

PPS/recycled PEEK/ carbon nanotube composites: Structure, properties and compatibility

Shuling Deng,¹ Zhidan Lin,¹ Lin Cao,¹ Jiaming Xian,¹ Chunyuan Liu²

¹College of Science and Engineering, Jinan University, Guangzhou 510632, People's Republic of China

²Department of Chemistry, Jinan University, Guangzhou 510632, People's Republic of China

Correspondence to: Z. Lin (E-mail: linzd@jnu.edu.cn)

ABSTRACT: Blends of poly(phenylene sulfide) (PPS) and recycled poly(ether ether ketone) (r-PEEK) were prepared using a twin-screw extruder. The carbon nanotube (CNT) added to the blends not only improved the compatibility of the two polymers, but also affected the morphology of the immiscible PPS/r-PEEK blends. R-PEEK always forms the dispersed phase and PPS the continuous phase in such blends. In the composite, CNT particles were observed in the PPS phase, mostly distributes in the interface between PPS and PEEK. The results show that r-PEEK improves the impact and tensile strength of PPS, but does not provide nucleation effect on PPS. However, CNT improved the flexural modulus of PPS/r-PEEK blends and promoted the crystallization of r-PEEK rather than that of PPS. The prepared PPS/r-PEEK blends provided larger electrical conductivity than neat polymers. Adding 20 wt % CNT to blend resulted in composite with the minimum volume resistivity, a reduction of four orders of magnitude, compared with that of the neat blend. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42497.

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INTRODUCTION

Poly(phenylene sulfide) (PPS) is a semicrystalline thermoplastic engineering polymer with some outstanding properties, such as high mechanical strength, superior thermal stability, excellent chemical resistance, and electrical conductivity.^{1–3} However, the application of neat PPS has been limited because of its relatively low glass transition temperature ($\sim 90^\circ\text{C}$) compared with its high melting temperature ($\sim 275^\circ\text{C}$) and its narrow processing temperature range, brittleness, and low strength. Compounding with other polymers is expected to be an effective way to obtain new materials via further improving the properties of polymer. Polymers, such as PA66,⁴ PEEK,⁵ PC,⁶ and rigid particles, such as tungsten disulfide (WS_2),⁷ silica (SiO_2),⁸ and carbon nanotube (CNT)^{9–11} have been successfully compounded with PPS.

Similar to PPS, poly(ether ether ketone) (PEEK), as a high-performance semicrystalline thermoplastic, is known for its thermal stability, corrosion resistance, and excellent mechanical and electrical properties. Now it is widely used in aerospace, automotive, electrical and electronics, and medical equipment industries.^{12,13} In addition to the high melting point and viscosity, PEEK is an expensive polymer, more than four times the price of other engineering thermoplastics, such as POM, PBT, and PA, which restricts its application in more other industries. However, none of studies has reported the application of

recycled PEEK (r-PEEK). To date, polymers recycling studies are only focused on PEEK reinforced with carbon fiber.^{14,15} Therefore, PPS blends with r-PEEK were prepared through compounding with a twin-screw extruder. As a consequence, the main goal of this study was to improve compatibility of the blends. For the immiscible blends, it has been observed that the addition of the third component may increase the compatibility and influence phase morphology of blends. For example, minor compatibilizing character of PP on HDPE/PA6 immiscible blends might be realized and an enhancement of impact strength and breaking elongation of composites can be observed.¹⁶ Nanofillers, such as silica and calcium carbonate, as compatibilizers in immiscible PLA/LDPE blends were also extensively studied.¹⁷ The results showed silica as a better potential compatibilizer than calcium carbonate for the given blends. Zou *et al.*¹⁸ found that clay can not only affect the phase morphology in PPS/PA66 blends, but also controls the phase inversion.

As one of the most important carbon products, CNT is commonly used to improve the properties of ABS,¹⁹ PA,^{20,21} PPS,^{9–11} PE,²² and some other polymers because of its excellent mechanical properties, electrical conductivity, and heat transfer performance. Generally, researches are focused on the thermal, mechanical, and crystallization properties of blends. In this

Table I. Samples Codes and Compositions of Blends and Composites

Samples	PPS (wt %)	r-PEEK (wt %)	CNT (wt %)
PPS	100	-	-
P80/PK20	80.0	20	-
P50/PK50	50.0	50	-
P20/PK80	20.0	80	-
r-PEEK	-	100	-
P80/PK20/C3	80.0	20	3
P80/PK20/C5	80.0	20	5
P80/PK20/C10	80.0	20	10
P80/PK20/C20	80.0	20	20

article, CNT acting as an inorganic compatibilizer was added to the blends to improve the compatibility of the two polymer phases and to reduce phase thickened. The effects of CNT on the mechanical, crystallization, and electrical properties of blends were investigated. Additionally, we investigated the effects of CNT on morphology and compatibility of polymer blends.

