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Effect of carbon nanotube (CNT) functionalization in epoxy-CNT composites

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Abstract: The effect of carbon nanotube (CNT) functionalization in altering the properties of epoxy-CNT composites is presented. The presence of functional groups effectively influenced the colloidal behavior of CNTs in the precursor epoxy resin and the hardener triethylenetetramine (TETA), which affected the synthesis process and eventually the interfacial interactions between the polymer matrix and the CNTs. The physical, thermal, and electrical properties of the composites exhibited strong dependence on the nature of functionalization. At a 0.5-wt% CNT loading, the enhancement in tensile strength was found to be 7.2%, 11.2%, 11.4%, and 14.2% for raw CNTs, carboxylated CNTs, octadecyl amide-functionalized CNTs, and hydroxylated CNTs, respectively. Glass transition temperatures (T_g) also varied with the functionalization, and composites prepared using hydroxylated CNTs showed the maximum enhancement of 34%.

Keywords: functionalized carbon nanotube; interfacial interaction; nanocomposites; physical properties; thermal properties.

1 Introduction

There has been much interest in nano-carbon-based composites and, in particular, carbon nanotubes (CNTs) [1–10]. The incorporation of small amounts of CNTs is known to improve properties such as mechanical strength, fracture toughness, thermal stability, permittivity, and electrical conductivity [11–17]. Epoxy has unique mechanical, thermal, and electrical properties, which makes it attractive for various applications such as fiber-reinforced composites, laminates, adhesives, and coatings [18–21].

However, cured epoxy is brittle, rigid, and shows poor crack propagation resistance and low impact strength [22, 23]. Researchers studied the mechanical, thermal, and electrical properties of epoxy-CNT composites thoroughly [24–27]. The application of an epoxy-CNT composite onto glass fibers have shown to reduce stress concentration [28] and enhanced electromagnetic shielding [29]. The influence of different types of CNTs with varying lengths and graphitizations on the properties of epoxy-CNT nanocomposites and the kinetics of curing liquid-crystal epoxy with CNTs were also investigated [30–32].

The capability to regulate the CNT dispersion into a polymer matrix is important in applications related to nanocomposites [33]. In general, the effective incorporation of nanomaterials (NMs) including CNTs into a polymer matrix depends upon the interactions with the polymer [34, 35]. The high specific surface area of the NMs provides a desirable interface; however, the uncertainty in interfacial bonding is a concern [36]. The CNTs have a high aspect ratio, but they entangle with each other and are difficult to disperse [37–39]. The introduction of functional groups on the CNT surface promotes efficient adhesion to the polymer and contributes to better dispersion [40–42]. While much was reported about the epoxy-CNT composites, specific interaction based on functionalization is yet to be studied. Another important factor is that the colloidal behavior of the CNT dispersions, which depends on the type of functionalization, is important in understanding their stability in the liquid phase precursors and eventually determines the polymer-CNT interactions in the solid composite. The objective of the present work is to study the influence of various CNT functional groups on the different properties of epoxy-CNT composites.

2 Materials and methods

2.1 Material synthesis

Epoxy resin (D.E.R.TM 332, epoxy equivalent weight 176) and an amine hardener (Triethylenetetramine, Tech., 60%) were used for this study. Anhydrous 1-butanol

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(99.8%) and xylene (ACS Reagent, 98.5%) were used as solvent for the epoxy and the amine hardener. Nitric acid (ACS reagent, $\geq 90.0\%$), sulfuric acid (99.9%), thionyl chloride (reagent grade, 97%), N,N-Dimethylformamide (ACS reagent, $\geq 99.8\%$) and octadecylamine (97%) were used for CNTs purification and functionalization. All of the materials were purchased from Sigma Aldrich Inc., Saint Louis, MO, USA.

