion in term of an entanglement-like transition and flow-induced alignment[40], we can imagine that molecules of high molecular weight can wrap themselves around the surfaces of nanotubes.

Scientists are enthusiastic to explore potential applications of both noncovalent modification approaches, which can manipulate nanotubes into ordered array without destroying their instinct structure.

Due to agglomerate structures, carbon nanotubes are very difficult to break down physically. Therefore, fabrication of homogeneous nanocomposites with carbon tubes remains a technical challenge. Generally, nanotubes-polymer composites were fabricated by direct mixing or in-situ polymerization. Obviously, in-situ polymerization is a better way for homogenous dispersions because nanotubes are more likely to disperse in a precursor monomer than in the polymer.

3. Carbon nanotube-Polymer Interface

This interface is very important because it will allow to produce a homogeneous and stable dispersion of the nanotubes in the polymer matrix. Moreover, a strong interaction will allow an optimal load transfer between the matrix and the nanotubes. Hence improved properties are expected.

It is found that interaction between pristine nanotubes and polymers is dependent on the choice of matrix polymer and also polymer conformation, thus the molecular structure may play a critical role in the interaction. Even with "best polymer", pristine graphite may not form strong interfaces. It has been proposed that funtionalizing nanotubes or chemical bonding might increase the interaction with polymer matrix, but it was found that some mechanical properties decrease after covalent chemical modification[41], and the structure of nanotubes would be destroyed partially. It seems that MWNTs are more suitable for chemical treatment because the inner graphene layers can be unreacted, thus the essential electronic structure can be retained, but less excellent properties than SWNT and weak interaction between layers make them not attractive for a lot of applications. Few mechanisms about adhesion, load transfer and deformation were investigated, which make it difficult to accurately predict behaviors of nanotube-polymer composites and fabricate "ideal" nanocomposites. Therefore, synthesis of more dispersible nanotubes, a more complete

understanding of interfacial chemistry and dispersion mechanism and better understanding of interaction between polymer matrix and carbon nanotubes are now the main focus.

In the case of MWNT, it has been demonstrated that wrapping of polymer ropes around the tube lattice occurs in a well-ordered periodic fashion and keep them suspended in solution indefinitely. Crystalline polymer nucleates from nanotube defects and each nanotube has a uniform coating of polymer. In the case of SWNT hybrids, the pitch of the polymer coil can accommodate individual nanotubes. SWNT ropes are destroyed due to an intercalation process of polymer. At low loading fractions, the tubes are sufficiently isolated and are unable to re-aggregate. "The polymer interact strongly with nanotubes of within a diameter range of 1.35-1.55 nm and weakly with tubes of smaller and higher diameters". However, the exact nature of polymer interaction with SWNT is not reported in these papers[42-45]. And the use of SWNT for mechanical reinforcement and thermal stabilization of the conjugated polymer were not further studied.

In order to achieve the good polymer-nanotube interface, various approaches have been proposed and studied. All of these approaches are intended to modify the nature of the nanotube surface. The approaches can be categorized in general, as follows.

3.1. Non-Covalent surface modification of the nanotubes

This approach of the surface modification of nanotubes involves a van der Waals attraction between the nanotubes and various molecules.

For example, a derivative of pyrene has been attached non-covalently to the sidewalls of nanotubes. The molecule used has a pyrenyl group, that can interact with the nanotube sidewalls, and on the other side the molecule has succinimidyl ester groups, that can attract amine functional groups of the polymer matrix.

By that attachment of the derivative of pyrene, the functionality of the nanotubes is changed, in order to be more attractive towards amines or other functional groups (Fig. 8).

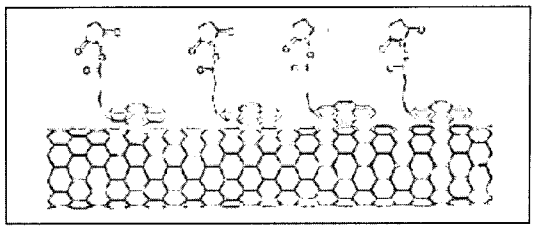


Fig. 8. Ester Derivative of Pyrene, attached to the nanotube walls[39].

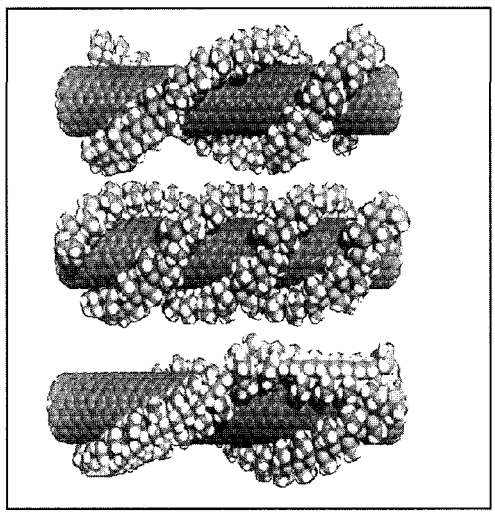
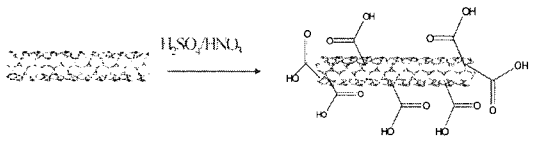


Fig. 9. Wrapping of a Nanotube by polymer chains – Illustration[46].

