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Preparation and Properties of Pyrene-Modified Multi- Walled Carbon Nanotube/Epoxy Resin Nanocomposites

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Summary: Nanocomposites of multi-walled carbon nanotube (MWCNT)/bis-phenol A type epoxy resin were prepared and physical properties of the nanocomposites were investigated. For the fine dispersion of MWCNT in the epoxy resin, MWCNT was modified with pyrene butyric acid (PBA) in the supercritical carbon dioxide (CO_2). The physical adsorption of PBA on the surface of MWCNTs was studied with a thermogravimetric analyzer and a transmission electron microscopy. The electrical surface resistivities of the nanocomposites showed threshold decreases due to percolations above the critical concentration of the MWCNT. The resistivities showed maximum depending on the concentration and the modification of the surface of the MWCNT with PBA. It is postulated that the dispersion of the MWCNT in epoxy resins resulted in dispersion systems which exhibit rheological properties similar to lyotropic liquid crystalline polymers. The surface resistivities of the MWCNT/epoxy systems reflected the morphological characteristics of the systems which also determined rheological properties of the systems.

Keywords: epoxy; liquid crystalline; multiwalled carbon nanotube; nanocomposite; pyrene

Introduction

Since Iijima discovered the carbon nanotubes (CNTs) in the cathode deposit with fullerene (C_{60}),[1,2] nanocomposites of CNTs and organic polymers have been studied to develop high performance materials of superior electrical, mechanical and thermal properties. The superior properties of carbon nanotube (CNT) offer exciting opportunities for the new composites. However, CNTs are easy to agglomerate, bundle together and entangle, leading to many defect sites in the composites, and limiting the efficiency of CNT in polymer matrices. For the fine dispersion of CNT, much progress has been made to introduce covalent bond of desired chemical groups to the ends and surfaces of the tubes[3]. A drawback of such chemical modification of the conjugated backbone of CNT is the corresponding loss of the strength and electrically conductive characteristics of the pristine CNT. In this study, surface modifications of multi-walled carbon nanotube (MWCNT) by π-π stacking or hydrophobic interactions using a pyrene derivative were investigated.[4–12] Especially, pyrene butyric acid (PBA) was employed to modify the surface of CNT by adsorption in supercritical carbon-dioxide (CO_2), which dissolves PBA and allows adsorption of PBA on the surface CNT effectively. Supercritical fluids (SCFs) have previously been used for efficient deposition of self assembled monolayers onto many high surface area materials because of their gas like diffusivity and liquid like density.[13,14] In addition, the solubility of pyrenes in supercritical carbon-dioxide (CO_2) is well known.[15–20] Nanocomposites based on the modified MWCNT and epoxy resins were prepared and the rheological

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and electrical properties of the nanocomposites were studied and discussed in this paper.

Experimental Part

Materials

All the raw materials were commercial products. Characteristics of the raw materials are given in Table 1.

Surface Modification of MWCNTs

The amount of PBA molecules necessary to saturate the surface of the MWCNT was estimated to be 14wt% by considering the cross section area of PBA, 0.7 nm^2.[12] Concentrations of PBA during the treatment of the MWCNTs in the autoclave of supercritical CO_2 were varied from 0 to 20wt% of the MWCNT. The autoclave was flushed with carbon dioxide and pressurized with the gas to the level of 5000 psi. And the mixture was stirred at 190 °C for 30 min and 200 rpm. MWCNT 'P-xx' denotes a MWCNT treated with xx% (by wt) of PBA in this paper.

Preparation of MWCNT/Epoxy Resin Nanocomposites

Nanocomposites of PBA-modified MWCNT/epoxy resin were prepared by dispersing a determined amount of PBA-modified MWCNT (P-CNT) in the epoxy resin. MWCNT/epoxy resin mixtures were sonicated for 3 hr at 300 W. Stoichiometric amounts of the hardener for the epoxy resin were then added to the dispersion and the whole mixture was mechanically stirred for 3 min and then cast into a silicone mold and cured at 190 °C for 4 hr.