EXPERIMENTAL

Materials

Poly(phenylene sulfide) (PPS-HB,) was obtained from Deyang Science and Technology Company (China) with relative density of 1.3 g cm^{-3} . R-PEEK (450G) was purchased from Victrex (Germany) with density of 1.32 g cm^{-3} . Carbon nanotube (CNT-3) was obtained from Shanghai Kajet Chemical (China) with outer diameter of 10–30 nm and length of 10–30 μm .

Preparation of Samples

Before the compounding process, all the materials were stored adequately in a vacuum oven at 100°C for 12 h. PPS powder, r-PEEK granules, and CNT were then homogenized and compounded in a twin-screw extruder according to the compositions presented in Table I to obtain PPS/r-PEEK blend and PPS/r-PEEK/CNT composite samples. The extrusion temperatures for compounding were set between 350°C and 400°C and the screw speed at 120 rpm. The blend of PPS/r-PEEK at 80/20 wt % was selected as matrix to study the effects of CNT addition on the properties of blends. Four PPS/r-PEEK compounds with CNT contents of 3, 5, 10, and 20 wt % were prepared in this study. After the compounding process, composite particles were used for DSC measurements. For examination of mechanical and electrical properties, composite particles were injection molded at 410°C to obtain standard test samples.

Characterization Techniques

Mechanical Examinations. Tensile, flexural, and impact tests were carried out according to ASTM standard methods. For each type of composite, five specimens were examined and the average values were reported. Tensile tests were conducted according to ASTM Standard D 638 using Type V specimen on a universal testing machine (Zwick/Roell Z005, Zwick Roell Testing Machines) at a crosshead speed of 50 mm min^{-1} . Static flexural tests were carried out according to ASTM Standard D 790 using the same testing machine mentioned above at a crosshead speed of 2 mm min^{-1} . Notched Charpy impact strength

tests were conducted according to ASTM D 256 Standard using a universal impact testing machine (ZBC-50, China Shenzhen SANS Testing Machine). The notches were made through gear cutting method.

Thermal Characterization. A 204F1 differential scanning calorimeter (NETZSCH,GER) was used to study the thermal behavior of PPS/GNP composites. Samples of 5–10 mg were accurately weighed for DSC examinations. All measurements were performed in a nitrogen atmosphere.

To examine the nonisothermal crystallization and melting behavior, a composite sample was rapidly heated to 380°C and held for 5 min. Subsequently, it was cooled to 60°C at the cooling rate of 10 K min^{-1} for the crystallization behavior observations. Then, the same sample was reheated to 380°C at 10 K min^{-1} for the melting behavior investigation.

Measurement of Electrical Conductivity. Wolfgang Warmbier SRM-110 surface impedance tester (Pinion Company, USA) was used to study the electrical conductivity. At least five specimens of each type of composite were tested to get an average value.

Morphology Examination. The specimens that were broken in the impact examinations were used for morphology studies. The fracture surfaces of the specimens were sputter-coated with gold before conducting microscopic observations with a Philips XL-30 environmental scanning electron microscope (ESEM) at an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Effects of CNT on Mechanical Properties

As is shown in Table II, when r-PEEK was added to the PPS, a significant enhancement in impact strength was observed compared with that of the neat PPS matrix, suggesting that the toughness of PPS was improved. The impact strength of PPS/r-PEEK blend increased to 52.6 J m^{-1} with the addition of 80 wt % r-PEEK. Moreover, the tensile strength of PPS exhibited an increasing tendency with the increase of r-PEEK content. Compared with neat PPS, the impact strength of blend increased by 15% with only introducing 20 wt % r-PEEK, whereas the impact strength of blend filled with 80 wt % r-PEEK increased by 30%. It is widely accepted that both PPS and r-PEEK provide higher strength and modulus than conventional plastics. There were small effects on flexural strength and modulus in the blend of two polymers. The mechanical properties examinations indicated excellent results for PPS/r-PEEK (80/20) blend in comparison with properties of neat PPS. Therefore, this blend was selected as matrix to study the effects of CNT.

Figure 1 shows the flexural characteristics of composites. The relationship between flexural strength and CNT contents for PPS/r-PEEK blend [Figure 1(a)] reveals that when P80/PK20 blend was filled with 3 wt % CNT, the flexural strength slightly decreased. To further increase the content of CNT, flexural strength stayed almost constant in a certain level. As shown in Figure 1(b), the flexural modulus monotonically increased with the increase in the amount of CNT particles. At 20 wt % CNT content, modulus increased by 24% relative to that of neat PPS.

