Electrical Properties of Poly(phenylene sulfide)/Multiwalled Carbon Nanotube Composites Prepared by Simple Mixing and Compression

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ABSTRACT: Poly(phenylene sulfide) (PPS)/multiwalled carbon nanotubes (MWNTs) conductive composites were prepared through the simple mixing of PPS granules with MWNT powder and subsequent compression. The electrical properties as a function of MWNT loading clearly showed a low percolation threshold of about 0.22 vol % and a high critical exponent value of 3.55 for composites prepared by this method. A comparison study with composites prepared via melt mixing was also carried out, where a random dispersion of MWNTs was achieved. There existed a striplike morphology of MWNTs in the PPS matrix and MWNTs were selectively located in strips caused by compression. The effects of temperature and pressure on the conductivity of the PPS/MWNT composites as prepared via simple mixing and compression are discussed. In addition, the conductivity also showed a dependence on the flow direction of the compression, with higher conductivity in the direction parallel to the flow direction than in the direction perpendicular to the flow direction. So the relationship of the processing and morphological properties was investigated in detail. The possible conductive mechanisms of conventional melt blending and preparation via sample mixing and compression are also discussed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 720–726, 2008

Key words: composites; conducting polymers

INTRODUCTION

Conductive polymer composites, including polymers filled with conductive particles, have a wide range of industrial applications. They are widely used as antistatic materials, self-regulating heaters, overcurrent and overtemperature protection devices, and materials for electromagnetic radiation shielding.[1–5] At present, the most commonly used filler material for the preparation of electrically conducting polymer composites is carbon black, wherein about 16 vol % carbon black is introduced to the composite through melt mixing.[6] With carbon nanotubes (CNTs), which have much better electrical conductivities and aspect ratios, discovered in 1991,[7] the use CNTs is of great interest for the preparation of composites with higher electrical properties.[8]

A minimum content can be defined at the point at which a significant network can be created and can cause electrical conductivity in polymer composites; this is known as the *percolation threshold*.[9] At points higher than this concentration, the composite is basically electrically conductive; otherwise, it is an insulator. The properties of a polymer/CNT composite material depend strongly on the uniformity of CNT dispersion. A lot of work has been done on the modification of CNTs and their dispersion in polymer matrices. One of the main foci has been to achieve polymer/CNT conductive composites with low percolation thresholds. For solution-casting films, supersonication has usually been applied, and percolation thresholds as low as 0.2–1 wt % have easily been obtained.[10–12] However, for melt mixing through screw shear, the percolation for composites has been remarkably high, ranging from 2 to 10 wt %.[13–15]

Until now, many processing methods, such as the multipercolation[16] and electrical field-induced methods,[17] have also been applied to prepare conductive composites with low percolation thresholds. One of the best methods is the so-called filler prelocalization method obtained by direct hot compacting of a

simple mixture of polymer powder and fillers. The earliest report found on the preparation of electrically conducting polymer composites via compression was originated from the groups of Turner[18] and Kusy.[19] The segregated network was established to explain the conductivity mechanism. Since then, several other investigations have followed, and different fillers, such as carbon black,[20] organic fillers,[21] metallic powder,[22] and ceramic,[23] have been molded into polymers via this method. In contrast to random distribution, segregated distribution has been achieved through the tendency of small conducting fillers to adhere to the surfaces or to segregate on grain boundaries of the much larger insulating matrix grains. The processing temperature has usually been lower than the melting point of polymer matrix. However, this method is limited to high-viscosity polymers, such as ultrahigh molecular polyethylene, which makes molding difficult in the melts. Meanwhile, the high viscosity of the polymer during processing is a retarding force, which minimizes the migration of filler into the polymer particles and the deformation of the polymer particles; thus, the obtained conductivity is limited.

In this study, both simple powder mixing and compression and melt blending were used to prepare poly(phenylene sulfide) (PPS)/multiwalled carbon nanotube (MWNT) conductive composites. Our purpose was twofold. One purpose was to compare the effect of the processing method and the resultant dispersion of MWNTs on the conductivity of the polymer/MWNT composites. The other was to investigate the effects of temperature and pressure used for the compression on the conductivity of the PPS/MWNT composites. The reason we chose PPS as a matrix is that PPS is a kind of promising engineering plastic with high temperature resistance combined with good mechanical properties, exceptional chemical and solvent resistance, high dimensional stability, and easy processability.[24,25] The conductive PPS/MWNT composites are expected to find applications in the fields of the automotive, industrial, and consumer goods sectors.

