

Investigation on the Miscibility of the Blends of Poly(methyl methacrylate) and Poly(styrene-*co*-acrylonitrile)

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ABSTRACT: The miscibility was investigated in blends of poly(methyl methacrylate) (PMMA) and styrene-acrylonitrile (SAN) copolymers with different acrylonitrile (AN) contents. The 50/50 wt % blends of PMMA with the SAN copolymers containing 5, 35, and 50 wt % of AN were immiscible, while the blend with copolymer containing 25 wt % of AN was miscible. The morphologies of PMMA/SAN blends were characterized by virtue of scanning electron microscopy and

transmission electron microscopy. It was found that the miscibility of PMMA/SAN blends were in consistence with the morphologies observed. Moreover, the different morphologies in blends of PMMA and SAN were also observed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 292–298, 2012

Key words: miscibility; PMMA/SAN blends; morphologies; SEM; TEM

INTRODUCTION

The investigation of the miscibility of polymer blends has attracted many researcher and research groups' attention because of the important academic study and increasing technological applications.^{1–11}

It is well-known that the performances of polymer blends with the lower critical solution temperature (LCST) or upper critical solution temperature (UCST) depend mainly on their phase structure and morphology. A few studies of the phase behavior of PMMA/SAN blends have been reported in the literature. It is believed that PMMA/SAN blends exhibit a LCST behavior, where polymer blends are miscible and homogenous for any composition at temperature below phase separation temperatures and a dispersed phase forms with temperature elevation.^{12–14}

It has been known that blends of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN) are miscible when the acrylonitrile (AN) content in SAN copolymer ranges between 9 and 33 wt %.^{15,16} The phase structures and morphologies of polymer blends can be characterized by means of many different methods such as optical microscopy,

infrared spectroscopy,^{17,18} atomic force microscopy (AFM)^{11,19}, nuclear magnetic resonance^{20,21}, small angle light scattering (SALS)^{22–25}, differential scanning calorimetry (DSC)^{9,15,16,26,27}, and dynamic mechanical analysis (DMA), etc. Electron microscopy is a powerful and conventional method, by which the phase separation can be observed easily, in the investigation of polymer structure and morphology, provided the compositions of polymer blends differ enough in refractive index. But there have been few articles that deal with the phase morphologies studied by electron microscopy method for PMMA/SAN blends systems.

In this work, we prepared styrene-acrylonitrile (SAN) copolymers by emulsion polymerization. The miscibility of PMMA/SAN blends was investigated by means of dynamic mechanical analysis and electron microscopy. The AN content of SAN copolymer and the temperature dependences of the phase morphologies of PMMA/SAN blends are discussed in detail.

EXPERIMENTAL

Materials

The PMMA resin used in this work is a commercial product of LG Company, Korea. Number molecular weight (M_n) is 60,000. Prior to each processing step, the PMMA resin was dried in a vacuum oven for 4 h at 80°C to remove absorbed water. Acrylonitrile (AN)

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TABLE I
Conversion Rates of SAN Copolymers with Different AN Contents

St/AN in SAN copolymer	SAN95/5	SAN75/25	SAN65/35	SAN50/50
Conversion rate (%)	99%	99%	99%	99%

and styrene (St) used in this study were supplied by Jilin Chemical Industry Group synthetic resin factory, Jilin, China. SAN copolymers with different AN contents were synthesized by emulsion polymerization in our Laboratory.

Synthesis of SAN copolymers

SAN copolymers were achieved by emulsion polymerization method. The oil-soluble initiator used in combination with a redox system was cumene hydroperoxide (CHP) in this work. The redox initiator system, CHP, sodium pyrophosphate (SPP), dextrose (DX), and iron (II) sulfate (FES) was used without further purification. The emulsion polymerization was performed in a 2L glass reactor under nitrogen at 65°C Deionized water, SPP, DX, FES, and KOH were added to the glass reactor and stirred for 10 min under nitrogen, then the mixture of St, AN, and CHP and chain transfer agent, *tert*-dodecyl mercaptan, was added in a continuous feeding way to the glass reactor. The polymers were isolated from the emulsion by coagulation and dried in a vacuum oven at 60°C for 24 h before being used. Determination of the conversion rates of the SAN copolymers were performed, and the results were listed in Table I.

