

Effect of Multiwalled Carbon Nanotubes on the Morphology and Electrical Properties of Polyamide 6/Polystyrene Blends Prepared via Successive Polymerization

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ABSTRACT: In this article, polyamide 6/polystyrene/multiwalled carbon nanotubes (PA6/PS/MWNTs) nanocomposites were prepared via successive *in-situ* polymerization. The effect of MWNTs on the morphology and electrical properties of polyamide 6/polystyrene (PA6/PS) blends was investigated in detail. Scanning electron microscopy and transmission electron microscopy analysis indicated that MWNTs were selectively located at the interface of PA6 and PS. The interface-localized MWNTs could act as compatibilizers, which resulted in the decreased size of PS domains in PA6 matrix and the delayed phase inversion of immiscible PA6/PS blends.

The PA6/PS interface was continuous in the MWNTs-filled (70/30) PA6/PS blends. Selectively located MWNTs at the continuous interface were connected with each other, which resulted in the establishment of a MWNTs conductive pathway in (70/30) PA6/PS blends. Electrical properties analysis indicated that the volume resistivity of (70/30) PA6/PS blends with 0.5 and 1.0 wt % MWNTs loading was decreased by about nine orders of magnitude. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E167–E174, 2012

Key words: carbon nanotubes; *in situ* polymerization; polymer blends; phase morphology; electrical properties

INTRODUCTION

Because of improvements in their mechanical and physicochemical properties over those of single-component systems, polymer blending has gained considerable interest in recent years. Both polyamide 6 (PA6) and polystyrene (PS) are commodity polymers that possess unique properties individually. Thus, a PA6/PS blend is expected to have commercial potential applications, such as engineering plastic,^{1,2} because it could provide a combination of the useful properties of its constituents. Because of the intrinsically different polarities of PA6 and PS, PA6/PS blends are immiscible and represent two-phase morphology with poor interfacial adhesion and exhibit poor mechanical properties. Therefore, it is essential to control and stabilize a desired type of morphology in PA6/PS blends to generate polymeric materials with favorable properties.^{3–9} Styrene copolymers, such as poly(styrene-*co*-maleic anhydride) (SMA), poly(styrene-*co*-acrylonitrile) (SAN) and maleated styrene-*b*-ethylene-cobutylene-*b*-styrene copolymer

(SEBS-*g*-MAH),¹⁰ poly(styrene-*g*-ethylene oxide) (SEO),^{11,12} graft copolymers of PS and PA6 (PS-*g*-PA6),¹³ maleated propylene-ethylene copolymer,¹⁴ were usually used as the compatibilizers of PA6/PS blends in a great number studies.

It is promising to use carbon nanotubes (CNTs) additives in polymer blends to achieve high performance and multifunctions because of the nanometer size, high aspect ratios, and more importantly, the extraordinary mechanical strength, high electrical and thermal conductivity.^{15–23} Furthermore, when incorporated into polymer blends, the nanofiller, such as CNTs,²⁴ carbon black,²⁵ organoclay,²⁶ and silica particles, could act as compatibilizers and affect the dynamic phase behavior and morphology of the polymer blends because of the strong adsorption of polymer on the surface of these fillers.^{27–31} Several researchers have reported both experimental results and theoretical predictions that CNTs can be used as a third component to improve phase morphology of the immiscible polymer blends. The effect of CNTs on the interfacial properties of immiscible blends is similar to that of compatibilizer.^{32–35} PA6/PS/organoclay nanocomposites had been studied by Kelnar²⁷ and Yang,³¹ respectively. However, there are few reports about PA6/PS/CNTs nanocomposites.

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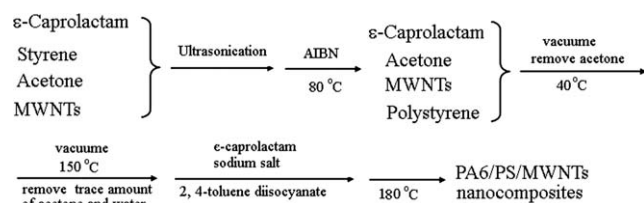


Figure 1 The scheme of the preparation procedure of MWNTs-filled PA6/PS blends.

On the other hand, most researches focus on the electrical properties of polymer blends containing CNTs in recent years. For CNTs-filled polymer blends, the electrical conductivity depends on the location of CNTs and on the blends morphology. The selective localization of CNTs in a continuous phase of immiscible polymer blends is a conceptual approach in achieving conducting blends utilizing very low concentration of CNTs. When CNTs were selectively located at the continuous interface of immiscible polymers blends, the electrical conductivity of the blends could be improved significantly with the lowest CNTs loading.^{32–47}

PA6/PS blends had been prepared via successive *in situ* polymerization in our previous works^{48–50} in which a novel phase inversion phenomenon was achieved. In these works, PS is the dispersed phase when it is present at less than 10 wt % in PA6/PS blends. Beyond 15 wt % PS, phase inversion occurs, and a transformation for PS from a dispersed phase to a continuous phase, and for PA6 from the matrix to a dispersed phase, is observed. Recently, PA6 magnetic microspheres with mean diameter of 7.7 μm and a narrow size distribution were obtained in our laboratory on the base of the above novel phase inversion in PA6/PS blends.⁵¹ Furthermore, the effect of montmorillonite on the morphologies and properties of PA6/PS blends via successive *in situ* polymerization was also studied in our laboratory.⁵²

In this study, MWNTs-filled PA6/PS blends were also prepared via successive *in situ* polymerization. Figure 1 shows the schematic illustration of the preparation procedures. The main aim is to investigate the effect of MWNTs on the morphology of PA6/PS blends. Furthermore, the increased electrical conductivity of PA6/PS/CNTs nanocomposites resulted from unusually selective location of MWNTs in PA6/PS blends was also studied in detail in this work.

