Modification of Epoxy Resins via *m*-chloroperbenzoic Acid-Epoxidized Carbon Nanotubes

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ABSTRACT: In this article, epoxidized carbon nanotubes (CNTs) are used to modify current epoxy resins. The produced epoxy groups on the nanotube surface significantly enriched nanotube chemistry and made them soluble in the organic solvents. Atomic force microscopy characterization indicated that epoxidized nanotubes were well dispersed in the organic solvent and most of them were isolated. Fracture surface of modified epoxy resins suggested that fracture toughness of the modified resins was significantly improved, demonstrating fracture characteristic of typical ductile materials. Epoxidized CNTs-modified epoxy resins demonstrated a 50% increase in the Young's modulus, 32% improvement in the tensile strength with 1 wt % loading. This study provides an effective way to synthesize novel epoxy resins. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3322–3326, 2009

Key words: carbon nanotubes; surface modification; nanocomposites; nanotechnology

INTRODUCTION

Epoxy resins are considered as one of the most important classes of thermosetting polymers. They have been extensively used in various fields of coating, high-performance adhesives, composite matrix, etc. Once cured, epoxy resins are characterized with high chemical and corrosion resistance as well as good mechanical and thermal properties. However, the effective using of these outstanding resins has been limited by their inherent brittleness. Many efforts have been attempted to improve their physical properties.[1–5] A popular method is to incorporate flexible elastomers into brittle epoxy network. Typical rubbery modifiers in the epoxy resins induce phase separation to form a "sea-island" structure, an irregular distribution of microscale rubbery inclusions throughout the resin.[1–4] Control over the scale and homogeneity of these inclusions may toughen epoxy resin and enable the preparation of useful new thermosetting materials. In addition, reactive block copolymers were used to modify epoxy resin for better performance.[5] However, embedding elastomers or block copolymers into epoxy resin decrease the elastic modulus while improving the brittleness.

Emerging carbon nanotubes (CNTs), tube-like supermolecules, provide an excellent alternative to modifying the existing epoxy resins. CNTs integrate amazing rigid and tough properties, such as exceptionally high elastic properties, large elastic strain, and fracture strain sustaining capability, which seem inconsistent and impossible in the previous materials.[6–12] The Young's modulus of single-walled carbon nanotubes (SWNTs) is around 1 TPa, five times greater than that of steel (200 GPa), while their density is only 1.2–1.4 g/cm^3.[6–13] This means that materials made of nanotubes are lighter and more durable. Guo and Guo[14] have measured the strength of a nanotube rope (consisting of 15 nanotubes) as high as 63 GPa. Beside their well-known extra-high mechanical properties, CNTs offer superior thermal and electrical properties: thermal stability up to 2800°C in a vacuum and 750°C in air, thermal conductivity about twice as high as diamond, and an electric current transfer capacity 1000 times greater than copper wire.[15] Effective incorporation of CNTs into epoxy resin will significantly improve resin brittleness, and also enhance strength, stiffness, electrical, and thermal conductivity.[16,17] In addition, modification of epoxy resins will also improve the fire-retardant properties. Therefore, using CNTs as novel modifiers will enable new thermosetting resins and lead to wider application of these resins.

However, CNTs tend to aggregate together and it is difficult to be effectively integrated into epoxy resins. In addition, CNT surface has to be modified to improve the compatibility between CNTs and epoxy
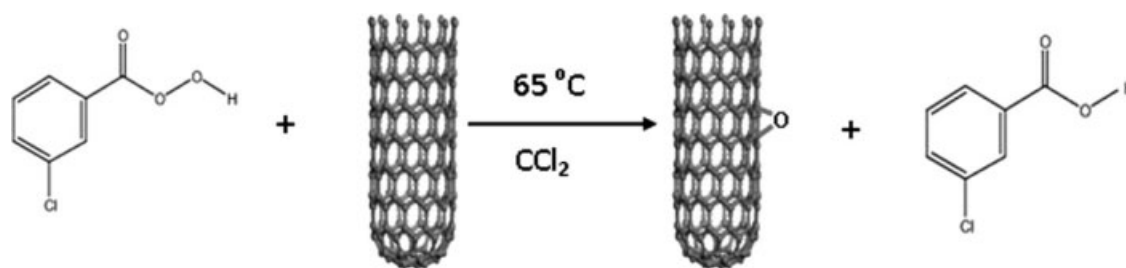
Figure 1 Scheme of nanotube epoxidation with *m*-CPBA.

resins. Hence, epoxidization of CNTs will be very useful. Wang et al. used *in situ* polymerization to graft epoxy groups to the CNT surface.[18,19] Jana and Verkade successfully used *m*-chloroperbenzoic acid (*m*-CPBA) to epoxide a phenol derivative in 2003.[20] Szakacs and Ivan also succeeded in using *m*-CPBA to epoxidize thermal-degraded poly(vinyl chloride) in 2004.[21] In this article, we use *m*-CPBA to epoxidize CNTs and achieve epoxidized supermolecules. These epoxidized nanotubes demonstrated exceptional miscibility in the epoxy resin. The chemical synthesis and property characterization were discussed.

