Effective Functionalization of Carbon Nanotubes for Bisphenol F Epoxy Matrix Composites

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Received: July 27, 2011; Revised: March 18, 2012

A brand-new type of multifunctional nanocomposites with high DC conductivity and enhanced mechanical strength was fabricated. Ionic liquid functionalized Carbon Nanotubes (CNTs-IL) were embedded into epoxy matrix with covalent bonding by the attached epoxy groups. The highest DC conductivity was $8.38 \times 10^{-1} \text{ S.m}^{-1}$ with 1.0 wt. (%) loading of CNTs-IL and the tensile strength was increased by 36.4% only at a 0.5 wt. (%) concentration. A mixing solvent was used to disperse CNTs-IL in the epoxy monomer. The dispersion and distribution of CNTs-IL in the polymer matrix were measured by utilizing both optical microscopy and scanning electron microscopy, respectively.

Keywords: carbon-carbon composites, mechanical properties, polymer-matrix composites, carbon nanotubes

1. Introduction

Over the past decade many researches have been done to improve polymer matrix composites by adding carbon nanotubes (CNTs)1-4. Polymeric matrices, such as polyethylene (PE)5,16, poly(methyl methacrylate) (PMMA)7,8, poly(vinyl alcohol)9,10, polyimide11,12, and polystyrene (PS)13-15, have been investigated for CNT/polymer composites fabrication. Among polymer composites, epoxy resins have high strength and are very important materials for aircraft, space shuttles, electronic products, and other industrial applications16-20.

Currently, there are two major challenges encountered in the successful fabrication of nanocomposites systems. One is uniform dispersion of CNTs; another is good adhesion between CNTs and the host polymer matrix. These two qualities must be achieved without destroying the integrity of the CNTs and the polymer21-25. Chemical functionalization of CNTs was explored as an effective method of achieving the aforementioned goal. A critical requirement for the production of high strength conductive nanocomposites was the proper control of the type and degree of the grafting on the tube walls. The degree of grafting should not be too high to avoid adversely disturbing the π-electron system in the tube walls. Also, all of the organic groups attached on the CNT wall will increase the contact resistance between individual CNTs and the bundles, or even insulate the CNTs from the polymeric matrix. This would allow a better compatibility between the CNTs and the polymer26. On the other hand, the functionalization of the CNTs reduces the length to diameter ratio, which can be detrimental for the overall conductivity, and leads to stabilization of the dispersion and the formation of an isolating polymer layer around the nanotubes in an unlikely case27. Thus a compromise may be necessary between better bonding and enhanced conductivity.

Ionic liquids (ILs), consisting of imidazolium cations and counter anions, have attracted increasing interest as fascinating materials for a wide range of synthesis, catalysis, electrochemistry, and liquid-liquid extractions. This is due to their remarkable properties such as non-volatility, non-flammability, high ion density, high ionic conductivity and so on28-32. A few polymer gel electrolytes containing ILs have been investigated to realize both high ionic conductivity and good mechanical property33. Polymer-in-IL electrolytes were also prepared by in situ polymerization of vinyl monomers in ILs34,35. Ohno’s group prepared the ionic liquid-type polymer films having flexible spacers between polymerizable groups and imidazolium cations36,37. Polymerization of IL itself was very effective, not only to transport target ions but also to improve mechanical property. However, polymeric ILs are usually flexible with low strength, and therefore limited in their applications.

In this work, we used ionic liquids with epoxy segment groups to functionalize CNTs for better conductivity and superior interfacial adhesion. A solvent-based method was developed to facilitate dispersion of functionalized CNTs. Both mechanical and electrical properties of the resulting composites are presented to show the effectiveness of IL functionalization.

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2. Experimental Details

2.1. Materials

The resin used was an epoxy Epon 862 (bisphenol F epoxy) with EpiCure curing agent W (Miller-Stephenson Chemical Company, Inc.). All other chemicals utilized in this research were purchased from Sigma-Aldrich Company and were used as received without further treatments.