Table II. Mechanical Properties of PPS/PEEK Blends and Its Composites

Samples	Impact strength (J/m)	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)
PPS	37.6 ± 0.9	73.4 ± 1.5	3200 ± 20.9	107 ± 17.2
P80/PK20	43.9 ± 1.1	84.2 ± 0.9	3210 ± 22.4	115 ± 18.6
P50/PK50	76.6 ± 0.8	88.8 ± 0.7	2930 ± 31.8	113 ± 12.9
P20/PK80	90.2 ± 1.3	95.1 ± 1.4	3030 ± 28.1	116 ± 13.4
r-PEEK	94.0 ± 1.5	89.85 ± 1.2	2790 ± 24.6	111 ± 15.2

In summary, r-PEEK improved the impact and tensile strength, whereas CNT increased the flexural modulus of PPS.

Effects of CNT on Crystallization and Melting Behavior

Crystallization process plays a crucial role on the properties of semicrystalline polymers; therefore, it was necessary to study crystallization and melting behavior of PPS and r-PEEK in matrix. Figure 2 shows crystallization and melting thermograms of PPS/r-PEEK blends at identical cooling rates in which T_c and T_m are crystallization and melting peaks' temperatures, respectively. The corresponding data of PPS and r-PEEK components in blends are listed in Table III. The T_c and T_m of PPS shifted to a lower temperature and the peak intensity decreased with increasing the r-PEEK content in the matrix. Moreover, T_c and T_m of r-PEEK tended to decrease with the addition of PPS and the peak intensity decreased. The T_c of both PPS and r-PEEK decreased, indicating that r-PEEK does not provide heterogeneous nucleation effect on PPS, which is different from the observations made by Zhang.²³ This may be attributed to the fact that r-PEEK with high viscosity limits the movement of PPS molecular chain.

Figure 3 shows an obvious change in the crystallization of r-PEEK in blend as a result of the addition of CNT. With increasing the CNT content to 20 wt % T_c increased by 5.5°C, suggesting that CNT promotes crystallization of r-PEEK. Despite this change in T_c , T_m did not reveal any significant change. However, both T_c and T_m intensity weakened. The composite containing 3 wt % CNT provided the best performance. The addition of

CNT basically reduced the crystallization temperature and peak intensity, probably because CNT particles hinder the molecular chain arrangement of PPS. The increase in melting temperature suggests improvement in the crystallization area of PPS. Blend sample filled with 10 wt % CNT revealed the largest crystallization and melting peak intensity.

Table III also lists the crystallization enthalpies (ΔH_c) and the degree of crystallinity (X_c) values calculated from the ratio of enthalpy of fusion normalized to that of polymers in compositions ($\Delta H_c/\Delta H_f$). In the calculations, ΔH_f is the heat of fusion of an infinitely thick PEEK and PPS crystals with the values of 130 and 80 J g⁻¹, respectively.^{24–26} The crystallinity values of all blend samples were observed lower than those of the neat polymers. With the addition of CNT to P80/PK20 blend, the crystallinity of r-PEEK increased, whereas that of PPS decreased. All the above results clearly indicate that PPS and r-PEEK form continuous and dispersed phases, respectively, and the CNT particles are selectively located in the PPS phase.

Electrical Properties of Blends and Composites

Figure 4 displays the volume resistivity of (a) PPS/ r-PEEK blends and (b) PPS/ r-PEEK/CNT composites. The volume resistivity reduced with increasing PPS loading because of an improvement in electrical conductivity. We observed a minimum volume resistivity of 10¹¹ Ω cm at 80 wt % loading of PPS, which exhibits a reduction of three orders of magnitude compared with that of neat PPS. This observation suggests that the blend (P80/PK20) initially builds a simple conductive

