

Influence of Carbon Fiber Surface Treatments on the Structure and Properties of Conductive Carbon Fiber/Polyethylene Films

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ABSTRACT: Effects of carbon fiber (CF) surface modification on the crystalline structure and both electrical and mechanical properties of conductive CF/high-density polyethylene (HDPE) films were studied. Three different types of surface-treated CF, epoxy-sized, unsized, and sized but thermally treated, were considered. It was found that the uniformity of the transcrySTALLINE zone around CF and the overall crystallinity of the polyethylene matrix decreased when epoxy-sized CF was used. Epoxy-sized CF caused a significant reduction not only in electrical resistivity and temperature coefficient of resistivity (TCR) but also tensile strength and coefficient of linear thermal expansion (CLTE) of composite films compared with that of unsized or sized CF that was thermally treated. We observed the systematic changes of TCR and CLTE values in accordance with CF surface modification and CF content in composite films. It was concluded that thermal expansion of the polymer matrix is the main reason for the positive TCR of CF/HDPE films. As the most probable reasons for decreased resistivity and strength of the CF/HDPE films with epoxy-sized CF, the diffusion of epoxy sizing agent into the polyethylene matrix and the formation of loosened semiconductive interphase structure in the film are considered. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2040–2048, 2002; DOI 10.1002/app.10500

Key words: conductive carbon fiber reinforced polyethylene film; carbon fiber surface modification; crystalline structure; electrical resistivity; tensile strength

INTRODUCTION

Electrically conductive polymer composites have been widely used in many industrial areas such as antistatic materials, materials for electromagnetic interference (EMI) shielding, heaters, and electrode systems.^{1,2} These composites have been

replacing metals and carbon-graphite materials in many technologically important areas because of its unique properties including low density, high conductivity, and mechanical strength as well as corrosion, wear, and chemical resistance. Among them, carbon fiber (CF)–reinforced thermoplastics (CFRTP) advantageously differ from others in terms of good balance of properties, processibility, and recyclability.^{3,4} These desirable properties make CFRTP one of the most prospective conductive composites. In this group of ma-

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terials CFRTP films based on discontinuous carbon fiber are attracting special interest because of the potential possibilities of their wide acceptance as EMI shielding materials for both small and large dimensions (e.g., from electronic devices to buildings) as well as for fabrication of laminated composites with large dimensions and gradient structure.

Like other composites, the structure and properties of conductive CFRTP films are determined by the physical and chemical structure of polymer binder and carbon fiber, interactions between them, CF content in the composite, and fabrication technology. Along with other parameters the physicochemical nature of the CF surface affects the electrical and mechanical properties of CFRTP films. As is well known in the literature, surface modification of CF is essential for improving the adhesion between the fibers and the polymer matrix and involves oxidation treatments as well as the use of coupling agents, wetting agents, and sizings.^{5,6} As a rule, commercially available CFs are surface oxidized and then sized. Usually, industrial manufacturers provide no information concerning the method used for surface treatment and the type of sizing agent used. In any case, although there are numerous publications about the effect of sizing agent on adhesion in the CF/polymer matrix system and mechanical properties of CF-reinforced polymer composites,^{7–11} the effect of the sizing agent on electrical properties has not been reported.

This study aims to evaluate the role of commercial epoxy sizing agent in the formation of structure and both electrical and mechanical properties of conductive CF/polyethylene (PE) films. Polyethylene was selected because its crystalline structure and electrical behavior are well known and it is an excellent polymer matrix for making soft and inexpensive CFRTP films.

EXPERIMENTAL

Materials

Powdery high-density polyethylene (HDPE, Grade M850, melt index = 4.7 g/10 min) from Yuhwa Hiden Co. (Korea) was used as polymer binder. The average size (diameter) of polymer particles used was less than 0.2 mm. The short-chopped (length of 1 mm) epoxy-sized CF [CF(S), Grade TZ-307] and unsized CF [CF(U), Grade TZ-507] from Tae-Kwang Co. (Korea) were em-

ployed as fillers. Epoxy-sized CF, which had been thermally treated at 573 K for 150 min [CF(ST)], was also used as a surface-modified CF filler for comparison.

