High Dispersion Ability of Fluorene-Based Polyester as a Polymer Matrix for Carbon Nanotubes

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ABSTRACT: The high compatibility of fluorene-based polyester (FBP-HX) as a polymer matrix for multiwalled carbon nanotubes (MWCNTs) is discussed. A low surface resistivity due to the fine dispersion of MWCNTs in FBP-HX and polycarbonate (PC) is reported. With a solution-casting method, a percolation threshold with the addition of between 0.5 and 1.0 wt % MWCNTs was observed in the MWCNT/PC and MWCNT/FBP-HX composites. Because of the coverage of FBP-HX on the MWCNTs, a higher surface resistivity and a higher percolation ratio of the MWCNT/FBP-HX composites were achieved compared with the values for the MWCNT/PC composites. In the MWCNT/FBP-HX composites, MWCNTs covered with FBP-HX were observed by scanning electronic microscopy. Because of the coverage of FBP-HX on the MWCNTs, FBP-HX interfered with the electrical pathway between the MWCNTs. The MWCNTs in FBP-HX were covered with a 5-nm layer of FBP-HX, but the MWCNTs in the MWCNT/PC composites were in their naked state. MWCNT/PC sheets demonstrated the specific Raman absorption of the MWCNTs only with the addition of MWCNTs of 1 wt % or above because of the coverage of the surface of the composite sheet by naked MWCNTs. In contrast, MWCNT/FBP-HX retained the behavior of the matrix resin until a 3 wt % addition of MWCNTs was reached because of the coverage of MWCNTs by the FBP-HX resin, induced by its high wettability. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2690–2695, 2010

Key words: carbon nanotube; composites; dispersions; polyesters

INTRODUCTION

Electronic devices are becoming increasingly compact. Components containing carbon compounds are designed to be compact for enhanced performance. To obtain enhanced performance in fillers in matrix resins, a fine dispersion of the fillers in the polymers is required.

Composite materials containing carbon black (CB), graphite, carbon fiber, and carbon nanotubes (CNTs) have been used in applications that require materials with special electrical and thermal conductivity properties (e.g., electromagnetic shielding, batteries).[1] After the discovery of multiwalled carbon nanotubes (MWCNTs) by Iijima in 1991,[2] the number of applications has increased tremendously because of their excellent mechanical, electrical, and optical properties. CNTs have also been used as reinforcement materials for polymers.[3,4] The high electric conductivity of CNTs make them suitable for use in electronic fields and makes it possible to prepare polymer composites with CNTs that have particular electrical conductivity or electrostatic discharge properties.[4] Although the surface modification of carbon fillers is an established method for producing excellent composite resins, the development of a matrix resin in which carbon fillers without such modification could be dispersed would provide a more efficient method of achieving high-performance composite materials.

The synthesis and application of various fluorene-based polymers (FBPs), synthesized from the end group of a side chain at the 9,9 position of fluorene moieties (Scheme 1), such as polyurethanes, poly (ether ether ketone)s, and polyesters, referred to as FBPs, have been reported.[5,6] Despite their high dispersion power, FBPs are also used in optical fields because of their high thermostability, transparency, and refractive index and low birefringence.[7–11] Fluorene moieties capable of forming supermolecules have also been used in biomedical fields as a bridging unit for DNA molecules.[12]

The cardo structure of FBPs, demonstrated in Scheme 1, makes it easy to achieve a fine dispersion of fillers, such as CB, CNTs, and organic pigments,.
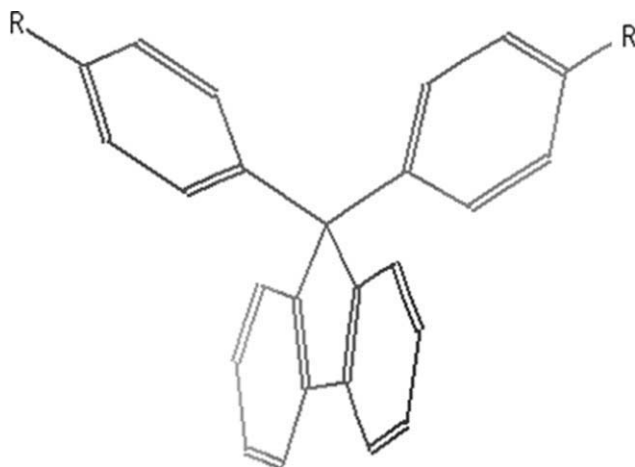
Scheme 1 Chemical structure of the FBP.