Characterization

Characteristics of PBA in the MWCNTs after the modification in the supercritical fluid were studied using a thermogravimetric analyger (TA, Q-50) by heating the samples from room temperature to 800 °C at 10 °C/min in the air. And the samples for transmission electron microscope were prepared by drying the copper grid immersed in the 0.002wt% dispersion of the MWCNT in N,N-dimethylformamide. Rheological properties of the nanocomposites were investigated employing a parallel-plate rheometer (TA, Advanced Rheometer 2000) in oscillation mode at 0.5% strain. Surface electrical resistivities of the nanocomposites were measured with a resistivity tester (SIMCO ST-3, DKK-TOA Co. SM8220).

Results and Discussion

Modification of MWCNT with PBA

TGA thermograms of MWCNTs after the treatment with PBA in supercritical CO_2 are given in Figure 1. Pristine MWCNT follows one step weight loss while PBA two step weight loss with increasing temperature in the air. When the PBA content of the modified MWCNT is less than 15wt%, the thermograms of the treated MWCNTs are similar to that of pristine MWCNT, showing one step weight loss. The MWCNT treated with 20wt% of PBA follow two step weight loss like neat PBA, implying the presence of free PBA which are not adsorbed on the surface of the MWCNT strongly. It is speculated that PBA which could not be adsorbed on the

Table 1.
Raw materials used in the preparation of the nanocomposits.

Materials	Grade	Manufacturer	Characteristics
Epoxy resin	YD-128	Kukdo Chemical	Bisphenol A based epoxy resin, Mn: 374 g/mol
Hardener	KBH-1098	Kukdo Chemical	Tetrahydrophthalic anhydride
MWCNT	CVD 95	Iljin Nanotech	Purity: 97% Diameter: 12 nm Length: 15 μm Density: 1.55 g/cm^3
PBA	Reagent	Aldrich	

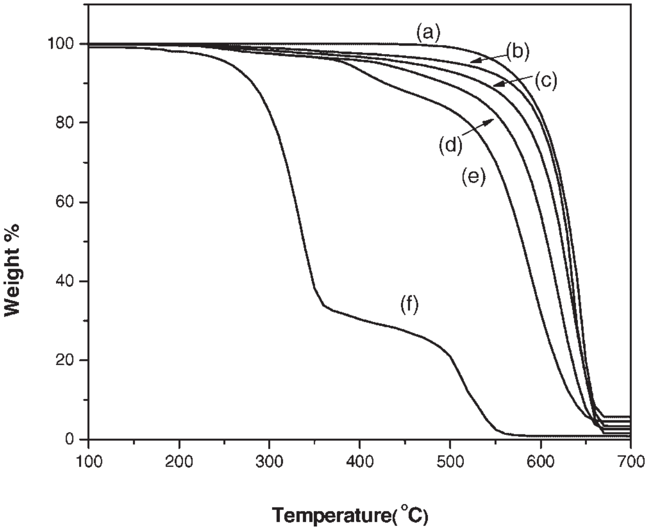


Figure 1.
TGA thermograms of various MWCNTs modified with PBA: (a) pristine MWCNT; (b) P-05; (c) P-10; (d) P-15; (e) P-20; (f) neat PBA.

