Investigation on Particular Morphology of Immiscible Polyamide 12/Polystyrene Blends

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ABSTRACT: In this article, a particular phase morphology of immiscible polyamide 12/polystyrene (PA12/PS) blends prepared via *in situ* anionic ring-opening polymerization of Laurolactam (LL) in the presence of PS was investigated. SEM and FTIR were used to analyze the morphology of the blends. The results showed that PS is dispersed as small droplets in the continuous matrix of PA12 when PS content is less than 5 wt %. When the PS content is higher than 10 wt %, two particular phase morphologies appeared. First, dispersed PS-rich particles with the spherical inclusions of PA12 can be found when PS content is between 10 wt % and 15 wt %. Then, the phase inversion (the phase morphology of the PA12/PS blends changes from the PS dispersed/PA12 matrix to PA12 dispersed/PS matrix system) occurred when PS content is higher than 20 wt %, which is completely different from traditional polymer blends prepared by melt blending. The possible reason for the particular morphology development was illuminated through phase inversion mechanism. Furthermore, the stability of the phase morphologies of the PA12/PS blends was also investigated. SEM showed that the particular morphology is instability, and it will be changed upon annealing at 230°C for 30 min. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2970–2976, 2012

Key words: phase morphology; anionic ring-opening polymerization; phase inversion; polyamide 12; blends

INTRODUCTION

The blending of miscible polymers for production of new tailor made materials at low cost has gained great interest in recent years, as this enables getting better mechanical properties over those of single-component systems. However, simple melt blending of two kinds of immiscible polymers such as polyamide 12 (PA12) and polystyrene (PS), generally results in poor phase morphology.[1] Both PA12 and PS are commodity polymers that possess unique properties individually. Thus, a PA12/PS blend is expected to have commercial potential applications because it could provide a combination of the useful properties of its constituents. Unfortunately, owing to the intrinsically different polarities of PA12 and PS, PA12/PS blends are immiscible and present a two-phase morphology with poor interfacial adhesion and exhibit poor mechanical properties. However, blends between polar and non-polar polymers are of particular interest, as this enables tailoring of important properties such as surface energy and adhesion.[2–5] So far, our studies on the blend of PA12 and PS are mainly focused on its special phase morphology.

As we all know, besides the thermodynamic factor, the final phase morphology can also be controlled by the phase separation kinetic factors, such as temperature, concentration, viscosity change, etc.[6,7] Studies of chemically induced phase separation create possibilities for controlling the final morphology of PA12/PS blends and enable preparation of special morphologies impossible obtained via conventional method such as mixing, hydrolytic polycondensation and so on. As was published, phase separation often occurs upon polymerization of the reactive solvent in solution of polymer/reactive solvent with respect to the incompatibility of most polymers. Lactams, such as Laurolactam (LL), caprolactam (CL), are one special group of reactive solvents, which have strong solvency for PS, PE and so on.[8–11] Furthermore, lactams can be polymerized via anionic ring-opening polymerization, which generally proceeds faster than the step growth polymerization. Alternatively, an *in situ* anionic polymerization technique is an effective way to control morphologies of PA12/PS blends, mainly from the angle of kinetics of phase separation. A series of monomer-casting PA12 *in situ* composites had

been synthesized using LL as reactive solvent.[8–10] The morphologies can be controlled by the dissolution/diffusion of polymers in reactive LL and the kinetics combined with the thermodynamics of reaction of systems.

In this article, a novel method has been developed for the synthesis of PA12/PS blends with particular morphologies. The target of our study is focused on obtaining blends between immiscible PA12 and PS via *in situ* anionic polymerization, starting from a homogeneous mixture of the LL and PS. First, the PS is dissolved in the LL solvent. Second, blends of immiscible PA12/PS are reliably synthesized by *in situ* anionic polymerization of the LL. The most interesting thing during the polymerization is that the secondary phase separation takes place at very low PS content (10 wt %), and the phase inversion occurs when PS content is more than 20 wt %, which is an unusual phenomenon impossible for polymer blends prepared by conventional mechanical blending.