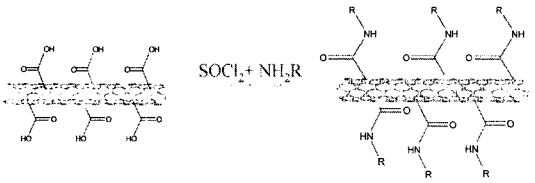
Another mechanism of non-covalent modification of the naotubes surface is called Wrapping. In that case, specific polymer chains are wrapped around the nanotubes in a helical shape (Fig. 9).

3.2. Covalent surface modification of the nanotubes

The covalent modification of the nanotube surface involves chemical reactions between the nanotubes carbon atoms and the chemical reagents. These reactions cause changes in the walls of the nanotubes, and therefore cause defects in the perfect structure of the original nanotubes.



Scheme 1. [47]



Scheme 2. [47]

Chemical modification of the nanotube can be achieved by a reaction with sulfuric and nitric acid, according to Scheme 1.

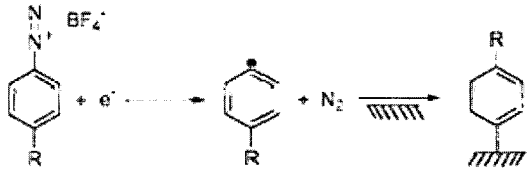
The conditions of the above reaction can cause cutting of the nanotubes length. The carboxylic acid functional groups that are formed on the nanotubes surface enable them to be dispersed readily in water. Moreover, hydrophilic polymer chains can interact with these nanotubes, in order to form a composite material, which its interface is based on the hydrogen bonding between the nanotubes and the polymer matrix.

Further reaction of the hydrophilic nanotubes with thionyl chloride, followed by a reaction with an amine terminated molecule, will transform the nanotubes into organic dispersable, according to Scheme 2.

The nature of the functional group, and in particular the R functional group in the amine reagent will determine the dispersion properties of the modified nanotubes.

The above modification can be followed by a chemical reaction with monomers or oligomers of the matrix, or only by weaker van der Waals attractions with the polymer chains.

Other chemical modifications of the nanotubes surface can be achieved by various approaches. One example is the plasma treatment of aligned and separated nanotubes, to cause functional groups to be



Scheme 3 . Electrochemical reduction of an aryl diazonium salt, giving a reactive radical that covalently attaches to a carbon surface[48].

attached covalently to the surface.

Another example is the reaction of an aryl radical on the nanotube surface, according to Scheme 3.

4. Carbon Nanotube Reinforced Thermosets

The carbon nanotubes-polymer composites were initially reported by Ajayan *et al*[49]. They just mechanically mixed the purified MWNTs with epoxy resin. Since then, attention has been paid to composite materials with uniform and high nanotubes loading. Carbon nanotube epoxy composites are most widely studied as nonconjugated polymer-based composites.

Sandler *et al*[50] reported that untreated carbon nanotubes were dispersed in an epoxy matrix. The use of carbon nanotubes not only reduces the percolation threshold to below 0.04 wt%, but also increases the overall conductivity. Although ultrasound in ethanol and the intense stirring process improves the dispersion of the nanotubes, it is not impossible to break up all the entanglements of the carbon nanotubes. Even on the millimeter scale the distribution of nanotubes is not uniform.

The matrix used in this study is an epoxy polymer based on bisphenol-A resin (Araldite LY 556, Ciba Geigy) and an aromatic hardener (Araldite HY 932, Ciba Geigy). The carbon nanotubes used are supplied under contract by Hyperion Catalysis International, Cambridge USA. They are generated by decomposition of hydrocarbon gases. The supplied powder consists, almost exclusively, of balls of loosely aggregated nanotubes that are non-coiled

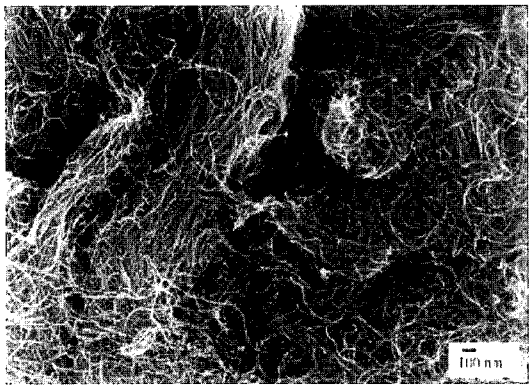


Fig. 10. SEM image of catalytically-grown nanotube matrial, as-supplied.

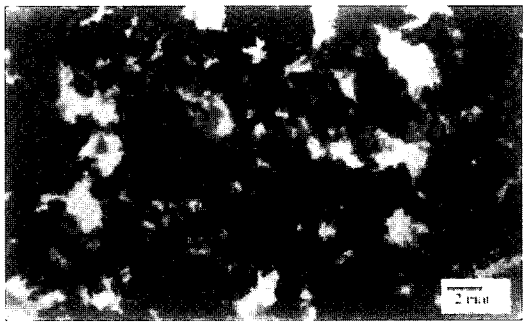


Fig. 11. Magnified transmission light photograph of the sample containing 0.0225 wt.% catalytically-grown carbon nanotubes, highlighting the formation of aggregates. The sample thickness was 0.5 cm.

but generally curved. Their outer diameter is about 10 nm and inner diameter of around 5 nm and they have a length of a few microns (Fig. 10).

Weight percentages ranging from 0.0225 to 0.15 wt% of the untreated catalytically-grown carbon nanotubes were dispersed in the resin. The necessary weight fractions were first dispersed in ethanol in an ultrasonic bath at room temperature for 1 h. After mixing the ethanol-based solution into the resin, the suspensions were stirred for 1 h at 2000 rpm. During the stirring process, the temperature of the resin was kept at 80°C using a silicone oil bath in order to maintain a low viscosity of the resin. In order to evaporate the ethanol the mixtures were placed in a vacuum oven at 80°C for 1 h. The mixtures were then stirred again for 1 h at 2000 rpm. After adding the hardener, the mixtures were stirred at 2000 rpm for 15 min. The epoxy was hardened in a vacuum oven at 140°C for 8 h.