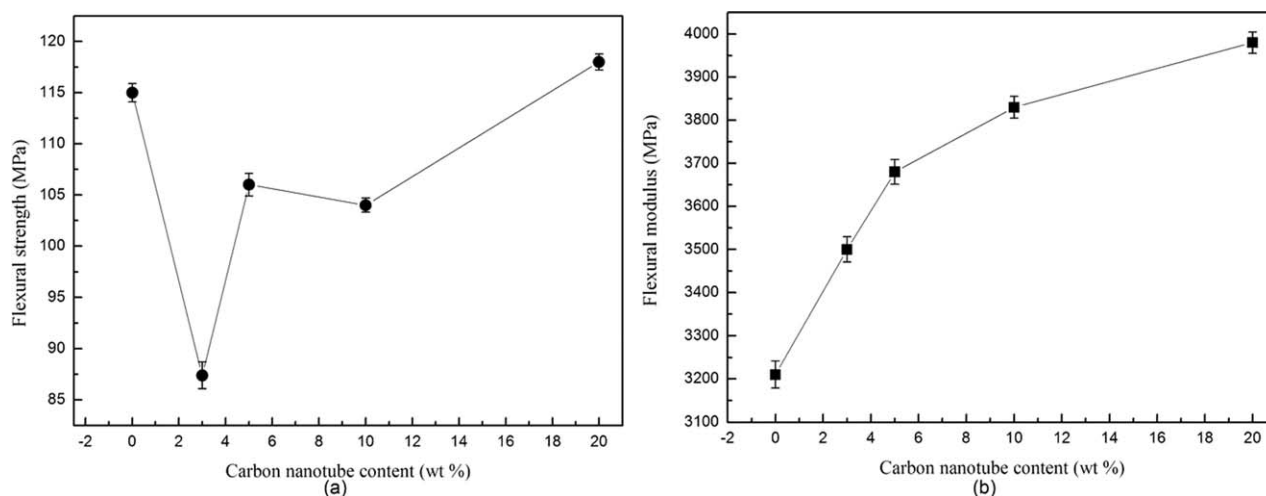


Figure 1. (a) Flexural strength and (b) flexural modulus of PPS/PEEK/CNT composites.

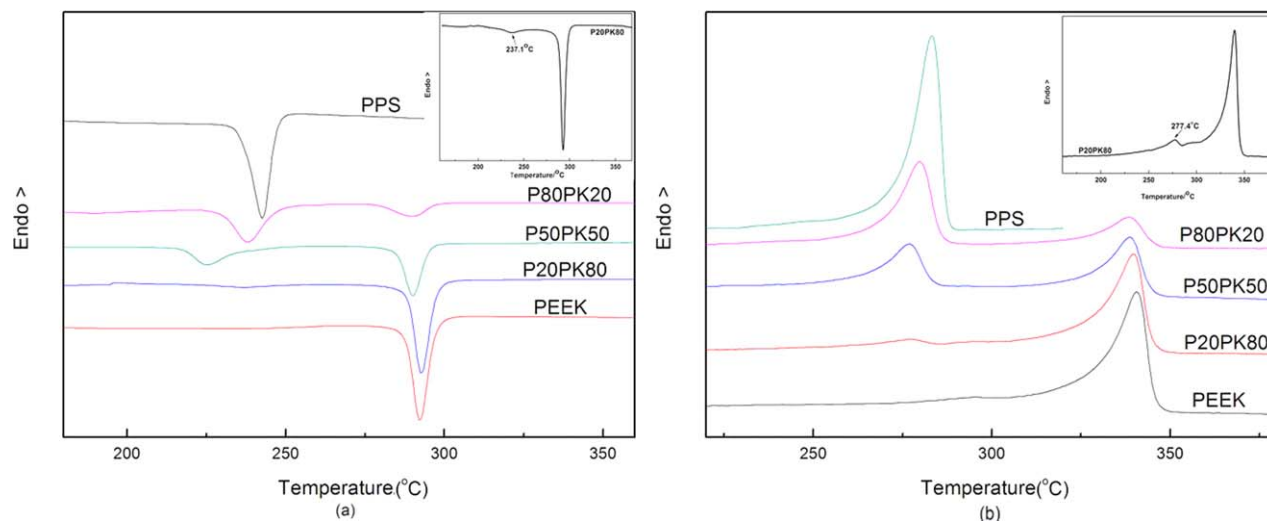


Figure 2. (a) DSC crystallization and (b) melting thermograms of PPS/PEEK blends with various r-PEEK contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. DSC Data of PPS and PEEK Component in Blends and Composites

Samples	T_c ($^{\circ}\text{C}$)		T_m ($^{\circ}\text{C}$)		ΔH_c (J/g)/ X_c (%)	
	PPS	r-PEEK	PPS	r-PEEK	PPS	r-PEEK
PPS	242.7	-	283.2	-	39.97/49.96	-/-
P80/PK20	238.1	289.7	279.9	338.4	23.61/29.51	6.869/5.284
P50/PK50	225.3	290.1	276.9	338.7	15.39/19.24	21.06/16.20
P20/PK80	237.1	292.8	277.4	339.9	3.039/3.799	32.07/24.67
r-PEEK	-	292.3	-	340.7	-/-	35.13/27.02
P80/PK20/C3	232.9	292.4	278.1	340.2	6.238/7.798	30.06/23.12
P80/PK20/C5	239.5	292.5	280.4	340.0	8.786/10.98	21.05/16.19
P80/PK20/C10	236.0	293.1	279.0	339.9	22.72/28.40	13.45/10.35
P80/PK20/C20	237.2	298.3	277.8	339.7	23.29/29.11	6.891/5.301