EXPERIMENTAL

Materials

LL was supplied by Degussa A.G. (Germany), and was used as received. *N*-Acetyl caprolactam (ACL) (analytical grade) as an activator was purchased from Aldrich Chemical Company (Germany). Sodium hydride (NaH) as an initiator was purchased from Shanghai Chemical Reagents Company (China), which contained 45 wt % mineral oil. Polystyrene (GPPS-232) was supplied by Shanghai SECCO Petrochemical co., Ltd.

Preparation of PA12/PS blends

A desired amount of PS was dissolved in melted LL monomer at 80°C under nitrogen. The mixture was stirred for 3 h at 140°C, and then a viscous and homogeneous transparent polymer–monomer solution was obtained. Afterwards, the solution was kept under vacuum at 140°C for 20 min to remove traces of water. NaH (0.4 wt %) was added under stirring and vacuumed for about 10 min. The analysis purity ACL (0.94 wt %), as an activator, was then added with stirring. The final mixture was immediately poured into a mold preheated to 170°C, and polymerized in oven at 170°C for 30 min. After polymerization, the products were cooled to room temperature slowly and extracted with boiling alcohol to eliminate the residual monomer for 10 h (the equilibrium conversion was about 93–96 wt %). Finally, PA12/PS samples with various amounts of PS were obtained, which were denoted as S5 (5 wt %), S10 (PS 10 wt %), S15 (PS 15 wt %), S20 (PS 20 wt %), and S25 (PS 25 wt %). The treatment processes of all

compositions were identical to ensure comparability and accuracy of the testing results.

Preparation of PA12 microspheres

The PA12/PS sample (i.e., S25) was shattered and immersed into tetrahydrofuran (THF) for 2 h to dissolve most of the PS. Then a Soxhlet extraction of the power with hot THF was carried out for 10 h to remove the remained PS completely. The powder finally got was dried for 1 h in a hood, and then further dried in a vacuum oven at 80°C for 12 h under a full vacuum. The PA12 microspheres were obtained finally.

Characterization

Scanning electron microscopy

SEM (Sirion200, FEI Company) was used to investigate the morphology of the blends. Before the observation, the samples were held in liquid N_2 and a brittle fracture was performed. The brittle-fractured surfaces of specimens were etched in THF for 8 h at room temperature to dissolve the PS phase. The etched samples were then dried at 80°C under vacuum for 10 h, and the surfaces of fracture specimens were gold-sputtered under vacuum before observation.

Fourier transform infrared spectroscopy

PA12 microspheres (20 mg) was initially ground with 300 mg of KBr for 10 min in an agate mortar, then a further 700 mg of KBr was added and the sample was ground for another 5 min. The mixture was molded into a disc. Pure ground KBr was used to obtain a reference spectrum. The procedure was done in a glove box in which pure nitrogen gas was made to flow. The discs were analyzed by FTIR using a Nicolet AVATAR 360 TT-IR spectrometer, and the spectra were recorded by coadding 100 scans in the wavenumber range from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}. The FTIR spectra were processed by curve-fitting analysis.

Monomer conversion

Monomer conversion was measured by first grinding up the dry polymer in a mill at room temperature and then carrying out a Soxhlet extraction of an accurately weighed (about 10 g) sample with hot alcohol for 24 h. The thimble containing the extracted sample was removed when the extraction was complete, allowed to dry for 1 h in a hood, and then further dried in a vacuum oven at 80°C for 24 h under a full vacuum. The sample was removed from the oven and placed in a desiccator to cool.

Once the sample had cooled to room temperature it was weighed and the percentage conversion calculated using eq. (1).

Percent monomer conversion
$$= [(W_b \times X) - (W_b - W_a)]/(W_b \times X) \times 100 \quad (1)$$

W_b is polymer weight before extraction. W_a is polymer weight after extraction. X is the LL content in the mixture.