EXPERIMENT

Materials

Single-walled carbon nanotubes (grade: purified, ash content $\leq$ 15 wt %) were purchased from Unidym with HiPco processing. *m*-Chloroperbenzoic acid (ACS grade), stabilized 97%, and chloroform were purchased from Fisher Scientific. Epoxy resin, epon862, was purchased from Shell.

Epoxidization functionalization

SWNTs were dispersed into chloroform under ultrasonic processing for 30 min at the power of 30 W. Then *m*-CPBA was added for 10-min ultrasonic process at the same power. Subsequently, all the suspension was transferred to the refluence setup for the chemical reaction. The reaction was controlled at 65°C for 2 h.

Then, the mixture after reaction was diluted with chloroform and filtered through 0.2-μm Teflon membrane, resulting in a thin film. This film was substantially washed with acetone, then ground, and dispersed into chloroform for the subsequent filtration. This washing processing was repeated for three times, and then the film was annealed at 60°C for 10 h and weighed for record. The dried film was ground and dispersed into chloroform for washing again. Then, the film was dried and weighed for record. When the recorded weight was almost the

same, the film was presumed to be clearly washed. Epoxidized SWNTs (e-SWNTs) were characterized with Raman spectroscopy (Renishaw) and FTIR (Thermo Nicole).

Preparation of modified epoxy resin

The resultant e-SWNTs membrane was broken into pieces and ground to black paste with mortar and pestle in a small amount of chloroform. A certain curing agent (based on the required curing ratio) was weighed and added to the e-SWNT paste. Subsequently, e-SWNT and curing agent were mixed in the chloroform solvent under cup-horn ultrasonic processing at 30–40 W for a half an hour. Epoxy resin was diluted and added to the SWNT suspension, resulting in a new mixture which was processed with cup-horn ultrasonic processing at the power of 12 W for 3 h. Finally, the mixture was placed under high-speed shearing at 2000 rpm/min for 3 h. The resultant mixture of e-SWNT and epoxy was left in the vacuum system for 12 h to remove the residual solvent. The final mixture was cast into a metallic mold and cured under hot-press at 177°C for 2.5 h. The subsequent postcure was conducted at 177°C for another 2 h. The pristine SWNT (p-
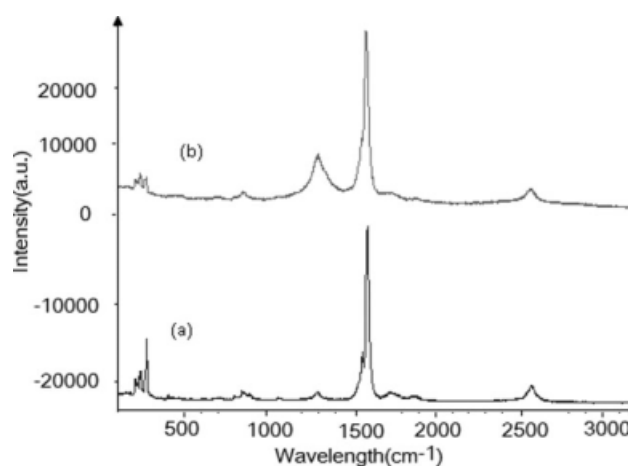

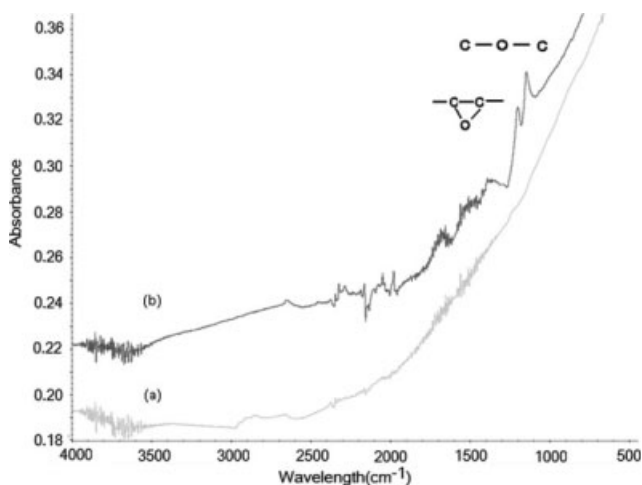**Figure 2** Raman spectrum of (a) pristine SWNTs and (b) epoxidized SWNTs.