Preparation of Samples

The samples of conductive CF/HDPE film were produced by novel, so-called electron-ion technology (EIT), in accordance with the scheme described previously.¹² Flat steel plates (200 × 200 × 3 mm) with Teflon coating were used as intermediate technological substrates. A thin polymer binder layer, called sublayer (thickness of 80–100 μm), was applied on the substrate by the vibro-spread method and melted in an oven at a temperature of 453 K for 10 min. Short-chopped CFs were electrodeposited onto the molten polymer sublayer in a specially designed fiber-feeding apparatus with brush screws, in which a high-intensity dc electric field was applied at a field strength of about 3 kV/cm. The density of the formed, aligned CF layer was about 25–30 g/m². The CF-filler content (C) in the resultant film was controlled in the range from 5 to 20 wt % by making changes in the mass of powder polymer binder. Forming of the obtained composition system was carried out by compression molding (Tetrahedron Press, USA) at 453 K under a pressure of 0.3 MPa for 2 min with preheating for 3 min and cooling on the substrate in air-conditioning. Antiadhesion Teflon film was used during the pressing process. The thickness of the fabricated films was varied from 140 to 550 μm.

Testing of Samples

The electrophysical properties of short-chopped CF were characterized by the resistivity and packing density of the fiber sample. The resistivity of short-chopped CF samples was measured by 6512 electrometer (Keithley Metrabyte, Taunton, MA). The CF sample (mass 3 g) was placed into a Teflon cylinder between two cylinder brass electrodes (diameter 30 mm), which were compressed under constant load of 49 N. Each measurement was carried out after exposition under the load for 60 s. The thickness of the compressed CF sample was evaluated by digital trammel. The resistivity ρ and packing density α of the CF sample were calculated using the following formulas:

$$\rho = \frac{(R_S - R_0)S}{\delta} \quad \text{and} \quad \alpha = \frac{M_S}{S\delta d}$$

where R_S and R_0 are the resistance of the electrode system with and without the CF sample, respectively; S is the area of the electrode; δ is the thickness of the sample; M_S is the sample mass; and d is the specific density of the CF (1.78 g/cm^3).

Optical microscopic analysis was carried out by polarized microscope Optiphot 2-Pol (Nikon, Japan). The fracture surface of CFRTP film samples was studied by scanning electron microscope (SEM S 2500S; Hitachi, Japan) at an accelerating voltage of 10 kV. The film samples for SEM were immersed in liquid nitrogen and fractured, then sputtered with a gold/palladium coating. Thermal analysis of film samples was carried out using DSC 7 (Perkin Elmer Cetus Instruments, Norwalk, CT) under conditions of nonisothermal crystallization in a nitrogen gas atmosphere. The samples (about 10 mg) were heated at a rate of 10 K/min to 473 K, kept for 5 min, and then cooled at 10 K/min to 303 K (first cycle); reheated again at 10 K/min to 473 K, and finally cooled at 10 K/min to 303 K (second cycle). Parameters of the melting and crystallization of film samples were determined from the second cycle of heating/cooling scans. X-ray diffraction (XRD) measurements of the films were carried out on a Geigerflex diffractometer (Rigaku, Japan) under a scanning rate of $5^\circ/\text{min}$ in low-angle range $2\theta = 10\text{--}40^\circ$. X-ray with wavelength $\lambda = 1.542 \text{ \AA}$ was used. The crystallinity was estimated as a ratio of both peak areas of the crystal to the total area including amorphous and crystalline parts. The crystallite dimension (crystallite or lamellar thickness) L was calculated by using the Scherrer formula¹³:

$$L = \frac{K\lambda}{\beta_0 \cos \theta}$$

where $K = 0.9$, a constant that is commonly assigned as a value of unity; β_0 is the breadth of the reflection corrected for instrumental broadening; and θ is the Bragg's angle. The transcrystalline region dimensions in the samples were estimated for the micrographs from polarized light microscopy.

