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Physical properties of phenol-anchored multiwall carbon nanotube/epoxy nanocomposite

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Abstract Surface functionalization of multiwall carbon nanotubes (MWCNTs) was carried out by introducing a ylide group containing anchored phenol structures. Epoxy nanocomposites filled with modified and pristine carbon nanotubes were prepared, and their mechanical, electrical, and thermal properties were evaluated. Mechanical properties such as tensile strengths and Young's moduli of the epoxy nanocomposites increased significantly with the addition of the modified MWCNTs compared to the pristine MWCNTs, due to the strong interaction between the modified MWCNTs and the epoxy matrix. Scanning electron microscopy of the fractured epoxy systems revealed that the functionalized MWCNTs were finely dispersed in the matrix, as opposed to the pristine carbon nanotubes. The epoxy/functionalized MWCNT nanocomposite had a lower surface electrical resistance than the epoxy/pristine MWCNT nanocomposite, confirming the effect of functionalization.

Keywords Epoxy · Functionalization · Ylide · Mechanical property · Multiwall carbon nanotube

Introduction

The discovery of carbon nanotubes (CNTs) has initiated research to determine their uses in many applications. One of the most intriguing applications of CNTs is polymer/CNT nanocomposites [1–3]. The outstanding mechanical, electrical, and thermal properties of CNTs make them ideal candidates for filler in lightweight

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polymer composites [4]. Polymer/CNT nanocomposites have been prepared using several methods, including solution blending, in situ polymerization, and melt mixing [5, 6]. Many reports are available concerning CNT/polymer composites using matrices such as polyethylene [7], polypropylene [8], poly (methylmethacrylate) [9], poly (vinyl carbazole), and polyamide [10]. Epoxy resin is widely used in electronics, paints, electrical insulators, printed circuit boards, and packaging materials. The incorporation of CNTs into an epoxy matrix can significantly improve its mechanical, electrical, and thermal properties. Breton et al. [11] investigated the influences of the microtexture, structure, and surface chemistry of catalytically grown MWCNTs on the elastic moduli of nanotube-based composites. Extensive investigations have been carried out by various researchers to improve the properties of CNT-filled epoxy systems [11–14]. In general, improving the properties in specific applications depends on the dispersion states of the carbon nanotubes in the epoxy matrix [15].

Even though CNTs are known as an excellent nano-reinforcement material for polymer matrices, the scope of their application in practical devices is limited due to poor dispersion in the polymer matrix, as well as the weak interfacial bonding between the CNTs and the matrix. The poor dispersion of CNTs in polymer matrices is caused by their tendency to become bundled due to the van der Waals forces between the nanotubes. This problem can be offset by introducing reactive functional groups that reduce the bundling of CNTs and enhance the polymer-filler interaction. Bae et al. [16] added acid-modified CNTs to liquid epoxy and studied their surface properties, cure kinetics, and mechanical and thermal properties [17]. Chen et al. [18] incorporated amine-functionalized carbon nanotubes into an epoxy matrix, and subsequently reported improved properties due to the formation of covalent bonding between the amino groups and the epoxy matrix. Shen et al. [19] studied the influences of amino-functionalized carbon nanotubes on the thermophysical properties of epoxy nanocomposites. Bae et al. [20] reported the influence of phenol-anchored carbon nanotubes on the surface characteristics. In this study, we prepared phenol-anchored MWCNTs and evaluated their effects on the properties of epoxy nanocomposites, including their tensile, flexural, thermal, and electrical characteristics.

Experimental

Materials

MWCNTs with an average diameter of 9.5 nm and an aspect ratio of 158 were obtained from Nanocyl (Belgium) and were used as received without any purification. *N*-(4-hydroxy phenyl glycine), formaldehyde, and dimethyl formamide (DMF) were obtained from Aldrich. Diglycidyl ether of bisphenol A (YD-128) with an epoxy equivalent weight (EEW) of 184–190 g/eq. and poly(aminoamine) (PAA) curing agent (G–A0533) were obtained from Kukdo Chemicals Co. (Korea).