Figure 3 FTIR of epoxidized carbon nanotubes. (a) Pristine SWNTs and (b) epoxidized SWNTs.

SWNT)-modified epoxy resin was prepared in the same procedure. The e-SWNTs-modified epoxy resin was prepared with 1% tube loading by weight. The e-SWNTs-modified epoxy resins were tested by tensile machine according to the ASTM D638, and their morphologies were characterized by scanning electron microscopy.

RESULTS AND DISCUSSIONS

In this article, *m*-CPBA is used to epoxidize carbon nanotubes, and the mechanism of epoxidation is the same as the previous research. The chemical reaction scheme was given in Figure 1. In the favored solvent, the oxygen atom at peroxide group attracts the delocalized electron at double bond, and this attraction will reduce the oxygen bonding in the peroxide group. Finally, the oxygen will break the peroxide bonding and form epoxy group in the previous double bond.

Functionalization reactions would introduce many SP^3 hybrids so that intensity of disorder band (1290 cm^{-1}) would be enlarged in comparison to the pris-
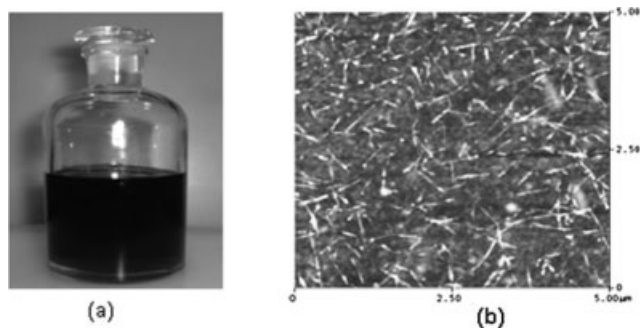

Figure 4 (a) Soluble epoxidized SWNTs and (b) AFM image of dispersed epoxidized SWNTs.

tine CNTs. In addition, the resonance Raman enhancement would be weakened or lost because of counteraction of grafted chemical groups, so the intensity of tangential mode (G-) could be diminished or lost.[22] Raman spectroscopy characterization of e-SWNTs is shown in Figure 2. Conspicuous increase in the disorder band intensity of functionalized SWNTs indicated covalent bond transformation on the SWNT surface. It also showed that the intensity of the RBM model was significantly reduced and almost disappeared because of interference with functionalized groups, which was consistent with high degree of functionalization. The evident undermined G- mode in e-SWNT further validated the covalent functionalization through epoxidization.

e-SWNTs were also characterized with FTIR, as shown in Figure 3. Although there were no visible peaks in the FTIR spectra of p-SWNTs, there existed several vibration peaks in the spectrum of functionalized SWNTs. The vibration peak that appeared in the frequency of 1250 cm^{-1} is due to the whole ring stretching of the epoxy group,[18–21,23,24] suggesting that the epoxy group existed in the functionalized SWNTs. In addition, the peak at frequency of 1138 cm^{-1} is attributed to ether asymmetric stretching.[23,24]
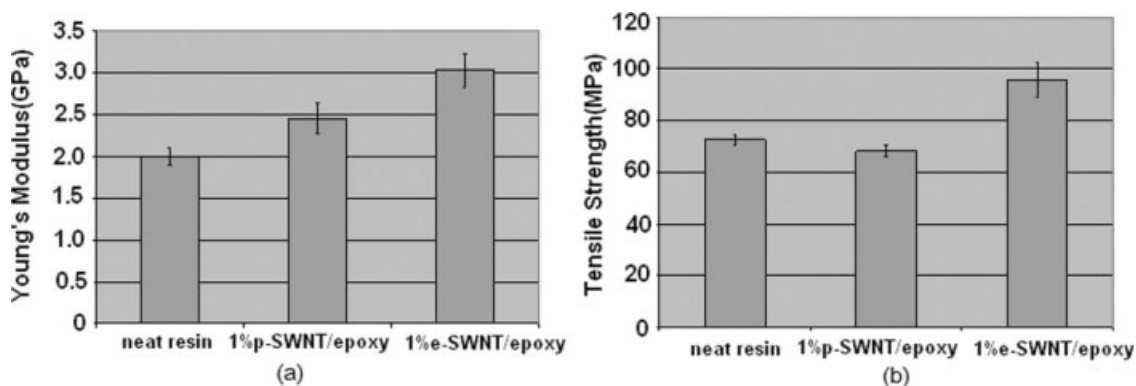