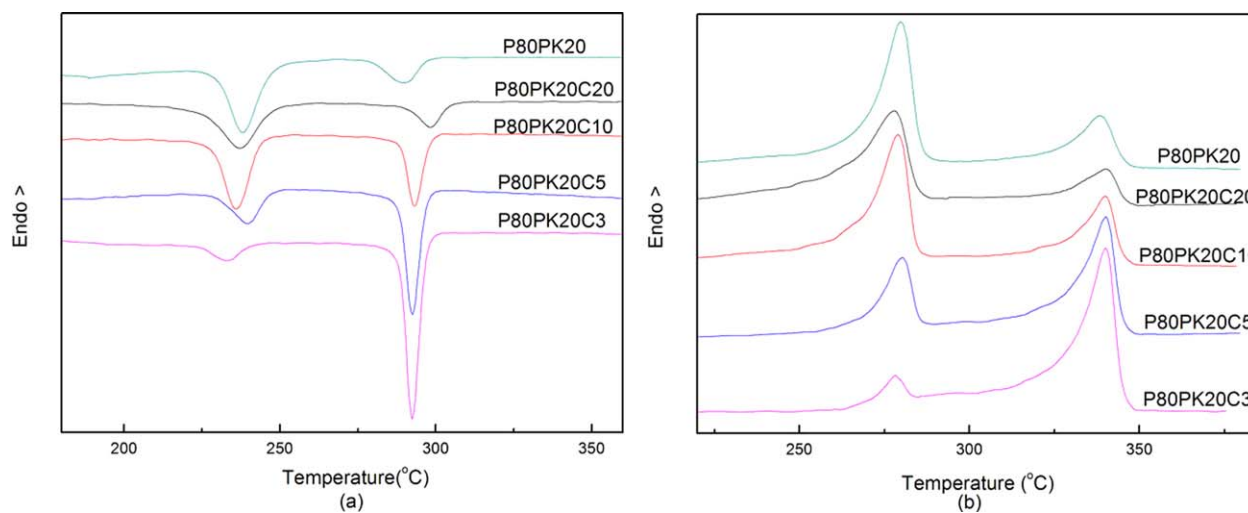


Figure 3. (a) DSC Crystallization and (b) melting thermograms of PPS/PEEK/CNT composites with various CNT contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

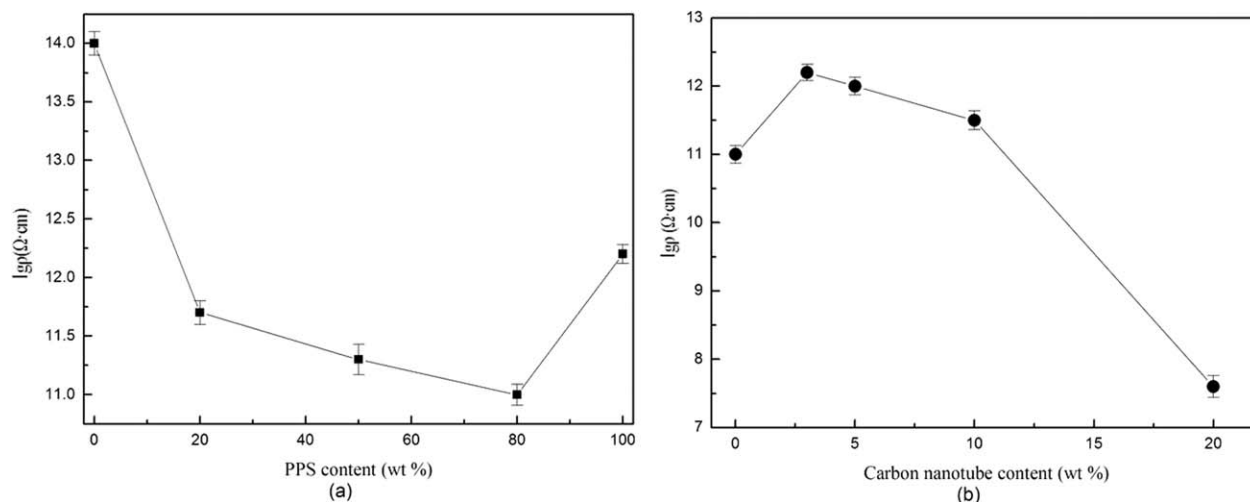


Figure 4. Volume resistivity of (a) PPS/PEEK blends and (b) PPS/PEEK/CNT composites.