The raw CNTs and CNT-OH (30-nm average diameter and $\sim 15\text{-}\mu\text{m}$ length) were procured from Cheap Tubes Inc., Brattleboro, VT, USA, and were purified with dilute nitric acid. Functionalization via carboxylation (CNT-COOH) and octadecyl amide(-CO-NH-C₁₈H₃₇) formation (CNT-ODA) were carried out in our laboratory in a Microwave Accelerated Reaction System (Mode: CEM Mars, CEM Corporation, Matthews, NC, USA) using procedures published before by our group [43, 44]. CNTs were treated with a mixture of concentrated sulfuric acid and nitric acid solutions at 140°C for 20 min in a microwave reactor. A carboxylic group was grafted over the CNT surface by this reaction. The CNT-COOH was then washed, filtered, and dried under vacuum at 80°C . Octadecyl amide-grafted CNTs (CNT-ODA) were prepared in two steps. First, the CNTs were reacted with thionyl chloride in dimethyl formamide solution to produce -COCl-functionalized CNTs in a 20-min microwave-induced reaction for 20 min at 70°C . It was then washed and dried. After modification, CNT-COCl was further treated with octadecyl amine for 10 min at 120°C under microwave reaction conditions. Excess ODA was removed by washing with ethanol followed by dichloromethane. It was then dried at room temperature under vacuum.

2.2 Dispersion of CNTs and preparation of composites

Because of the agglomeration tendency of the CNTs, uniform dispersion into the polymer matrices is believed to be one of the most important issues related to composite synthesis [45, 46]. The ultrasonic dispersion method is considered an effective, less time consuming compared to conventional dispersing systems, though direct ultrasonication is known to damage CNTs and reduce tube length [47–49]. In this study, a mixed solvent (xylenes and butanol, 1:1 by weight), which was compatible for both CNTs and polymer was used to disperse the CNTs. After mechanically stirring for 30 min, the CNT-mixed solvent dispersion was placed in a sonication bath for 3 h. The solvent allowed the dissipation of the local energy input, thus, reducing the tube damage. Epoxy resin was then added under stirring condition to the dispersion for 1 h.

The mixed solvent was removed completely from the system under vacuum at 70°C for 12 h. The solvent-free CNT-polymer dispersion was allowed to cool under vigorous stirring, and this was followed by the addition of the hardener. The resin was cured at room temperature for 24 h and annealed at 60°C for 6 h.

2.3 Characterization

2.3.1 Colloidal behavior of CNTs in epoxy resin and TETA

Dynamic light scattering (Beckman Coulter N4 Plus) was used to characterize the colloidal behavior of different types of CNTs dispersed in epoxy resin and TETA. The dispersions of CNTs ($250\text{ mg}\cdot\text{l}^{-1}$) were prepared in xylene-butanol solution under sonication for 3 h. Polymer solution was prepared by adding 5 wt% of epoxy resin or TETA to the dispersion under stirring condition for 10 min. The dispersion of various functionalized CNTs was prepared using a similar procedure described above. The stability of the CNT dispersion was monitored for a period of 6 h.

2.3.2 Composite characterization

Scanning electron microscope (SEM) (LEO 1530 VP), thermogravimetric analysis (TGA, Perkin=Elmer Inc.), transmission electron microscopy (TEM, Hitachi H-7500), and differential scanning calorimetric (DSC, Perkin-Elmer Inc.) were used to characterize the composites. The colloidal behavior of the CNTs in epoxy resin solution (xylene-butanol, 1:1) was also explored. A three-dimensional (3-D) image of the surface was taken using a digital microscope (Keyence) to study the surface roughness and the distribution of CNTs. Instron 8516 was used to study the mechanical properties of the composite materials. Tensile strength measurements were carried out using dumbbell-shaped specimens at a fixed cross-head movement of 3 mm per min at room temperature. The surface hardness of the composites was measured using the Leco Microindentation Hardness Testing Systems at a fixed load of 25 gf. The reproducibility of the data was measured by repeating the experiments three times. The relative standard deviation was found to be less than 1%.

2.3.3 Electrical conductivity

Electrical resistivity of a material was a measure of the restriction of electric current flow through the material, usually expressed in terms of volume resistivity.