Preparation of epoxy/CNT nanocomposites

Functionalized MWCNTs were prepared using *N*-(4-hydroxy phenyl glycine), formaldehyde, and DMF. The detailed functionalization procedures are described in a previous work [20]. Pure and azomethine ylide-functionalized carbon nanotubes were designated as NT_P and NT_G, respectively. Epoxy/CNT nanocomposites containing 1–3 wt% CNTs were prepared, and both pristine and functionalized carbon nanotubes were dispersed in the acetone solvent (50 mL) for 60 min. A calculated amount of the epoxy resin was dissolved in 100 mL of acetone, and the CNTs were then added. The resulting solution was then subjected to sonication for 60 min. The samples were dried in a vacuum oven at room temperature to partially remove the solvent before being stirred with a high speed mixer. Amine hardener was added, and the solution was stirred for an additional 30 min. The samples were then dried in a vacuum oven to remove the solvent. The samples were transferred into Teflon plates, degassed for 4 h, cured at 80 °C under vacuum for 2 h, and finally cured for an additional 2 h at 120 °C to complete the crosslinking reaction. Epoxy nanocomposite samples were designated as ENT_x, where E represents the epoxy resin, and NT_P and NT_G represent pristine and modified CNTs, respectively.

Characterization

Characterization studies of pure and phenol-anchored carbon nanotubes were performed using various tools. Fourier transform infrared spectroscopy (FT–IR) results were collected using a Perkin-Elmer 2000 spectrophotometer in the range of 4,000–400 cm^{-1} with a resolution of 4.0 cm^{-1} and an average scan number of 32. Elemental analysis was conducted using an elemental analyzer (Flash EA112, CE Instruments, Italy).

Mechanical properties including the Young's moduli and tensile strength of the epoxy nanocomposites were determined following the ASTM D 638. The measurements were carried out using a universal testing machine (INSTRON 8871) at a crosshead speed of 3 mm/min. Dimensional changes in the epoxy nanocomposites were measured using a thermal mechanical analyzer (Q 400EM, TA Instrument) in the range of 24–150 °C at a heating rate of 10 °C/min. Before the measurements, the specimens were annealed in a furnace at 150 °C for 2 h. The electrical properties of the epoxy nanocomposites were determined using a two probe method with a Keithley 2001. Field emission scanning electron microscopy (FE-SEM) (LEO SUPRA 55, Carl Zeiss, Germany) was used to investigate the carbon nanotube dispersion in the fractured tensile specimens.

Results and discussion

Table 1 shows the elemental analysis results of the pristine (NT_P) and modified CNT (NT_G) samples, revealing that nitrogen atoms are introduced on the functionalized carbon nanotube surface, and confirming the presence of azomethine ylide groups on the surface. The atomic concentration of the nitrogen atom is about

Table 1 Elemental analysis of pristine and azomethine ylide functionalized MWCNT

MWCNT	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Others (%)
Pristine CNT (NT_P)	86.0	0.0	0.0	14.0
Modified CNT (NT_G)	74.2	3.0	2.7	20.1

2.7% (0.15 mmol) in the modified CNT (NT_G) sample, while nitrogen atoms are not detected in the NT_P. The extent of azomethine ylide functionalization on multiwalled carbon nanotubes is similar to our previously reported result for single wall carbon nanotubes [20]. As the moles of nitrogen in the nanotube surface are equivalent to the number of phenol structures introduced onto the nanotube surface, it is possible to calculate the number of anchored groups on the nanotube surface, which is estimated to be 23 anchored phenol structures/1,000 carbon atoms.