All the cured epoxy samples but the one containing the lowest filler weight fraction of 0.0225 wt.% appeared completely black to the naked eye. It is interesting to note that even on the millimetre scale the distribution of nanotubes is not uniform. Figure 11 shows that there are regions with a dearth of nanotubes, whilst higher density regions percolate across the sample. The conductivity of the nanocomposites were measured using sample lengths of about 75 mm. This length is more than an order of magnitude larger than the maximum variation in the carbon nanotube density and therefore provides a valid measurement of the bulk conductivity.

Allaouia *et al*[18] have reported the formation of rubbery epoxy matrix reinforced with MWNT. Epoxy polymer matrix was prepared by mixing 15 parts by volume of epoxy resin (bisphenol A-epichlorhydrine) with 2 parts of aromatic hardener (triethylenetetramine). Epoxy resin contains one or more epoxide groups that serve as cross-linking points when the resin reacts with the hardener to form long chains, the polymerization. The over-aged hardener used in this work produced a rubbery epoxy matrix. The hardener has an impact on the matrix structure and the cross-linking ratio and by this way the molecular motions.

CNTs used in this study were synthesized by (CVD) thermal decomposition of hydrocarbon gas. Benzene was used as carbon source, thiophene as growth promoter, ferrocene as catalyst and hydrogen as carrier gas. The relative ratio of different components in the reaction system was controlled by adjusting the carrier gas flow rate. Through controlling the reaction time and relative components of benzene, thiophene and ferrocene, carbon nanotubes and carbon nanofibers of different diameter and structure can be obtained.

The obtained MWNTs have diameters in the

range of 15-400 nm, the mean diameter being 100 nm, and average length a few hundreds microns (Fig. 6). They are highly entangled and randomly organized. There are some catalyst particles, amorphous carbon and onions as impurities.

The as-prepared CNTs material consists of aggregates of different sizes. The bigger ones are millimetric or even centimetric. This would be an obstacle to the uniform dispersion of MWNT into the epoxy matrix. A procedure of two steps was followed. The MWNT were first dispersed in methanol solution under magnetic agitation to reduce the maximum size of the aggregates to about 100 m. After complete evaporation of methanol, the obtained MWNT powder was then directly added to the epoxy resin bisphenol A/aromatic hardener mixture. Finally, it was injected into sample moulds after manual homogenization. The 4 wt.% samples were very viscous and the homogenization process was difficult. The samples were placed between two metal plates under pressure to reduce porosity forming during hardening.

The optical microscope observations revealed the presence of porosities and CNTs aggregates (small size for the 1 wt.% composites and large for the 4 wt.% samples). On the polished surface of samples, there are some zones with very high local CNT concentrations, as shown in Fig. 12a. The distribution of CNTs is more homogeneous in the 1 wt.% samples (Fig. 12b).

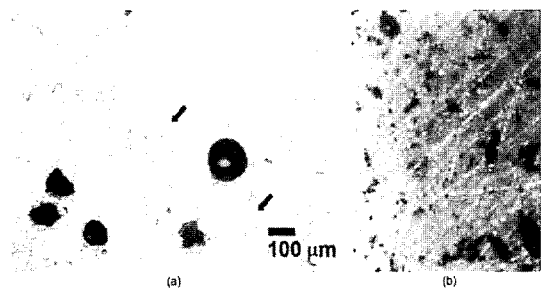


Fig. 12. (a) Optical micrographs of the surface of the 4 wt.% CNT composite. The porosities are marked by white arrows and the zones of very high local CNT concentration by black arrows. (b) Optical transmission light micrograph of the surface of 1 wt.% CNT composite.

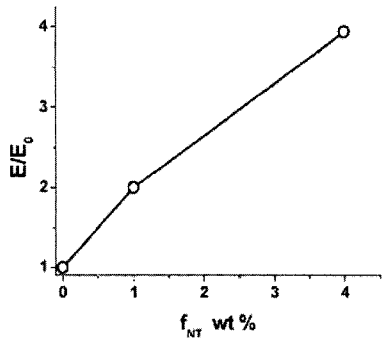


Fig. 13. Normalized Young's modulus of the composites.

Even the dispersion is very poor, the improvement in modulus has been observed linearly with nanotube concentration [Fig. 13].

Puglia *et al*[51] report nanocomposites prepared from DGEBA epoxy resin, a diethylene triamine (DETA) hardener and an AP-grade nanotubes (SWNTs) (CarboLex). The material consisted of packed bundles of SWNTs 12-20 Å in diameter. There were approximately 30 nanotubes per bundle (with an average bundle diameter of 100 Å) several micrometers in length (data provided by Carbolex).

For composite production, SWNTs were sonically dispersed for 2 h in the liquid epoxy resin before curing. All samples were then cured with DETA with a stoichiometric weight ratio DETA/DGEBA= 1:7.248, using a cure schedule with a temperature ramp from 30 to 250°C at a heating rate of 10°C min-1. Two concentrations of nanotubes were analysed: 5% and 10% specified as the weight phr with respect to the cured resin.

Using Raman spectroscopy and microscope, they have concluded that there is an opening of the nanotube bundles produced by the intercalation of the resin (Fig. 14). However, for the 10% DGEBA/ DETA-SWNT composites no further intercalation of the polymer and at higher nanotubes concentrations no further dispersion of the nanobundles occurred.