Preparation of PMMA/SAN blends

PMMA/SAN blends were prepared by mixing PMMA resin with SAN copolymers on a thermo Haake mixer. The rotating speed was set at 70 rpm, and the temperature was set at 190°C.

Elemental analysis

The elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer. Data for the elemental analysis was listed in Table II.

TABLE II
Data for the Elemental Analysis Used in This Work

SAN copolymer	SAN95/5	SAN75/25	SAN65/35	SAN50/50
C	89.96%	85.41%	83.80%	80.22%
H	7.570%	7.296%	7.144%	6.882%
N	1.319%	5.916%	7.832%	11.63%
AN content of SAN	5.0%	22.4%	29.7%	44.1%

TABLE III
Torque Values for Polymers Used in This Study

Polymer	PMMA	SAN95/5	SAN75/25	SAN65/35	SAN50/50
Torque (N/m)	12.4	6.1	8.4	10.3	11.8

DMA analysis

The PMMA/SAN blends were compression molded to obtain bars that are suitable for DMA measurements. The PMMA/SAN blends were melted at 190°C for 5 min, and then a slight pressure was applied. The melted samples were cooled under pressure until solid bars were obtained. These bars were sized 20 × 3 × 1 mm³. The apparatus used is the Netzsch DMA242 (Germany). The scans were carried out in single cantilever mode. The dynamic mechanical measurements were performed over a temperature range from 20 to 150°C at a constant heating rate of 3°C/min, and at a frequency of 1 Hz.

Examination of optical properties of PMMA/SAN blends

Transmittance of each sample was measured by using a photometer (WGW) at room temperature. Specimens with the thickness of 1 mm were cut from the compression-molded sheet for testing.

Rheological properties

The rheological measurements were performed on a Thermo-Haake mixer. The rotating speed was set at 70 rpm, and the temperature was set at 190°C. Torque values of PMMA and SAN copolymers were listed in Table III.

Scanning electron microscopy

The miscibility of PMMA/SAN blends was investigated by scanning electron microscopy (SEM), model Japan JSM-5600. The sample surface was cut at room temperature with a glass knife until a smooth surface was obtained; thereafter, the samples were etched in glacial acetic acid at room temperature for 2 h to remove PMMA phase and coated with a gold layer for SEM observation.

Transmission electron microscopy

The specimens of PMMA/SAN blends were cut to 60 nm in thickness using a microtome at room temperature, and the samples were not stained for sufficient contrast between two phases. A JEM-2000EX TEM operated at 200 kv was used to study the miscibility of the PMMA/SAN blends.

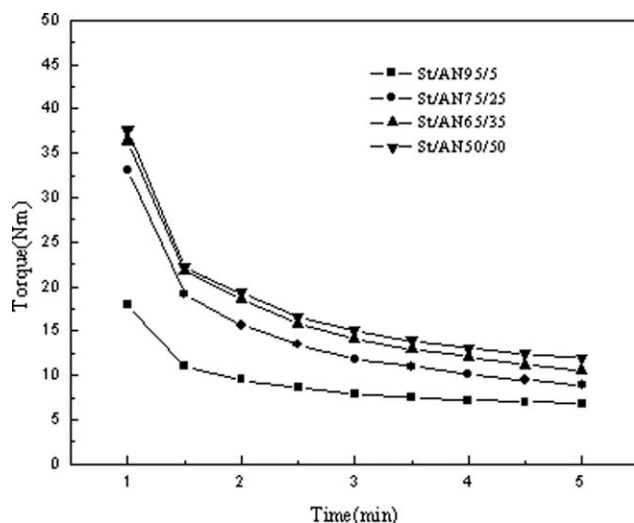


Figure 1 Evolution of torque with time for the PMMA/SAN blends with different AN contents in SAN copolymers.