Volume resistivity (ρ_v) can be defined as,

$$\rho_v = \frac{A}{t} R_m (\Omega \cdot \text{cm})$$

where A = the effective area of the measuring electrode in cm^2 , t = the thickness of the test specimen in cm, and R_m = the measured resistance in ohms.

The volume resistivity and surface resistance of various composites were measured using a Keithley 6715B electrometer. The specimens for the surface resistance measurements were prepared using two electrodes painted with conducting silver ink. The active area was $1 \times 1 \text{ cm}^2$.

3 Results and discussion

3.1 Colloidal behavior of various CNTs

A strong interfacial physico-chemical affinity of the CNTs with the polymer matrices enhances the dispersibility of the CNTs and overall performance of the composite materials. The introduction of functional groups on the CNTs' surfaces not only impairs the strong attractive interactions between the CNTs, themselves, but also alters the wettability and dispersibility in the liquid precursors. These led to an improved interfacial bonding with the composite [50–52].

Figure 1 shows the photographs of various CNT dispersions in dilute epoxy solution in a xylene-butanol mixture when the mixture was allowed to stand for 6 h. The CNTs

tend to agglomerate, and the large aggregates tend to settle out. It was observed from the figure that the stability of the CNTs increased with the introduction of surface functionalization. The size of the aggregates was smaller, and they remained dispersed for a longer period of time. The surface functionalization reduced the strong van der Waal forces between the individual CNTs, thus, decreasing the agglomeration tendency, and the functional groups increased interactions with the solvent molecules. While -COOH and -OH are highly polar, the amide groups (-CO-NH-) and non-polar octadecyl groups (-C₁₈H₃₇) make CNT-ODA highly stable in the mixed polar-nonpolar (butanol-xylene) solvents. The dispersion of pure CNTs showed relatively poor stability, which was followed by CNT-COOH, while the other two were very stable for the 6-h period shown in Figure 1.

The particle size of various CNTs in the mixed solvent as well as in the presence of epoxy and TETA was measured by dynamic light scattering. The interfacial modification of the CNTs via functionalization was critical to the distribution of the CNTs in the polymer matrix and has significant effects on the final properties of the CNT epoxy nanocomposites. Figure 2A and B shows the stability of various CNT agglomerates in the presence of epoxy and TETA. These figures represent those particles that were in the suspension and had not settled out. The increase in particle size indicates the aggregation tendency of the corresponding nanotubes, which may lead to poor dispersibility into the polymer matrix during fabrication. Among all of the CNTs, the particle size of CNT-ODA was found to be the smallest followed by CNT-OH, CNT-COOH, and raw CNT. The larger particle size was attributed to the higher agglomeration tendency [53].

Figure 1: Photographs of various CNT dispersion in dilute epoxy solution (xylene-butanol (1:1) mixture) when the mixture was allowed to settle for 6 h. (A) CNT-ODA; (B) CNT-OH; (C) CNT-COOH; (D) CNT-raw.

Figure 2: Particle size of various f-CNTs in (A) epoxy resin solution and (B) TETA solution from 0 to 25 min (5 wt% in xylene-butanol 1:1).

3.2 Characterization of the CNT-composite

Figure 3A and B shows the 3-D optical images of the nanocomposite surfaces. The images provide nanometer-level profile and roughness. It is clear from the images that the epoxy-CNT composites have relatively less planar surface in comparison to pure epoxy. The presence of the CNTs in the polymer matrix hindered the flow of the binder, hence, showing a poor planarity of the composites.

Figure 4 shows the SEM images of the cross-section of the fractured surface. These show the distribution of the CNTs within the matrix. Figure 4A shows the original CNTs, and the images of the f-CNTs were similar to what were reported before and are not included for

brevity [44, 54]. Cross-sectional views of the SEM images of the different epoxy-CNT composites are shown in Figure 4B–F. The raw CNTs did not appear to disperse uniformly in the composite matrix, and better dispersion was observed for the f-CNTs. The dispersion of the CNTs into the polymer matrix exhibited a similar type of behavior as observed in the liquid phase. The functionalization of the CNTs reduced the agglomeration tendency and promoted uniform distribution in the polymer matrix.