The volume resistivity of conductive film samples (length 140–150 mm, width 20 mm) was evaluated using a four-probe method according to ASTM D 991-89. A 2553 dc voltage current standard (Yokogawa Electric Works, Japan), 6512 electrometer (Keithly Metrabyte), and 3466A digital multimeter (Hewlett-Packard, Palo Alto, CA) were used as a stabilized power supply, voltme-

ter, and milliammeter, respectively. Temperature dependency of the resistivity of films was examined by measuring the resistivity while heating the electrode assembly with film in an electric furnace in the temperature range 295–353 K at heating rate of 0.5 K/min. The resistivity and thermal coefficient of resistance (TCR) were calculated as average values for four to six film samples. The tensile strength of the films was determined on standard dumbbell-shaped test specimens (overall length 65 mm; width and length of narrow section 3 and 10 mm, respectively) according to ASTM D 638-95 using MTS 45/G testing machine (MTS, USA) at the deformation rate 10 mm/min. The CLTE of films was evaluated by a standard test method (ASTM E831-93) using film samples (length 8 mm, width 5 mm) and TMA 2940 thermomechanical analyzer (TA Instruments, New Castle, DE) at a heating rate of 5 K/min in the temperature range 298–358 K. The tensile strength was calculated as an average of 18–25 samples, whereas CLTE and TCR were determined as averages of three samples. Statistical preparation of obtained data was carried out at a 95% confidence level.

RESULTS AND DISCUSSION

Changes of Crystalline Structure of Polymer Matrix

As is known, the performance of polymer composite is determined, in many respects, by the physicochemical structure and properties of the filler. Therefore, it is expected that CF surface modification by epoxy sizing or thermal treatment of sized fibers will change both fiber properties and the interaction between the CF and the polymer matrix resulting from structural modification of an interphase in the polymer composite. There have been many publications that confirm the possibility of structural transformation of the polymer matrix caused by CF surface modification. It has been reported that the presence of CF in a semicrystalline polymer matrix affects the crystalline structure and morphology development during crystallization of the polymer.^{14–17} The type of CF is known to affect the nucleation at the fiber surface and the interphase in the form of a transcrystalline zone whose thickness can extend to the order of a few tens of micrometers.¹⁴ For CF/poly(*p*-phenylene sulfide) composites, in particular, an inverse relationship was found between the nucleating efficiency of various types of

Table I Effects of CF Surface Modification on Properties of CF Samples

Carbon Fiber	Resistivity ($\Omega \cdot \text{cm}$)	Packing Density
CF(U)	1.02	0.086
CF(S)	9.31	0.114
CF(ST)	1.44	0.069

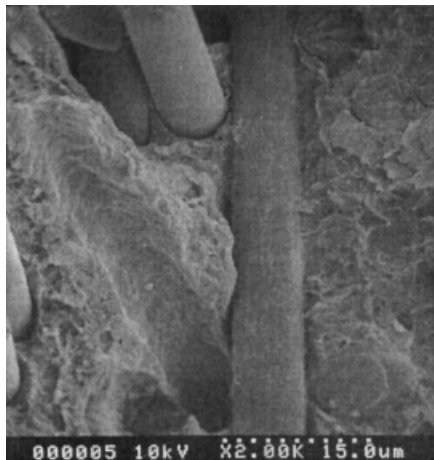
CF toward the low-polarity polymer and the value of the polar component of the CF surface energy.¹⁵ It means that the interaction between CF and polymer binder is enhanced when the value of the CF surface energy is low. From this viewpoint, the epoxy sizing with high polarity should decrease the nucleating efficiency and interaction between CF and either nonpolar or low-polarity polymers such as HDPE or poly(*p*-phenylene sulfide). However, microscopic observations in polarized light and DSC analysis of CF/poly(*p*-phenylene sulfide) composite samples with sized and desized CFs (sized CFs were washed in dichloromethane) indicated that the sizing agent did not affect either the morphology or the crystallization mechanism of the poly(*p*-phenylene sulfide) matrix.¹⁶ In this connection, it was necessary to study the effect of CF surface treatment on the crystalline structure of the interphase zone in the CF/HDPE composite.