RESULTS AND DISCUSSION

Rheological properties

Figures 1 and 2 show the evolution of torque and temperature versus time for the PMMA/SAN blends with different AN contents in SAN copolymers. It can be seen from Figure 1, compared to PMMA/SAN25, PMMA/SAN35, and PMMA/SAN50 blends, PMMA/SAN5 blend has the lowest torque value since there is the weak intramolecular interaction in the blend. It was found that the torque values of these blends increase with the increase of AN contents in SAN copolymers for the strong intermolecular interactions. Therefore, PMMA/SAN5, PMMA/SAN35, and PMMA/SAN50 are not miscible system.

Figure 2 illustrated the relationship between the actual temperature in the mixer and mixing time for

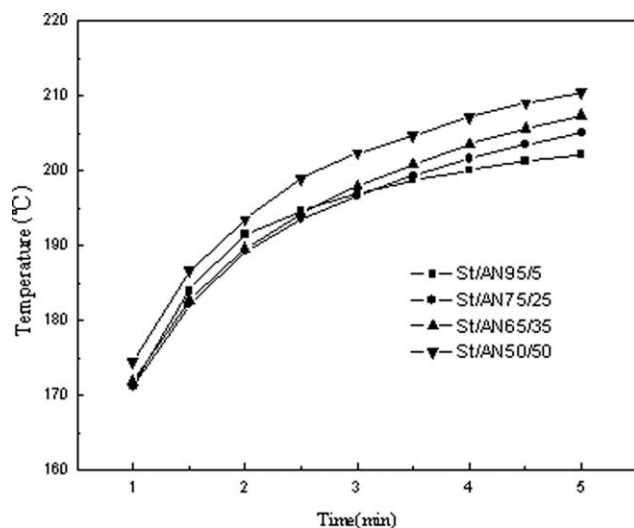


Figure 2 Evolution of temperature with time for the PMMA/SAN blends with different AN contents in SAN copolymers.

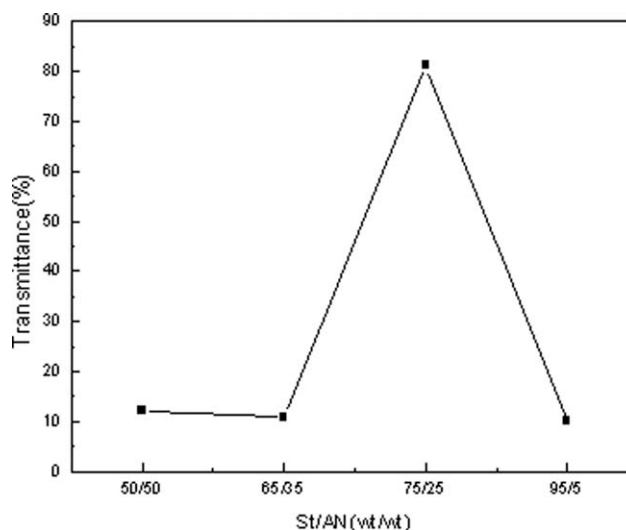


Figure 3 Relationship between the transmittance of the PMMA/SAN blends and AN content in SAN copolymer.

PMMA/SAN blends. The actual temperature in the mixer increases rapidly during a short time interval, and it reaches 202°C for the PMMA/SAN5 blend, which is higher than the setting temperature 190°C due to viscous heating of the polymer. As for the PMMA/SAN25, PMMA/SAN35, and PMMA/SAN50 blends, the temperature in the mixer gets higher. This is due to the viscous heating of highly viscous PMMA/SAN blends.