2.2. Preparation of the CNT-ILs/Epoxy nanocomposites

Preparation of the CNT-ILs/Epoxy nanocomposites is depicted in Figure 1. The imidazole functionalized CNTs were prepared according to our previously reported procedures\textsuperscript{38,39}. The carboxylic acid group was converted to acid chloride by treatment with SOCl\textsubscript{2} (reflux for 24 hours). Excess SOCl\textsubscript{2} was then removed by vacuum distillation. The resulting functionalized CNTs with acid chloride was reacted with excess amount of 3-aminopropylimidazole at 120 °C for 24 hours under nitrogen atmosphere. The resulting black solid was filtered with a 0.2 micro poly(tetrafluorethylene) (PTFE) membrane and successively washed with anhydrous tetrahydrofurane (THF). This was followed with 1 M aqueous HCl solution, saturated NaHCO\textsubscript{3} solution, and water until the pH of the filtrate was 7.0. Elemental analysis indicated that 0.76 mmol.g\textsuperscript{–1} of imidazole segment was incorporated into the CNT surface.

To introduce the epoxy group, the imidazo-functionalized CNTs were bathed with excess amounts of epichlorohydrine at 90 °C for 48 hours. After filtration, the resulting ionic liquid-functionalized CNTs with epoxy group were washed several times with acetonitrile, and dried under vacuum at 60 °C for 24 hours, which were used for the preparation of the CNT-ILs/Epoxy nanocomposites.

2.3. Characterization

The reference epoxy resin was prepared by mixing Epon 862 with EpiCure curing agent W under mechanical stirring for 30 minutes, then degassing the mixture in a vacuum oven at 80 °C for 30 minutes. The mixing ratio of Epon 862 and EpiCure W was 100:26 (v/v). After removing the bubbles, the mixture was transferred to stainless steel dog-bone molds and cured at 120 °C for 4 hours. The cured test samples were then trimmed and machined for thermal and mechanical characterization.

For the preparation of the CNTs-IL/epoxy nanocomposites, CNTs-ILs and curing agent were added into a mixed solvent (acetone: ethanol ratio is 1:3), then sonicated for 4 hours at room temperature and additional 3 hours at 60 °C. Subsequently, Epon 862 was added and shear mixed with the CNTs-IL/ EpiCure W mixture at 80 °C for 30 minutes and sonicated for an additional 30 minutes. Finally, the resulting mixture was degassed in a vacuum oven at 80 °C for 2 hours. The curing cycle of CNTs-IL/epoxy nanocomposites was the same as that of the pristine epoxy. Figure 1 illustrates the fabrication procedures of the CNTs-IL/epoxy nanocomposites.

The tensile testing was performed using a micro tensile machine (Instron 4411) at room temperature. A scanning electron microscope (JEOL SM-71010) was used to examine fracture surfaces. Fourier transform infrared (FTIR) spectra were recorded with a JASCO Fourier transform infrared spectrometer, which is operated from 700 to 4000 cm\textsuperscript{–1} at room temperature with a nitrogen flow rate of 100 cubic centimeters per minute (ccpm). DC conductivity was measured by a standard two-probe method and the electrodes were fixed with silver coating on both sides of the samples.
3. Results and Discussion

In the composite fabrication process, the epoxy functionalized CNT-ILs and curing agent were initially fragmented aggregates in a mixing solvent under ultrasonication. After solvent evaporation, CNT-ILs interacted with the diamine with the aid of curing agent, and further chemically bonded with the Epon via an amidation reaction. Due to the ionic interaction of the imidazolium ions and high surface energy of CNTs, CNT-IL tended to aggregate heavily. Figure 2 presents the microscopy photographs of CNTs-IL dispersed in curing agent without (Figure 2a) and with (Figure 2b) mixing solvent. From Figure 2a, the size of CNT aggregates is about 30-50 µm, however there is no obvious CNT aggregates in Figure 2b. The imidazolium-functionalized CNTs bearing hydrophilic Chlorine anion were found to convert the hydrophobic surface of CNT to hydrophilic. After screening various solvent systems, a mixture of ethanol and acetone (3:1, v/v) was found to favor the uniform dispersion of the CNTs-IL. There was no obvious aggregation inside the epoxy, due to covalent chemical bonding between the CNTs-IL and epoxy, as well as the fact that they hardly aggregated inside the epoxy matrix during the curing process. Moreover, even as the content of the CNTs-IL increased to 1.0 wt. (%), there was no obvious morphology change in the composite because of the perfect dispersion system of the CNT-IL formed inside the epoxy matrix in micro level and following SEM result could provide more evidences in nano-level.

