

Electrical and Thermal Properties of Composite of Liquid Crystalline Polymer Filled with Carbon Black

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ABSTRACT: The electrical resistivity and thermal conductivity of a liquid crystalline polymer (LCP) filled with a commercial carbon black (CB) of various volume fractions (ϕ) is investigated. The percolation threshold (ϕ_c) is found at about 3%, and the resistivity (ρ) as a function of $(\phi - \phi_c)$ satisfies the exponential function. Although the pure LCP is highly anisotropic in thermal and mechanical properties after processing, the composite samples exhibit no preferential direction for electrical conduction. Samples of ϕ below ϕ_c exhibit a negative temperature coefficient of resistivity while those above ϕ_c show almost no temperature dependence from room temperature to 200°C. In addition, the samples at lower ϕ have higher thermal conductivity in the LCP flow direction than those measured in the transverse and thickness directions, and they approach the same value at higher ϕ . This result indicates that preferential molecular alignment of the matrix LCP is responsible for the behavior of the thermal conductivity of the composites. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1549–1555, 2001

Key words: carbon black; liquid crystalline polymer; electrical resistivity; thermal conductivity; anisotropic properties

INTRODUCTION

Conventional extrinsic conducting polymers including carbon black (CB)-filled polyethylene or styrene butadiene rubber have found many applications, such as antistatic protection packages, flexible-conducting ribbons, self-regulating heaters, and resettable fuses for power surge protection. Numerous investigations were conducted to study this class of conducting polymers^{1–4} and to develop various conducting composites based on other polymer matrices such as polyimide,⁵ poly(vinylidene fluoride) blended with polyethylene,⁶ or liquid crystalline polymer (LCP) with polysul-

fone.⁷ Some of the studies concentrated on anisotropic conduction of polymers filled with carbon fibers or flakes.^{8–10}

The working temperature of most flexible polymer-based composites is relatively low. Some thermoplastics can withstand temperatures higher than 200°C, including a class of thermotropic LCPs. Because of their rigid rod-like structure, LCP molecules preferentially align in the flow direction during processing, thus enhancing the mechanical strength and thermal conductivity¹¹ in the fibril direction. These advantages make LCPs attractive polymers for advanced applications.

Pure LCP is an electrical insulator with a resistivity (ρ) on the order of 10^{13} Ω cm, but an LCP can be modified to become a conductor by being filled with carbon fiber (e.g., the resistivity of Vectra B230 from Hoechst Celanese is on the order of 10^3 Ω cm and its heat deflection temperature is

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about 190°C) and sacrificing the impact strength. The investigation of CB in anisotropic matrices has received relatively little attention whereas CB-filled flexible polymers and synthetic rubbers that are both isotropic matrices have been studied extensively. Therefore, in the present study, we prepared the CB loaded thermotropic LCP and measured the electrical resistivity and thermal conductivity of the samples in three orthogonal directions. The molecular orientation of the samples was determined by the X-ray diffraction method.

EXPERIMENTAL

Sample Preparation

The thermotropic LCP used in this work was Vectra A950 produced by Hoechst Celanese Co. It is copolyester of about 70 mol % *p*-hydroxybenzoic acid and 30 mol % 6-hydroxy-2-naphthoic acid¹² with a density 1.4 g/cm³. The conductive CB powder used was HG-4 (Southern Chemicals of China) with a conductivity of 0.33 Ω cm. Its specific surface area was 1080 m²/g, the average particle size was 33 nm, and the density was 1.9 g/cm³. For the preparation of the composites, the LCP pellets were ground to powder form in a cryogenic grinder at liquid nitrogen temperature and mixed with CB powder in a blender. The CB volume fractions (ϕ) were 1–7 and 10%. The mixture was blended at 290°C in a single-screw extruder (Randcastle RCP0250) with a length/depth ratio of 24:1 and equipped with a 1-mm conical die. The extruded CB/LCP rods were chopped into pellets, transferred to a hot press machine, and heated to 290°C for 20 min. Thin film samples were obtained by pressing the molten mixtures into a stainless steel 0.2 × 5 × 20 mm³ mold as shown in Figure 1. The molded films were then quenched in room temperature water. Because the rigid rod-like LCP molecules are easily aligned in the flow direction, the melted LCP composites were injected and forced to flow along the length of the mold, so that the quenched samples would be anisotropic in the sense of molecular orientation. We defined the LCP flow direction as the *X* direction, and the *Y* direction was perpendicular to *X* in the sample plane. The *Z* direction was normal to the sample plane. The films were cut into 5 × 5 mm² squares of for resistivity and thermal diffusivity measurements in the three orthogonal directions.