EXPERIMENTAL

Materials

The MWNTs used in this study were prepared by chemical vapor deposition. They were purchased from Organic Chemical Limited Co. (Chengdu, China). The lengths were about 15 μm, the outer diameters ranged from 40 to 50 nm, and the purity was about 95%. The density of the MWNTs was 2.1 g/cm^3.

PPS, type PPS30, purchased from Hong He Technological, Ltd., Co. (ZiGong, China), was used in this study in the form of a powder. The melting point was

about 282°C. The powder showed a typical complex, cauliflower-like morphology with an average particle size of 100–200 μm. The density of PPS was 1.35 g/cm^3.

Sample preparation

To obtain the mixture of PPS powder and MWNTs, ethanol was chosen as a liquid medium (a nonsolvent for PPS) to disperse the MWNTs. A 20-mL solution containing 1 g of MWNTs was ultrasonicated for 15 min. Then, PPS powder was immediately added to the suspension for another 15 min of sonication. After extraction and drying at a temperature of 80°C in a vacuum oven overnight, the mixture of PPS powder and MWNTs was obtained.

The obtained mixture was directly compressed into plates with different temperatures and different pressures. The mold we used was homemade. It was sealed to avoid pressure dissipation. The mold put unidirectional downward pressure on the mixture. The sample of pressed plates used for electrical property measurement had a diameter of 18 mm with a thickness of 1 mm. The MWNT loading was varied from 0.05 to 5 wt %. The volume fraction of nanotubes in the composites (φ) was calculated as

$$\varphi = [1 + (C_P \rho_f)/(C_f \rho_p)]^{-1} \tag{1}$$

where C_f and C_P are the weight contents of the nanotubes and polymer, respectively, and ρ_f and ρ_p are the densities of the nanotubes and polymer, respectively.

Another preparation method, melt blending, was also used for comparative study. The melt blending of PPS and MWNTs was conducted with a mixer (Haake RS600, Bersdorff, Germany) at a temperature of 290°C for 10 min. The blends were also pressed into plates of the same size as the compressed blends for electrical measurement.

Characterization

Electrical property testing

The resistivity of the PPS/MWNT composites was measured along the flow direction, which was the same as the compression direction, with impedance spectroscopy by application of the two-probe method at room temperature. The copper network was immersed into the two surfaces that contact with the electrodes in order to remove contact resistance. We measured the resistance of samples and converted it to conductivity by taking into account the sample dimensions. The values of electrical conductivity (σ) were estimated with the following equation:
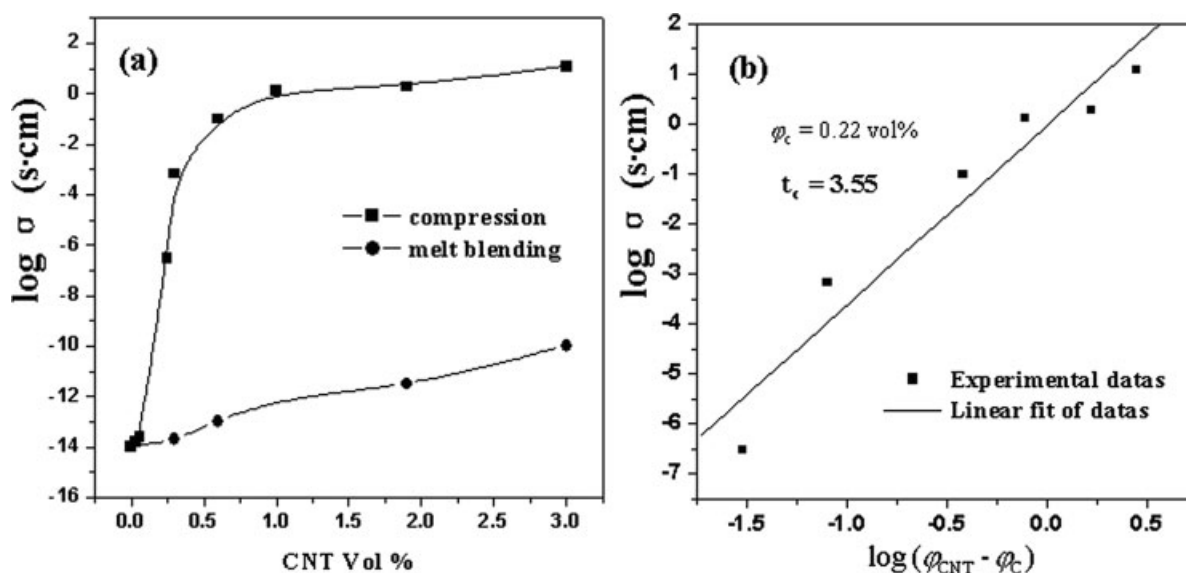
$$\sigma = h/(RS) \tag{2}$$