Thermogravimetric curves obtained for DGEBA

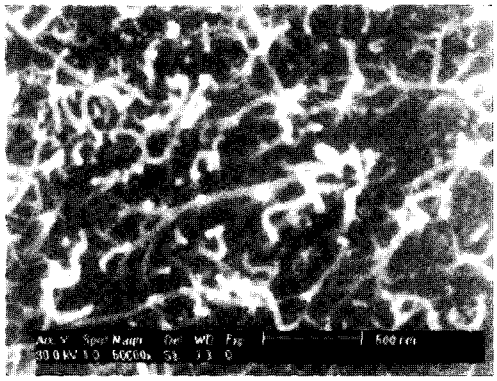


Fig. 14. SEM images of 5% DGEBA/DETA-SWNT composit.

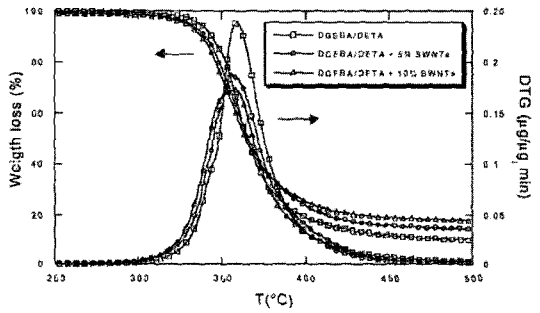


Fig. 15. TG curves in nitrogen (heating rate 10 °C/min) of the DGEBA/DETA system and DGEBA/DETA-SWNT composites.

and DGEBA-SWNT composites are reproduced in Figure 15, which show that the DGEBA-SWNT composites exhibit a lower thermal stability. The higher weight loss is clearly evident at the lowest reinforcement content with a slight further decrease with the SWNT concentration.

Goinya *et al*[52] were modified the arc-grown MWNT (produced at TUHH or obtained by MER Inc.) by heating with an excess of a mixture of sulphuric and nitric acid in order to remove impurities of carbon black and graphite nanoparticles. These oxidised MWNTs were separated by centrifugation and membrane micro-filtration (Millipore Durapore Membrane) and washed with distilled water and acetone.

In a second step the oxidized nanotubes were heated with an excess triethylenetetramine, again separated by centrifugation and membrane microfiltration, and finally washed with acetone. For the preparation of the nanocomposites, a suspension of oxidized MWNTs in acetone and of amino-functionalised nanotubes in acetone were sonicated for 30 min and finally slowly dispersed in heated epoxy resin (Ruetapox 0164/LV). After cooling down to room temperature the hardener was added to each of the two samples and finally cured for 24 h at room temperature.

This procedure improves the interaction with the matrix is comparable to previous work by Chen *et al.*[28] using an ionic functionalisation to improve the stability of single wall carbon nanotube (SWCNT) suspensions. In order to remove amorphous carbon, the nanotubes were treated with oxidising inorganic acids. Besides the fast removal of these thermodynamically less stable impurities, a much slower oxidation of the nanotubes, starting at structural defects and at the caps of the tubes, occurs. Through this treatment the outer shells were destructed to some extent, but carboxylic groups appear on the surface. The reaction of the oxidized nanotubes with triethylenetetramine leads to a mixture of covalently and ionically bonded amines on the surface of the nanotube. The ionic form of the functionalised nanotubes can be transformed into the covalent bonded amide by removing water while heating in vacuum. The main reasons for the choice of this functionalisation are: (i) the advantage of high yields and (ii) in particular the possibility of scaling up this procedure to larger scales, which is necessary for a potential technical application. The investigation via TEM showed that the agglomeration could be reduced by the introduction of functional groups. The steric and electrostatic repulsion of the functional groups lead to a better dispersion of the nanotubes (Fig. 16).

The presence of carboxylic acid groups on the surface enables a better dispersion of CNTs and reduces the amount of impurities. The nanotube/matrix interactions of oxidized MWCNTs and the

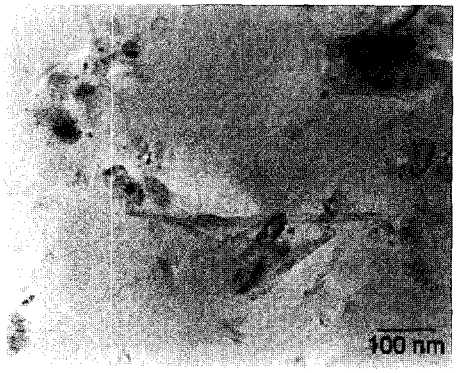


Fig. 16. TEM image of oxidised MWCNTs embedded in epoxy resin. The tubes are completely dispersed in the matrix due to the appearance of carboxylic groups on the surface.

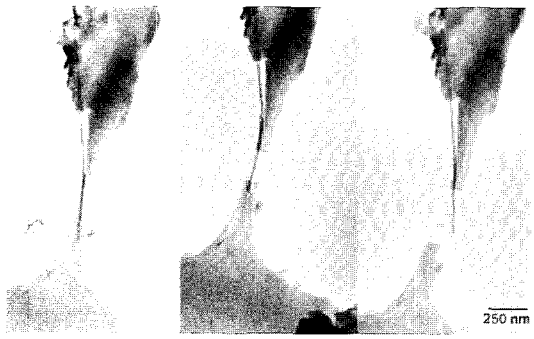


Fig. 17. A weak interaction between the epoxy matrix and the nanotube leads to pull-out.