RESULTS AND DISCUSSION

Morphology of MCPA6/PS blends

In situ polymerization system during the process of polymerization of reactive solvent, the morphology is determined by many factors, such as thermodynamics, kinetics, polymerization rates, interphase interaction, viscosity characteristics of the components, and so on.[7] In this article, LL is reactive solvent, and PA12/PS samples with different weight ratios of PS are prepared by the *in situ* anionic ring-opening polymerization of LL in the presence of PS. To study the morphology of the composites, a complete view on the phase morphology development of the PA12/PS blends is necessary. Figure 1(a–e) shows the SEM micrographs of S5-S25. And the SEM micrographs of S5, S10, S20, and S25 etched by THF are given in Figure 1(a′,b′,d′,e′), respectively.

In Figure 1(a′), the sample corresponds to that in Figure 1(a) was etched by THF to render the observed morphology as clear as possible. The black domains correspond to the extracted PS phase. It shows that the PS phase is dispersed as small droplets in the continuous matrix of PA12. The size of the droplets obviously increases with increasing amounts of PS, as can be seen in Figure 1(b,b′,c,c′). With PS content increasing from 10 wt % to 15 wt %, besides the particles with larger size, some dispersed PS-rich particles with the spherical inclusions of PA12 can be observed. This phenomenon, dispersed particles with inclusion of the continuous phase matrix, is so-called secondary phase separation.

The secondary phase-separation process may take place in reaction-induced phase separation, which results in dispersed particles with inclusion of the continuous phase matrix.[12] It usually occurs when the blend first pass into the metastable region and then into the unstable region such that some nucleation and growth precedes spinodal decomposition, or the composition of the coexisting phases changes due to continuous polymerization of the reactive monomers such that they themselves become unstable.[13] In our study, PS can be completely dissolved in melted LL. Before the LL anionic ring-opening

polymerization, the mixture of PS and LL is a viscous and homogeneous transparent polymer–monomer solution. However, PS has a poor miscibility with PA12, so the phase separates in the early stage of the polymerization. Just as the same time, the PS-rich phase forms due to the relatively low viscosity of the composites. Then, the further phase separation occurs just in the separated phases. Because of the quick polymerization rate of LL, the diffusion between PA12-rich phase and PS-rich phase would be hindered by the rapid increase of viscosity of the system. As a consequence, the individual PS-rich phase with the spherical inclusions of PA12 appears, and the phase separation becomes more obvious with increasing PS content in the composites.

Once the PS content is higher than 20 wt %, the blend morphology shows a significant change. The phase morphology of the PA12/PS blends changes from the PS dispersed/PA12 matrix to PA12 dispersed/PS matrix system. This phenomenon is so-called phase inversion. SEM micrographs of the blends with 20 wt % and 25 wt % PS are given in Figure 1(d,d′,e,e′). As shown in Figure 1, the PA12 phase is nearly spherical, and the PS component exists mainly in the gap of PA12 spheres, though the PS might not entirely enwrap the PA12 particles. And the diameter and size distribution of the PA12 spheres changes with the composition of the blends. In Figure 1(d,d′), the size of PA12 microspheres is about several to 80 μm. The particle size is poorly uniform, and some strange spheres, such as a bigger sphere joined with one or two little spheres, can be even observed. The above phenomena prove that the PS exists in the gap through the dispersed PA12 spheres, but it does not entirely enwrap the PA12 particles. However, with increasing PS content up to 25 wt %, phase inversion completes, and the PA12 particles are almost completely isolated by the PS matrix. The PA12 spheres become much smaller (no bigger than 50 μm in diameter) and more uniform, as can be seen in Figure 1(e,e′).