Figure 1 (a) Electrical conductivity versus MWNT content of PPS/MWNT composites prepared by compression and melt mixing. (b) Electrical conductivity as a function of excess concentration ($\varphi_{CNT} - \varphi_c$) for the calculation of t. φ_{CNT} = volume fraction of CNT.

where R is the volume electrical resistance measured experimentally (Ω), h is the thickness of the samples between the two electrodes (m), and S is the sample area contacting the electrodes (m^2). When the volume resistance of the samples was below 10^3 Ω, a profound ohmmeter (SW-II, HengXun, SuZhou, China) was used for testing. A high-resistance meter (PC68, Cany, ShangHai, China) was used to measure the volume resistance of samples beyond 10^4 Ω.

Morphology as observed by scanning electron microscopy (SEM)

SEM was used to examine the micromorphology of the fractured surfaces of the samples. The images were observed under an acceleration voltage of 20 kV with a Jeol JSM-5900LV (Tokyo, Japan) for the SEM experiments.

Morphology as observed by optical microscopy

The geometry of conductive channels on a large scale was observed by optical microscopy (Hirox KH-3500, Tokyo, Japan).

RESULTS AND DISCUSSION

Electrical conductivity of the PPS/MWNT composites

Figure 1 shows the electrical conductivities of the PPS/MWNT composites prepared by compression and conventional melt mixing as function of MWNT volume fraction. The results were obtained by the samples prepared at a temperature of 285°C and a

pressure of 20 MPa. For simple mixing and compressing samples, it was obvious that the conductivity of compressed composites jumped by many orders of magnitude when the MWNT content reached the percolation threshold, which was about 0.22 vol %. However, for melt-blended samples, the conductivity showed only slight increases with increasing MWNT loading up to 3.0 vol %, and the conductivity was much lower than that of the compressed samples. According to percolation theory, the conductivity increases dramatically above a certain MWNT concentration as a result of the percolation of the conductive MWNTs. So for the melt-mixed composites, the MWNT loading in this study did not reach the percolation threshold. On the other hand, for the simple mixing and compressing composites, the increased conductivity above the critical concentration (i.e., the percolation threshold) could be characterized by a universal law:[9]

$$\sigma \propto (\varphi_{MWNT} - \varphi_c)^t, \text{ for } (\varphi_{MWNT} > \varphi_c) \qquad (3)$$

where the σ is the electrical conductivity of the composites, φ_{MWNT} is the volume fraction of the nanotubes, φ_c is the percolation threshold, and t is the critical exponent in the conducting region. The best fits of the conductivity data of the compressed composites to the log–log plots of the power laws gave the following values: $\varphi_c = 0.22 \pm 0.02$ vol % and $t = 3.55 \pm 0.20$, as shown in Figure 1(b).

SEM experiments were used to investigate the conductive network in the composites prepared by both compression and melt blending. Figure 2 shows the morphologies of the fractured surfaces of compo-
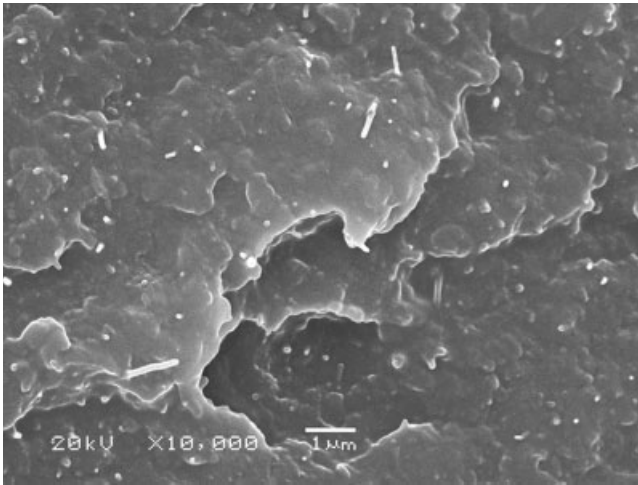
Figure 2 SEM images of the fractured surfaces of PPS/MWNT composites prepared by melt blending. The MWNT loading was 3 vol %.