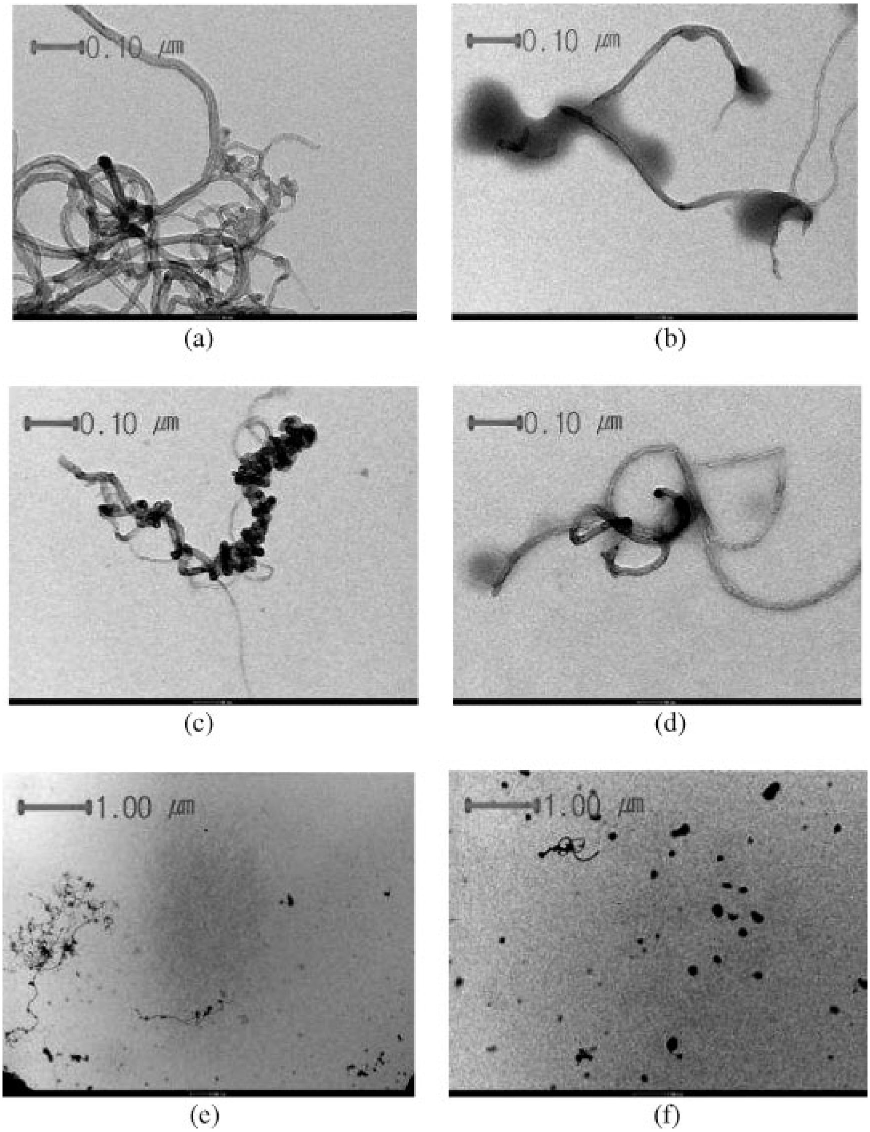
surface by π-π stacking follows degradation behavior of neat PBA.[10,17] It seems that there is little PBA in excess after treatment when the concentration of PBA is less than 15% (by wt). TEM images of the MWCNTs are shown in Figure 2. Less entanglement was observed in TEM images of the MWCNTs with increasing the concentration of PBA in the treatments. Furthermore, black spots which are believed to be PBA in excess were observed when the concentration of PBA is above 15wt%. It is worthwhile to note that the theoretical maximum amount of PBA which can be adsorbed on the surface of MWCNT is 14%, assuming the area of adsorbed by one PBA molecule is 0.7 nm^2.[12] The proper amount of PBA for the modification of the MWCNT seems to be similar to the amount necessary to saturate the surface of the MWCNT theoretically, 14wt%.

Rheological Properties of MWCNT/Epoxy Nanocomposites

In Figure 3, storage moduli (G′) of the MWCNT/epoxy resin mixtures are given. With increasing the concentration of MWCNTs, the mixtures showed solid like properties, i.e., the slope of G′ versus frequency decreased. But the changes of G′ with frequency depending on the concentration and the surface treatments were complicated. However, one common feature is that the mixtures show maximum values of G′ with increasing the concentration of MWCNT and the maximum value was dependant on the surface treatment. In general, most solutions or dispersions show increase of viscosity or storage modulus with increasing the concentration of fillers. It is of interest to note that lyotropic liquid crystalline polymers show maximum and minimum values in viscosities with increasing the concentration due to rigidity of molecules. Rheological properties observed in the MWCNT/epoxy resin systems can be attributed to rigidity of MWCNTs dispersed in epoxy resins similar to lytropic liquid crystalline systems.