In a previous report, the fine dispersion ability of CB in FBPs was proven.[13,14]

In this report, we discuss the fine dispersion of carbon fillers with a high aspect ratio in FBP. MWCNTs were used as high-aspect fillers for FBPs. Commercially available polycarbonate (PC) was used for comparison.

EXPERIMENTAL

Materials

PC (Panlite L-1225L, Teijin Chemicals, Ltd., Tokyo, Japan), with a weight-average molecular weight of 35,400, and fluorene-based polyester (FBP-HX; Osaka Gas Chemicals, Osaka, Japan), with a weight-average molecular weight of 25,800 (as shown in Scheme 2), were used as the matrix resins. MWCNTs (NC 7000, Nanocyl Japan, Nara, Japan), with an average diameter of 10 nm and an aspect ratio of over 1000, were used as the filler in the matrix polymers. The MWCNTs were directly used in the experiment without further treatment. Chloroform (guaranteed reagent (GP) grade, Nacalai Tesque, Kyoto, Japan) was used as the solvent for the polymer and the dispersion solvent for the MWCNTs.

Sample preparation

Preparation of the MWCNT/polymer composites

A solution blending method was applied to investigate the dispersion mechanism of the MWCNTs in the matrix polymers. A 10 wt % polymer solution was prepared in CHCl$_3$. The desired amount of MWCNTs was dispersed in the 10 wt % solution of polymer by mechanical stirring; this was followed by sonication of the dispersion for 45 min. The dispersion state of the MWCNTs in the 10 wt % polymer solutions was evaluated by the stability of the

dispersion. A MWCNT/polymer composite was prepared by the evaporation of the solvent from the previously described mixture. The MWCNT/polymer composites were hot-pressed into thin sheets at 250°C and 40 MPa for evaluation.

Preparation of the samples for scanning electronic microscopy (SEM) observation

We prepared MWCNT/polymer samples for SEM observation by first dipping the composite sheets into liquid nitrogen for 2 min and then breaking them by bending. The broken MWCNT/FBP-HX composite sample with 3 wt % MWCNTs was dipped into CHCl$_3$ for 5 min along the broken cross section of the sample and wiped lightly with filter paper. This was the sample designated as 2e in Figure 2 (shown later).

Evaluation of the CNT/polymer

Surface resistivity

For the MWCNT/polymer composite, the MWCNT sheets prepared by hot pressing were cut into 10 × 10 mm^2 squares, and a gold layer was spin-coated on the sheets. The electrical conductivity of the gold-coated composite sheets was determined by application of a direct current, and their resistances were then determined with an electric resistance meter (Loresta-GP MCP-T600, DIA Instruments Co., Ltd., Kanagawa, Japan). The surface resistivity of the sheets was calculated from the following standard relation:

$$\rho = R \times RCF$$

where ρ is the surface resistivity (Ω/square), R is the electrical resistance (Ω), and RCF is the resistivity

FBP-HX

PC
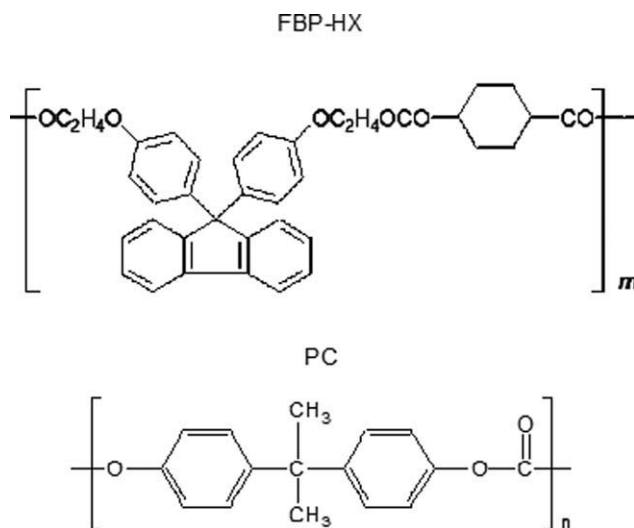
Scheme 2 Chemical structures of the FBP-HX and PC.

correction factor (correlated to the shape and size of the sample and also correlated to the measuring position; in this experiment, RCF = 10.5 was applied).