The successful functionalization of the azomethine ylide groups on the carbon nanotube surface is further supported by the FT–IR results. Figure 1 shows the FT–IR spectra of the NT_P and NT_G samples. The appearance of the new peaks in the FT–IR spectra of NT_G at 2927 cm^{-1} corresponds to the –CH asymmetric stretching vibrations of the aromatic and $–CH_2$ groups present in the azomethine ylide groups, confirming the successful functionalization of the carbon nanotubes. This is further supported by the peaks at 1575, 1476, and 1438 cm^{-1}, which are due to the phenolic ring, –CH bending vibrations of the phenolic ring, and –CH bending vibrations of the azomethine ylide groups, respectively. The formation of the azomethine ylides is further supported by the appearance of a peak at 1376 cm^{-1}, along with the small hump at 1279 cm^{-1}, which correspond to the –CNC stretching and –CN stretching of the tertiary amine group, respectively.

The mechanical properties (including the tensile strength and Young's modulus) of the epoxy nanocomposites with varying CNT loadings are investigated and the

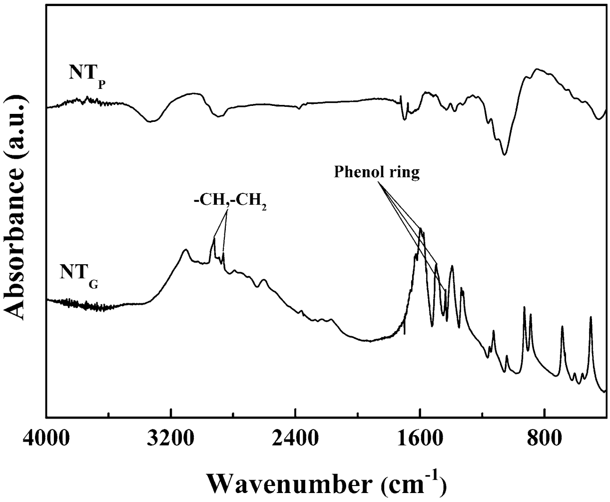


Fig. 1 FT–IR spectra of pristine (NT_P) and functionalized (NT_G) MWCNTs

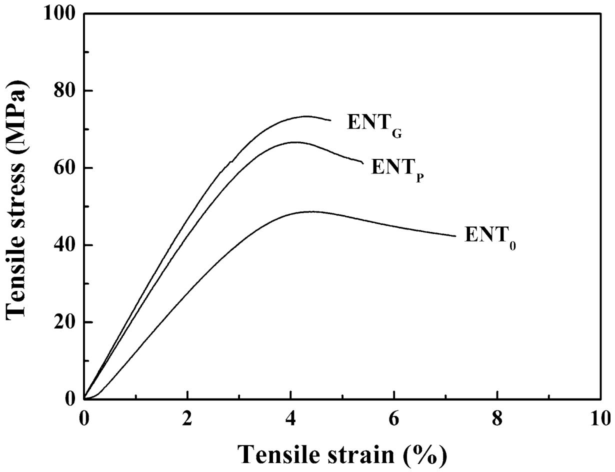
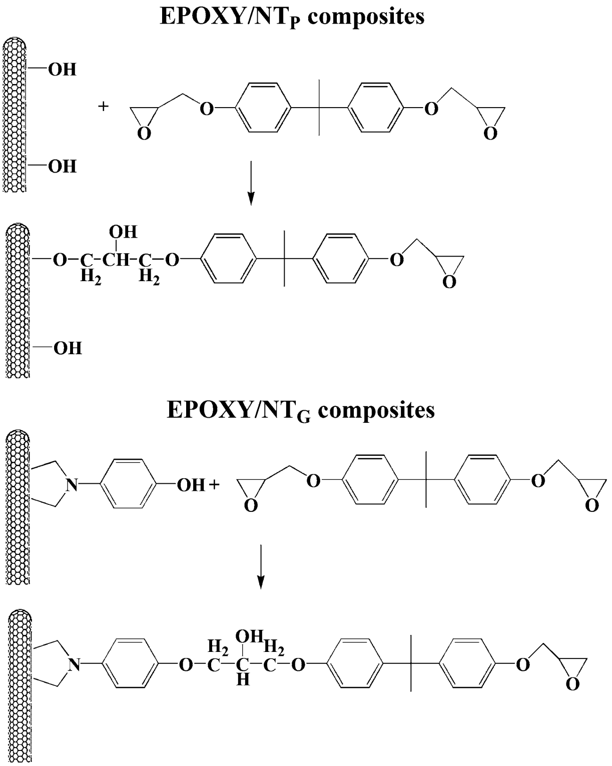