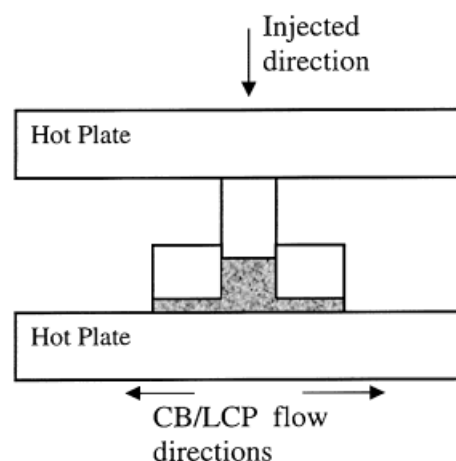


Figure 1 A schematic diagram showing the injection by the hot press and the LCP flow directions.

Resistivity Measurements

The current–voltage (*I*–*V*) characteristics of the samples were measured. The applied voltage ranged from 0 to 100 V; the current passing through the samples was monitored by measuring the voltage drop on a standard resistor in series with the samples. The two-point and four-point methods were employed to measure the dc resistivity of the samples. The latter method was applied for lower resistivity samples. In order to avoid self-heating, the voltage was applied for about 1 s for each measurement point. The temperature dependence of the resistivity was measured in a vacuum chamber in which the temperature could be controlled up to 200°C.

Thermal Conductivity Measurements

The determination of the thermal diffusivity (*D*) of the samples was accomplished by the laser flash radiometry technique. The details of this method were given previously.¹³ In brief, for the determination of *D* across the thickness direction, the sample was irradiated by a 10-ns pulsed laser with a 532-nm wavelength (Quanta-Ray Nd/YAG) on the front surface. The thermal radiation from the rear surface was focused onto a liquid nitrogen cooled HgCdTe IR detector by a germanium lens. For the measurement of *D* in the transverse direction, the circular laser beam was focused into a line by a cylindrical lens and radiated on the sample. The thermal radiation was detected from the rear surface at a distance away from the heat source. The signal received by the IR detector was amplified and fed to a digital storage oscilloscope.

The experiment was performed by averaging the signals obtained in 20–100 laser shots. The averaged signal as a function of time was transferred to a microcomputer and then fitted to a theoretical expression to give the D . The thermal conductivity (K) of the sample was calculated from the relation

$$K = dC_p D \quad (1)$$

where d is the density and C_p is the specific heat. The density of the samples was measured by the flotation method and the specific heat was determined by a differential scanning calorimeter (Perkin–Elmer DSC-7) at a heating rate of 10 K/min.

Orientation Determination

The preferential orientation of the LCP molecules was determined by wide-angle X-ray diffraction. Aperiodic meridional X-ray reflections arising from diffraction by the oriented molecular chains with a random comonomer sequence¹⁴ were observed. The azimuthal intensity distribution of the strongest meridional reflection at $2\theta = 43^\circ$ of the Ni filtered Cu $K\alpha$ line was recorded with a Philips Xpert diffractometer equipped with a goniometer. The orientation function (f) was calculated by the following equation:

$$f = \frac{1}{2} (3 \langle \cos^2 \alpha \rangle - 1) \quad (2)$$

where α is the angle between the axis of the diffracting unit and the polymer flow direction and $\langle \cos^2 \alpha \rangle$ is the average of the azimuthal intensity distribution over all azimuthal angles. The f value is for a sample with perfectly molecular alignment whereas f would equal zero for random orientation.