Determination of the transmittance of the PMMA/SAN blends

Determination of the transmittance of polymer blends is the convenient method for investigating the miscibility. It is well known that a stable homogeneous mixture is transparent, whereas an unstable nonhomogeneous mixture is turbid unless the components of the mixture have identical refractive indexes. If a stable homogeneous mixture, transition from the transparent to the turbid state can be brought about by variations of temperature, press, or composition of the mixture. Figure 3 shows the relationship between the transmittance of the PMMA/SAN blends and AN content in SAN copolymer. It can be seen from Figure 3 that the transmittance of the PMMA/SAN25 blend reaches 81.2%. It is found that the PMMA/SAN25 blend is transparent, which indicated that when AN content in SAN copolymer is 25%, PMMA and SAN are miscible. The miscibility of the blends of PVC/ODMS,²⁸ PAA/PVA,²⁹ and PVC/PHC³⁰ was investigated by determining the transmittance of the blends.

Dynamic mechanical analysis (DMA)

The most commonly used method for investigating the miscibility in polymer-polymer blends or partial

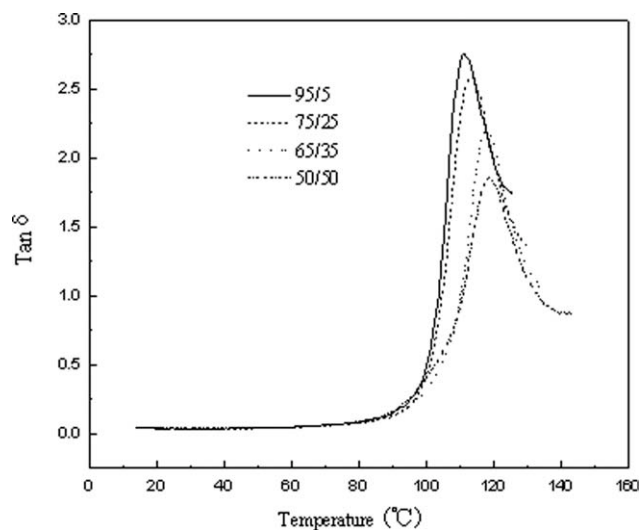
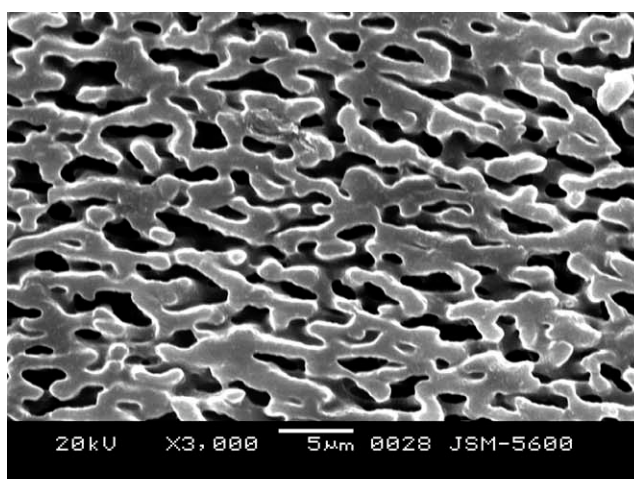
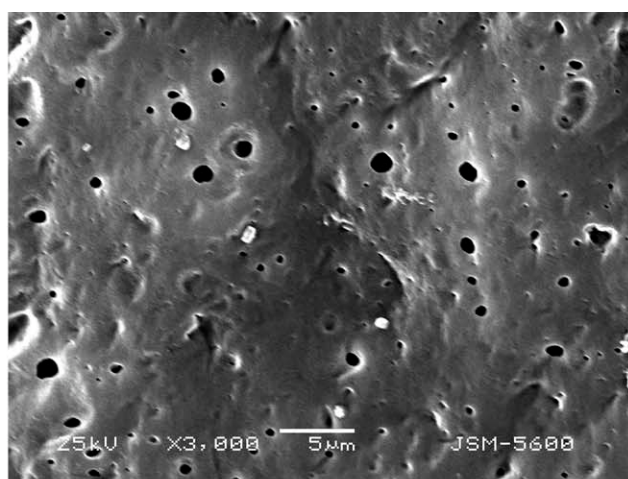


Figure 4 Temperature dependence of loss tangent ($\tan\delta$) for the PMMA/SAN blends.