According to the results of chemical analysis of epoxy-sized and desized CF, carried out earlier by ESCA methods,¹⁶ the surface of both CFs is characterized compositionally by carbon, oxygen, and nitrogen atoms. However, the amount of oxygen that derives from C—O, C=O, and O—C=O bonding on the surface of sized CF is greater than that of the desized CF. Thermogravimetric analysis revealed that washed epoxy sizing agent had a maximum rate of thermal decomposition at 573 K.¹⁶ Therefore, the decomposition and partial curing of the residue of the epoxy sizing agent (residue mass is about 2 wt % of the initial one) under thermal treatment should lead to a drastic decrease in the resistance of the CF sample. Experimental results presented in Table I confirm this and show that the epoxy-sized CF sample has higher resistivity and packing density than that of unsized CF as a result of the creation of a semiconductive shell of epoxy resin on the CF surface. At the same time, the resistivity and packing density of the thermally treated CF(ST) sample are lower than those of CF(S) because of

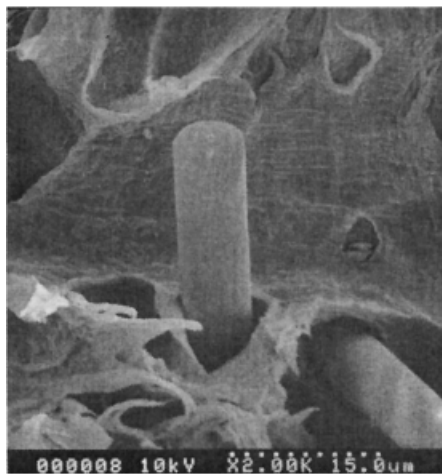
the thermal degradation of this epoxy shell by thermal treatment and probably the increased rigidity of short-chopped fibers.

Thus, the CF treatments, modifying both the chemical structure of fiber surface and the inter-fiber resistance, will change the molecular interaction of the CF with HDPE binder and properties of CF/HDPE films. However, experimental assessment of the effect of CF surface treatment on wetting in the CF/HDPE system, using measurement of contact angle of a molten polymer drop on the CF surface by the tangent method,¹⁸ has shown that the wetting was not significantly changed under CF modification. Only a slight increase of contact angle value for CF(S) compared with that for CF(U) and CF(ST), caused by higher polarity of CF surface attributed to higher oxygen content, was found. This agrees with results of SEM study of the fracture surface of CF/HDPE samples. An analysis of SEM micrographs of fracture surface for film samples presented in Figure 1 indicates the following. First, all samples are slightly delaminated. Second, the surface of CF, pulled out from the polymer matrix, looks different: CF(ST) has a slightly rough surface, whereas CF(U) and CF(S) have a visually smooth surface with fixed thin particles of polymer matrix. Finally, CF(U) appears fixed into the HDPE matrix more strongly than was either CF(S) or CF(ST), given that hole sizes on the fracture surface for CF(U) are less than those for CF(S)- or CF(ST)-reinforced films. The latter may provide evidence that interaction in the CF/HDPE system is reduced when CF(S) is used.

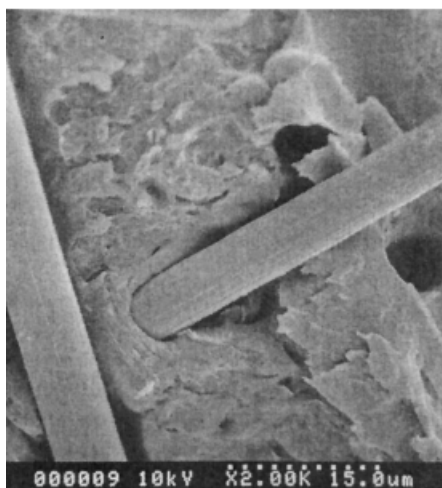
Microscopic analysis of thin model samples of CF/HDPE composite with CF(U), CF(S), and CF(ST), specially fabricated at the same conditions, has shown that the effect of CF surface modification on the transcrystalline zone near the CF surface in the CF/HDPE system is not strong. It is easy to find from micrographs presented in Figure 2 that the thin (5–15 μm) transcrystalline zone is formed in all CF/HDPE films. However, the thickness and uniformity of this zone depends on CF surface structure: the average thickness of the transcrystalline zone around CF(S) is higher than that around either CF(U) or CF(ST), although uniformity is lower. Obtained data lead to the conclusion that CF(ST) and CF(U), compared with CF(S), have a higher nucleating ability in the polyethylene matrix. As a result, the crystallinity of polyethylene filled with CF(S) is less than that filled with either CF(U) or CF(ST), as indi-