To study the possible formation mechanism of the particular phase inversion morphology, the hydrolytic polycondensation reaction has also been adopted to polymerize LL in the presence of PS for preparation of PA12/PS blends with 25 wt % PS. The other conditions are exactly the same as those in the anionic ring-opening polymerization. The SEM result (Fig. 2) shows that the PS is dispersed as the minor phase in the PA12 matrix, which is obviously different to that of PA12/PS blends with the same PS content obtained from *in situ* anionic ring-opening polymerization of LL [Fig. 1(e,e′)]. The same investigations had also been discussed in our previous researches.[14–16] We speculate that the *in situ* anionic ring-opening technique of LL plays a pivotal role in determining the morphology
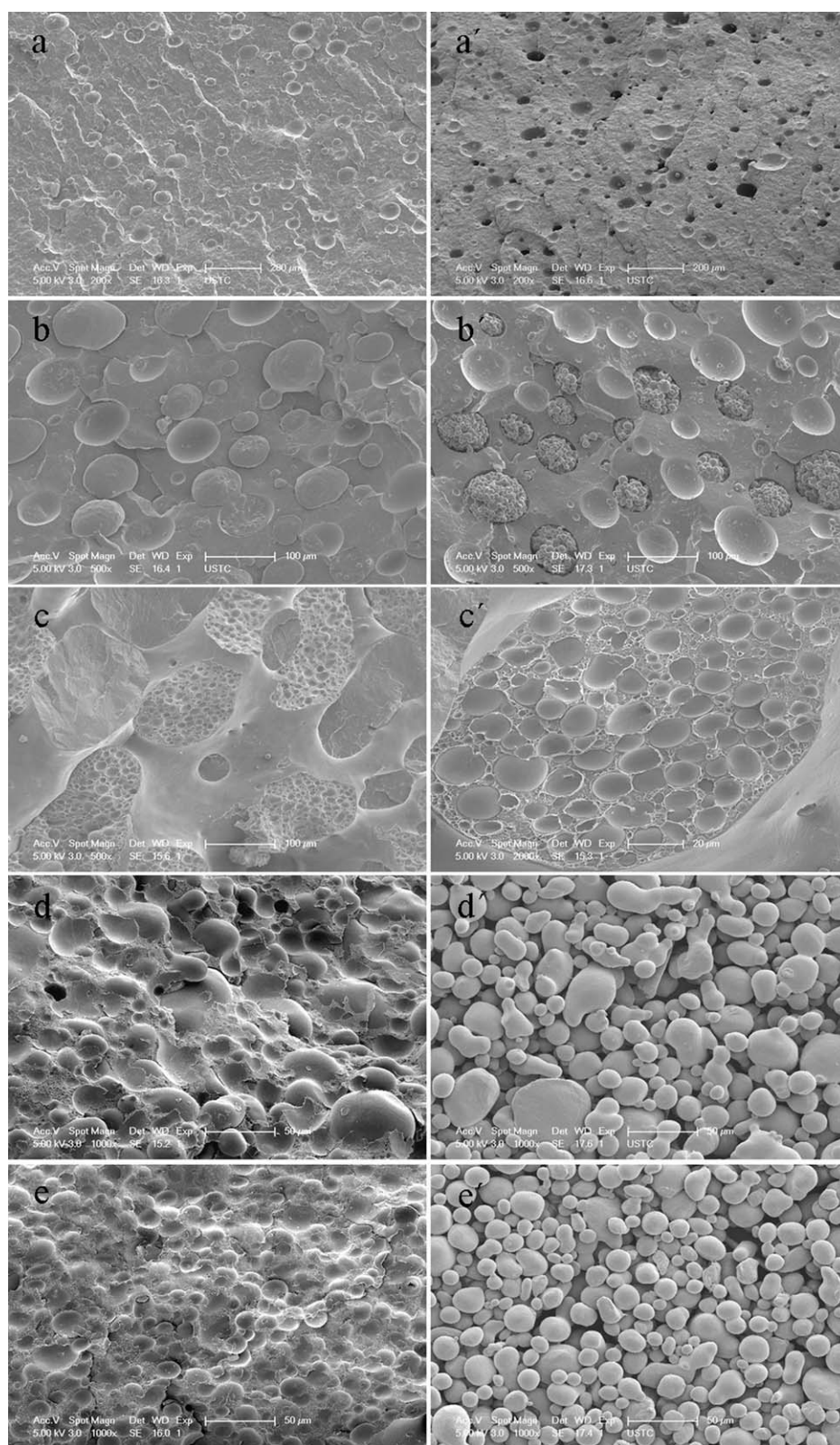
Figure 1 SEM micrographs of PA12/PS blends: (a and a′) S5, (b and b′) S10, (c and c′) S15, (d and d′) S20, (e and e′) S25. a′, b′, d′, and e′ represent PA12/PS blends etched with THF.