sites obtained by melt blending. The MWNTs were randomly dispersed in the PPS matrix without serious aggregation. No percolation threshold was observed in the range of MWNT loading. Generally speaking, the electrical properties of polymer/CNT composites depend strongly on the uniformity and connection of CNTs in the matrix. Two basic microstructures for random dispersion can be generated: (1) random but isolated and (2) random but continuous.[18,19] It is obvious that the latter is the optimum geometry for conductive composites and provides the best contact between neighboring fillers. For

PPS/MWNT composites, as shown in Figure 2, the MWNTs were well dispersed but isolated from each other, which led to a higher percolation value, although for the compressed composites, the earlier percolation could be contributed by the different morphology and MWNT distribution, as shown in Figure 3(a). Different from the random dispersion, there existed a strip filled with MWNTs in the matrix, as shown by the bright domain. It is obvious that the strip was filled with CNTs, as shown in Figure 3(b). If Figure 2 is compared with Figure 3(b), a zoomed-in portion of Figure 3(a), under the same magnitude, the density of the MWNTs was remarkably higher in the strip. Hence, the contact and interconnection between the MWNT were largely strengthened; thus, the electrical properties were enhanced. Only smaller amounts of CNTs were needed to establish the conductive network for a system with MWNTs selectively located in the strips than for a system with randomly distributed MWNTs. So the agglomeration of conductive fillers, to some extent, was favorable for the formation of infinite interconnected clusters and thereby enhanced the electrical performances of the composites.[26] However, for the domains around the strips, there were no CNTs in the matrix, as shown in Figure 3(c). In summary, the CNTs were selectively located in the strips on a large scale.

For the conductivity and t, generally, t is about 1.1–1.3 for a two-dimensional system, whereas a higher value, in the range 1.6–2.0, is found for a three-dimensional system. The t value of the com-
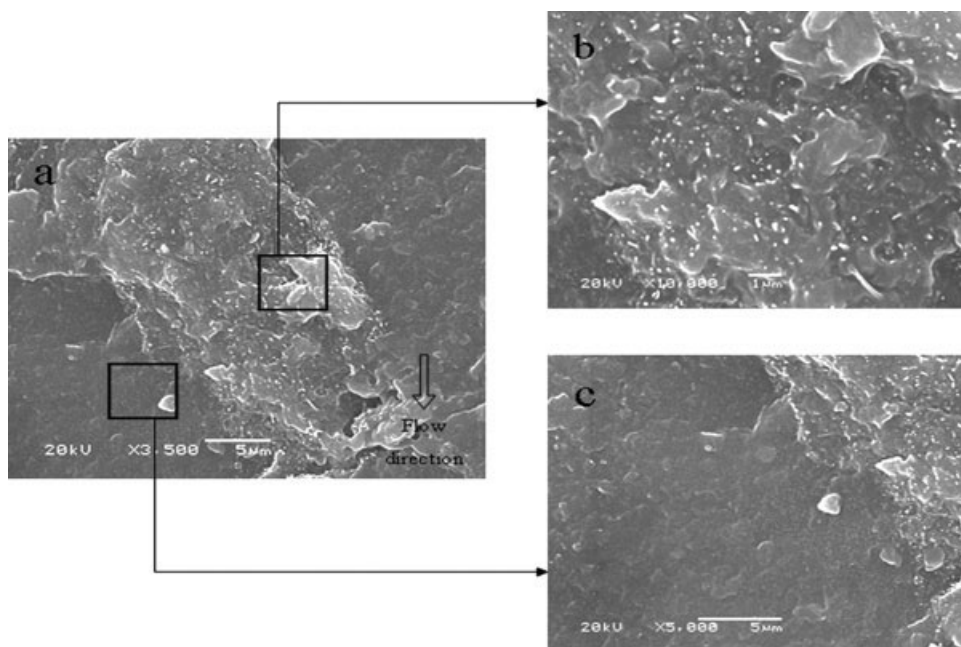