RESULTS AND DISCUSSION

I–V Characteristics

The I–V characteristics of the 1 and 7% CB volume fraction samples in the X, Y, and Z directions were measured at room temperature and the results are shown in Figure 2. Figure 2(a) shows that even when the applied voltage was about 100 V, the current passing through the sample was just a few nanoamperes, which is a typical value for an insulating polymer. This result implied

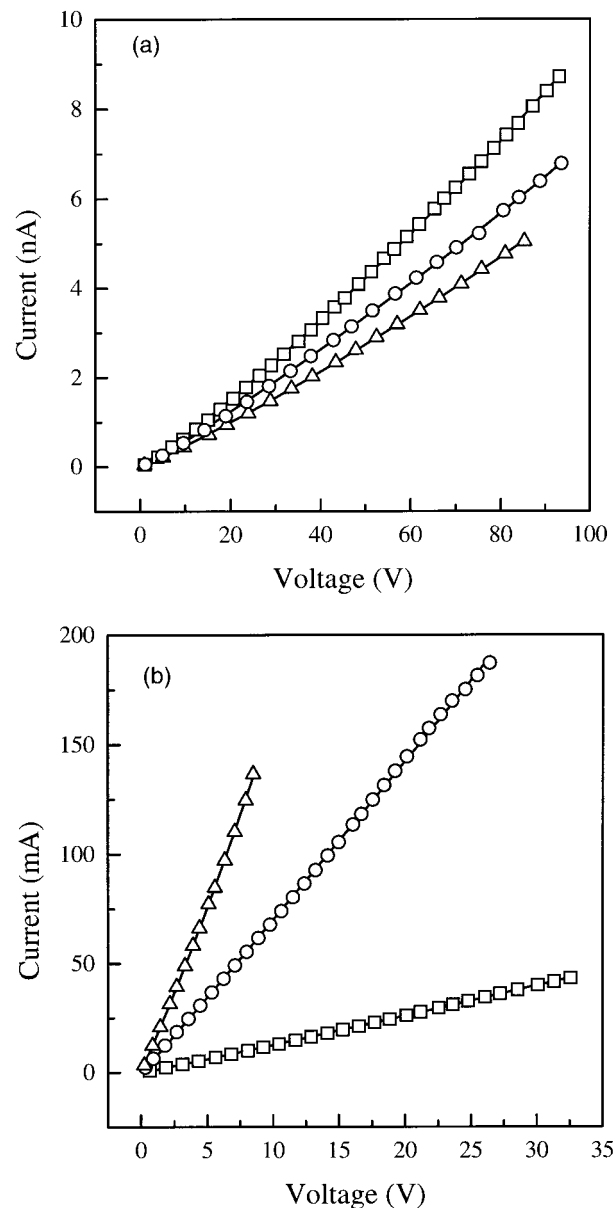


Figure 2 The I–V characteristics of (a) 1% CB and (b) 7% CB composite samples in the (□) X, (○) Y, and (△) Z directions.

that for this low CB volume fraction the LCP matrix was responsible for the electrical conduction. The slightly nonlinear I–V relation as shown in the figure further verified this point. Electrical conduction in polymers is usually attributed to ionic transport in an applied electric field. The activated ion concentration and the ion drift mobility were proportional to the exponential of the electrical field, resulting in a non-ohmic I–V relation. In the 7% CB [Fig. 2(b)] the magnitude of the current was on the order of a few hundred milli-