a)

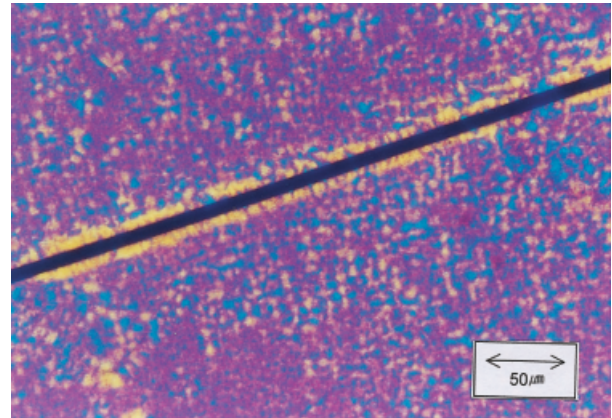


b)

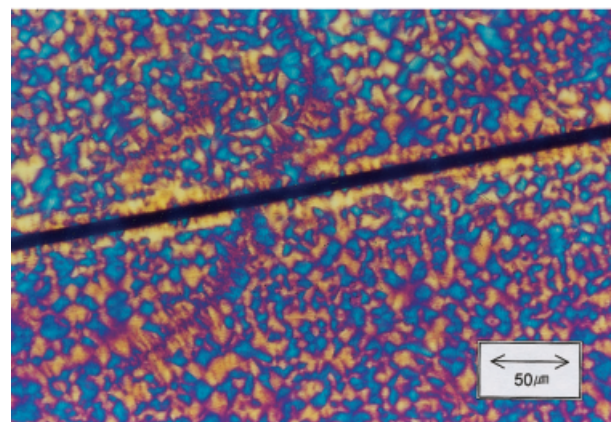


c)

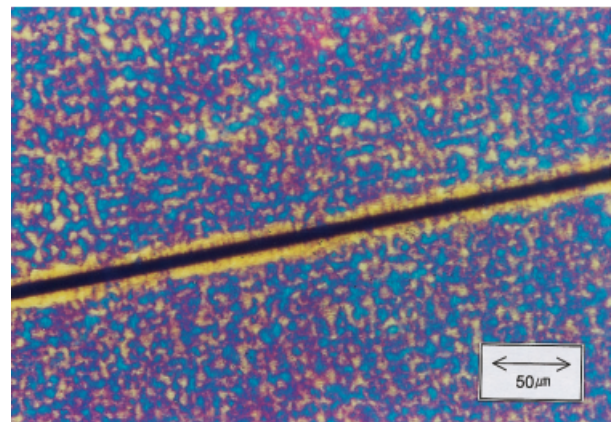
Figure 1 SEM images of fracture surface of (a) CF(U)-reinforced, (b) CF(S)-reinforced, and (c) CF(ST)-reinforced CF/HDPE films with filler content $C = 20 \text{ wt } \%$ ($\times 2000$).



(a)



(b)



(c)

Figure 2 Optical micrographs of CF/HDPE system with (a) CF(U), (b) CF(S), and (c) CF(ST) ($\times 275$).

cated by DSC data and XRD results, as presented in Table II and III.