EXPERIMENTAL

Materials

MWNTs were purchased from Chengdu Organic Chemistry Co., Ltd. The diameter of MWNTs is

about 10–20 nm. Styrene, azodiisobutyronitrile (AIBN), 2, 4-toluene diisocyanate (TDI), and ϵ -caprolactam sodium salt (NaCL) were purchased from Shanghai Chemical Reagent Corp (Analysis Grade). Styrene was distilled under reduced pressure. Commercial grade ϵ -caprolactam (CL) was obtained from Nanjing Oriental Chemical Company.

Preparation of MWNTs-filled PA6/PS blends

In a typical experiment, 1.0 wt % MWNTs-filled (80/20) PA6/PS blends were prepared following the two steps below:

1. Polymerization of styrene in the presence of CL and MWNTs

First, 1.0 g of MWNTs, 80 g of CL, 20 g of styrene, and 20 g of acetone were added into a three-necked flask with stirring. After 1 h ultrasonication, the above mixture was purged with dry nitrogen for 30 min to remove oxygen from the reaction flask, followed by addition of 0.04 g of AIBN. Then, the mixture was polymerized at 80°C for 24 h with stirring. Afterwards, the mixture was vacuumed at 40°C to remove acetone, and a viscous PS/CL/MWNTs mixture was obtained.

2. Preparation of MWNTs-filled PA6/PS blends

The obtained PS/CL/MWNTs mixture was vacuumed at 150°C for 20 min to remove residual styrene monomer, trace amount of acetone, and water. Then, 0.32 g of NaCL was added with stirring for 5 min. After that, 0.32 g of TDI was added with stirring. Finally, the mixture was immediately poured into a mold preheated to 180°C and polymerized in an oven at 180°C for 20 min, and subsequently, the 1.0 wt % MWNTs-filled (80/20) PA6/PS blends were obtained after slowly cooling to room temperature.

The unfilled and 1.0 wt % MWNTs-filled (95/5, 90/10, 85/15, and 70/30) PA6/PS blends, 0.5 and 1.5 wt % MWNTs-filled (90/10, 80/20, and 70/30) PA6/PS blends were also prepared via the method mentioned above. The content of MWNTs, CL, and styrene were determined by the different compositions of MWNTs-filled PA6/PS blends. AIBN was used as a initiator of radical polymerization of styrene; the amount of which was determined by the content of styrene in the mixture. NaCL and TDI were used as the catalyst and activator for anionic ring opening polymerization of CL, respectively; the amount of which were determined by the content of CL. Acetone was used as a predispersant of MWNTs, CL, and styrene, which could ensure the

mixture is liquid. The amount of acetone was determined by the content of CL.

Characterization

Scanning electron microscopy

The morphology of MWNTs-filled PA6/PS blends was examined with a scanning electron microscopy (SEM) (JSM LV-5610, JEOL). The samples were held

in liquid N₂ and a brittle fracture was performed. Specimens were etched with tetrahydrofuran (THF) to dissolve the PS homopolymers. The etched surface was coated with gold before observation.

Transmission electron microscopy

The location of MWNTs was observed by a transmission electron microscopy (TEM) (JEM-2100F, JEOL). The samples were ultramicrotomed with a