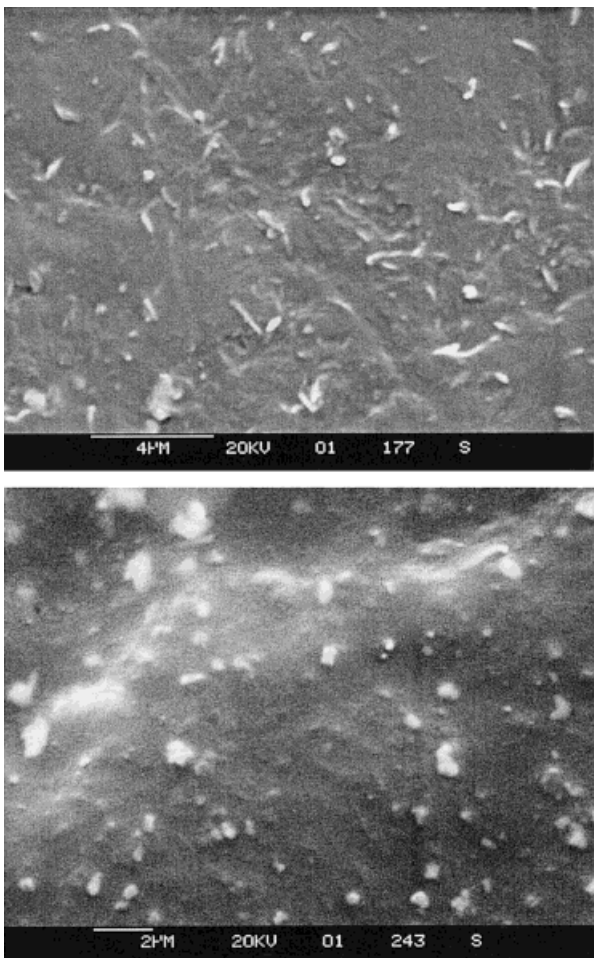


Figure 3 SEM micrographs of (a) 1% CB and (b) 7% CB-filled LCP. The CB aggregates can be clearly observed in the 7% sample.

amperes, because the current passed directly through the CB network. At this volume fraction the CB aggregates dispersed in the LCP were in contact and formed a continuous network that resulted in a linear ohmic I–V behavior for this sample. Figure 3 gives the SEM pictures of the 1 and 7% samples. The CB aggregates for the 7% sample are discernable and it was these aggregates that formed a continuous network throughout the sample that was responsible for the conduction.

Volume Fraction Dependence of Resistivity

Figure 4 depicts the resistivity (ρ) of the composites at room temperature versus the CB volume fraction, which clearly shows that ρ is critically dependent on the CB volume fraction. For low volume fractions the magnitudes of ρ remained on

the order of $10^9 \Omega \text{ cm}$. However, a sudden drop in ρ occurred for ϕ above 3%, which was attributed to the percolation behavior of the conducting phase in the composites. The relatively low percolation threshold in CB-filled polymer systems is not uncommon⁶ if the CB agglomerates in the polymer matrix and forms conductive networks.¹⁵ On the other hand, as shown in Figure 4, the resistivity measured for the three directions of the samples did not show obvious differences at low volume fractions. Above the percolation threshold, although the resistivity in the three directions at one specific volume fraction (4%) exhibited large differences (ρ was about 40 times greater in the Z direction than in the X direction), no large difference was found for other volume fractions. For the 5% samples the ρ was even larger in the X direction than in the Z direction. Thus, anisotropy in the resistivity is not so apparent from Figure 4.

According to percolation theory,¹⁶ the resistivity above the percolation threshold (ϕ_c) is a function of the excess volume fraction ($\phi - \phi_c$) and can be expressed by the equation

$$\rho = \rho_o(\phi - \phi_c)^{-\beta} \quad (3)$$

where ρ_o is a constant and β is the exponent that accounts for the geometry of conducting particles. Plotting the resistivity against the excess volume