Figure 3 SEM images of the fracture surfaces of PPS/MWNT composites prepared by simple mixing and compression. The MWNT loading was 3 vol %.

pressed composites was a little higher than the universal value. Usually, for three-dimensional systems, t values have been found to be higher than the universal value in the literature.[27–29] Recently, many reports have shown that many systems do not obey the universal percolation theory. Particularly, multipercolation in multiphase conductive systems do not match the universal law. In Foulgers's study,[30] a high exponent ($t = 3.1$) was obtained and was attributed to the multipercolation of the high density polyethylene/carbon black (HDPE/CB) blends. However, obviously, this was not the case for the PPS/ MWNT composites in this study. For the single-phase conductive, similar to PPS/MWNT, the high value of t was determined by other factors. For the CB/poly(vinyl chloride) composites in Balberg's study,[31] the high value of t (6.4) was attributed to the tunneling–percolation model[32] caused by nonrandom dispersion of the particles in this system. In this study, the CNTs were selectively located in the strips, sometimes in the form of aggregates. So with regard to the conductive mechanism, the tunneling conduction would have come into being between the strips when the distance of two strips was not close enough. Also, similar investigations by Lisunova et al.[33] revealed that the high t was attributed to the contacting charge transfer within the conductive phase of the MWNTs. The agglomeration of CNTs in the strips may have caused contacting charge transfer in the PPS/MWNT composites, which resulted in the high value of t. Consequently, the complex geometry of the conductive phase in the matrix was the key to the derivation from the universal laws. In summary, the anisotropic distribution of conductive CNTs, the tunneling conduction, the contacting charge transfer, and the complex geometry of the conductive phase in the matrix were likely to make the conducting composites deviate from the classical percolation theory, which resulted in a high value of t.

Effect of temperature and pressure on the conductivity of the PPS/MWNT composites as prepared via simple mixing and compression

Because the PPS/MWNT composites prepared via simple mixing and compression showed much better conductivity, hereafter, we focus on this system and the effects of processing parameters, including temperature and pressure, which will help us understand the formation of the special strips. Figure 4 shows the conductivity as a function of compression temperature with various MWNT contents. The conductivity showed a slight decrease in the temperature range 220–260°C and increased again with a further increase in temperature. This result was somewhat difficult to understand at first glance. After we considered possible softening around 220–260°C and
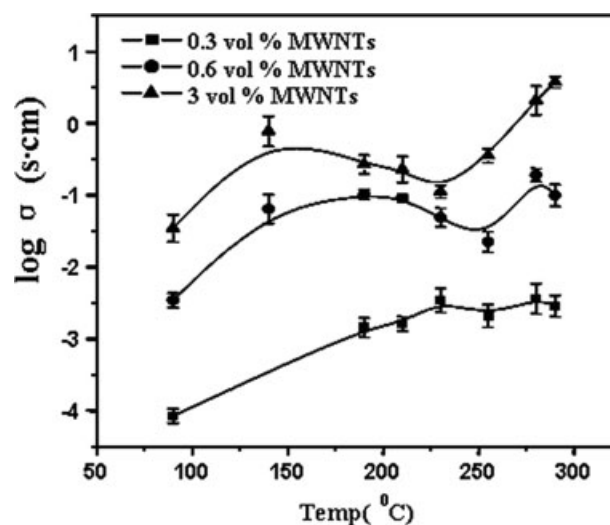

Figure 4 Electrical conductivities of the PPS/MWNT composites at different process temperatures with various MWNT contents. The molding pressure was 20 MPa.