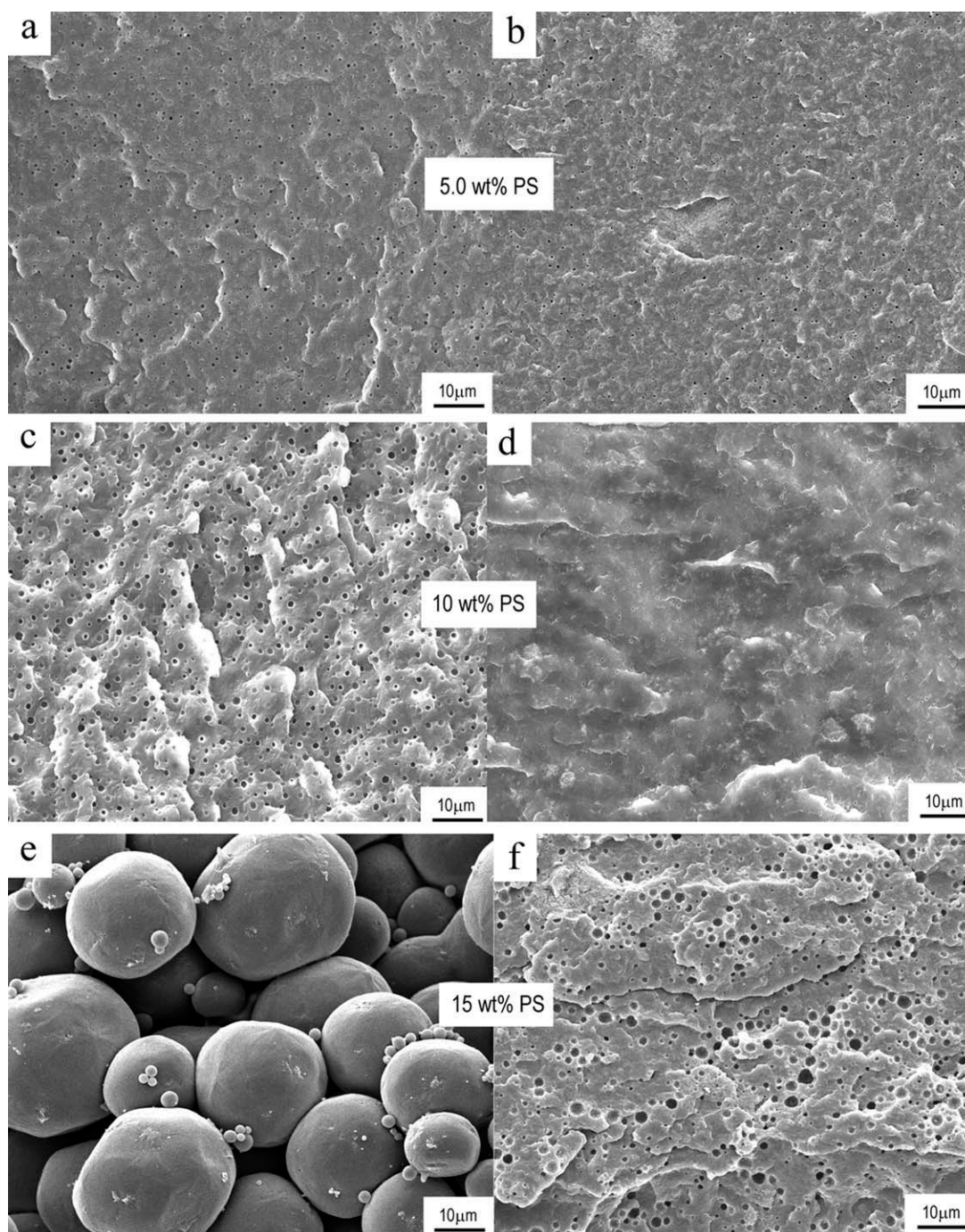


Figure 2 SEM images of the THF etched fracture surface of the blank PA6/PS blends (a,c,e,g, and i) and 1.0 wt% CNTs-filled PA6/PS blends (b,d,f,h, and j).

diamond knife on a Leica Ultracut UCT microtomed at -20°C to give 70-nm-thick sections. The sections were transferred to carbon-coated Cu grids of 200 meshes.

Broadband dielectric spectrometer

Broadband dielectric spectrometer (Concept 40, NOVOCONTROL) was used to determine the volume resistance of sheet samples (diameter 30 mm, thickness 1.0 mm) at room temperature.

RESULTS AND DISCUSSION

Microscopic morphology of MWNTs-filled PA 6/PS blends

Figure 2 gives the SEM images of the THF etched fracture surface of the blank PA6/PS blends and 1.0 wt % MWNTs-filled PA6/PS blends. The black domains correspond to the extracted PS phase [Fig. 2(a–d),f,h], and the microspheres [Fig. 2(e,g,i,j)] are PA6 spheres.^{48–50} As the results showed in our previous works,^{48–50} the phase morphology of PA6/PS blends gradually changes from the PS dispersed/

PA6 matrix to PA6 dispersed/PS matrix with increasing PS loading. With the same loading of PS, the size of the discrete PS domains in MWNTs-filled PA6/PS blends reduces remarkably when compared with that in blank PA6/PS. For blank PA6/PS blends (Fig. 2(e,g,i)), the phase inversion occurs at a PS content of 15 wt % in which the phase morphology of the PA6/PS blends changes from the PS dispersed/PA6 matrix to PA6 dispersed/PS matrix system. However, with the addition of MWNTs, it does not occur until at a PS content of 30 wt % [(Fig. 2(b,d,f,h,j)]. Moreover, when the content of MWNTs is increased to 1.5 wt %, the phase inversion of PA6/PS blends with 30 wt % PS loading is hindered. Discrete PS spherical domains are dispersed in the PA6 matrix again, as shown in Figure 3(c).

Location of MWNTs in the PA6/PS blends

To explore the mechanism of the morphological change of PA6/PS blends with the addition of MWNTs, it is necessary to investigate the location of MWNTs in the blends. SEM images of the MWNTs-filled PA6/PS blends show that MWNTs are mainly