Dispersion state and structure

The dispersion of the MWCNTs in the 10 wt % solutions of FBP-HX and PC in chloroform was achieved by simple mechanical stirring. The MWCNTs in dispersion did not aggregate or precipitate, even after 48 h of rest at room temperature.

The dispersion of the MWCNTs in the composite was observed by SEM (S-2460N, Hitachi, Ltd., Tokyo, Japan). The sheets prepared by hot pressing were quenched in liquid nitrogen and broken by bending. The cross sections of the broken sheets were coated with gold and observed by SEM.

Thermal analysis

The thermal properties of the MWCNT/polymer composite films were evaluated by differential scanning calorimetry (DSC) with a Thermoplus DSC 8020 calorimeter (Rigaku Corp., Tokyo, Japan) in the range from room temperature to 250°C at a heating rate of 10°C/min.

The midpoint value, where the endotherm of the glass transition reached half-height, was used to evaluate the glass-transition temperature (T_g) of the polymer and MWCNT/polymer composites.

Raman spectroscopy of the MWCNT/polymer composites

Raman spectroscopy was carried out with a 532-nm laser (Holoprobe 532, Kaiser Optical Systems, MI, Ann Arbor). The scanning of the samples was performed at wave numbers from 100 to 4400 cm^{-1}.

RESULTS AND DISCUSSION

Surface resistivity of the MWCNT/polymer composites

According to a theoretical simulation we published previously,[14] the adsorption energy of fluorene structures, such as FBP-HX, to graphite structures is higher than that for bisphenol structures, such as PC. A fine dispersion of MWCNTs in a matrix polymer will result in a low surface resistivity. In contrast, a coverage of the matrix polymer on the MWCNTs will disturb the electrical pathways between the MWCNTs; thus, MWCNTs covered with matrix polymer should have a higher surface resistivity than uncoated or naked nanotubes.

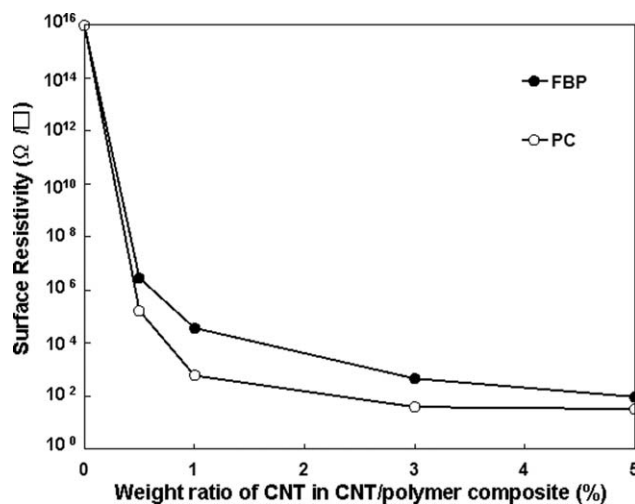Figure 1 shows the surface resistivity of the MWCNT/polymer composites prepared by the solu-

Figure 1 Surface resistivity of the MWCNT/FBP-HX composites prepared by solution casting with different weight ratios of MWCNTs: (●) MWCNT/FBP-HX and (○) MWCNT/PC composites.

tion-casting method. Both the composites of MWCNTs with PC and FBP had a low percolation ratio between 0.5–1.0 wt %. The high dispersion power of PC and FBP on the MWCNTs induced the low surface resistivity of the composites, and because of the coverage of FBP on the naked MWCNTs, a higher surface resistivity of MWCNT/FBP-HX was achieved than for MWCNT/PC. The reason for this phenomenon was the coverage of FBP-HX on the MWCNTs. This resulted in both a higher surface resistivity in the MWCNT/FBP-HX composites and the higher percolation ratio of the MWCNT/FBP-HX composites when compared with the values for the MWCNT/PC composites.