An introduction of CF in the polyethylene matrix caused reduction of the crystallinity of

Table II Effect of CF Surface Modification on the Melting and Crystallization of CF/HDPE Films (C = 20 wt %, $\delta = 0.19 \pm 0.05$ mm)

Carbon Fiber	Crystallization Peak Temperature (K)	Melting Temperature (K)	Polymer Crystallization Enthalpy (J/g)	Polymer Melting Enthalpy (J/g)
CF(U)	393	411	166	170
CF(S)	393	411	155	161
CF(ST)	393	411	166	174

HDPE, although there were no changes in temperatures of both melting and crystallization processes. Obtained XRD results indicated that the crystallite (lamellar) dimension is reduced in CF/HDPE film compared with that of unfilled HDPE (Table III). The crystalline structure of films reinforced with CF(S) and CF(ST) is characterized by reduced crystallite dimension than that with CF(U). Assuming that the epoxy sizing agent can penetrate into the HDPE matrix to create a physical blend in the interphase region, this will lead to the formation of a loosened irregular transcrystalline zone, decreasing the overall crystallinity of the HDPE matrix.

Effect on the Electrical and Mechanical Properties

Table IV shows that CF surface modification causes significant changes of structure-sensitive properties such as volume resistivity and tensile strength of CF/HDPE composite film. From Table IV, contrary to the values of CF resistivity (Table I), CF/HDPE film reinforced with CF(S) has an appreciably lower volume resistivity than the film reinforced with either CF(U) or CF(ST). These experimental results can be explained in the following way. Taking into account the diffusion of epoxy resin molecules into polyethylene at a depth up to 1 μm during thermoforming,¹⁹ the

lower value of the electrical resistivity for CF(S)-reinforced films can be attributed to the diffusion of the sizing agent or epoxy oligomers into HDPE layers in the interphase region during the preparation of the films. This phenomenon should cause the formation of semiconductive channels between HDPE layers and CF, given that the electrical conductivity of epoxy oligomers is higher than that of HDPE by 8–10 orders of magnitude.²⁰ At the same time, the presence of the epoxy sizing agent changes the morphology in the interface region and leads to the forming of weaker boundary layers of polymer binder, resulting in a reduction of the strength of films with CF(S). In this context, the higher value of the resistivity of CF(ST)-reinforced film, compared with that of the CF(U)-reinforced one, is probably caused by the increase of contact resistance between CF elements of conductive network in the film mainly attributed to cured remnants of degraded epoxy sizing agent on the CF(ST) surface. These remnants can have high resistivity and make for slightly worse wetting and bonding on the CF/HDPE interface. As a result, CF(ST)-reinforced film will have increased resistivity and lower strength.

To understand the mechanism of the influence of CF surface modification on the electrical properties of CF/HDPE films, the temperature dependency of the resistivity and thermal expansion of

Table III XRD Test Results of the Crystallinity and Crystallite Dimension in HDPE and CF/HDPE Films (C = 20 wt %, $\delta = 0.19 \pm 0.05$ mm)

Polymer Film	Crystallinity (%)	Crystallite Dimension (\AA)
HDPE	63	197
CF(U)/HDPE	51	170
CF(S)/HDPE	49	166
CF(ST)/HDPE	52	165

Table IV Effects of CF Surface Modification on Properties of CF/HDPE Films (C = 20 wt %, $\delta = 0.19 \pm 0.05$ mm)

Carbon Fiber	Resistivity ($\Omega \cdot \text{cm}$)	Tensile Strength (MPa)
CF(U)	2.23 ± 0.33	48.6 ± 3.3
CF(S)	0.22 ± 0.02	26.2 ± 1.2
CF(ST)	6.21 ± 0.81	40.3 ± 2.4