Fig. 2 Tensile stress–strain curves of epoxy (ENT$_o$) and epoxy/MWCNT nanocomposites. CNT loading is 1 wt%

results are displayed in Figs. 2 and 4. Figure 2 shows the stress–strain curves of the epoxy nanocomposites with 1 wt% CNTs. The addition of 1 wt% of pristine carbon nanotubes (NT$_P$) in the epoxy matrix (ENT$_P$) increases the Young's modulus and tensile strength, but the strain decreases relative to that of the pure epoxy system. The addition of modified carbon nanotubes (NT$_G$) into the epoxy matrix (ENT$_G$) further improves the Young's modulus and tensile strength. The increases in the modulus and tensile strength of the CNT-filled system can be attributed to the epoxy–carbon nanotube interaction. This interaction facilitates the load transfer between the carbon nanotubes and the polymer matrix, thereby leading to the distribution of applied stress in the matrix, and resulting in the improved mechanical properties. Possible interaction mechanism between CNT and epoxy is shown in Fig. 3. Phenolic –OH groups introduced on the carbon nanotube surface (NT$_G$) can react with the epoxy groups as proposed in Fig. 3. This type of interaction between the NT$_G$ and epoxy leads to an increased modulus and tensile strength. Even though it is rare, pristine carbon nanotubes also can possess a certain degree of phenolic –OH groups that are generated on the nanotube surface during the purification step.

Figure 4a, b shows the tensile properties of the epoxy nanocomposites at various carbon nanotube loadings. The tensile strength and Young's modulus of ENT$_P$ leveled off at a certain pristine CNT loading ($\sim$1–2 wt% CNTs), while those of ENT$_G$ increased with increasing CNT content. The different loading trends of the two different CNTs can be attributed not only to the degree of interfacial interactions between the CNTs and epoxy, but also to the uniformity of dispersion. Bae et al. [20] reported that the functionalization of single wall carbon nanotubes with azomethine ylide resulted in uniform dispersion of the CNTs in the solvents. Similarly, strong interactions of the ylide groups on the NT$_G$ surface with the epoxy resulted in a more uniform distribution of NT$_G$ in the epoxy matrix compared to that of NT$_P$.



EPOXY/$\mathrm{NT_P}$ composites

EPOXY/$\mathrm{NT_G}$ composites

Fig. 3 Possible interaction reaction mechanism between epoxy and MWCNTs

This phenomenon is further supported by the FE-SEM morphological characterization results of the tensile-fractured samples shown in Fig. 5. The SEM image of $\mathrm{ENT_P}$ shows localized carbon nanotube clusters with some nanotubes buried in the epoxy matrix. Alternatively, the SEM image of $\mathrm{ENT_G}$ shows well-distributed carbon nanotubes, the majority of which are buried in the epoxy matrix. From these observations, $\mathrm{ENT_G}$ shows more uniformly dispersed MWCNTs than does $\mathrm{ENT_P}$.

Figure 6 shows the dimensional changes of the epoxy/carbon nanotube composites. The dimensional change is drastically reduced by loading 1 wt% of both pristine and modified MWCNTs in the epoxy matrix ($\mathrm{ENT_p}$ and $\mathrm{ENT_G}$). However, an increase in temperature results in a more prominent reduction in dimensional change in the case of $\mathrm{ENT_G}$, when compared to $\mathrm{ENT_P}$. This behavior can also be attributed to the interactions between the MWCNTs and the epoxy, as well as to the uniform dispersion of the MWCNTs. Uniform distribution and the strong interaction of $\mathrm{NT_G}$ with epoxy molecules hinders the mobility of the epoxy molecules, resulting in reduced dimensional change.