Fine dispersion of MWCNTs in FBP-HX as observed by SEM

The MWCNTs in the composite materials as prepared by the solution method showed significant differences in the PC and the FBP-HX polymer matrices. The fluorene structure of FBP-HX had a strong π–π interaction with the graphite structure on the surface of the MWCNTs. This improved the compatibility of the MWCNTs with the FBP-HX polymer through a process that is not yet clear. The MWCNTs were separated at the nanometer level in the FBP-HXs. The fine dispersion of the MWCNTs in FBP-HX and PC resulted in the low surface resistivity of both kinds of MWCNT/polymer composites, even those which contained low weight ratios (0.5–1.0 wt %) of MWCNTs.

SEM observation of the cross section of the MWCNT/FBP-HX composite indicated that the FBP-HX matrix polymer covered the surface of the MWCNTs [Fig. 2(b)]. However, this was not true for
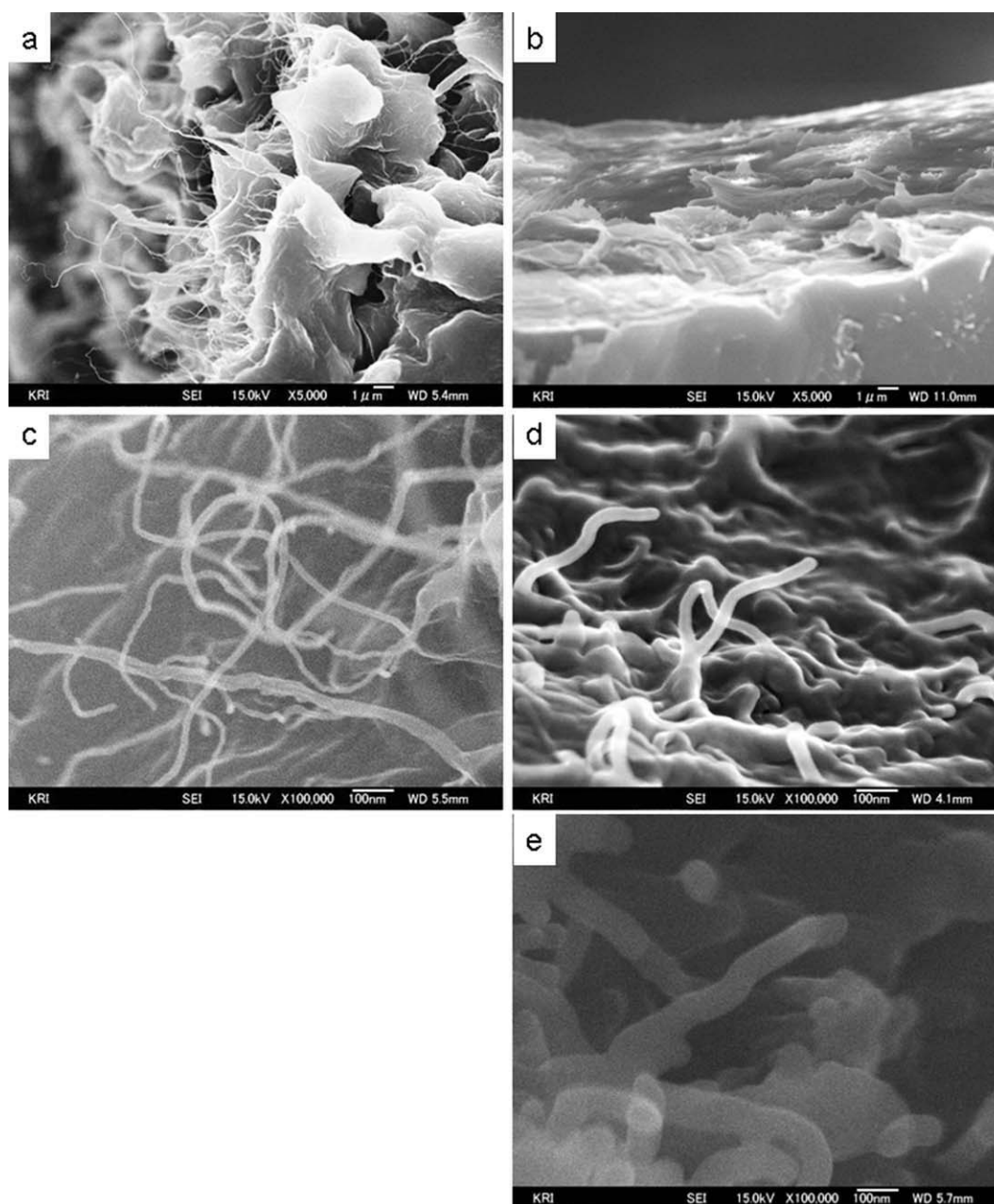
Figure 2 Cross sections of the MWCNT/polymer composites observed by scanning electronic microscopy. (a) MWCNT/PC composites with 3 wt % MWCNTs at 5000× magnification, (b) MWCNT/FBP composites with 3 wt % MWCNTs at 5000× magnification, (c) MWCNT/PC composites with 3 wt % MWCNTs at 100,000× magnification, (d) MWCNT/FBP composites with 3 wt % MWCNTs at 100,000× magnification, and (e) swollen MWCNT/FBP composites with 3 wt % MWCNTs at 100,000× magnification.