development of the PA12/PS blends. First, compared to other polymerization techniques, such as classical hydrolytic polycondensation (total conver-

sion needs about several hours depending on the conditions used), anionic ring-opening polymerization is a much faster material generation process
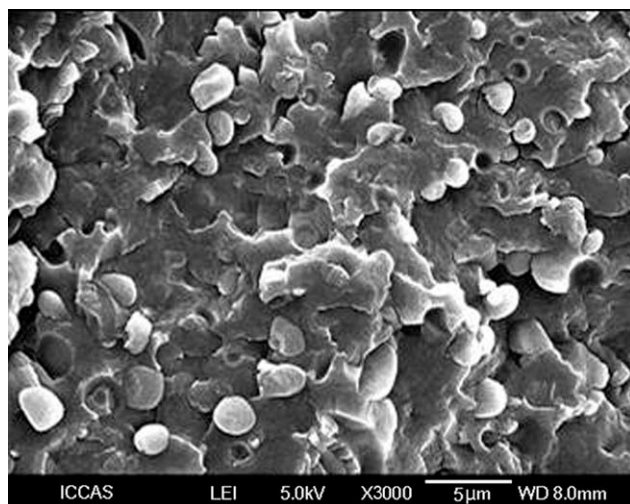
Figure 2 SEM micrograph of a 75/25 PA12/PS blend obtained by the hydrolytic polycondensation of LL in the presence of PS.

(total conversion needs only a few minutes). Second, anionic polymerization can be operated at a temperature comparatively lower than the melt point of PA12 while higher than the T_g of PS. Before the anionic polymerization of LL, the LL molecules are dispersed among the interspace of the PS molecular chains. During the anionic polymerization of LL, the PA12 contracts into solid-state spheres during the faster polymerization of LL and is dispersed among the softened PS once the PS content is high enough to envelop the PA12. So, the PA12 is dispersed as spherical particles among the PS continuous phase with the PS content higher than 20 wt %.

FTIR analysis of PA12 microspheres

Just as mentioned above, once the PS content is higher than 20 wt %, secondary phase separation

disappears, and phase inversion occurs. The phase morphology of the PA12/PS blends changes from the PS dispersed/PA12 matrix to PA12 dispersed/ PS matrix system. We speculate that the spherical droplets dispersed in the continuous PS matrix are PA12 spheres. To prove this speculation, the spheres in the PA12/PS blends with 25 wt % PS had been collected. The obtained spheres are measured by FTIR spectroscopy (Fig. 3).

FTIR spectra of polyamide are usually recorded in two regions: 4000–2800 cm^{-1}, where the characteristic bands of OH, NH and CH are to be found,[17,18] and 1800–1100 cm^{-1}, where the absorption characteristic of the amide group is located.[19] The broad band centered about 3300 cm^{-1} is a complex band of the NH group of polyamide.[20] The stretching vibration of the NH group may split into bands at 3444 cm^{-1} and 3310 cm^{-1}, which are assigned to free and hydrogen-bonded NH stretching modes, respectively.[21,22] The CH stretching mode of amide is located at 2990–2850 cm^{-1}.[23,24] The peaks at 1640 cm^{-1} and 1550 cm^{-1} correspond to the N—C=O and C—N—H vibrations, respectively, which are usually identified as amide I and amide II modes in secondary amides.[21] In comparison to pure PS, the spheres shows only typical polyamide peaks in Figure 3, and the peaks at 1601 cm^{-1} and 1493 cm^{-1} corresponding to the aromatic C=C of PS, are not found in the spectra of microspheres. So, we speculate that the spherical droplets dispersed in the continuous matrix are PA12.