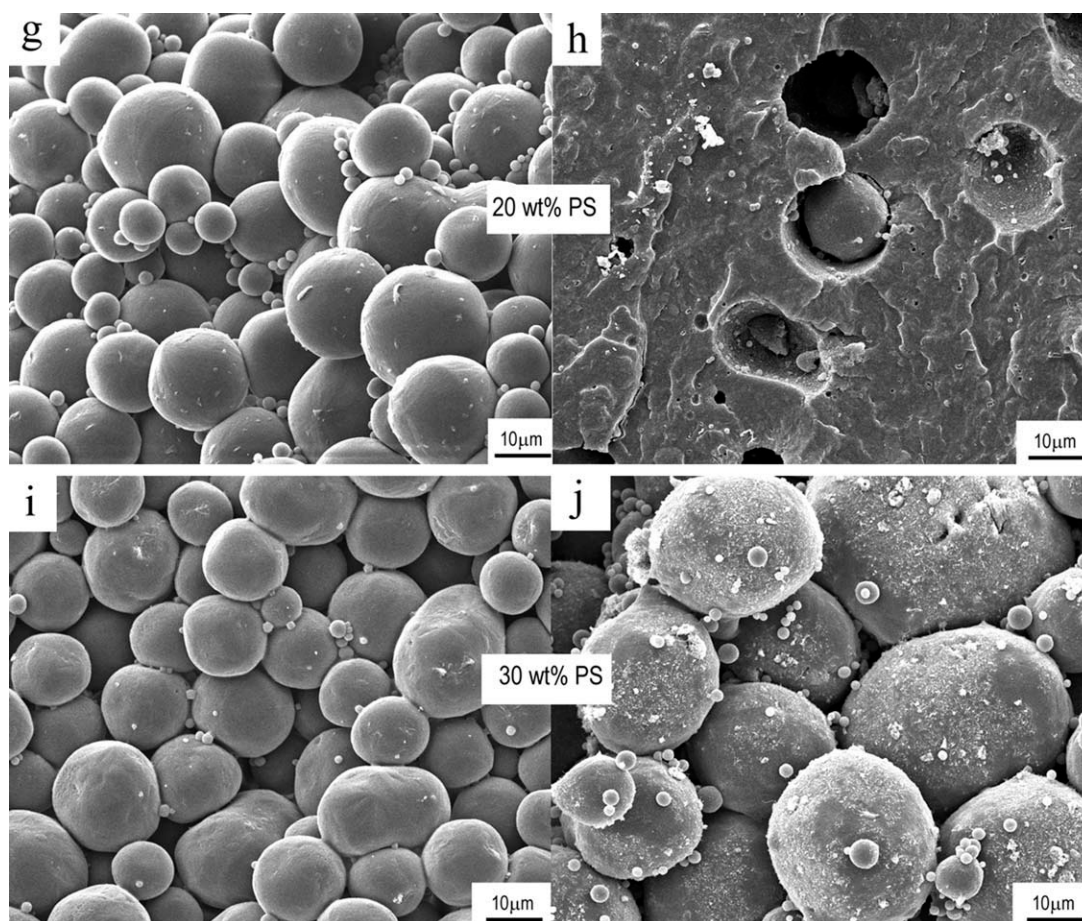


Figure 2 (Continued)

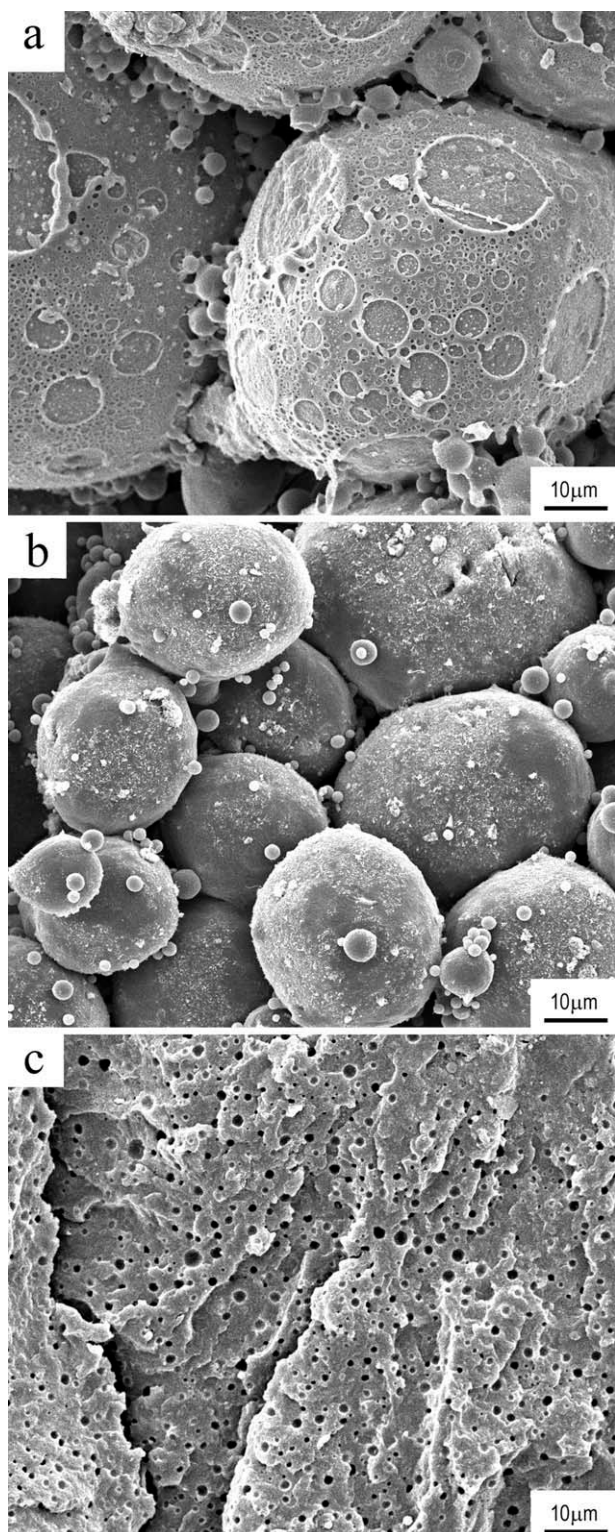


Figure 3 SEM images of THF etched fracture surface of (70/30) PA6/PS blends with (a) 0.5 wt% MWNTs, (b) 1.0 wt% MWNTs, and (c) 1.5 wt% MWNTs.

located at the bottom of the dark holes in the PA6 continuous phase and there are hardly any MWNTs in the PA6 matrix, as shown in Figure 2(b,d,f,h) and Figure 4(a). When PS is the continuous phase [Fig.