network. In contrast, at a low loading of CNT (less than 10 wt % content), the volume resistivity of PPS/r-PEEK/CNT composites were slightly larger. This effect is probably because the addition of a small amount of CNT to blends destroys the built-up network structure rather than perfecting it, resulting in smaller electrical conductivity. The composite filled with 20 wt % CNT exhibited an average volume resistivity reduction of

four orders of magnitude in comparison with the neat matrix, indicating formation of a complete conductive network. At percolation threshold, the volume resistivity sharply decreases, but beyond the percolation concentration, the additional filler loading does not significantly reduce the resistance of the composite.²⁷ Composites showed a percolation threshold at between 10 and 20 wt % CNT content, whereas the percolation threshold

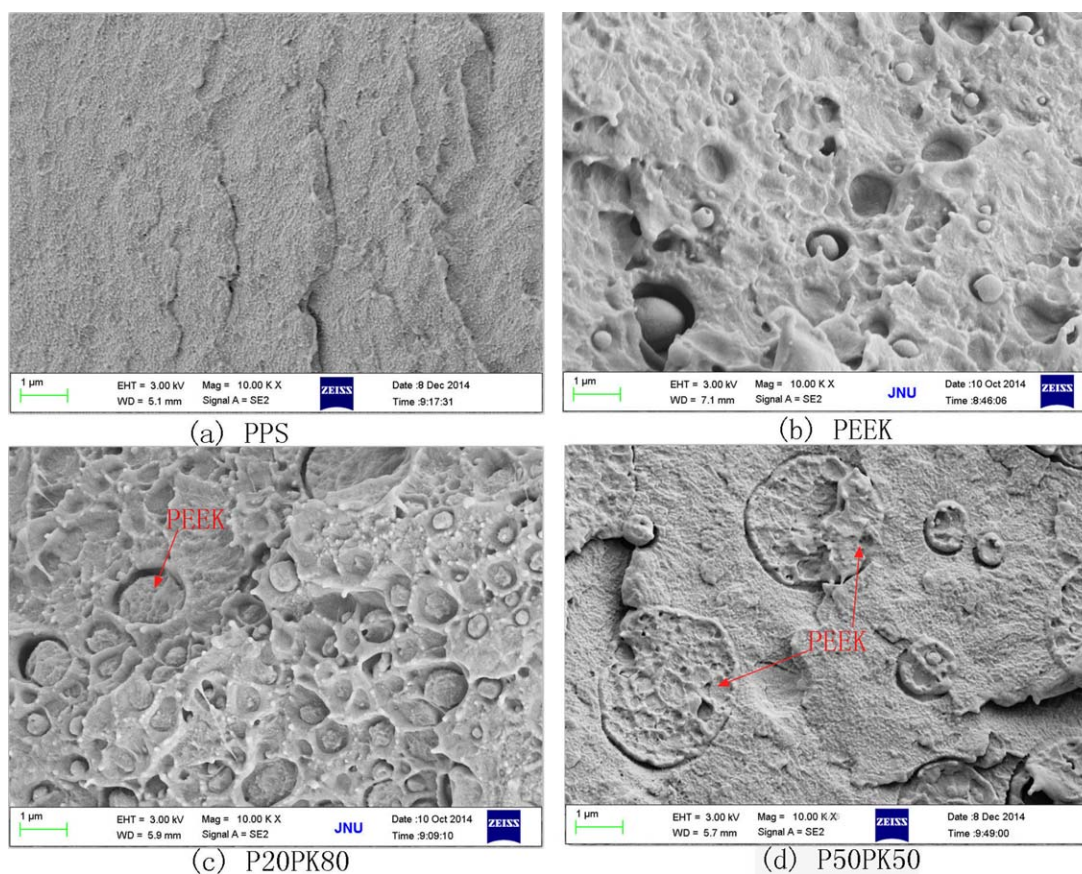


Figure 5. Scanning electron micrographs of PPS/PEEK blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