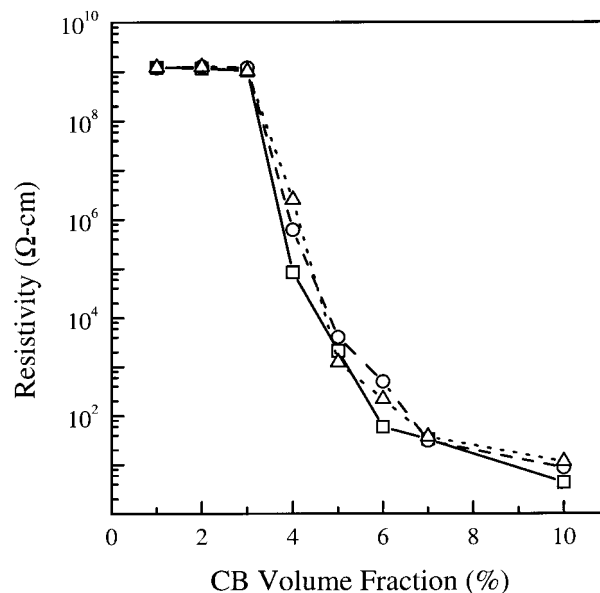


Figure 4 The resistivity measured in the three directions of the CB/LCP samples as a function of the volume fraction in the (□) X, (○) Y, and (△) Z directions.

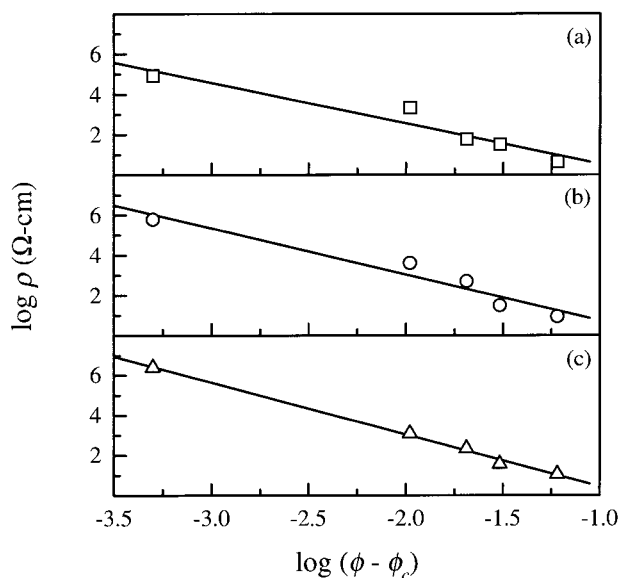


Figure 5 The log–log plot of the resistivity of CB/LCP composites as a function of the excess volume fraction for the (a) X , (b) Y , and (c) Z directions. The straight lines represent the best fits to the data with $\phi_c = 0.0395$. The slopes of the lines are (a) -2.02 , (b) -2.3 , and (c) -2.6 .

fraction in a log–log scale allows one to obtain β from the slope of the straight line. As shown in Figure 5, when ϕ_c is taken as 0.0395, the β obtained from the linear least-squares fit of the data were 2.02, 2.3, and 2.6 for the X , Y , and Z directions, respectively. These different β values for the three directions characterize anisotropy in resistivity at room temperature. The values are slightly above the normal range of 1.65–2 for spherical and randomly distributed conducting particles.¹⁷ However, these values agree with other reported values,^{15,18,19} although the published data were based on flexible polymer matrices.

Temperature Dependence of Resistivity

The resistivities of the samples in the three directions as a function of temperature were measured in the range from room temperature to 200°C. There were three types of temperature dependence for samples having different CB volume fractions. Below the percolation threshold, in the range of 1–3% as shown in Figure 6, the resistivity dropped from 10^9 to 10^6 Ω cm as the temperature was raised from room temperature to 200°C. At low temperature there was no obvious change, but it decreased significantly at a temper-

ature above 60°C. A similar temperature dependence of ρ for CB-filled butyl rubber, which had CB loading below percolation, was reported.³ In the present study, all three samples exhibited similar features in this temperature range, despite the difference in the CB volume fraction. It was mentioned that the ionic current is an exponential function of the reciprocal of the absolute temperature. This suggests that the decrease in resistivity as the temperature rose was a result of thermally activated ionic conduction in the LCP matrix.

The results in Figure 7 show that the 4 and 5% samples that were above the percolation threshold showed almost no change at low temperatures but were obviously increased at high temperatures. This can be understood by the thermal expansion of the CB/LCP system. At high temperatures the thermal expansion of the connecting CB network reduced the number of connecting paths in the network, resulting in a slightly increasing resistivity. For the higher CB volume fractions (6, 7, and 10%) the thermal expansion no longer reduced the number of connecting paths enough to reduce the resistivity.