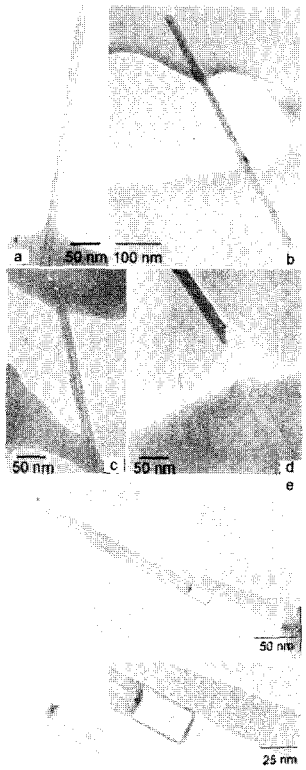


Fig. 18. TEM image of functionalised MWNTs: (a) Matrix covers the surface of the carbon nanotubes which indicates an improved interaction; (b and c) Nanotubes should improve the fracture toughness by bridging micro-cracks and proes in the matrix; (d and e) Telescopic pull-outs substantiate the evidence of improved interactions.

epoxy resin seem to be still weak and as a consequence of this, the stress transfer from the matrix to the tube is low and pull-outs of the CNTs from the surrounding matrix were observed (compare Fig. 17). A further chemical derivatisation seems to be useful in order to make the outstanding properties of the carbon nanotubes accessible for an application as a reinforcing filler in epoxies. This derivatisation of the oxidised MWNTs was achieved by a reaction with triethylenetetramine. These introduced functional groups lead to covalent bonds with the epoxy resin. The TEM-micrographs (Fig. 18) of functionalised nanotubes in the same epoxy resin shows CNTs that are completely covered with matrix. A further evidence for a strong interaction is telescopic pull-out, which is a typical damage mechanism for MWNTs under tensile load (Fig. 18e). The outermost layer, which is directly bonded to the matrix, remains in the matrix, while the inner-tube bridges the crack. The interactions between the shells of a MWNT seems to be weaker than those to the matrix, as we can assume only van-der-Waals forces between the shells.

They also observed some examples with matrix remaining on the caps and along sidewalls of the CNT. Initial points for the oxidation of the MWNTs are the caps and structural defects along the sidewalls, where accordingly the density of functional groups is higher than on the non-oxidised sidewalls, which enables the matrix bonding.

Finally, they have stressed that the oxidation

leads, besides the introduction of functional groups, to structural defects, which may decrease the potential strength of the nanotubes. They suppose that the degree of oxidation and accordingly, the degree of functionalisation has a certain influence on the mechanical properties of the resulting composite. A widely destructed surface leads to a debonding of the nanotube whereas the inner concentric tubes are pulled out and parts of the outer shells, which are bonded to the matrix, remain in the matrix.

Gong *et al.*[53] reported the fabrication of nanocomposites based on an AP (as-prepared)-grade carbon nanotube (MWNT) (Carbolex at the University of Kentucky) and bisphenol A epoxy resin with hydroxylated polyamine hardener H-917 (Composite Materials Inc, Arlington, WA). A typical preparation of the carbon nanotube-epoxy composites is as follows: 19.2 mg Polyoxyethylene 8 lauryl, $(CH_3(CH_2)_{11}(OCH_2CH_2)_7OCH_2CH_3)$ or $C_{12}EO_8$ (Sigma) was dissolved in 0.5 g acetone in a small beaker. 25.2 mg carbon nanotube was added to the as-prepared C12EO8 solution. This mixture was sealed with a plastic film (Parafilm) and magnetically stirred for 15 min with a stir-bar at room temperature. Then 2.0 g epoxy and 0.5 g hardener were added. This produced a viscous suspension. The suspension was sealed and stirred for another 15 min until it appeared to be homogeneous. The mixture was poured into a mold with a dimension of 20×3×1 mm, cured at room temperature overnight, followed by an elevated temperature cure at 80°C for 2 h and 120°C for 2 h.

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (SEM) revealed that the received carbon nanotubes have a diameter from 2 to 4 nm. A small fraction of the carboneous materials are made of partially disordered spherical particles. Examination of the cross-section TEM image suggests that the partially disordered particles are also made of short carbon nanotubes centered around the nickel particles used in the preparation of the carbon nanotubes. The surface area of the as-received carbon nanotubes, as measured by nitrogen adsorption technique, is 252 m^2/g.

They pointed out that even with the addition of the surfactant, complete homogeneous dispersion of the nanotubes was not achieved. The gas-phase synthesized carbon nanotubes usually contain agglomerate structures that can be very difficult to breakdown physically. There are regions with more carbon nanotubes, and regions with less carbon nanotubes. More carbon nanotubes are observed within the domains of an agglomerate. However, the addition of surfactant into carbon nanotubee composite increased significantly the storage modulus and glass transition temperature (T_g) while the addition of the surfactant by itself in the epoxy matrix has little effect on the glass transition temperature, but decreases the storage modulus. The decrease of the modulus by the surfactant is expected because the surfactant functions as a plasticizer (Table 1).

Lau *at el*[54] reported the nanocmposites produced from two different types of nanotubes (raw SWNT soot grown by the HiPCO method[12] or vapor grown carbon fibers (VGCF) from Applied Sciences, Inc) and Shell Chemicals Epon 862 epoxy resin and Air Products Ancamine 2435 dimethane-amine curing

Table 1. Storage moduli and transition temperatures of the epoxy and carbon nt composite samples

	G' (GPa)			T_g(C)	
Samples	-60°C	-20°C	20°C	tan	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% NT	2.12	1.90	1.60	72	53
(d) Epoxy + $C_{12}EO_8$ + 1% NT	2.54	2.18	1.80	88	64

agent. The SWNT material contained approximately 15-25 wt% Fe catalyst in the form of isolated nanoparticles.