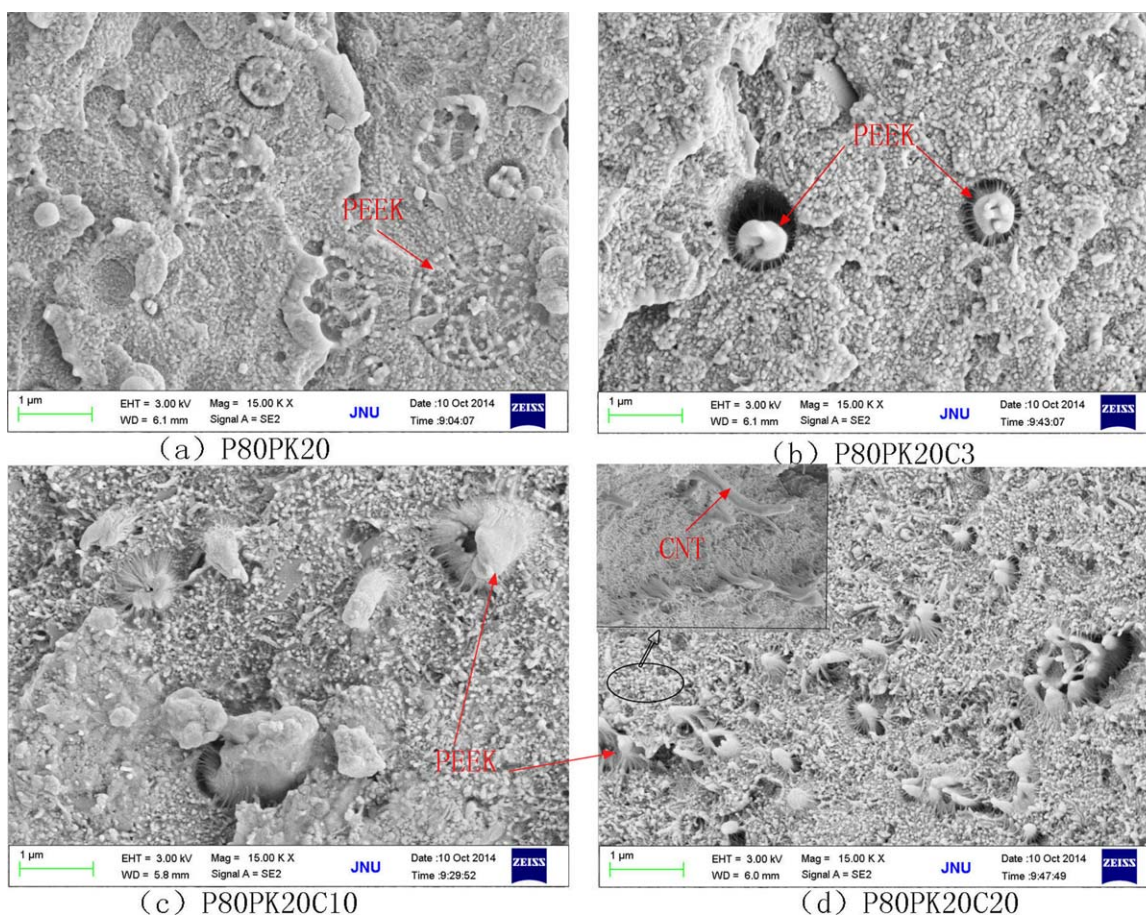


Figure 6. Scanning electron micrographs of PPS/PEEK/CNT composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the nanocomposites is about 10 wt %. A sudden decrease in resistivity was observed at this point.

Microstructures of PPS/PEEK Blends and Composites

The SEM micrographs of the PPS/ r-PEEK blends are given in Figure 5. The r-PEEK forms a continuous phase in which the spherical particles are evenly distributed in this phase [Figure 5(b)]. In P20/PK80 blend micrograph, r-PEEK particles are dispersed in PPS continuous phase. Although having a mass fraction of 80% of the total mass, r-PEEK still appears as an irregular or globular granules distributed. At the same time, PPS provides a continuous structure, thus a continuous morphology is formed. With addition of further PPS, the two-phase interface becomes blurry, indicating at this condition a better affinity between the two polymers [Figure 5(d)]. Increasing the PPS content by 80 wt %, as shown in Figure 6(a), no interface can be seen. A conductive network was set up with good mechanical performance and electrical conductivity in blend.

The SEM micrographs of P80/PK20 blend containing different amounts of CNT are shown in Figure 6. We found that with the addition of CNT, the interaction between r-PEEK and PPS becomes stronger. At an earlier stage of blending, r-PEEK is individually dispersed in matrix, thus, indicating no interaction between r-PEEK particles because of the large distance between them. Then, as the distance between r-PEEK particles becomes

shorter, r-PEEK interacts further with PPS. When the CNT content is 20 wt %, r-PEEK particles contact with each other, forming a perfect network structure in the matrix. At smaller loadings of CNT (less than 10 wt %), the interaction between r-PEEK and PPS is restricted and r-PEEK particles are simply dispersed in PPS continuous phase. Consequently, the simple conductivity network of blend is broken down. That is why the electrical conductivity of blends containing less CNT decreased. As shown in Figure 6(d), CNT exists in the PPS continuous phase not as dispersed phase, but promotes r-PEEK cohere with PPS via acting as an inorganic compatibilizer. CNT particles prefer to locate in PPS phase, which hinder the free movement of PPS macromolecular chains, thus reducing the crystallinity.