It was reported that fatigue crack growth suppression in epoxy nanocomposites strongly depends on the CNT properties and can be reduced by improving the nanotube dispersibility [55]. It is clear from the cross-sectional images that the nature of the fracture was quite different in the presence of the CNTs. The fracture surface of pure epoxy was also flatter and smoother. The cleavage planes in the pure epoxy were in a radiating pattern indicating a brittle fracture associated with low-impact resistance and fracture toughness [56]. The fracture surfaces of the composites were quite different where the CNTs served as reinforcing fibers. The surface of the composite was significantly rougher indicating an improved polymer chain interaction leading to enhanced interface crack resistance and toughness [57].

The TEM images of various CNTs in a polymer matrix are shown in Figure 5. A high-energy ultrasonic probe was used to disperse various CNTs in a toluene-xylene mixed solvent, and then, the dispersed suspension was mixed with a dilute solution of epoxy in similar solvent mixtures, again with ultrasonic agitation. The low viscosity of the dilute polymer solution permitted the CNTs to allocate freely through the polymer matrix. The drops of the mixed solution were placed on copper TEM grids. The thin-film specimen of the various epoxy-CNT composites were prepared by evaporating the mixed solvents.

TEM images of (A) epoxy-CNT-raw, (B) epoxy-CNTs-COOH, (C) epoxy-CNTs-OH, and (D) epoxy-CNTs-ODA are

Figure 3: 3-D optical images of (A) pure epoxy surface, (B) epoxy-CNTs-raw composite surface from digital microscope (Keyence; scale bar: red 67.7, yellow 38.7, green 29.06, and dark blue 0.0 l m).

Figure 4: SEM images of (A) CNT-raw; the cross-section image of (B) pure epoxy, (C) epoxy-CNTs-raw composite, (D) epoxy-CNTs-COOH composite, (E) epoxy-CNTs-OH composite, (F) epoxy-CNTs-ODA composite.

shown in Figure 5A–D, respectively. As can be seen from all of the figures, the raw nanotubes contained some disordered carbon impurities. The length of the multiwalled nanotubes varied by tens of nanometers to several micrometers and in the outer diameter from about 15 to 30 nm. From the figures, it was observed that the CNTs were embedded in the epoxy matrix, although the difference in agglomeration tendency was not obvious from these images.

3.3 Mechanical properties

The mechanical performances of the composite materials are strongly influenced by the phase morphology developed during mixing of the CNTs and the polymers, and the interfacial adhesion between the phases. Good dispersion and strong interactions of the CNTs is important for enhancing the mechanical properties of the composites

Figure 5: TEM images of (A) epoxy-CNTs-raw, (B) epoxy-CNTs-COOH, (C) epoxy-CNTs-OH, (D) epoxy-CNT-ODA.

[58]. The implementation of surface functionalization was expected to enhance the performance of the epoxy composites through better interfacial bonding as well as better dispersion. The colloidal behaviors of various CNT forms were expected to be an indicator of dispersibility in the final composites.

The tensile strength and elongation at the break of various epoxy-CNT composites at different concentrations of CNTs into the polymer matrix are compared in Figure 6A and B. The zero CNT concentration represents the pure epoxy. Figure 6A clearly demonstrates a significant enhancement in tensile strength at relatively low CNT

Figure 6: Tensile properties of pure epoxy and epoxy-nanocomposites at different CNT loading. (A) Tensile strength; (B) Elongation at break (%).

loadings. It is also clear from the figure that the f-CNTs exhibited better tensile strength than the raw CNTs. This was attributed to the superior dispersion of the f-CNTs as well as stronger interfacial interactions with the polymer matrix.