Care was taken to disperse carbon material uniformly through the composite. Carbon materials were dispersed ultrasonically for as long as 48 hours in an organic solvent (dichloroethane or N-N dimethylformamide) to promote the formation of a stable suspension. The epoxy resin was subsequently dissolved in the carbon/solvent mixture; high quality dispersal was indicated by the formation of a smooth emulsion. This solution was placed under vacuum to remove trapped air. After degassing, samples were placed on a hotplate at 130°C for an hour to completely evaporate the solvent. The curing agent was added, and the samples cured at room temperature for two to four days followed by a 2 h post-cure bake at 120°C. Loading was studied up to 5 wt%; Fig. 19 shows that the SWNTs were well dispersed in the material on the micrometer scale, with random tube/rope orientation. Samples were black, however, indicating that the dispersal was still not ideal.

They also observed that "Pyrograf-III" vapor grown carbon fibers (VGCF) have an average diameter of 200 nm and lengths from several microns to over 10 mm. During sample production (mixing, sonication) these fibers tend to break to lengths below 100 μm.

Barrera[55] has emphasized that SWNTs, without a doubt, require initial purification to remove fullerenes, amorphous carbon and unwanted catalyst. A degree of separation of the nanotubes can be obtained in toluene. The initial agglomerated form of SWNTs limits somewhat the ability to produce dry SWNT dispersed in epoxies and other polymer matrices. Use of high-shear mixing is playing a role and when coupled to elongational flow, should prove useful in giving aligned nanotube composite forms.

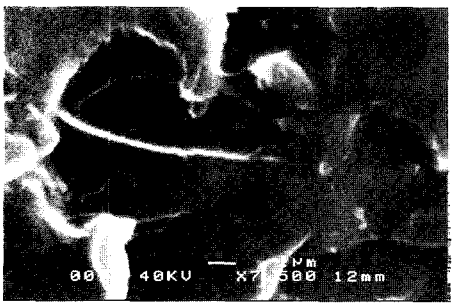


Fig. 19. Scanning electron micrograph of 1 wt% SWNT-epoxy composite. Randomly oriented nanotube bundles are clearly visible throughout the matrix.

Vaccarini *et al*[56] have prepared the nanocomposites from epoxy resin (Ciba Araldite LY556 with HTHT972 hardener) and arc-SWNT (purified in nitric acid and annealed at 1600°C under nitrogen atmosphere). The SWNTs (0-35 wt%) were dispersed in CH_2Cl_2 is then sonicated with the epoxy. Due to the high SWNT loading, only poor dispersion and modest improvement in Young modulus have been observed.

Spindler-Ranta *et al*[57] have produced the nanocomposites from Dow DER 383 bisphenol A epoxy resin with Hunstman Jeffamine T-403 triamine hardener and Carboflex AP-grade MWNT (with between 50-70 purity, without further purification) using the procedure reported by Gong *et al*[53] with high power ultrason (900 W) up to 90 min. The nanocomposites at low loading of 1 wt% has a good dispersion of the clusters but not of the individual NTs. At 5 wt% loading, poor dispersion and voids have been observed. No improvement in compression strength can be obtained.

Breton *et al*[58] have modified the MWNT (synthesized by catalytic decomposition of acetylene on CoxMg(1-x)O solid solution at 600°C) by sodium hypochloride 12° Cl at ambient temperature, then annealed at 2400°C under Argon. High energy sonication has been used to prepare the nanocomposites (3-6 wt% NT). The oxidation has shortened down the NT length, however, it improved the interface. Thus, its nanocomposite properties are higher than those with unmodified NT.

Ajayan *et al*[59] have fabricated epoxy-SWNT bun-

dles (5% wt), loaded in tension and compression and looked at the Raman spectroscopy results as a function of applied strain. Hypothesize that the transfer between matrix and NT may be limited, because the NTs are slipping within the bundles. Failure that they see at large crack distances is not tube failure, but rather bundles falling apart. They get this result because of constant values of the Raman peaks (indicating that the individual tubes are not being strained). They also looked at CNT-carbon composite pellets. Show some results of the CNTs on the fracture surface, but really don't discuss much.

Watson *et al*[60] have reported the formation of polyimide nanocomposites. 0.0060 g of nanotube and 10 ml of dimethylformamide was placed in an ultrasonic bath for periods ranging from 16 to 24 h before adding to the monomers for producing the nanocomposite. The addition of carbon nanotube reduced slightly the tensile strength but significantly the modulus while increased slightly the tensile modulus of the thin film polyimide. In addition, it also reduced the optical transmission of the film due to a poor dispersion of carbon nanotubes.

Park *et al*[61] have also prepared the polyimide nanocomposites in a similar way. A dilute SWNT solution, typically around 0.05 wt% in dimethylformamide (DMF), was prepared by homogenizing for 10 min (750 rpm with a 6 mm diameter rotor) and sonicating for one and a half hours in an ultrasonic bath (40 kHz). After stirring the SWNT solution for 10 min, the diamine (APB) was added into the SWNT solution. The SWNT and diamine mixture continued to be stirred for 30 min before adding the dianhydride (6FDA). The entire reaction was carried out in the flask immersed in an ultrasonic bath (40 kHz) until the solution viscosity increased and stabilized. Additional stirring was continued overnight to form the SWNT-poly(amic acid) solution without sonication. Solid content for SWNT-poly(amic acid) was 15% (w/w) in DMF. Acetic anhydride and pyridine were used as catalysts to imidize the SWNT-poly(amic acid) chemically.