the MWCNT/PC composite; this indicated that PC had a lower compatibility with the MWCNTs [Fig. 2(a,c)].

Figure 2(a,b) demonstrates the differences between the status of MWCNTs in PC and FBP-HX. In Figure 2(b), almost none of the MWCNTs are separated from the matrix resin. In Figure 2(a), naked MWCNTs can be observed spilling out from the matrix resin.

The MWCNTs in FBP-HX, as observed by SEM, had diameters of 30 nm [Fig. 2(d)]. This was about 1.5 times that of the naked MWCNTs (20 nm); this provided more evidence for the fine dispersion of MWCNTs in FBP-HX and the strong interaction between MWCNTs and FBP-HX. It means that an FBP-HX layer 5 nm covered the MWCNTs. The covered layers of FBP-HX became swollen in chloroform. The diameters of the MWCNTs covered with FBP-HX increased to 60–70 nm after they were swollen in CHCl$_3$ [Fig. 2(e)].

All of this evidence showed that FBP-HX covered the surface of MWCNTs without further treatment.
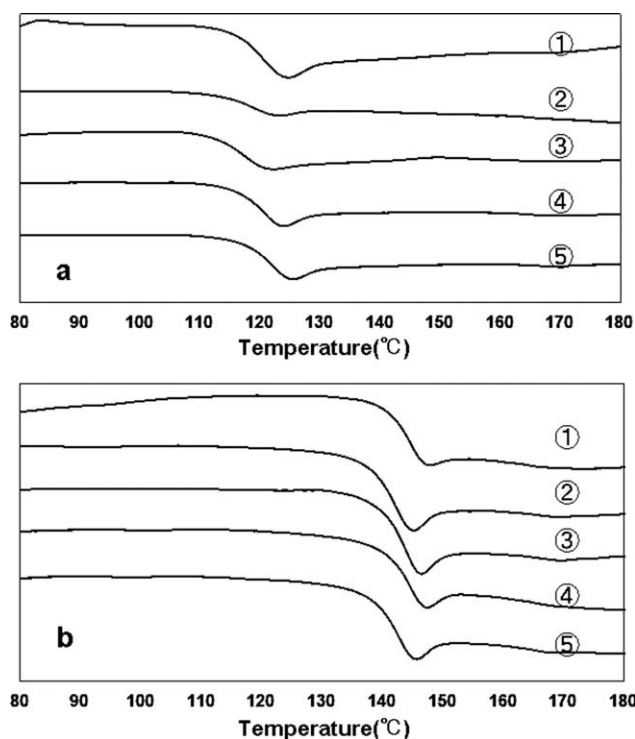
Figure 3 Shift in T_g of the matrix resin due to the addition of MWCNTs. (a,b) FBP-HX and PC composites with different amounts of dispersed MWCNTs: (1) neat resin, (2) composite with 0.5 wt % MWCNTs in the matrix resin, (3) composite with 1.0 wt % MWCNTs in the matrix resin, (4) composite with 3.0 wt % MWCNTs in the matrix resin, and (5) composite with 5.0 wt % MWCNTs in the matrix resin.