the melting of the PPS powder above 260°C, the observed change in conductivity as a function of compression temperature could be explained as following. First, the MWNTs and PPS powder were premixed in low-power, high-frequency sonicators. This would have enhanced the exfoliation of MWNT bundles without much breakage of the tubes. When the solvent was removed, PPS particles were coated by the MWNTs. At low processing temperatures, called *cold compression* (below the melting point of PPS), the morphological change caused by compression could be described as in Angelos and Turner's article.[18] The cold compression made the mixed powders pack together more tightly. So increased conductivity was observed. In the range 220–260°C, the decrease in conductivity was caused by a high degree of intermixing between the MWNTs and PPS chains at the interfacial region due to the softening of PPS. The interpenetration of PPS chains into the MWNT districts led to an increase in contacting resistance. An optical micrograph of the segregated network of MWNTs in the composites is shown in Figure 5(a). MWNTs in the black domains of the photo were coated on the surface of PPS particles and dispersed in the boundary between two PPS particles, as indicated in Figure 5(a). A similar effect of the temperatures has been discussed for metal/polymer and polymer/carbon black systems.[20,22] However, when the temperature increased to the melting point of PPS, the melting caused an immediate volume expansion, and the unidirectional pressure induced the polymer to flow along the pressure direction. The lightweight CNTs attached on the surface of polymer particles would have moved with the polymer flow, and the strips full of CNTs were produced. Figure 5(b) shows the morphology of the fractured surfaces, which con-

firmed that the MWNTs were indeed located along with the PPS flow direction under pressure. In the photo, the MWNTs are located in the strips along the flow direction, as shown by the arrows in Figure 5(b). Similar studies on flow-induced orientations of high-aspect-ratio fillers have been reported in literature.[34,35] This phenomenon was more obvious for the composite with a high content of MWNTs. A high content of MWNTs may have led to more conductive channels along the flow direction under the unidirectional pressure. Thus, an obvious increase in conductivity was observed above the melting point of PPS.
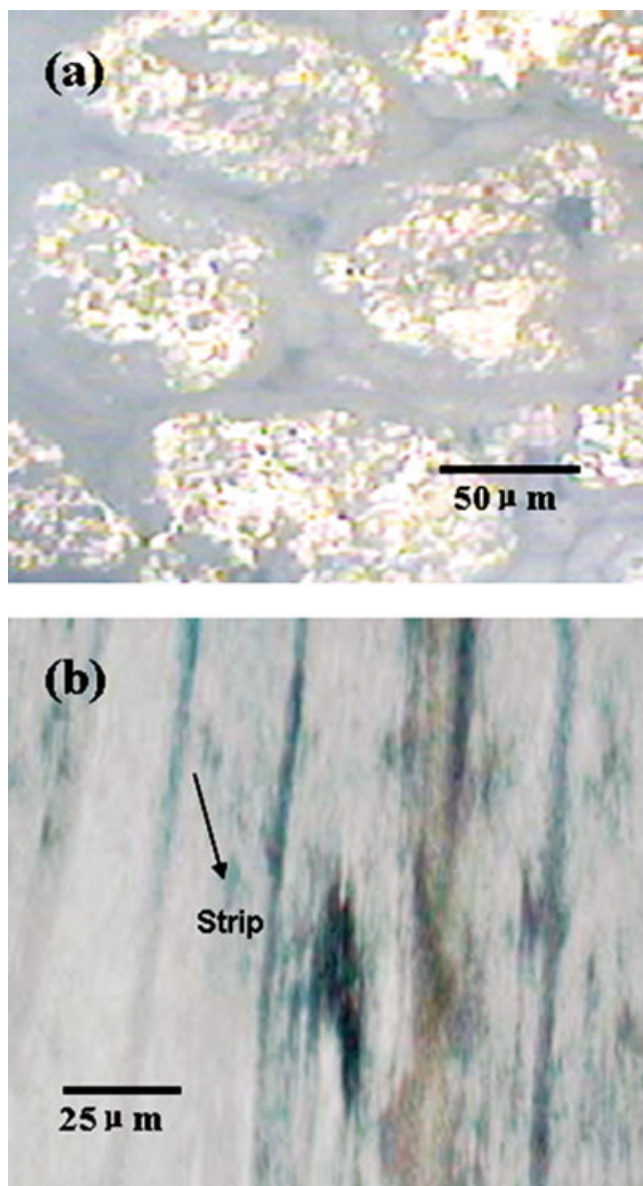

Figure 6 Electrical properties of the PPS/MWNT composites prepared by compression at different pressures with different process temperatures.