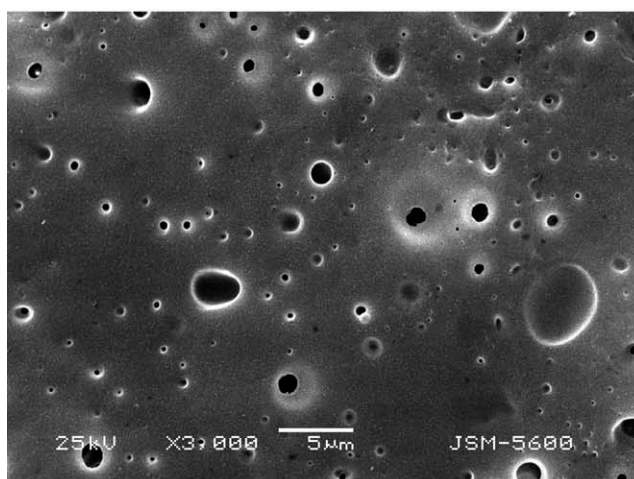
phase mixing in such blends is through determination of the glass transition in the blend versus those constituents. It is well known that if a polymer blend is miscible, there will be a single glass transition between the T_g 's of the components with a sharpness of the transition similar to that of the compositions. Figure 4 illustrates the relationship between $\tan\delta$, the ratio of loss modulus (E'') to storage modulus (E'), and temperature. It can be seen from the plot of $\tan\delta$ versus temperature that two separate transitions between those of the constituents may result, depicting one composition PMMA phase and the other composition SAN phase in PMMA/SAN50 and PMMA/SAN35 blends. It can be also seen that a single or unique transition occurs in PMMA/SAN5 blend, but PMMA and SAN forms two-phase structure. This is because that the transition of PMMA phase covers that of SAN5 for similar transitions. It is found that there is a single transition in



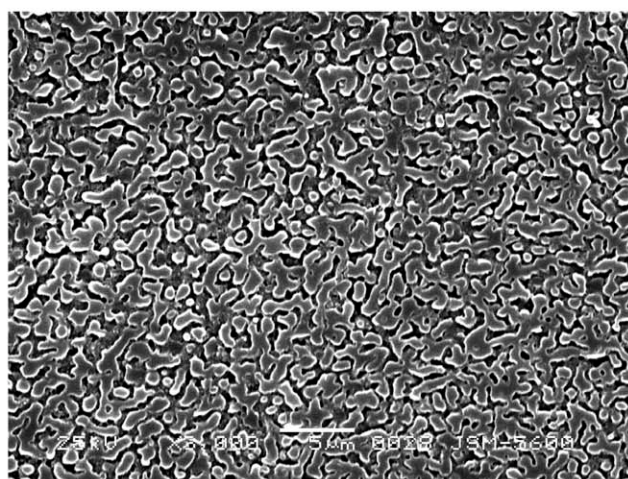
(a)



(b)



(c)



(d)

Figure 5 SEM photographs of the PMMA/SAN blends under 190°C with different ratio of St to AN: (a) 50/50, (b) 65/35, (c) 75/25, and (d) 95/5.