Volume Fraction Dependence of Thermal Conductivity

The D values along the flow, transverse, and thickness directions of the composites were mea-

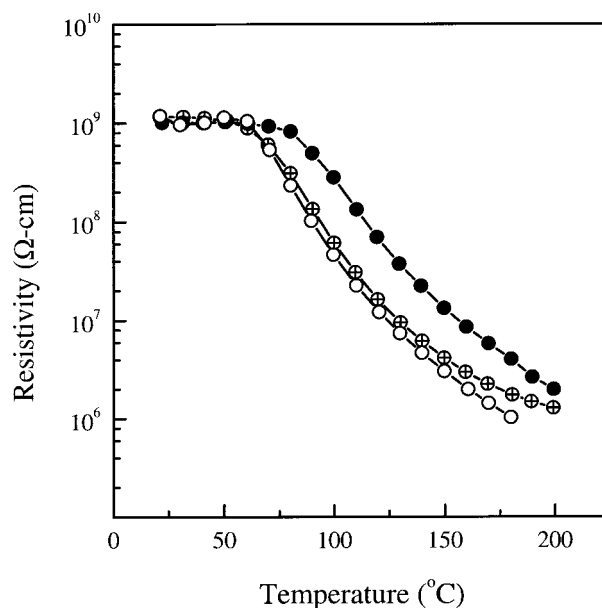


Figure 6 The temperature dependence of the resistivity in the flow direction of CB/LCP composites below ϕ_c : (●) -1 , (⊕) -2 , and (○) -3% .

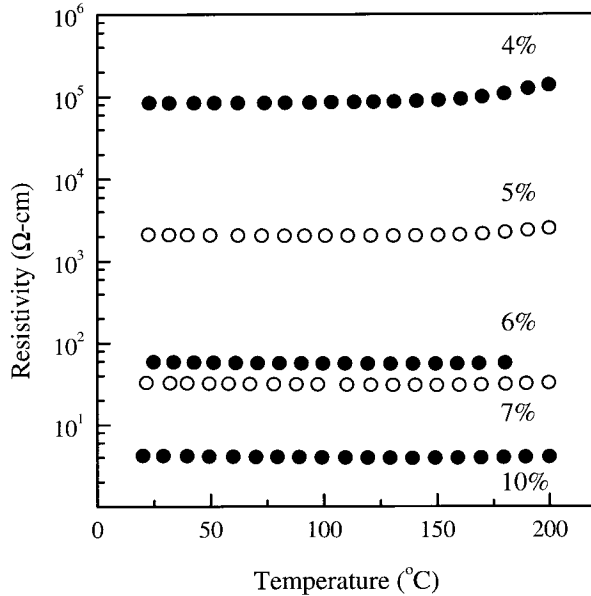


Figure 7 The temperature dependence of the resistivity in the flow direction above ϕ_c . The percentages shown next to the curves are the CB volume fractions of the samples.

sured by the laser flash radiometry method. From D the volume fraction dependence K_x , K_y , and K_z (i.e., K along all the corresponding directions) was obtained and is shown in Figure 8. It can be seen

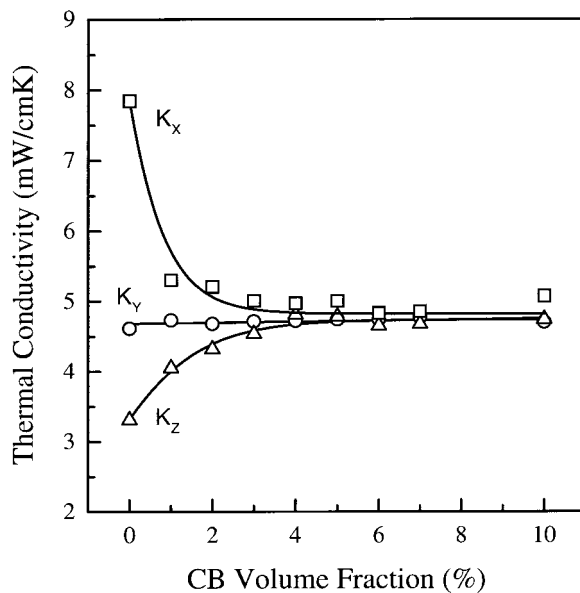


Figure 8 The thermal conductivity of CB/LCP composites plotted against the CB volume fraction in the (\square) X, (\circ) Y, and (\triangle) Z directions. The solid lines are to guide the eye.