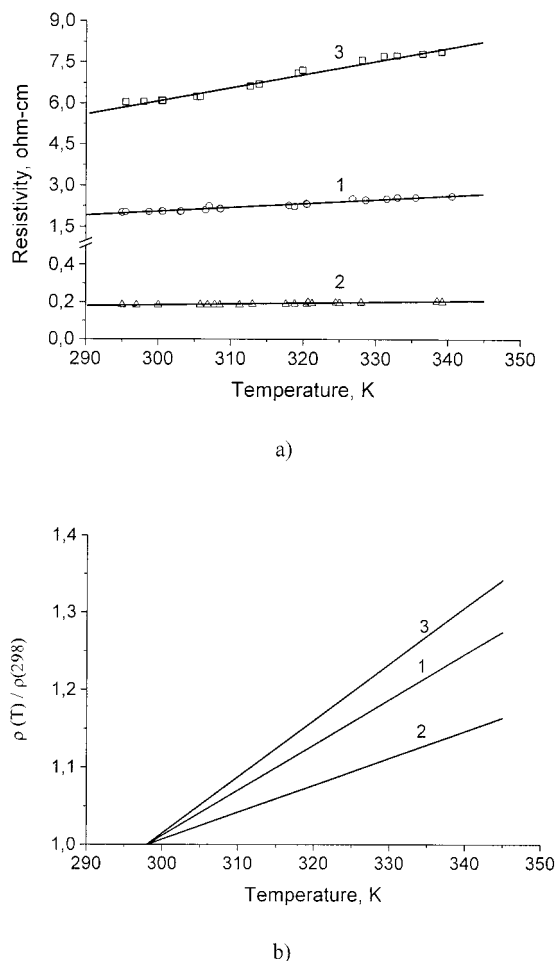


Figure 3 Temperature dependency of volume resistivity (a) and ratio of current resistivity to initial resistivity at 298 K (b) for HDPE films reinforced with (1) CF(U), (2) CF(S), and (3) CF(ST) ($C = 20$ wt %; $\delta = 0.19 \pm 0.05$ mm).

film samples were evaluated. As is known, the investigation of temperature dependency of the resistivity allows us to obtain information about the conductivity mechanism and to predict the conductive behavior of materials under service conditions.^{21–26} It is especially important for applications of conductive polymer composites such as thermistors, sensors, or self-controlled heaters.²⁷ In general, as the temperature of a material increases, the resistance of most conductors increases and that of insulators decreases. For polymer dielectrics it is found that electrical resistivity decreases exponentially with temperature.²¹ This is evidence of the activated character of conduction in polymers. Similar behavior has been found in polymer composite systems with metal particles² and carbon black²² as well as in laminated plastics reinforced with continuous CF.²³

It was also found that the increase of resistivity with temperature is a common phenomenon for quite a number of conductive polymer composites in which the powder filler content is beyond the critical threshold point.^{24–26} Several theoretical models have been proposed to explain the positive TCR phenomenon in polymer composites filled with conductive powders.^{26,27} According to these models, thermal expansion plays an important role in the positive TCR effect. Unlike materials mentioned above, it is hard to find information about the temperature dependency of electrical resistivity of discontinuous CF-reinforced polymer composites. Meanwhile, this is of particular interest in connection with the negative sign of both TCR and CLTE for PAN-based CF that distinguishes them from other fillers. Negative TCR and CLTE imply that their resistance and length, respectively, decrease with an increase of temperature.^{2,4,6,7}

Figure 3 shows the temperature dependency of volume resistivity for CF/HDPE films fabricated with CF(U), CF(S), and CF(ST). The resistivity of films shows a nearly linear increase with temperature growth in the service temperature range [Fig. 3(a)]. Both the resistivity value and the slope of temperature dependency were different among films with different CF [Fig. 3(b)]. Average values of TCR and CLTE obtained for these films are given in Table V, which shows that minimal values of TCR and CLTE are found for CF(S)-reinforced HDPE film, and maximal values for HDPE film filled with CF(ST). TCR and CLTE values mainly have a positive sign for all CF/HDPE films. The good correlation in TCR and CLTE values allows us to conclude that thermal expansion of the polymer matrix is the primary reason for the positive TCR and CLTE values of CF/HDPE films. Indeed, according to the latest understanding of electrical conduction of polymer composites, electrical current flows through a network of conductive particles in the composite and

Table V Variations of TCR and CLTE Values Depending on CF Surface Modification for CF/HDPE Films ($C = 20$ wt %, $\delta = 0.19 \pm 0.05$ mm)

Carbon Fiber	TCR (10^{-4} K^{-1})	CLTE (10^{-6} K^{-1})
CF(U)	59 ± 13	55 ± 8
CF(S)	35 ± 5	39 ± 3
CF(ST)	73 ± 18	81 ± 15