Stability of the morphology during annealing

The stability of the phase morphologies during annealing has also been investigated. The PA12/PS blends were annealed at 230°C (higher than PA12 melt point) for 30 min under vacuum. For the blends
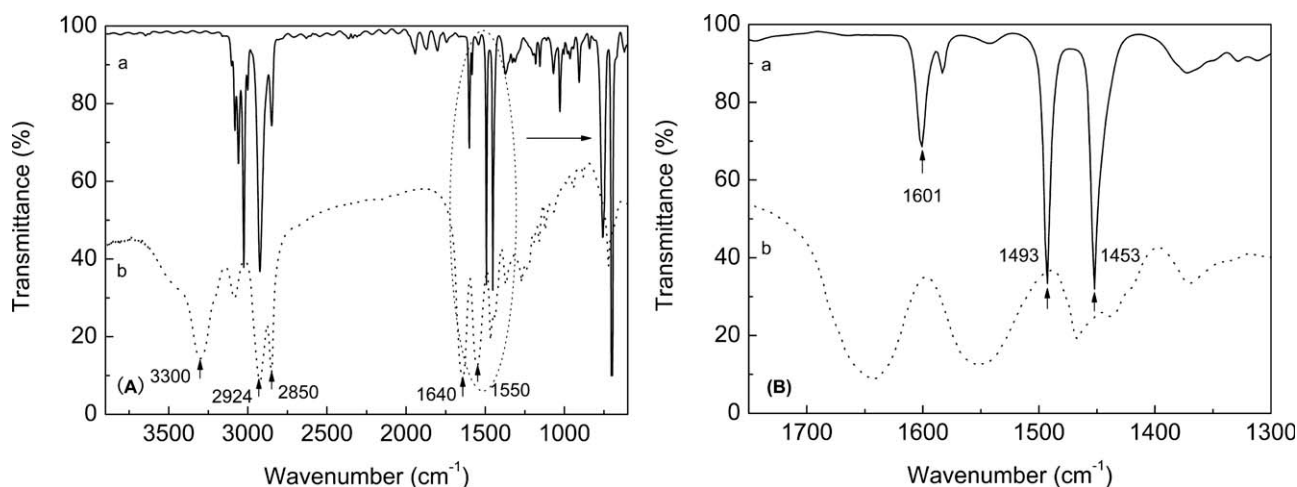