4(b,c)], MWNTs are mainly located at the surface of PA6 spheres, and the PS matrix does not contain MWNTs. It is generally believed that MWNTs are

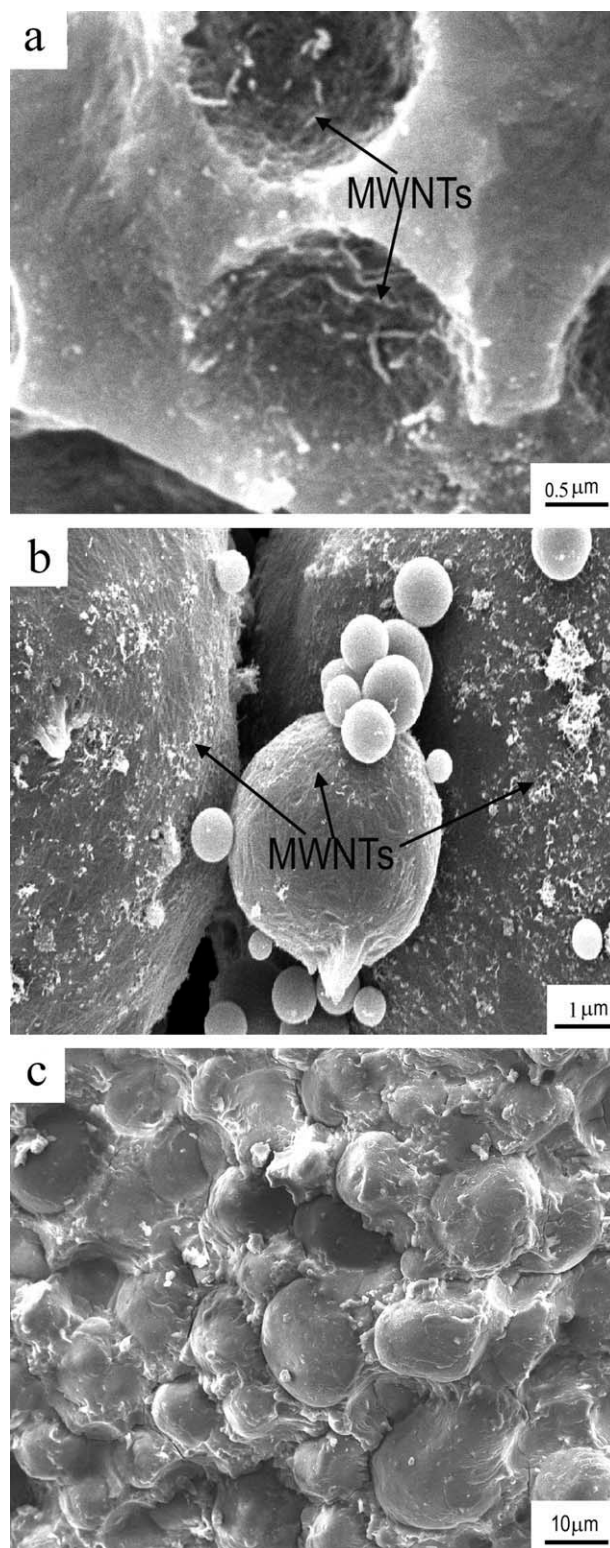


Figure 4 SEM images of the fracture surface of 1.0 wt% MWNTs-filled (80/20) PA6/PS blends (a), (70/30) PA6/PS blends (b and c). The surface of (a) and (b) was etched with THF.