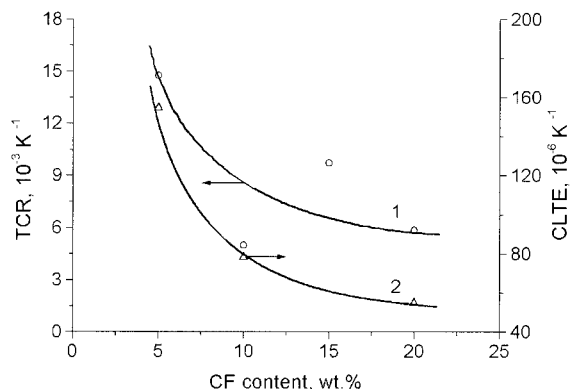


Figure 4 Variations of thermal coefficient of resistance (1) and coefficient of linear thermal expansion (2) with CF(U) content in CF/HDPE film ($\delta = 0.14\text{--}0.55$ mm).

conductivity is mainly determined by the physicochemical nature, size, and aspect ratio of filler particles as well as degree of filling and the proximity of conductive particles to one another.^{1,2,22}

In conductive composites some part of conductive particles can physically contact each other, but usually most of the particles are in close proximity, separated only by a thin layer of polymer binder. This polymer layer may act as an insulating gap or energy barrier for electron transport between conductive particles. Electrons can jump (or tunnel) across this isolating gap, creating current flow between conductive particles. The ability of an electron to jump a gap, under a given electrical field, increases exponentially with temperature. However, as the temperature increases, the effect of increasing gap width resulting from thermal expansion of the polymer matrix will predominate, leading to an overall increase of the resistance of the polymer composite. This is confirmed by the concentration dependency of TCR for CF/HDPE films, as shown in Figure 4. Figure 4 shows that both TCR and CLTE values are decreased by several times with increasing CF content from 5 up to 20 wt %. As CF content increases, the average distance between fibers, corresponding to the gap width for electron hopping, will reduce. The extent of the increase of the average distance or gap width under heating should decrease. As a result, the extent of the temperature dependency of resistivity becomes weak and the TCR value is decreased. Concentration dependency of CLTE for CF/HDPE films is mainly caused by the relative amount of CF and HDPE in the composite film, each of which has a different coefficient of linear thermal expansion

(higher value for HDPE). Thus, correlated changes of TCR and CLTE with CF content are evidence that they are closely connected with each other. Therefore, it is apparent that the observed effects of CF surface modification on TCR are primarily caused by changes of CLTE and result from modification of the structure and micro-mechanical properties of CF/HDPE films. At present the observed CLTE changes cannot be explained quantitatively because a satisfactory theory and models of thermal expansion of random discontinuous fiber-reinforced composites have not yet been developed.²⁸

CONCLUSIONS

The effects of short-chopped CF surface modification on the structure and on the electrical and mechanical properties of CF/HDPE films were studied using three different types of CF surfaces: epoxy-sized, unsized, and sized but thermally treated. It was observed that these different CF surfaces generate a morphological change of the transcrystalline zone formed along the fiber surface and affect the electrical and mechanical properties of the composite films. The epoxy-sized CF/HDPE system showed a less-uniform distribution of the transcrystalline zone and lower crystallinity of polymer matrix because of the negative effect of epoxy molecules on the formation of polyethylene transcrystals around the fibers, leading to lower electrical resistivity and tensile strength of the films. These results indicate the important role of interphase morphology to control the electrical properties of the composite films, given that epoxy-sized CF itself had a higher value in electrical resistance compared with that of the other two systems. Moreover, it was also observed that both the temperature coefficient of resistance and the thermal coefficient of linear expansion of the composite film were reduced simultaneously with the increase of CF content and had minimum values for epoxy-sized CF/HDPE film. It was concluded from this that thermal expansion of the polymer matrix, which depends on crystalline structure and fiber-polymer interaction, can be a reason for the positive temperature coefficient of electrical resistance.

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