3.1. FTIR

FTIR spectra can provide the evidence for the variation in the thermal and mechanical properties of the different samples in terms of their molecular structures. The spectra of the CNT-ILs and amine-curing agent mixture before and after curing were observed to have approximately the same absorption bands since the loading of CNTs-IL was low in the wide-spectra. Figure 3 shows the FTIR spectra of solution of CNTs-IL dispersed in curing agent. Curve shows the sample (a) before and (b) after heating. The important characteristic of the uncured epoxy group on the CNTs (spectrum a) is the major band at 1260 cm\(^{-1}\) (peak A) and 917 cm\(^{-1}\) (peak B) with a shoulder at 858 cm\(^{-1}\) (peak C), which was assigned to epoxy ring mode. Nevertheless, the major band is split into two bands (939 and 870 cm\(^{-1}\)) and the shoulder disappears after the long-term heating process, which can be observed in spectra b. Although these differences were small, FTIR could detect low concentration of CNTs-IL indicating that the epoxy ring disappeared. This was a result of the bonding built between the CNTs-IL and amine group of curing agent. The study of the evolution of the imidazolium functional group on the cured samples through their typical infrared absorption was difficult, due to the band overlapping of the absorption of other groups in the resin. Figure 4 shows the IR reflection spectra of the CNT-IL/epoxy composite. The conjugated strong peaks around 1570 and 1630 cm\(^{-1}\) were observed and attributed to the carbon-nitrogen-carbon or carbon-carbon bonds of epoxy resin, respectively. Observation on the evolution of the amino groups on the cured samples through their infrared typical absorption were difficult due to the band overlapping of the absorption of other groups in the resin.

3.2. Morphology of fracture surface

The purpose of this study was check the distribution of the conductor inserted in the insulator by using the SEM. SEM is capable of providing (pseudo) three-dimensional morphological information on single wall carbon nanotube (SWNT) networks in conductive SWNT/polystyrene (PS) nanocomposites at nanometric resolution by monitoring the sample in the charge contrast imaging mode. Before testing, there was no metal covering treatment. Figure 5 illustrates a uniform dispersion at microscale and shows that the material is microscopically homogeneous on the surface of samples with and without 0.5 wt. (%) CNTs-IL loading. The pristine CNTs were observed to be present mainly in the form of agglomerates, whereas the CNTs-IL were dispersed more uniformly, confirming a much better dispersion of CNTs-IL in epoxy matrix. Local charging of the polymer matrix around the SWNTs may have rendered the average diameter of the CNTs to be one order of magnitude larger than the value measured for an individual CNT by other measuring methods. The charge only could be hold in

![Figure 2](image-url)

**Figure 2.** Optical microscopy pictures taken of the nanotube dispersions (1 mg.mL\(^{-1}\)) in curing agent: without solvent (a) and with mixing solvent (b).
sliding and pull out at the surface since CNT have the high strength, suggesting a limitation of load transfer. This phenomenon can be explained in terms of improved interfacial interaction between the CNTs and epoxy matrix with solvent assistant. In comparison, the CNTs-IL using mixing solvent system showed good homogeneity and dispersion on the fracture surface. A number of tubes were found to be broken rather than just pulled out of the surface, indicating a strong interfacial bonding between the epoxy matrix and the functionalized nanotubes, and this bonding has the same strength level with CNT, so we presume it is covalent interaction. As the loading percentage of the CNTs-IL increased, good dispersion was still achieved, and most of the CNTs-IL were embedded in and tightly held to the matrix. Epoxy matrix were covalently attached on the CNTs-IL surface via the curing process after functionalization (Figure 1), resulting in an increase of the tensile strength and foundation of conductive net.