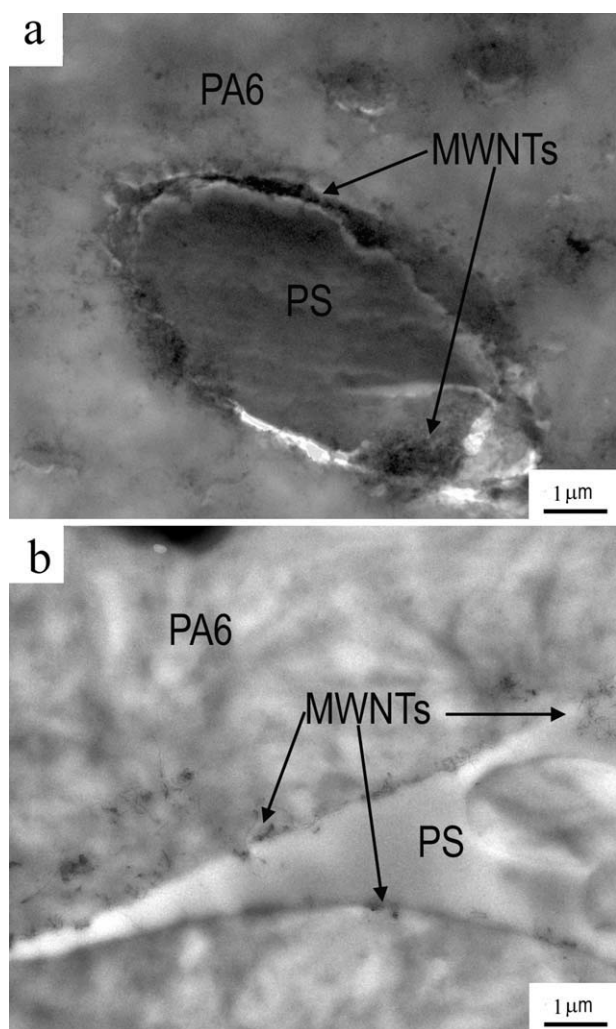


Figure 5 TEM images of 1.0 wt% MWNTs-filled (80/20) PA6/PS blends (a) and (70/30) PA6/PS blends (b).

confined at the interface of PA6 and PS but not dispersed into the matrix.

To further confirm the location of MWNTs, TEM observation (Fig. 5) was also used to investigate the morphology of the blends. In Figure 5(a) and (b), PS and PA6 is the dispersed phase respectively. The images show that MWNTs exist exclusively at the interface region of PA6/PS in both blends regardless of the PS or PA6 dispersed phase. This interesting selective location of MWNTs is due to the poor wettability of MWNTs by both PA6 and PS, and thus MWNTs are expelled from both PA6 and PS phases and banished to the interface region between PA6 and PS.

The selective localization of the CNTs has also been observed on some ternary nanosystems,^{33,39,41,44} which was prepared by either functionalized CNTs or special extrusion process. CNTs are mainly located in one of the polymer phases in those blends. In this work, MWNTs-filled PA6/PS blends are prepared via *in situ* successive polymerization

with raw MWNTs. Because of the poor wettability of MWNTs by PA6 and PS, they are excluded to the interface between PA6 and PS, which resulted in their selective localization at the PA6/PS interface.

Electrical properties of CNTs-filled PA6/PS blends

Figure 6 shows influence of MWNTs loading on the volume resistivity of the blends with different PA6/PS weight ratio. For the blends of (90/10) and (80/20) PA6/PS, the volume resistivity showed almost the same value even though the MWNTs content was increased from 0.5 to 1.5 wt %, and the slightly change is probably due to the instrumental inaccuracy. However, (70/30) PA6/PS blends showed quite different volume resistivity. For blends with 0.5 and 1.0 wt % MWNTs, obvious decrease of the resistivity could be observed, and the volume resistivity was decreased by about nine orders of magnitude. While with further increasing MWNTs loading to 1.5 wt %, an abrupt increase in volume resistivity occurred again for (70/30) PA6/PS blends. These results indicate that the electrical conducting ability of (70/30) PA6/PS blends with 0.5 and 1.0 wt % of MWNTs is much better than that of the other blends. In (70/30) PA6/PS blends with MWNTs content of 0.5 and 1.0 wt %, densely stacking of PA6 microspheres results in a continuous interface region of PA6 and PS, as shown in Figure 4(c). MWNTs confined at the continuous interface region are bridged into direct contact and the electrical conductivity can be imparted, which results in the fabrication of a conductive pathway in the blends. However, for the MWNTs-filled (90/10, 80/20) PA6/PS blends [Fig. 2(b,d,f,h)] and 1.5 wt % MWNTs-filled (70/30) PA6/PS blends [Fig. 3(c)], PA6/PS interface region has little or no continuity, which is believed to be responsible for the insulating behavior of these blends.

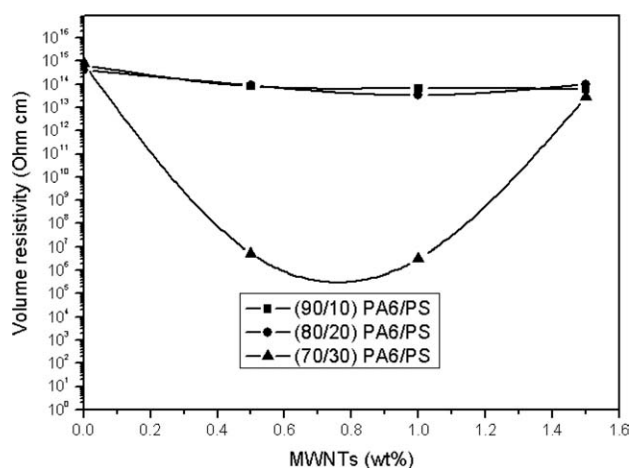


Figure 6 Influence of MWNTs loading on the volume resistivity of various PA6/PS blends composition.