Effect of CNT on Compatibility of Blend

Figure 7 schematically shows the components of blend and composite. Particles of r-PEEK are dispersed in PPS phase even if its content is greater in matrix, which is attributed to its higher melting point and special flow characteristic. Keeping intact particles, r-PEEK homogeneously dispersed in continuous phase without interaction with PPS. The compatibility of polymers improved when CNT was added to the blend matrix. The particles of CNT were observed in the PPS phase as well as especially in the interface between PEEK and PPS. Without directly affecting on r-PEEK, CNT acts as a medium to enhance

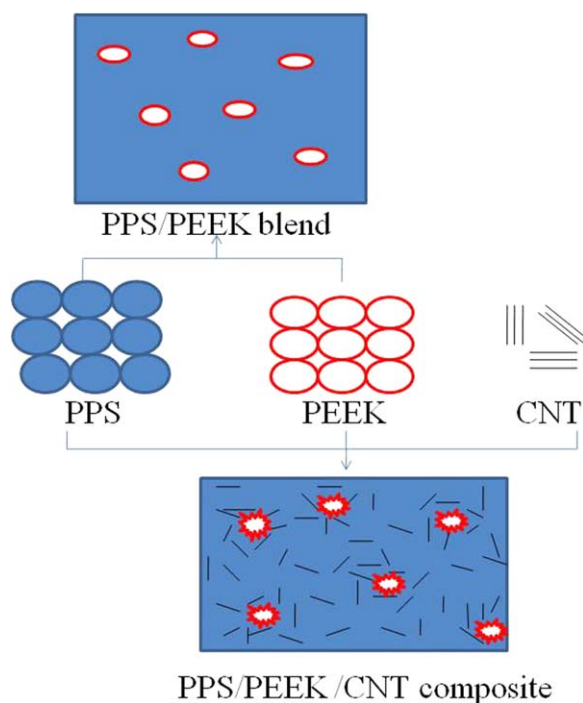


Figure 7. Phases in PPS/PEEK blend and its composites with CNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blending of matrix, which promotes the interaction of PPS and r-PEEK. Because of the presence of CNT, the friction of r-PEEK with PPS increases and the rigid macromolecular chains of r-PEEK become more flexible. As a result, r-PEEK with larger surface area interacts with PPS and improves the compatibility of two phases. Moreover, the movement of PPS macromolecular chains is blocked, whereas that of r-PEEK chains becomes less restricted. It also explains why with the addition of CNT, r-PEEK in the blend has larger crystallinity with easier crystallization than PPS. The composite structure prevented the stress concentration because of the improvement of compatibility, thus leading to increase in the flexural modulus.

CONCLUSIONS

The mechanical properties, crystallization, and melting behavior as well as electrical conductivity of PPS/r-PEEK blends and their composites with CNT were characterized. The effects of CNT on morphology and compatibility of blend were also examined. In this study, the recycled PEEK was used to improve the impact and tensile strength of PPS. Although the flexural properties of both polymers basically remained stable, however, the addition of CNT improved the flexural modulus of PPS/r-PEEK blends. The crystallization temperature and crystallinity of all blends were smaller than those of the neat polymers, indicating that they did not promote crystallization on each other. With the addition of CNT to P80/PK20 blend, the crystallinity of r-PEEK increased, whereas that of PPS decreased. For PPS, the largest crystallization and melting peak intensity were observed at 10 wt % CNT-filled composite. When CNT content was increased to 20 wt %, mainly the crystallization temperature of r-PEEK

increased. In general, CNT promotes the crystallization of r-PEEK to a certain extent.

The P80/PK20 blend exhibited the smallest volume resistivity, a reduction of three orders of magnitude, compared with that of neat PPS. The percolation threshold of composite appeared at near 10 wt % of CNT. The r-PEEK particles with granular morphology dispersed in PPS continuous phase, compatible with PPS, were observed. It is interesting to note that CNT particles exist in PPS phase and they are mostly distributed in the interface between PPS and r-PEEK, acting as an inorganic compatibilizer to improve the compatibility of PPS/ r-PEEK blend.

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