Figure 7 shows the surface electrical resistances of the $\mathrm{ENT_P}$ and $\mathrm{ENT_G}$. As expected, the surface resistivity of the epoxy nanocomposites decreased drastically with the addition of a small amount of MWCNTs (1 wt%), and it tended to level off around ca. 2 wt%. It is also observed that the surface resistivity of the $\mathrm{ENT_G}$ is

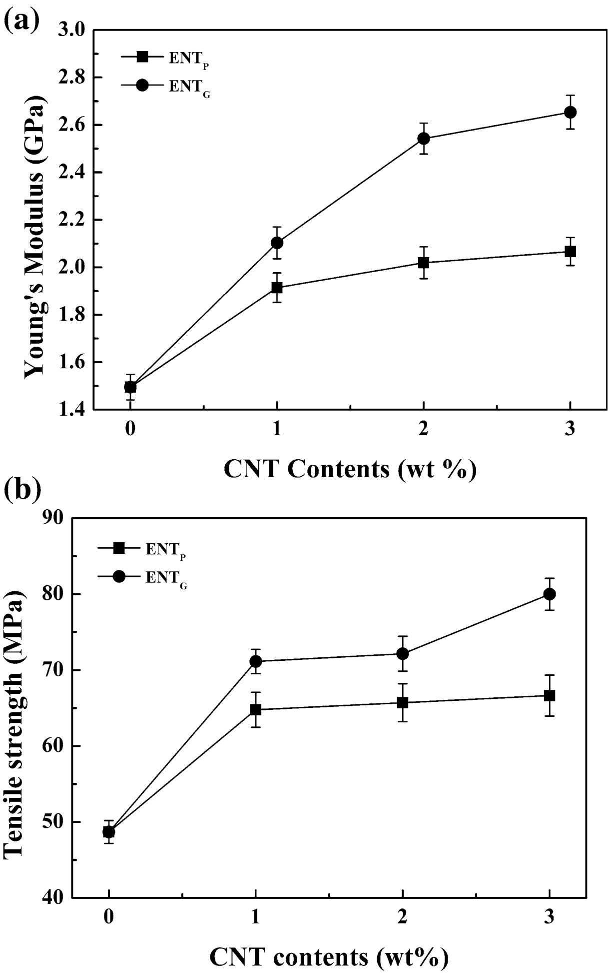


Fig. 4 Variation of **a** Young's modulus and **b** tensile strength of epoxy nanocomposites (*ENT*$_p$ pristine MWCNT, *ENT*$_G$ functionalized MWCNT)

about two orders of magnitude lower than that of ENT$_\mathrm{P}$ across the range of nanotube loading, which is attributed to the improved MWCNT dispersion in ENT$_\mathrm{G}$. As shown in Fig. 5, surface functionalization of the MWCNTs induces uniform distribution in the epoxy matrix, and well-dispersed, functionalized carbon nanotubes can form an efficient conductive network that reduces the surface resistivity of the epoxy matrix.

Conclusions

Surface functionalization of the MWCNTs leading to the development of the anchored phenol groups was performed through azomethine ylide functionalization,

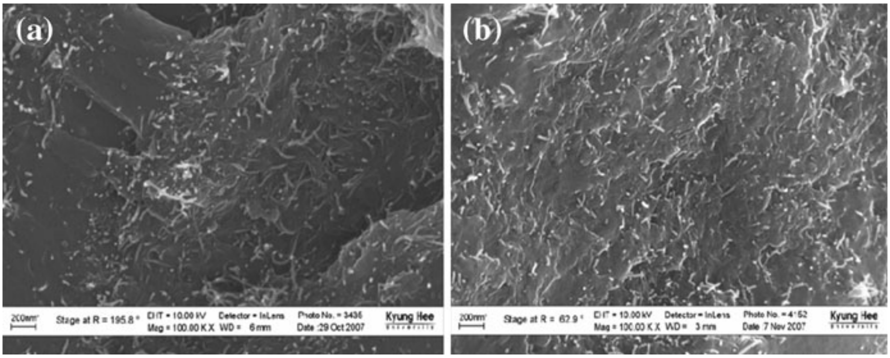


Fig. 5 FE-SEM images of tensile fractured **a** epoxy/pristine MWCNT and **b** epoxy/functionalized MWCNT nanocomposites (CNT loading = 1 wt%)