Surface Electrical Resistivity of MWCNT/Epoxy Nanocomposites

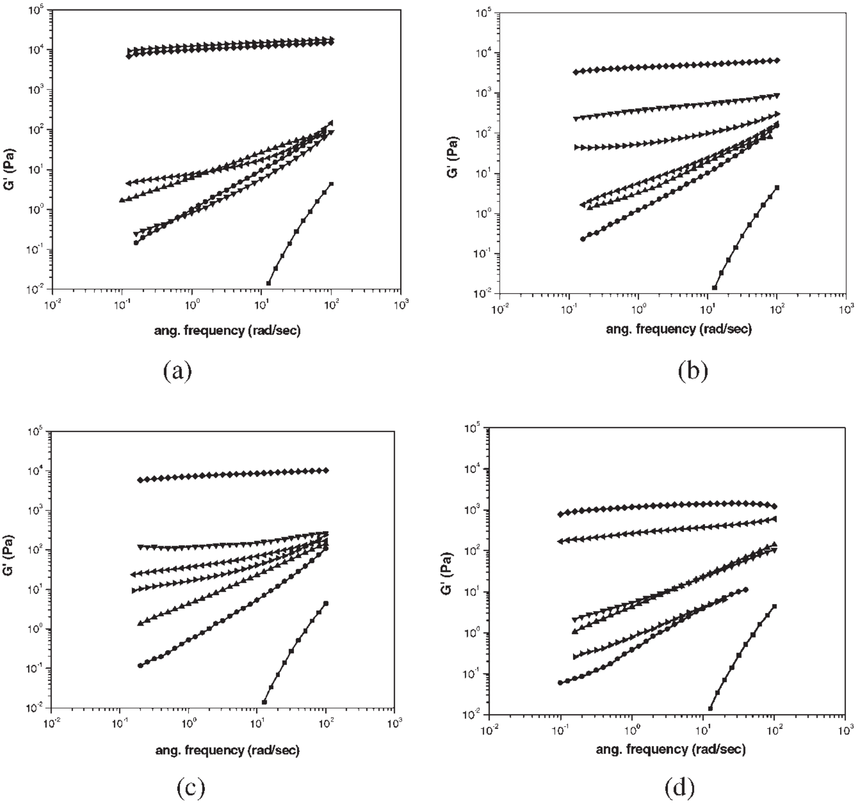
Surface electrical resistivities (SERs) of the nanocomposites investigated are shown in Figure 4. With increasing the content of



(a) (b) (c) (d) (e) (f)

Figure 2.
TEM images of various PBA-modified MWCNTs: (a) pristine MWCNTs; (b) P-10; (c) P-15; (d) P-20; (e) P-15 in low magnifications; (f) P-20 in low magnifications.

MWCNT in the nanocomposites, threshold decreases of SER are observed and attributable to percolation of MWCNTs. It is of interest to notice that maximum and minimum of SERs are observed with further increasing of the MWCNT content after the threshold decrease. In general, percolation of CNTs in polymer nanocomposites accompanies large increase of viscosity or modulus and threshold decrease of electrical resistivity. In Figure 3, we observed large increase of G′ and maximum and minimum of G′ with increasing the MWCNT content in the nanocomposite. Change of rheological and electrical properties relects the dispersion of the MWCNTs in the nanocomposites. It is speculated that maximum and minimum



(a)

(b)

(c)

(d)

Figure 3.

Storage modulus (G′) versus frequency of PBA-modified MWCNT/epoxy mixtures prepared from pristine MWCNT (a), P10 (b), P15 (c) and P20 (d) in different concentration of MWCNT (by wt) at 25 °C: (■) 0%; (●) 0.1%; (▲) 0.3%; (▼) 0.5%; (◀) 0.7%; (▶) 0.9%; (◆) 1.5%.