3.3. Mechanical properties of the CNTs-IL/Epoxy nanocomposites

Typical stress–strain behavior from the tensile tests is shown in Figure 7. All specimens failed immediately after the tensile stress reached their respective maximum stress. The stress–strain curves showed considerable non-linearity before reaching the maximum stress, but no obvious yield point was found in the curves. Five specimens were tested for each condition; the average obtained from these tests is listed in Table 1. Epoxy-functionalization not only improved the dispersion of MWNTs in the polymer matrix but also enhanced the tensile properties as shown in Figure 7. For the CNT-ILs/epoxy system, the tensile strength increased with the increase of the CNTs-IL content. The introduced strong chemical bonding between the CNTs-IL and the epoxy molecules resulted in good compatibility between these two phases. The average tensile strength of the nanocomposite with an addition of 0.5 wt. (%) CNTs-IL was 25% higher than that of the pristine EPON 862 epoxy. For the CNT/epoxy nanocomposites with a CNTs-IL loading of 0.1 wt. (%), the tensile strength only increased slightly. Conventionally, inorganic/organic
and voids arising from the high amounts of the CNTs-IL added to the system. A strong interaction between the CNTs and the polymer matrix was proved by the increase in the tensile strength and better dispersion of nanotubes. The dispersion of the CNTs in epoxy resin influenced its strengthening effect. CNTs-IL composites exhibited the highest increase in strength due to the fact that the CNTs-IL created a covalent bondage with the polymer matrix, thus becoming an integral part of the overall structure. The improvement in tensile strength in the case of the compatible CNTs-IL/epoxy nanocomposites can be attributed to the load transfer from the epoxy matrix to tougher CNTs-IL reinforcement via strong chemical bonding. Furthermore, ions on the CNTs-IL surface were better dispersed in the epoxy. The mixed solvent increased the surface polarity and induced the incorporation of CNTs into the matrix, which resulted in a larger improvement in the ultimate strength.

In other hand, the too much CNTs could lead more defects in the polymer matrix which will decrease the stress. 0.5% of IL-CNT is the best concentration ratio in our case.

3.4. Electrical properties of the CNTs-IL/Epoxy nanocomposites

The enhanced electrical conduction with the addition of carbon nanotubes (at low CNT concentrations) to the epoxy can be explained by the occurrence of conductive pathways at a critical filler concentration (percolation threshold).

Table 1 is the comparative data of the DC conductivity of the CNTs-IL/epoxy nanocomposites as a functional CNT content. It shows that conductivity increased with the increase of the CNTs-IL content for both types of systems. However, the CNTs-IL/epoxy system showed a lower percolation threshold (lower than 0.1 wt. %) than that of the CNTs/epoxy system (around 0.5 to 0.6 wt. %). The reason may be explained as follows: ionic liquid served as the high effective conductive pathway and reduced contact resistance between the well-dispersed CNTs. Therefore π-electrons of CNTs can easily get across the insulating polymer resin by CNTs and ionic liquid conductive matrix. Moreover with the increase of CNT percentage, the CNTs-IL/epoxy system can achieve a conductivity of $8.38 \times 10^{-3} \text{ S.m}^{-1}$ with a 1.0 wt. % addition, which is the highest conductivity data for CNTs/epoxy systems reported until now.

The epoxy functionalization significantly improved the compatibility between the epoxy and CNTs. The reaction of the epoxy resin with the functional groups on the nanotube surface formed an electrically insulating epoxy layer, which increased the distance between individual tubes, and made the tunneling of electrons from tube to tube more difficult. According to the percolation theory, electrical paths are made up of conductive inclusions in the direct contact. Short CNTs reinforced composites usually have a percolation threshold of 5-10 wt. % of the CNTs. Above the percolation threshold, the CNTs provide a three-dimensional conductive path, while ionic liquid builds a new ionic pathway between the individual CNTs, which have same ion-conductive mechanism in ionic conductive polymer as electrolyte materials. Additionally since ionic liquid functioned at defect sites of CNTs, which caused the main withdraw of CNT conductivity, ionic liquid fraction...
could be used instead to fix and repair those defects partially to increase the conductivity of CNT itself\(^9\). This gives rise for future investigation of a new possible electro-path under potential applied.

4. Conclusion

In summary, we report a new multifunctional epoxy composite fabricated with ionic liquid functionalized CNTs, an epoxy group and a mixing solvent dispersion. When embedded in a polymer matrix, CNTs-IL demonstrated an enhanced in DC conductivity and in tensile strength. CNTs-IL also outperformed other carbon nanotube-based fillers in terms of increased the tensile strength of the composite system. This material offers a new solution for the development of new generation of high-conductivity, high-strength and lightweight multifunctional composites for potential applications in aerospace.

Acknowledgements

This paper is based on work supported by the NBIT Program funded jointly by the Ministry of Science and Technology of Korea and the US Air Force Office of Scientific Research.

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