The effect of pressure on the conductivity of the PPS/MWNT composites is shown in Figure 6. The conductivity increased with increasing pressure when the compression temperature was higher than the melting point of PPS. Higher pressure led to the easier flow of PPS, so the conductive channel could be more easily formed. However, when the temperature was lower than the melting point of PPS (ca. 260°C), the conductivity decreased with increasing pressure. Under these conditions, the conductive mechanism was attributed to the segregated network. As reported before, an increase in pressure can cause the interpenetration of filler into the polymer and eliminate the effects of conductive channels in the segregated network.[22]

For a composite with filler preferentially arranged along flow direction, it is logical to determine the direction dependence of conductivity. Thus, the conductivities at directions parallel and perpendicular to the flow induced by compressing were investigated, and these are shown in Figure 7. The conductivity at the parallel direction was higher than that at the perpendicular direction; notably, a conductivity five orders of magnitude higher was seen at a lower concentration of nanotubes. Similar studies that used spin coating,[36] extrusion,[37] and shear inducement[38] have already reported the anisotropy dispersion of high-ratio fillers. This is important for the preparation of polymer composites with anisotropic conductivity.

Figure 5 Optical micrographs of the fracture surfaces of (a) PPS/MWNT composites obtained at a temperatures of (a) 250 and (b) 285°C. Both of the samples were molded at a pressure of 20 MPa. The volume fraction of CNTs was 3 vol %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
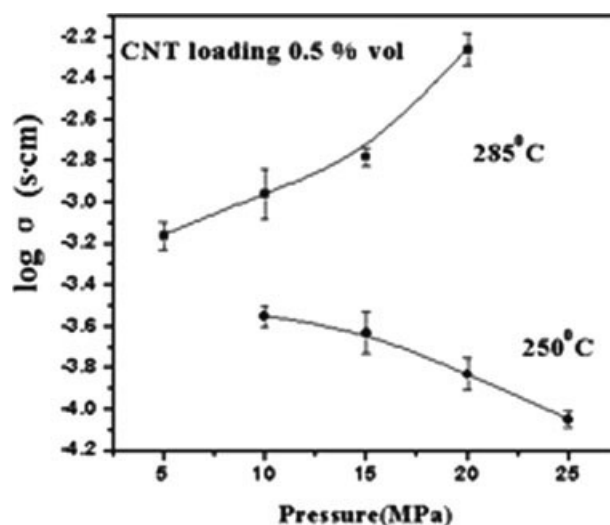
CONCLUSIONS

In summary, a conductive PPS/MWNT composite with a low percolation threshold was successfully
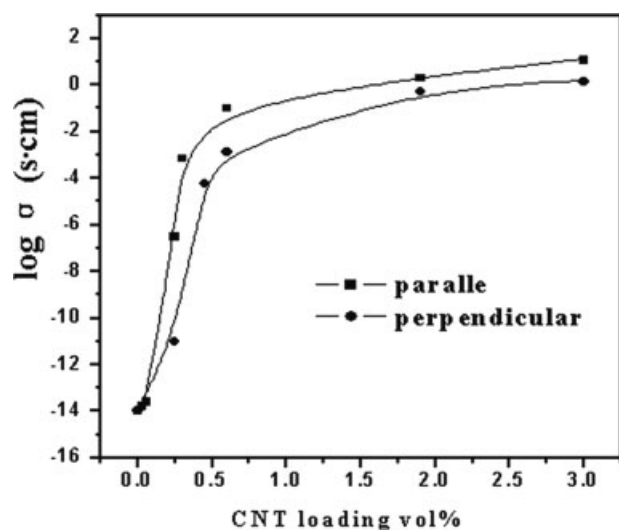
Figure 7 Electrical conductivities of the PPS/MWNT composites measured at parallel and perpendicular flow directions.

prepared with simple mixing and compression technology. A comparison study between conventional melt blending and compression was carried out. For melt blending, because of the random but isolated dispersion of MWNTs, the conductivity was comparatively low. The composites prepared by compression had a low percolation value, 0.22 vol %, with a higher t of 3.55. The ultralow percolation threshold value was caused by the special geometry of the conductive network. The formation of the geometry of network was dependent on the processing parameters: temperature and pressure. The effects of temperature and pressure on the conductivities of the PPS/MWNT composites as prepared via simple mixing and compression have been discussed in detail. During compression, the MWNT particles were preferentially aligned along the flow direction of PPS, which resulted in antistrophic conductivity behavior.

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