Figure 5 (a) Young's modulus and (b) tensile strength of modified epoxy resins.
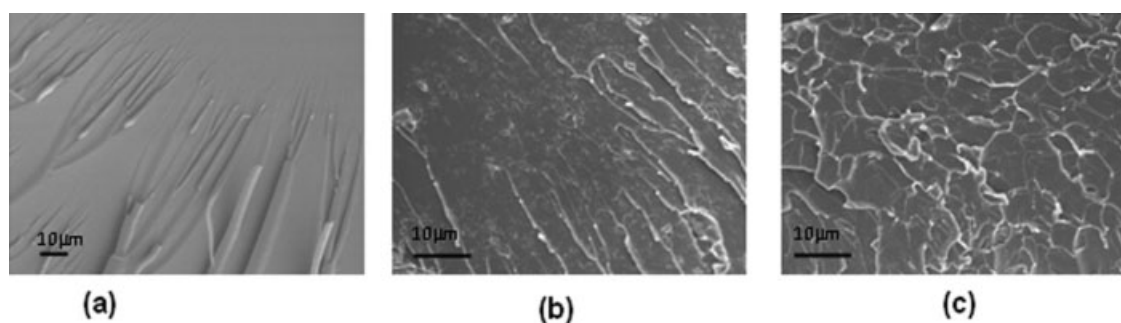
Figure 6 Fracture surface (a) unmodified epoxy resin, (b) Pristine SWNT-modified resin, and (c) epoxidized SWNT-modified resin.

The experimental results indicated that the e-SWNTs can be dissolved in the dimethyl formamide with high concentrations, whereas p-SWNTs are not soluble. The solution was stable and uniform. The solution was sampled and characterized with AFM, as shown in Figure 4. Most of the nanotubes were dispersed into the isolated state.

The e-SWNTs-modified epoxy resins were tested and the results are shown in Figure 5. For the unmodified epoxy resin, the average tensile strength and Young's modulus were found to be 72.6 MPa and 2.0 GPa, respectively. When the 1 wt % p-SWNTs were used to modified epoxy resins, the test results indicated that the average strength and modulus were 68.1 MPa and 2.4 GPa, respectively. The tensile strength did not show any improvement while the modulus was slightly enhanced. However, when 1 wt % e-SWNTs were used to modify epoxy resins, the tensile strength of modified resins was found to be enhanced to 95.8 MPa, about 32% increase. The Young's modulus was enhanced to 3.03 GPa, which is about 50% improvement in contrast to the neat resin. The noticeable improvement of the tensile strength suggested that the e-SWNTs were very effective to modify current epoxy resins.

The fracture surfaces of cured epoxy resin were examined by SEM and are shown in Figure 6. The unmodified epoxy resin fracture surface [Fig. 6(a)] demonstrates typical features of brittle fracture. The "river-like" fracture pattern shows the crack evolution initiated from the crack source. After the crack source was initiated, the crack propagated rapidly because of the brittleness. During propagation, more and more cracks occurred. Different cracks may propagate at different levels. When those cracks met together, "river-like" patterns were formed. The area between the "river-like" patterns is very smooth because of the rapid crack propagating. In the p-SWNT-modified resins, similar "river-like" fracture patterns are observed just like unmodified resins, but the river-like facture patterns are much finer, indicating improved fracture toughness. In the contrast, the fracture surface of e-SWNTs-modified res-ins appeared coarser and ductile. The whole surface consisted of many microvoids and dimples, and looked rough and irregular. This feature of fracture surface suggested that the crack moved slowly and was accompanied by a large amount of plastic deformation. Therefore, e-SWNTs significantly improved the toughness of the pristine epoxy resins.

CONCLUSIONS

Epoxidized CNTs were achieved by oxidation of *m*-CPBA. These epoxidized nanotubes were soluble in the organic solvent and were able to be dispersed in isolated states. Fracture surface of epoxidized CNTs-modified epoxy resin suggested that the fracture toughness of the modified resins was significantly improved, demonstrating fracture characteristic of typical ductile materials. Epoxidized CNTs-modified epoxy resins demonstrated a 50% increase in the Young's modulus and 32% improvement in the tensile strength with 1 wt % loading. This study provides an effective way to synthesize novel epoxy resin. The further experiments will be carried out to investigate the rheological behavior of these modified epoxy resins.

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