It was observed in Figure 6A that all of the f-CNTs exhibited better tensile properties at low CNT loadings. The rate of enhancement at low CNT loading was found to be higher compared to what was observed at higher CNT loading. Compared to the pure epoxy, at 0.5 wt% loading, the enhancement in tensile strength were found to be 7.2, 11.2, 11.4, and 14.2 for raw CNTs, CNTs-COOH, CNTs-ODA, and CNTs-OH composites, respectively. This was quite higher than what was reported (3%–8.5% enhancement) for high CNT and CNT-COOH loadings [53]. The tensile strength of epoxy-CNTs-ODA showed a different trend compared with the other composites. It increased up to 0.5 wt% and then began to decrease. At lower concentrations, the enhanced dispersion of CNTs-ODA led to a higher tensile strength compared to the CNTs-COOH and the raw CNTs. However, the presence of the long octadecyl ($-C_{18}H_{37}$) at a high concentration may influence the

cross-linking and close packing of the polymer chains, which negatively affected the mechanical properties.

It is interesting to observe that among the f-CNTs, epoxy-CNTs-OH exhibited a higher tensile strength compared to the others, followed by epoxy-CNTs-ODA and epoxy-CNTs-COOH up to 0.5 wt% of CNTs. This trend was slightly different from what we observe in particle size distribution analysis where the CNT-ODA exhibited better dispersibility than CNT-OH. Therefore, the enhancement in tensile strength was attributed to specific interactions between the hydroxyl groups ($-OH$) of the CNTs and the polymer matrix. This is shown in Figure 7A. Similar types of interactions also took place with CNT-ODA and/or CNT-COOH and are shown in Figure 7B and C. The presence of large octadecyl groups may hinder the close packing of the polymer chains, and poor dispersibility of CNT-COOH may affect the overall tensile strength of the composites.

Figure 6B shows the effect of various CNT content on elongation at break (EAB). It is clear from the figure that an increase in CNT content led to the reduction in EAB in all composites. The epoxy-CNTs-OH exhibited a higher reduction in EAB, and this was attributed to a better interaction with the epoxy matrix. The epoxy-CNTs-ODA showed a different trend where EAB first decreased up to 0.5 wt% and then remained unchanged or increased slightly. This was attributed to the presence of large octadecyl groups into the matrix, which may have prevented the interactions of the amide group with the functional groups present in the epoxy. Both tensile strength and EAB results indicate that an optimum amount of CNTs-ODA is needed for the optimization of the nanocomposite mechanical properties.

The surface hardness was measured using Vickers microhardness, and the value for pure epoxy was found to be 17.2 HV. The results are presented in Table 1. An enhancement by ~18% was observed for all other CNT composites. It is clear that a small amount of CNTs can significantly improve the microhardness.

3.4 Thermal properties of epoxy-CNT composites

The thermal properties of the nanocomposites typically depend upon the nature of the polymer matrix, orientation, and dispersion of the NMs, and the interfacial thermal boundary resistance between the matrix material and the nanoparticles [59]. The change in the thermal properties of the different nanocomposites is reflected in their glass transition temperatures (T_g) and thermogravimetric analysis profiles.

Figure 7: Interactions of the CNTs with epoxy and TETA. (A) CNT-OH; (B) CNT-ODA; (C) CNT-COOH, and (D) raw CNTs (no specific interactions).

Table 1: Different properties of pure epoxy and epoxy nanocomposites.

Sample	T_g (°C)	Microhardness (HV)	Volume resistivity ($\Omega \cdot \text{cm}$)	Surface resistance of 1 cm ² area (Ω)
Epoxy-pure	77.8	17.2	1.31×10^{11}	7.1×10^9
Epoxy-CNTs-COOH	86.9	20.4	1.64×10^9	1.04×10^9
Epoxy-CNTs-OH	103.2	20.2	1.81×10^9	1.17×10^9
Epoxy-CNTs-ODA	84.9	19.8	1.12×10^9	1.23×10^9
Epoxy-CNTs-raw	95.5	20.8	0.8×10^9	0.9×10^9