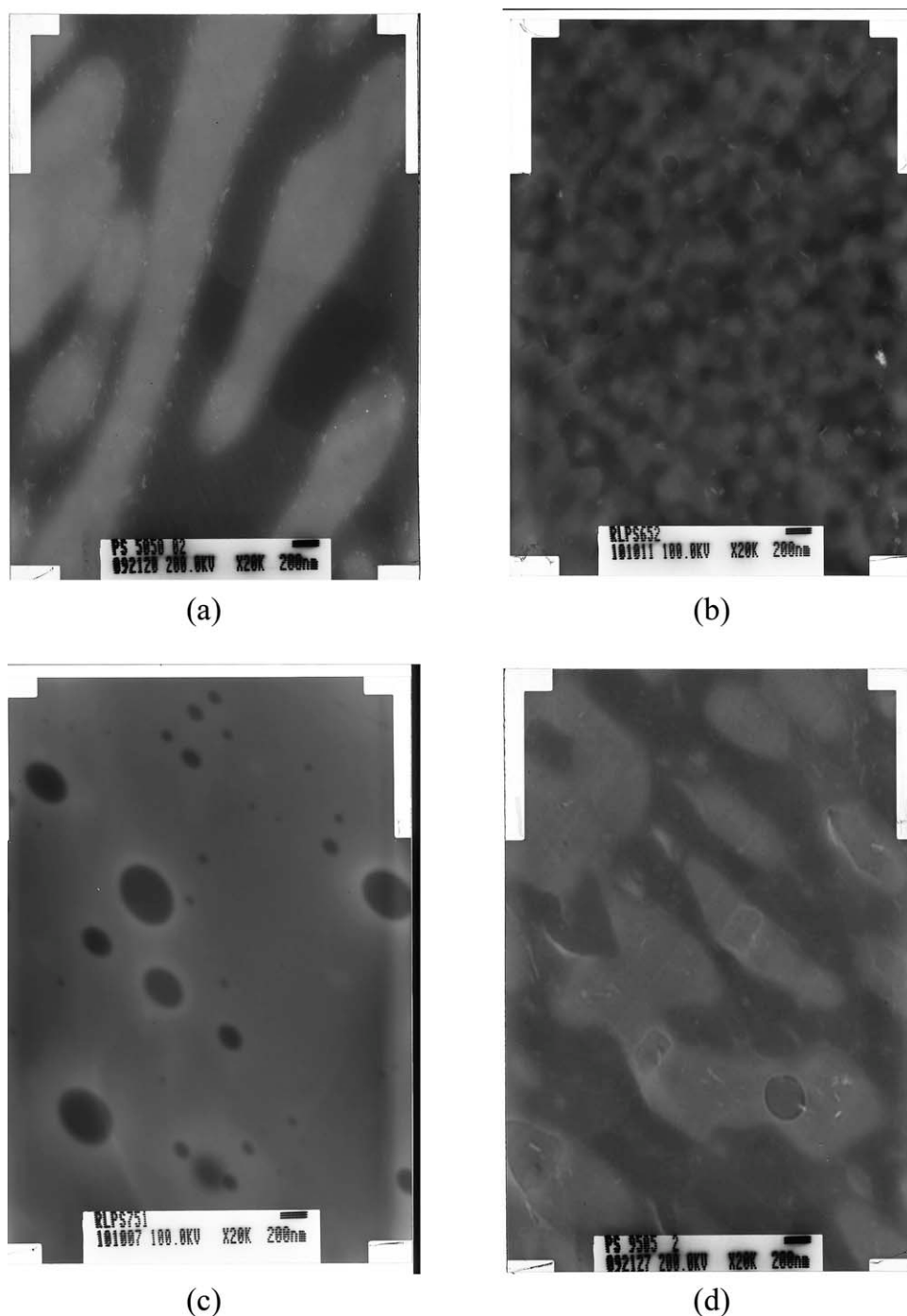


Figure 6 TEM photographs of the PMMA/SAN blends under 190°C with different ratio of St to AN: (a) 50/50, (b) 65/35, (c) 75/25, and (d) 95/5.

PMMA/SAN25 blend, which indicates that PMMA and SAN25 form homogeneous system.

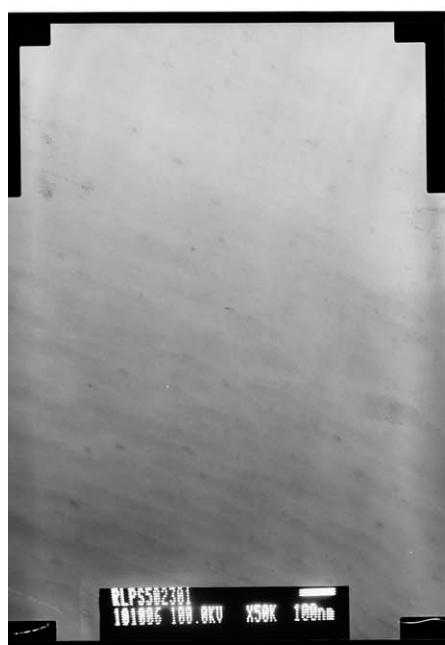
Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to investigate the miscibility of PMMA/SAN blends. In Figure 5, all the specimens were etched with glacial acetic acid for 2 h at room temperature to remove