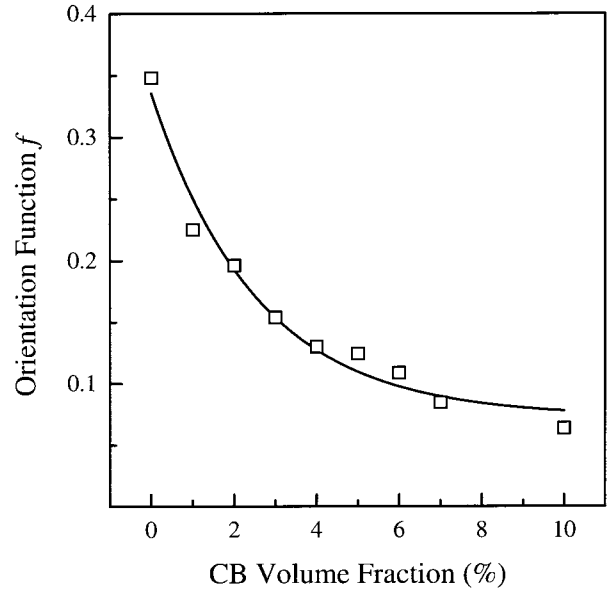


Figure 9 The orientation function (f) of CB/LCP composites versus the volume fraction. The solid lines are to guide the eye.

that the K_x decreased at lower ϕ and became constant with increasing ϕ . On the other hand, the K_z increased as the ϕ increased and approached the same value at larger ϕ as K_x . The K_y remained almost constant at all volume fractions. The anisotropy of the samples due to shear flow in the mold was evident in the thermal conductivity. As shown in Figure 9, the orientation parameter f decreased with increasing ϕ , meaning that CB hindered LCP molecular alignment (i.e., pure LCP had the highest f value with preferential alignment along the flow direction). As ϕ increased the molecular alignment in the LCP became weaker; this was verified by the small f at higher ϕ . As a matter of fact, the molecular alignment of the composites was the main factor that affected the thermal diffusion.¹¹ Because the covalent bonds along the chains were much stronger than the interchain forces, a higher thermal conductivity in the flow direction could be expected. Moreover, the LCP molecules tended to align parallel with the mold wall, thereby giving the lowest K in the thickness direction that was perpendicular to most of the molecular chains. As ϕ increased the composites became more isotropic, so that the K values obtained in the three directions reached the same value of about 4.5 mW/cm K . The upper limit of K of CB was about 3.75 mW/cm K .²⁰ It seems that the thermal conduction of CB did not make an obvious contribu-

tion to the thermal conductivity of the composites up to 10% CB, except as a hindrance to the alignment of LCP molecules.

CONCLUSIONS

The percolation threshold of a CB/LCP composite is found at a CB volume fraction just above 3%, indicating CB agglomerates in the LCP matrix. There are almost 6 orders of magnitude changes in ρ from the insulating to the conducting state. The resistivity bears an exponential relation to the excess volume fraction of the threshold, and the exponent is in fair agreement with some reported values. No particular direction can be identified as the preferred conduction direction throughout the volume fraction range investigated. The temperature dependence of the resistivity of the composites at a low CB volume fraction can be understood by means of the thermally activated ionic conduction, while the high CB volume fraction samples exhibit no significant temperature dependence of the resistivity. From the results of the thermal conductivity measurements, the difference in the thermal conductivities in the three orthogonal directions are the result of the molecular alignment within the LCP matrix. The CB aggregates do not make dominant contributions to the thermal conductivity as they do in electrical conductivity.

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