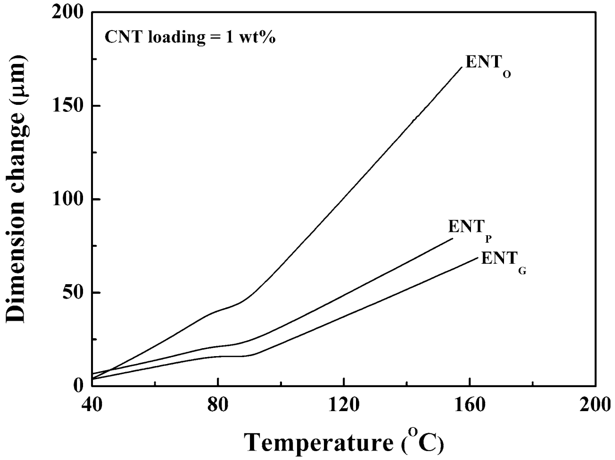


Fig. 6 Dimensional change of epoxy nanocomposites as a function of temperature. (*ENT*$_o$ without MWCNT, *ENT*$_P$ pristine MWCNT, *ENT*$_G$ functionalized MWCNT)

and the resulting properties were evaluated using characterization tools such as FT–IR and elemental analysis. Successful formation of the azomethine ylide groups with anchored phenol structures was confirmed via FT–IR, which showed a strong peak at 1376 cm^{-1} corresponding to the –CNC– stretching vibration. The elemental analysis results revealed that about 23 phenol groups were introduced per 1,000 carbon atoms. The effects of the phenol-anchored carbon nanotubes on the tensile moduli, tensile strengths, and flexural strengths of the epoxy nanocomposites were investigated. The observed properties were improved from those of pure epoxy or epoxy/pristine CNT nanocomposites. Significant improvements in the properties were corroborated by the improved interfacial interactions between the epoxy matrix and modified carbon nanotubes through the anchored phenol structure,

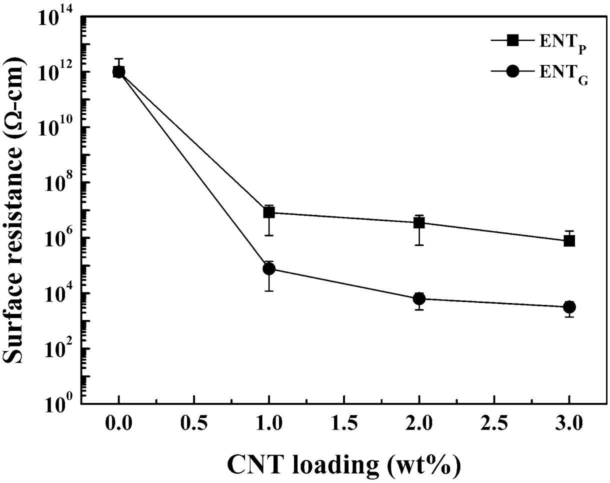


Fig. 7 Surface electrical resistances of epoxy nanocomposites with various CNT content (*ENT*$_P$ pristine MWCNT, *ENT*$_G$ functionalized MWCNT)

as well as the uniform distribution of CNTs in the matrix. FE-SEM studies of the tensile fractured epoxy nanocomposite samples further demonstrated the effective dispersion of the modified carbon nanotubes. Epoxy/modified CNT composites showed reduced dimensional change compared to that of epoxy/pristine CNT composites and pure epoxy, and the behavior became more significant with increasing temperature. The surface electrical resistivity of epoxy/modified CNT composites was about two orders of magnitude lower than that of epoxy/pristine CNT composites for all of the evaluated experimental MWCNT loadings.

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