The fine dispersion of the MWCNTs was the result of the strong interaction between the FBP-HX and the MWCNTs.

Variation of T_g

T_g is the temperature at which an amorphous solid, such as a glass or polymer, becomes brittle on cooling or soft on heating. In polymers, T_g is often expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. From this definition, we can see that the introduction of relatively stiff materials (e.g., CNTs) will interfere with the flow process and, hence, increase T_g.[15]

It is shown in Figure 3 and Table I that the increase in T_g for FBP-HX in the MWCNT/FBP-HX composites was due to the physical wrapping of the MWCNTs by the matrix resin. Although not the chemical modification of CNTs, the immobilization of FBP molecules around the CNTs occurred. So, the matrix polymer (FBP-HX) was restricted by the CNTs. The reinforcements of the filler with a high aspect ratio were explained by the network-forming

method.[16] According to Favier's theory, the incomplete nature of the network of the filler induces a reduction in the polymer's properties. This was reflected by the data that we obtained at low additions (0.5–1.0 wt %) of CNTs in polymer matrix. Above the ratio of network forming, further addition of filler resulted in a greater reinforcing effect of the filler in the polymer matrix.

For the MWCNT/PC composites, the matrix polymer PC had a low interaction with the MWCNTs. Therefore, it underwent only a minor change in its T_g. Although the addition of MWCNTs resulted in the improvement of the thermal dynamic properties for both the MWCNT/polymer composites, the driving force for the wrapping of MWCNTs by PC and FBP was small. Therefore, the effect of the MWCNTs on the thermal dynamic properties was not that obvious, as demonstrated by the DSC data.

Raman spectra of the MWCNT/polymer composites

The Raman spectra of MWCNT/polymer composites are shown in Figure 4. For the MWCNT/PC composites [Fig. 4(a)], a 1 wt % addition of MWCNTs was enough to homogenize the mobility of the materials in the composites. A peak around 1780 cm^{-1}, which is known to result from the vibration of the carbonate groups of PC, disappeared because of the addition of MWCNTs in PC. The Raman spectra of the MWCNT/PC composites with MWCNTs weight ratios higher than 1.0 wt % were similar to the spectrum of the MWCNTs alone (1340 cm^{-1} for the defects of MWCNTs and 1590 cm^{-1} for the G band of MWCNTs). This showed that the MWCNTs in PC were separated out from the resin and mainly covered the surface of the composites without a covering of PC on them.

In the case of the MWCNT/FBP-HX composites [Fig. 4(b)], a specific peak arising from the stretching of the phenyl groups on the fluorene moiety was observed around 1450–1500 cm^{-1}. The peak remained up to a 3 wt % addition of MWCNTs in