Figure 3 FTIR spectra of (a) pure PS and (b) microspheres prepared after the dissolution of the PS phase from the PA12/PS blend: S25. (A) 600–4000 cm^{-1} and (B) 1300–1800 cm^{-1}.
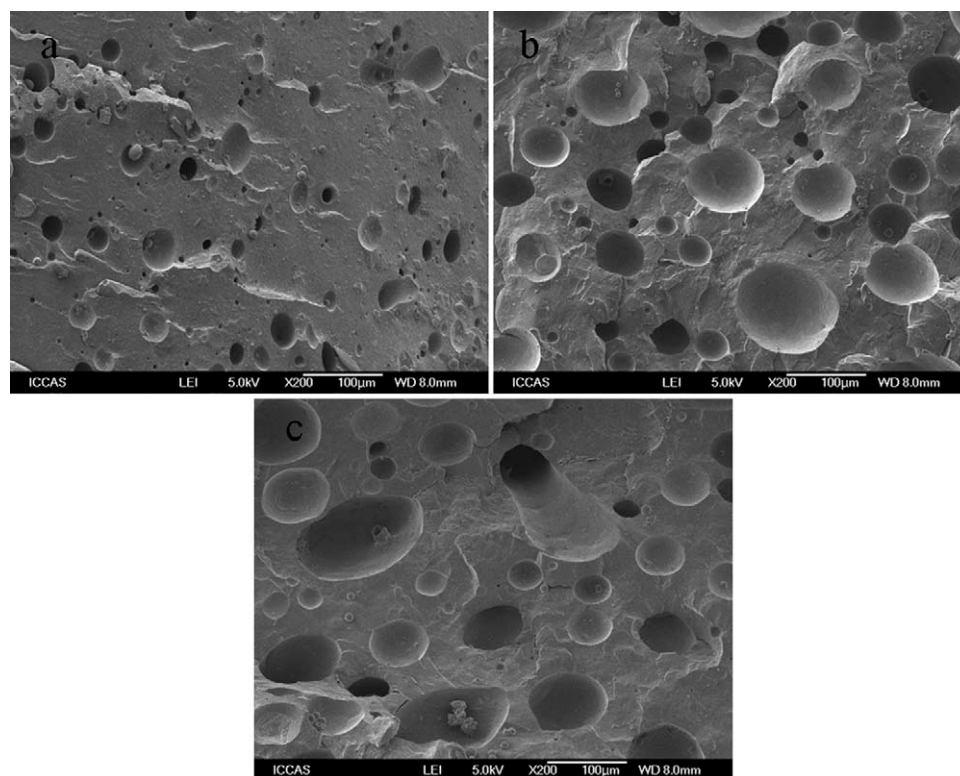
Figure 4   SEM micrographs of PA12/PS blends after annealing for 30 min at 230°C: (a) S10, (b) S20, and (c) S25.

with 10 wt % PS, the secondary phase separation morphology and the dispersed PS-rich particles with the spherical inclusions of PA12 disappears. The size of the PS dispersed particles obviously decreases. For the annealed PA12/PS blends with 20 wt %, 25 wt % PS, the initial phase inversion morphology is broken-up and droplet-matrix morphology has developed, in which PS particles with sizes of tens of micrometers are dispersed in the PA12 continuous phase [Fig. 4(b,c)]. The results presented above show that the morphology of PA6/PS blends is not stable to thermal treatment.

The instability of the PA12/PS blends can be attributed to the poor miscibility between PS and PA12, and the superiorities of the LL anionic polymerization. Compared to the classical hydrolytic polymerization, the faster reaction speed (total conversion needs only a few minutes) and the lower reaction temperature (lower than T_m of PA12 but higher than T_g of PS) of the LL anionic polymerization hinders the phase separation of immiscible PA12/PS blends, and favors the preservation of the original state of the PS/LL mixture. So, their morphologies are non-equilibrium intermediate structures. Once the blends are annealed for enough time at higher temperature than PA12 melt point, their phase morphologies will be destroyed and change toward a state closer to the thermodynamic equilibrium. That is why these particular morphologies, secondary phase separation and phase inversion,

can be observed in the anionic ring-opening polymerization but not in the traditional hydrolytic polycondensation reaction of the polyamides.

CONCLUSION

In summary, a series of PA12/PS blends were synthesized by a facile approach. SEM revealed that the particular phase morphology of the composites could be manipulated by varying the content of PS. PS is dispersed as small droplets in a continuous matrix of PA12 when it's content less than 5 wt %. Between 10 wt % and 15 wt %, the size of the droplets obviously increases with increasing PS content, and dispersed PS-rich particles with the spherical inclusions of PA12 can be observed. Beyond 20 wt %, phase inversion occurs, and the phase morphology of the PA12/PS blends changes from the PS dispersed/PA12 matrix to PA12 dispersed/PS matrix system.

The particular phase morphology development of the immiscible PA12/PS blends can be ascribed to the great superiority of the LL anionic ring-opening polymerization. First, LL anionic polymerization is a faster PA12 generation process (total conversion within only a few minutes). Second, LL anionic polymerization is operated at comparatively lower temperatures (lower than the melt point of PA12 while higher than the T_g of PS). For the immiscible

PA12/PS blends, such particular morphology is instability, and it will be changed upon annealing at 230°C (higher than PA12 melt point) for 30 min.

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