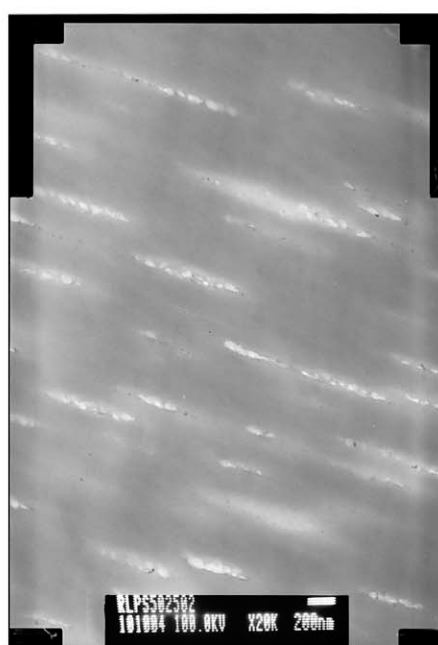
the PMMA phase. Figure 5(a) presents the morphology of the PMMA/SAN50 blend. When PMMA is mixed with SAN50, a co-continuous phase structure of PMMA/SAN50 blend is obtained. In this blend, phase separation is found, which indicates the immiscibility of PMMA and SAN50. Figure 5(b) displays the SEM micrograph of the PMMA/SAN35 blend. It can be seen that in this blend the holes left on the surface is PMMA, indicating that PMMA and SAN35



(a)



(b)



(c)

Figure 7 TEM photographs of the PMMA/SAN blends with different temperature: (a) 190°C, (b) 230°C, and (c) 250°C.

is not miscible system. Different from Figure 5(a,b), with the decrease of the AN contents in SAN copolymers, it is found that, from Figure 5(c), in PMMA/SAN25 blend dispersion is very fine and some miscibility is observed. It will be considered in more detail in next section on the miscibility of PMMA/SAN25 blend. As can be seen from Figure 5(d), there is co-continuous phase structure in the PMMA/SAN5 blend and phase domain size of PMMA/SAN5 blend

is smaller than that of PMMA/SAN50 blend, which indicates PMMA and SAN5 is immiscible.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) has been widely used in polymer-polymer studies. Figure 6 demonstrates TEM micrographs of PMMA/SAN blends with different AN contents in SAN

copolymers. It can be seen from Figure 6(a,d) that the dark areas are the PMMA-rich regions and the bright areas are the SAN-rich regions, indicating that PMMA/SAN50 and PMMA/SAN5 blends form inhomogeneous system. It is found from Figure 6(b) that the PMMA/SAN35 blend has formed the alveolate phase structure and the phase separation has occurred. However, for PMMA/SAN25 blend, a miscible or homogeneous system, from Figure 5(c), was observed.

All the PMMA/SAN blends prepared at different temperatures were also characterized by TEM. As an example, the TEM micrographs of PMMA/SAN25 blends prepared at different temperatures are shown in Figure 7. From Figure 7(a), it is found that the PMMA/SAN25 blend prepared at 190°C exhibits the homogeneous morphology just like that of the PMMA or the SAN copolymer. It can be seen from Figure 7(b) that the PMMA/SAN25 blend prepared at 230°C is miscible system, but phase separations have occurred in local regions. From the Figure 7(c), we can find that the PMMA/SAN25 blend prepared at 250°C has formed continuous region and the phase separations has occurred.