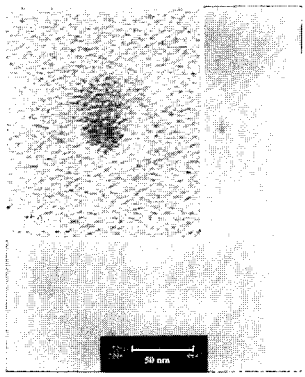


Fig. 20. TEM micrograph of 1.0 vol% SWNT-CP2 nanocomposite, The inset shows SWNT bundles dispersed in the polymer matrix at higher magnification.

An efficient dispersion of SWNT bundles in a polymer matrix was achieved. This method included in situ polymerization with SWNT and sonication during the reaction. The pre-dispersed SWNT dispersion remained stable throughout the reaction under sonication, producing a reasonably transparent, electrically conductive SWNT-CP2 nanocomposites at very low SWNT loading. The resultant SWNT-polymer nanocomposite exhibited significant conductivity enhancement (10 orders of magnitude) at a very low loading (0.1 vol%) without significantly sacrificing optical transmission. Mechanical properties as well as thermal stability were also improved by the incorporation of the SWNT. TEM study of the nanocomposite, such as in Figure 20, showed a bundle diameter range of 2-20 nm.

References

1. Iijima S. : Nature, **56** (1991) 354.
2. http://www.pa.msu.edu/cmp/csc/nasa/main.html
3. Ebbesen, T. W. : Carbon Nanotubes: Preparation and properties, CRC Press, Baca Raton, FL (1997).
4. Rinzler, A. G., Hafner, J. H., Nikolaev, P., Lou, L., Kim, S. G., Tomanek, D., Nordander, P., Cobert, D. T. and Smalley, R. E. : Science (1995) 2691.
5. Van de Heer, W. A., Chatelain, A., Ugarte, D. : Science, **270** (1995) 1179.

6. Collins, P. G., Zettl, A., Bando, H., Thess, A. and Smalley, R. E. : Science, **278** (1997) 100.
7. Wagner, H. D., Lourie, O., Feldman, Y. and Tenne, R. : Appl. Phys. Lett., **72** (1998) 188.
8. Dagani, R. : Chem. Eng. News, June **7** (1999) 25.
9. Wang, Z. L., Poncharal, P., de Heer, W. A. : First IUPAC Workshop on Advanced Materials: Nanostructured Systems, Hong Kong, **14-18** (1999).
10. Feist, T. P. As quoted in ref 5.
11. Calvert, P. D. : Nature, **399** (1999) 210.
12. Carren, S. A., Ajavan, P. M., Blau, W. J., Carroll, D. L., Coleman, J. N., Dalton, A. B., Davey, A. P., Drury, A., MaCarthy, B., Maier S. and Strevens, A. : Adv. Mater, **10** (1988) 1091.
13. mdob.larc.nasa.gov/summary01/B1_GILBERT.pdf
14. Bower, C., Kleinhammes, A., Wu, Y. and Zhou, O. : Chem. Phys. Let. **288** (1998) 481.
15. Zhao, J : Report on Dispersion of Carbon Nanotubes and Their Polymer Composites, Department of Materials Science and Engineering, University of Cincinnati (2001).
16. Bechinger, C., Rudhardt, D., Leiderer, P., Roth, R. and Dietrich, S. : Phys. Rev. Let. **83** (1999) 3960.
17. Rudhardt, D., Bechinger, C. and Leiderer, P. : J. Physics-Condensed Matter **11** (1999) 10073.
18. Allaouia, A., Baia S., Cheng, H. M., and Bai, J. B. : Comp. Sci. Tech. **62**(15) (2002) 1993.
19. http://www.rpi.edu/locker/25/001225/public_html/nano_02/eitana/eitana/Ami%27s%20Website/characterization%20of%20interface.htm
20. Tiano, T., Roylance, M. and Gassner, J. : Int. SAMPE Tech. Conf. **32** (2000) 192.
21. Boul, P. J., Liu, J., Mickelson, E. T., Huffman. C. B., Ericson, L. M., Chiang, I. W., Smith, K. A., Colbert, D. T., Hauge, R. H., Margrave, J. L. and Smalley, R. E : Chem. Phys. Let. **310** (1999) 367.
22. Liu, J., Casavant, M. J., Cox, M., Walters, D. A., Boul, P., Lu. W., Rimberg, A. J., Smith, K. A., Colbert, D. T. and Smalley, R. E. : Chem. Phys. Lett. **303** (1999) 125-129.
23. Ausman, K. D., Piner, R., Lourie O. and Ruoff, R. S. : J. Phys. Chem. B. **104** (2000) 8911.
24. Liu, J., Rinzler, A. G., Dai, H. J., Hafner, J. H., Bradley, R. K., Boul, P. J., Lu, A., Iverson, T., Shelimov, K., Huffman, C. B., RodriguezMacias, F., Shon, Y. S., Lee, T. R., Colbert, D. T. and Smalley, R. E. : Science, **280** (1998) 1253.
25. Krstic, V., Duesberg, G. S., Muster, J., Burghard, M. and Roth, S. : Chem. Mater., **10** (1998) 2338.
26. Duesberg, G. S., Muster, J., Krstic, V., Burghard, M., Roth, S., Appl. Phys. A: Mater. Sci. Process., **A67** (1998) 117.
27. Jin, Z. X., Huang L., Goh, S. H., Xu, G. Q. and Ji, W. : Chem. Phys. Lett. **332** (2000) 461.
28. Chen. J., Hamon, M. A., Hu, H., Chen, Y., Rao. A. M., Eklund, P. C. and Haddon, R. C. : Sience, **282** (1998) 95.
29. Mickelson, E. T., Chiang, I. W., Zimmerman, J. L., Boul, P. J., Lozano, J., Smalley, R. E., Hauge, R. H. and Margrave, J. L. : J. Phys. Chem. B **103** (1999) 4318.
30. Brenner, D. W. S., Mcwkill, J. P. and Shenderova, O. A. J. : Br. Int. Soc., **51** (1998) 137.
31. Garg, A. and Sinnot, S. B. : Chem. Phys. Lett. 1998, 295, 273.
32. Lu, K. L., Lago, R. M., Chen, Y. K., Green, M. L. H., Harris, P. J. F. and Tsang, S. C. : Carbon, 34 (1996) 814.
33. Shaffer, M. S. P., Fan, X. and Windle, A. H. : Carbon, **36**(11) (1998) 1603.
34. Wong, S. S., Joselevich E., Woolley, A. T., Cheung, C. L. and Lieber, C. M. : Nature, **394**(2) (1998) 52.
35. Riggs, J. E., Guo, Z., Carroll, D. L. and Sun, Y. P. : J. Am. Chem. Soc. **122** (2000) 5879.
36. Riggs, J. E., Wakker, D. B., Carroll, D. L. and Sun, Y. P. J. : J. Phys. Chem. B., **104** (2000) 7071.
37. Yudasaka, M., Zhang, M., Jabs, C. and Iijima, S. : Appl. Phys. A, **71** (2000) 449.
38. Koshio, A., Yudasaka, M., Zhang, M. and Lijima. S. : Nano Lett., **1**(7) (2001), 361.
39. Chen, R. J., Zhang, Y. G., Wang, D. W. and Dai, H. J. : J. Am. Chem. Soc., **123** (2001) 3838.
40. (a) Star, A., Stoddart, J. F., Steuerman, D., Diehl, M., Boukai, A., Wong, E. W., Yang, X., Chung, S., Choi, H. and Heath, J. R. : Angew. Chem. Int. Ed., **40** (2001) 1721. (b) Shaffer, M. S. P., Windle : A. H. Macromolecules, **32** (1999) 6864-6866
41. Garg, A. and Sinnott, S. B. : Chem. Phy. Lett. 295 (1998) 273.
42. Curran, S. A., Ajayan, P. M., Blau, W. J., Carroll, D. L., Coleman, J. N., Dalton, A. B., Davey, A. P., Drury, A., McCarthy, B., Maier, S. and Strevens, A. : Adv. Mater., **10**(14) (1998) 1091.
43. Dalton, A. B., Stephan, C., Coleman, J. N., McCarthy, B., Ajayan, P. M., Lefrant, S., Bernier, P., et. al. : J. Phys. Chem. B, **104** (2000) 10012.
44. McCarthy, B., Coleman, J. N., Curran, S. A., Dalton, A. B., Davey, A. P., Konya, Z., Fonseca, A., et. al. : J. Mater. Sci. Lett., **19** (2000) 2239.
45. Dalton, A. B., Blau, W. J., Chambers, G., Coleman, J. N., Henderson, K., Lefrant, S., McCarthy, B., et. al. : Synth. Met. **121** (2001) 1217.
46. O'Connell, M. J. : Chem.Phys. Lett., **342** (2001) 265.
47. Liu, J. : Science, **280** (1998) 1253.
48. Bahr, J. L. : J. Am. Chem. Soc, **123** (2001) 6536.
49. Ajayan, P. M., Stephan, O., Colliex, C. and Trauth, D. :