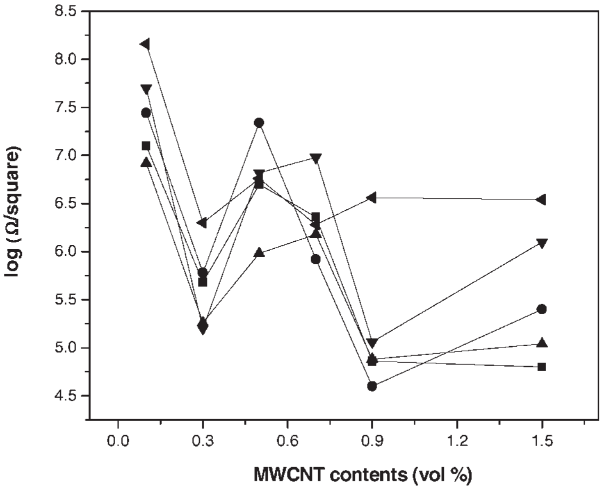


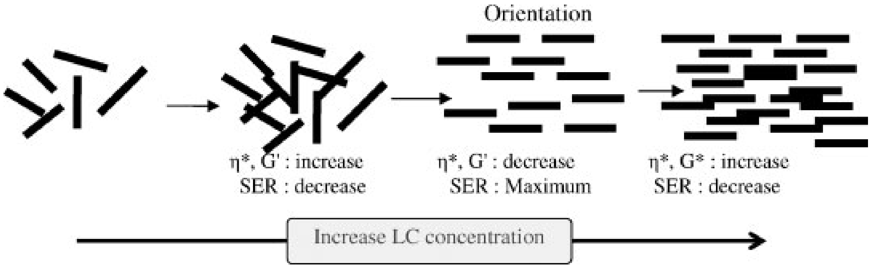
Figure 4.

Surface electrical resistivity of the nanocomposites based on different PBA-modified MWCNT and the epoxy resin: (■) pristine MWCNTs; (●) P05-MWCNTs; (▲) P10-MWCNTs; (▼) P15-MWCNTs; (◀) P20-MWCNTs.

Table 2.
Anisotropic SER of the nanocomposites investigated

Sample Code*	SER in one direction (A) Log(Ω/square)	SER in perpendicular to A direction Log(Ω/square)
P00-C0.5	6.70	10.6
P05-C0.5	7.34	12.6
P10-C0.7	6.18	10.8
P15-C0.7	6.86	9.2
P20-C0.9	6.56	11.0

xx and yy of sample code, Pxx-C-yy, denote the PBA content (wt%) of MWCNT and the MWCNT content (vol %) of the nanocomposites respectively.



Scheme 1.
Change of the dispersion of MWCNTs in epoxy resins with increasing the concentrations similar to a lyotropic liquid crystalline system.

of G′ and SER imply the orientation of MWCNTs in the nanocomposites like lyotropic liquid crystalline systems. Further increase of the concentration of the MWCNT after percolation is expected to induce orientation of MWCNT due to its rigidity. In order to confirm the possible orientation of the MWCNTs in the nanocomposites, SERs were measured in different directions and the results of measurements are given in Table 2. Table 2 show that the nanocomposites showing maximum in SER exhibits anisotropic SER values. Thus, due to rigidity of the MWCNTs in epoxy resin before cure, the dispersion of the MWCNT show a concentration dependency shown in Scheme 1 like lyotropic liquid crystalline systems.

Conclusion

Rheological properties and electrical resistivities of the nanocomposites based on a bis-phenol A type epoxy resin and PBA-modified MWCNT were studied. Rheological properties of the nanocomposites before cure and surface resistivities after cure showed interesting relationships and were attributed to the dispersion properties similar to lyotropic liquid crystalline systems. It is postulated that the modification of MWCNT with PBA in supercritical CO_2 improves the dispersion of MWCNT in the nanocomposites and affected the alignment of MWCNT in the epoxy resin.

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