TABLE I
Variation of the T_g Values of the MWCNT/Polymer Composites

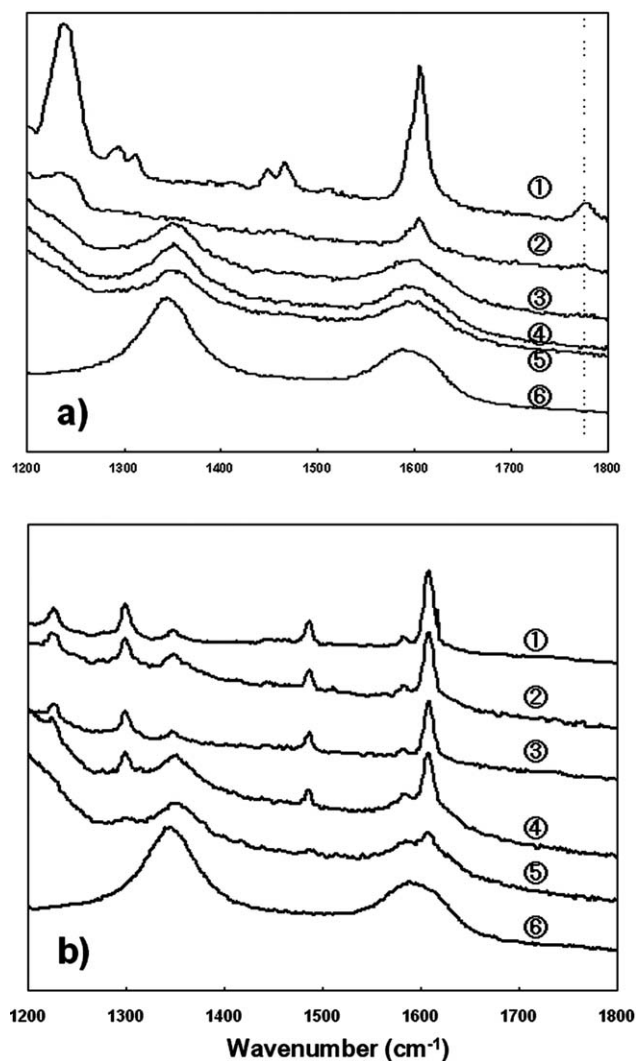|	T_g (°C)	$T_{g\text{Composite}}/T_{g\text{Matrix}}$
PC	143.6	1
PC–CNT 0.5 wt %	140.9	0.98
PC–CNT 1.0 wt %	142.5	0.99
PC–CNT 3.0 wt %	143.2	0.997
PC–CNT 5.0 wt %	143.6	1
FBP-HX	119.4	1
FBP–CNT 0.5 wt %	118.2	0.99
FBP–CNT 1.0 wt %	116.2	0.973
FBP–CNT 3.0 wt %	119.2	0.998
FBP–CNT 5.0 wt %	120.7	1.011

Figure 4 Raman spectra of the MWCNT/polymer composites. (a,b) PC and FBP-HX composites with different amounts of MWCNTs: (1) neat resin, (2) composite with 0.5 wt % MWCNTs in the matrix resin, (3) composite with 1.0 wt % MWCNTs in the matrix resin, (4) composite with 3.0 wt % MWCNTs in the matrix resin, (5) composite with 5.0 wt % MWCNTs in the matrix resin, and (6) MWCNTs.

CONCLUSIONS

The fine dispersion of MWCNTs in FBP-HX and PC resulted in low surface resistivity in both kinds of MWCNT/polymer composites, even those containing low weight ratios (0.5–1.0 wt %) of MWCNTs.

FBP-HX-covered MWCNTs were observed in the MWCNT/FBP-HX composites; however, for the MWCNT/PC composite, the MWCNTs remained separate from the matrix polymer. Because of that, a higher surface resistivity and a higher percolation ratio were achieved for the MWCNT/FBP-HX composites compared with the values for the MWCNT/PC composites.

T_g of the matrix polymer was lower at lower concentrations of MWCNTs in the polymer. At higher concentration ratios, that is, above 5 wt % MWCNTs incorporated with the polymer, an increase in T_g was observed. The relative increase in T_g for FBP-HX was higher than that for PC for the MWCNT/polymer composites.

Raman spectroscopy of the MWCNT/polymer composite sheets with a 3 wt % addition of MWCNTs indicated that the MWCNTs in the MWCNT/PC composites covered the surface of the sheets in their naked form, but the MWCNTs in the MWCNT/FBP-HX sheets were distributed homogeneously in the bulk and were covered with FBP-HX.

FBP-HX. In the MWCNT/FBP-HX composites with a weight ratio higher than 5 wt %, this specific peak disappeared

Because of the coverage of FBP-HX on the MWCNTs, the mobilities of the polymer and the MWCNTs was almost the same; smaller amounts of naked MWCNTs moved to the surface of the MWCNT/FBP-HX composites. As per the increased diameter of the MWCNTs in FBP-HX compared to naked MWCNTs in PC, the Raman spectra provided more evidence for the fine dispersion of MWCNTs in FBP-HX because of the strong interaction between the FBP-HX matrix and the MWCNT filler.

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