Science, **265** (1994) 1212.
50. Sandler, J., Shaffer, M. S. P., Prasse, T., Bauhofer, W., Schulte, K. and Windle : A. H. Polymer **40** (1999) 5967.
51. Puglia, D., Valentini, L., Armentano, I. and Kenny, J. M. : Diamond and Related Materials; Journal in Press.
52. Gojnya, F. H., Nastalczyka, J., Roslaniecb, Z. and Schulte, K. : Chem. Phys. Lett.; in Pres.
53. Gong, X., Liu, J., Baskaran, S., Voise, R. D. and Young, J. S. : Chem. Mater. **12**(4) (2000) 1049.
54. Lau, A. K.-T. and Hui, D. : Comp. Part B: Eng. **33**(4) (2002) 263.
55. Barrera, E. V. : JOM, 38 (2000).
56. Vaccarini, L., Desarmot, G., Almairac, R., Tahir, S., Goze, C. and Bernier, P. : Mol. Nanostruct. : Elec. Prop. Novel Mater. **544**(1) (2000) 521.
57. Spindler-Ranta, S. and Bakis, C. E. : 4th Internaltional SAMPE Symposium, 1775 (2002).
58. Breton, Y., Salvetat, J. P., Desarmot, G., Delpeux, S., Sinturel, C., Beguin, F. and Bonnamy, S. : Mol. Nanostruct. : Elec. Prop. 633 (2002) 574.
59. Ajayan, P., Schadler, L., Giannaris, C. and Rubio, A., Adv. Mater. **12**(10) (2000) 750.
60. Watson, K. A., Smith, J. G. and Connell, J. W. : 33rd International SAMPE Technical Conference, 1551 (2001).
61. Park, C., Ounaies, Z., Watson, K. A., Crooks, R. E., Smith Jr, J., Lowther S. E., Connell, J. W., Siochi, E. J., Harrison, J. S. and St Clair, T. L. : Chem. Phys. Lett. 364 (2002) 303.