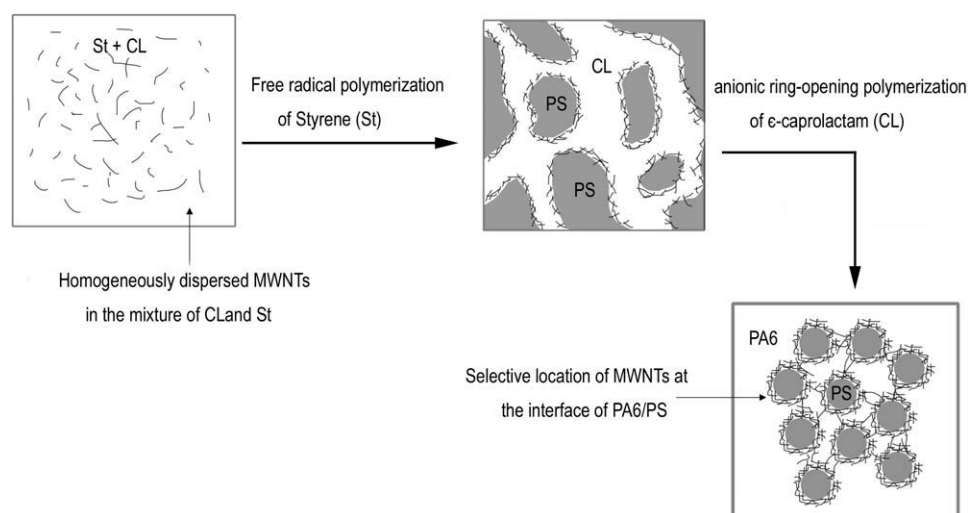


Figure 7 Schematic diagrams of unique mechanism of the unusual phase morphology and electrical properties of MWNTs-filled PA6/PS blends.

Unique mechanism of the unusual phase morphology and electrical properties of MWNTs-filled PA6/PS blends

MWNTs were dispersed homogeneously in the mixture of styrene and ε-caprolactam monomer with the aid of power ultrasonic wave before polymerization as shown in Figure 1. In the polymerization, MWNTs were excluded to the interface of the mixture and tended to “aggregate” forming interface-localized MWNTs clusters containing styrene and ε-caprolactam monomer, which resulted in the generation of PA6 and PS molecules in the MWNTs clusters. These interface-localized MWNTs clusters containing PA6 and PS molecules could be looked as an amphiphilic compatibilizer of PA6/PS blends and enhance the interface interactions between PA6 and PS effectively. Both the decreased size of the PS domains and the increased phase inversion concentration of PA6/PS blends are due to the compatibilization of the interface-localized MWNTs clusters.

CONCLUSIONS

MWNTs-filled PA6/PS blends were successfully prepared by *in situ* successive polymerization. Because of the poor wettability of MWNTs by PA6 and PS, MWNTs were selectively located at the interface of PA6 and PS. The interface-localized MWNTs could act as a compatibilizer of PA6/PS blends and resulted in both the decreased size of the PS domains and increased phase inversion concentration. For the (70/30) PA6/PS blends, the PA6/PS interface was continuous. Interface-localized MWNTs could be connected with each other in the continuous interface, and thus a conductive MWNTs pathway could be created, which was effective to decrease the volume resistivity. The method pre-

sented in this study is relatively facile but still reasonably controllable to prepare conductive commodity polymer blends.

References

- Holger, W.; Quaas, G.; Wittmann D. DE Pat. 10024933 A1 (2001).
- Jing, J. L.; Chen, G. X.; Sun, C. R. CN Pat. 1357566 A (2001).
- Jo, W. H.; Park, C. D.; Lee, M. S. *Polymer* 1996, 37, 1709.
- Dedecker, K.; Groeninckx, G. *Macromolecule* 1999, 32, 2472.
- Koulouri, E. G.; Kallitsis, J. K.; Hadziioannou, G. *Macromolecule* 1999, 32, 6242.
- Vander Hart, D. L.; Feng, Y.; Han, C. C.; Weiss, R. A. *Macromolecule* 2000, 33, 2206.
- Villarreal, M. E.; Tapia, M.; Nuño-Donlucas, S. M.; Puig, J. E.; González-Núñez, R. *J Appl Polym Sci* 2004, 92, 2545.
- Zhang, X. Q.; Son, Y. G. *J Appl Polym Sci* 2003, 89, 2502.
- Guo, T. Y.; Song, M. D.; Hao, G. J.; Zhang, B. H. *Eur Polym J* 2001, 37, 241.
- Cheng, C. C.; White, J. L. *Polym Eng Sci* 1993, 33, 923.
- Jannasch, P.; Wesslen, B. *J Appl Polym Sci* 1995, 58, 753.
- Jannasch, P.; Wesslén, B. *J Appl Polym Sci* 1998, 70, 1887.
- Zhang, C. L.; Feng, L. F.; Gu, X. P.; Hoppe, S.; Hu, G. H. *Polym Eng Sci* 2007, 48, 5940.
- Li, Y.; Wang, D.; Zhang, J. M.; Xie, X. M. *J Appl Polym Sci* 2011, 119, 1652.
- Gao, J. B.; Itkis, M. E.; Bekyarova, E.; Hu, H.; Kranak, V.; Yu, A. P.; Haddon, R. C. *Z. J Am Chem Soc* 2006, 128, 7492.
- Rasheed, A.; Dadmun, M. D.; Ivanov, I.; Britt, P. J.; Geohegan, D. B. *Chem Mater* 2006, 18, 3513.
- Moniruzzaman, M.; Winey, K. I. *Macromolecules* 2006, 39, 5194.
- Liu, T. X.; Phang, I. Y.; Shen, L.; Chow, Y.; Zhang, W. D. *Macromolecules* 2004, 37, 7214.
- Xu, G. Y.; Du, L. C.; Wang, H.; Xia, R.; Meng, X. C.; Zhu, Q. R. *Polym Int* 2008, 57, 1052.
- Carlos, V. S.; Martínez-Hernández, A. L.; Fisher, F. T.; Ruoff, R.; Castaño, V. M. *Chem Mater* 2003, 15, 4470.
- Liu, I. C.; Huang, H. M.; Chang, C. Y.; Tsai, H. C.; Hsu, C. H.; Tsiang, C. C. *Macromolecules* 2004, 37, 283.
- Hu, N. T.; Zhou, H. W.; Dang, G. D.; Chen, C. H.; Jing, J.; Zhang, W. J. *Polym Int* 2008, 57, 927.