The T_g depends upon the motion of the polymer chains and a sharp decrease in the free volume in the presence of the secondary elements (CNTs). The presence of the CNTs, which are dimensionally similar to the polymer chain-building units, are known to influence the alignment of the polymer chains and, thereby, alter the T_g . The presence of the CNTs was reported to affect the structure of the cured epoxy, thereby, affecting T_g [60]. Jin et al. reported an improved glass transition temperature (11°C increment) of dodecylamine-treated CNT epoxy nanocomposites [61]. However, the reduction in T_g in the presence of nanomaterials was also reported [40, 41]. Khare et al. studied the T_g of various CNT-based epoxy nanocomposites and observed

that the weak matrix-filler interactions cause the inter-phase region in the nanocomposite to be more compressible [62, 63]. A simulation also showed that the dynamic heterogeneity and the fraction of the immobile domains in crossed-linked structures increase rapidly below T_g [64].

Table 1 shows the T_g of the composites with different f-CNTs studied here. The composite prepared using CNT-OH showed an enhancement as high as 34%. This is attributed to the strong binding through the -OH interactions of the polymer molecules to the CNT surface, thereby, decreasing their mobility (as shown in Figure 7A). The low enhancement in the CNT-ODA composite was attributed to the presence of the bulky octadecyl ($\text{C}_{18}\text{H}_{37}$) groups in

the CNT surface, which restricted the close packing of the polymer chains. The relatively low enhancement of the CNT-COOH was attributed to the preferential adsorption of the basic curing agent on the acidic CNTs leading to a non-stoichiometric balance in the overall curing system, which would result in a decrease in the cross-link density to reduce T_g [41, 65].

The TGA was carried out in a flow of nitrogen at a temperature ramp rate of 10°C/min. The results are shown in Figure 8. The trend in the initial degradation up to 300°C was different for the different composites. The composite prepared from CNT-OH showed a better initial thermal stability. The ODA group in t\CNT-ODA began to degrade at low temperature leading to a rapid drop in mass.

3.5 Electrical conductivity

Typical epoxy is nonconductive, and the incorporation of CNTs improved the conductivity [66]. Table 1 presents the volume resistivity and surface resistance of pure epoxy and the various CNT-based composites at 0.5 wt% loading.

It is clear from the table that the conductivity of the composites improved with the incorporation of the CNTs in the polymer matrices. Among all of the composites, raw CNTs showed the highest improvement in conductivity because the CNTs were undamaged [67]. CNT agglomeration could also favor the formation of a percolating network for current flow [68–70]. This was attributed to the fact that the colloidal behavior of the raw CNTs was relatively poor and led to surface agglomeration. Figure 9 shows the surface resistance and volume resistivity of the CNT-OH composite as a function of CNT loading. It is clear from the figure that with an increase in the CNT concentrations, there was a sharp decrease in the surface as well as volume resistivity.

Figure 8: TGA curve of pure epoxy and various CNT composites.

Figure 9: Electrical resistance of epoxy-CNT-OH composite with the variation of CNTs.

4 Conclusions

Various functionalized CNTs were synthesized, and their colloidal behavior in the presence of epoxy resin and TETA was studied. The influence of interfacial interaction between the CNT surface and the polymer matrix were discussed. The nature of functionalization and their specific interactions with the polymer chains affected the physical, thermal, and electrical properties of the composites. For example, the enhancement in tensile strength was found to be 7.2%, 11.2%, 11.4% and 14.2% for raw CNTs, carboxylated CNTs, octadecyl amide-functionalized CNTs, and hydroxylated CNTs, respectively at 0.5 wt% CNT loading. Functionalization of the CNTs improved the glass transition temperature of the epoxy composites, and CNTs-OH showed highest enhancement (34%) in T_g . The addition of the CNTs in the polymer matrix also reduced the electrical resistance reasonably. The variation in the re-aggregation behavior of the CNTs in the presence of a polymer and TETA indicates specific interactions between the CNTs and the polymer matrix system. A direct comparison with other data is difficult because of the wide variation of epoxy resin, hardener, CNTs, degree of functionalization, and processing techniques.

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