CONCLUSIONS

A set of SAN copolymers with different AN contents were synthesized by emulsion polymerization processes, and then PMMA/SAN blends were prepared by mixing PMMA resin with SAN copolymers. The effect of AN contents in SAN copolymers and temperatures on the miscibility was investigated for blends of PMMA and SAN. The results indicated that when AN contents in SAN copolymers were 5, 35, and 50%, the PMMA/SAN blends formed two phase system, and PMMA was miscible with SAN copolymer containing 25% AN. It was found that for the PMMA/SAN25 blend phase separation took place with the increase of the temperature. The predicted results were in qualitative agreement with the experimental results of this study.

References

1. Aoki, Y. J.; Tannka, T. *Macromolecules* 1999, 32, 8560.
2. Eguiburu, J. L.; Iruin, J. J.; Fernandez-Berridi, M. J.; San Roman, J. *Polymer* 1998, 39, 6891.
3. Wen, G. Y.; Sun, Z. Y.; Shi, T. F.; Yang, J.; Jiang, W.; An, L. J.; Li, B. Y. *Macromolecules* 2001, 34, 6291.
4. Zuo, M.; Peng, M.; Zheng, Q. *Polymer* 2005, 46, 11085.
5. Pathak, J. A.; Colby, R. H.; Kamath, S. Y.; Kumar, S. K.; Stadler, R. *Macromolecules* 1998, 31, 8988.
6. You, J. C.; Shi, T. F.; Liao, Y. G.; Li, X. L.; Su, Z. H. *An, L. J. Polymer* 2008, 49, 4456.
7. Yang, H.; Han, C. D.; Kim, J. K. *Polymer* 1994, 35, 1503.
8. Higashida, N.; Kressler, J.; Inoue, T. *Polymer* 1995, 36, 2761.
9. Kim, E.; Kramer, E. J.; Wu, W. C.; Garrett, P. D. *Polymer* 1994, 35, 5706.
10. Zheng, Q.; Du, M.; Yang, B. B.; Wu, G. *Polymer* 2001, 42, 5743.
11. Wen, G. Y.; Li, X.; Liao, Y. G.; An, L. J. *Polymer* 2003, 44, 4035.
12. Du, M.; Gong, J. H.; Zheng, Q. *Polymer* 2004, 45, 6725.
13. Bernstein, R. E.; Cruz, C. A.; Paul, D. R.; Barlow, J. W. *Macromolecules* 1977, 10, 681.
14. Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* 1983, 16, 753.
15. Fower, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* 1987, 28, 2145.
16. Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* 1987, 28, 957.
17. Naito, K.; Johnson, G. E.; Allara, D. L.; Kei, T. K. *Macromolecules* 1978, 11, 1260.
18. Schafer, R.; Zimmermann, J.; Kressler, J.; Mulhaupt, R. *Polymer* 1997, 38, 3745.
19. Magonov, S. N.; Elings, V.; Papkov, V. S. *Polymer* 1997, 38, 297.
20. McBrierty, V. J.; Douglass, D. C.; Kwei, T. K. *Macromolecules* 1978, 11, 1265.
21. Feng, H.; Ye, C.; Feng, Z. *Polym J* 1996, 28, 661.
22. Hashimoto, T.; Kumaki, J.; Kawai, H. *Macromolecules* 1983, 16, 641.
23. Edel, V. *Macromolecules* 1995, 28, 6219.
24. Kyu, T.; Saldanha, J. M. *Macromolecules* 1988, 21, 1021.
25. Peng, M.; Zheng, Q. *Chinese J Polym Sci* 2000, 18, 565.
26. Song, M.; Hammiche, A.; Pollock, H. M.; Hourston, D. J.; Reading, M. *Polymer* 1995, 36, 3313.
27. Hsu, W. P. *J Appl Polym Sci* 1999, 74, 2894.
28. Lerma, M. S.; Iwamoto, K.; Seno, M. *J Appl Polym Sci* 1987, 33, 625.
29. Park, H. C.; Meertens, R. M.; Mulde, M. H. V. *J Membr Sci* 1994, 90, 265.
30. Nguyen, T. Q.; Essamri, A.; Clement, R. *Makromol Chem* 1987, 188 1973.