23. Lu, X. F.; Chao, D. M.; Zheng, J. N.; Chen, J. Y.; Zhang, W. J.; Wei, Y. *Polym Int* 2006, 55, 945.
24. Nayak, G. C.; Rajasekar, R.; Das, C. K. *J Mater Sci* 2011, 46, 2050.
25. Tan, Y. Q.; Song, Y. H.; Cao, Q.; Zheng, Q. *Polym Int* 2011, 60, 823.
26. Moghbelli, E.; Sue, H. J.; Jain, S. *Polymer* 2010, 51, 4231.
27. Kelnar, I.; Rotrekl, J.; Jiří, K.; Kaprálkova, L. *Polym Int* 2008, 57, 1281.
28. Wu, D. F.; Zhou, C. X.; Zhang, M. *J Appl Polym Sci* 2006, 102, 3628.
29. Mallette, J. G.; Guej, L.; Marquez, A.; Manero, O. *J Appl Polym Sci* 2001, 81, 562.
30. Pérez, L. D.; Sierra, L.; López, B. L. *Polym Eng Sci* 2008, 48, 1986.
31. Yang, J. T.; Sun, L.; Xiang, S. F.; He, J. L.; Gu, Li. C.; Zhong M. Q. *J Appl Polym Sci* 2008, 110, 276.
32. Zou, H.; Wang, K.; Zhang, Q.; Fu, Q. *Polymer* 2006, 47, 7821.
33. Meincke, O.; Kaempfer, D.; Weickmann, H.; Friedrich, C.; Vathauer, M.; Warth, H. *Polymer* 2006, 45, 739.
34. Das, A.; Stöckelhuber, K. W.; Jurk, R.; Saphiannikova, F. J.; Lorenz, H.; Heinrich, G. *Polymer* 2008, 49, 5276.
35. Bose, S.; Bhattacharyya, A. R.; Kulkarni, A. R.; Pötschke, P. *Compos Sci Technol* 2009, 69, 365.
36. Reddy, K. R.; Jeong, H. M.; Lee, Y.; Raghu, A. V. *J Polym Sci Pol Chem* 2010, 48, 1477.
37. Nogales, A.; Broza, G.; Roslaniec, Z.; Schulte, K.; Sjö, I. I.; Hsiao, B. S. *Macromolecules* 2004, 37, 7669.
38. Pötschke, P.; Bhattacharyya, A. R.; Janke, A. *Carbon* 2004, 42, 965.
39. Wu, M.; Shaw, L. *J Appl Polym Sci* 2004, 99, 477.
40. Khare, R. A.; Bhattacharyya, R. R.; Kulkarni, A. R.; Saroop, M.; Biswas, A. *J Appl Polym Sci* 2004, 46, 2286.
41. Bose, S.; Bhattacharyya, A. R.; Bonder, A. P.; Kulkarni, A. R.; Pötschke, P. *J Polym Sci Pol Phys* 2008, 46, 1619.
42. Bose, S.; Bhattacharyya, A. R.; Khare, R. A.; Kulkarni, A. R.; Pötschke, P. *Macromol Symp* 2008, 263, 11.
43. Wu, M.; Shaw, L. *J Power Sources* 2004, 136, 37.
44. Wu, D. F.; Zhang, Y. S.; Zhang, M.; Yu, W. *Biomacromolecules* 2009, 10, 417.
45. Su, C.; Xu, L. H.; Zhang, C.; Zhu, J. *Compos Sci Technol* 2011, 71, 1016.
46. Cayla, A.; Campagne, C.; Rochery, M.; Devaux, E. *Synth Met* 2011, 161, 1034.
47. Khare, R. A.; Bhattacharyya, A. R.; Kulkarni, A. R. *J Appl Polym Sci* 2011, 120, 2663.
48. Pei, A. H.; Liu, A. D.; Xie, T. X.; Yang, G. S. *Macromolecules* 2006, 39, 7801.
49. Pei, A. H.; Liu, A. D.; Xie, T. X.; Yang, G. S. *J Appl Polym Sci* 2007, 105, 1757.
50. Pei, A. H.; Liu, A. D.; Xie, T. X.; Yang, G. S. *Macromol Chem Phys* 2006, 207, 1980.
51. Liu, Y.; Xie, T. X.; Yang, G. S. *J Mater Sci* 2011, 46, 5050.
52. Liu, Y.; Chen, Z. M.; Xie, T. X.; Yang, G. S. *J Mater Sci* 2010, 46, 2700.