Morphology and Thermal Behavior of MCPA6/SAN Blends Prepared by Anionic Ring-Opening Polymerization of ε-Caprolactam

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ABSTRACT: In this article, a series of blends of monomer casting polyamide 6 and styrene-co-acrylonitrile (MCPA6/SAN) were prepared by in situ anionic ring-opening polymerization of ε-caprolactam. Their morphology and thermal behaviors were investigated by means of scanning electron microscope, differential scanning calorimeter, and wide-angle X-ray diffraction (WAXD), respectively. The SAN phase had much finer domain in MCPA6/SAN than that in the PA6/SAN blends prepared by melt blending of PA6 and SAN. All the melting and crystallization parameters of MCPA6/SAN blends decreased gradually with the increase of SAN content, while the melting temperature was almost unchanged. These results were due to the hydrolysis reaction of SAN that occurred during the anionic polymerization of ε-caprolactam. In addition, WAXD results showed that only α crystal forms existed in the MCPA6/SAN blends. In addition, the mechanical property of MCPA6 was improved obviously by incorporating a certain amount of SAN. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1357–1363, 2006

Key words: monomer casting polyamide 6; styrene–acrylonitrile; anionic ring-opening polymerization; morphology; crystallization properties

INTRODUCTION

In the recent decades, a great number of literatures existed related to modification of polyamide 6. The blend components covered various polymers, among which styrenic copolymers, such as acrylonitrile–butadiene–styrene (ABS), SAN, hydrogenated styrene–butadiene–styrene, have been widely investigated because of the significant commercial interest, especially ABS and SAN.[1–13]

Because of thermodynamical immiscibility, the polyamide-containing binary blends usually exhibited poor phase dispersion and interfacial adhesion, which in turn resulted in unsatisfactory mechanical properties. Therefore, there were extensive interests in improving their compatibility. One of the preferable routes was reactive compatibilization, in which graft or block copolymers were formed in situ during melt processing in terms of appropriate reactive functionalities. It had emerged as an effective way of solving the problem associated with incompatible polymer mixtures.[14]

Jafari et al. studied the effects of added styrene–acrylonitrile–maleic anhydride (SANMA) on the thermal behavior and morphology of multicomponent blends based on PA6, PA6/SAN, and PA6/ABS.[15,16] Paul and coworkers used imidized acrylic polymers or SANMA terpolymer as a compatibilizer for PA6/ABS and PA6/SAN blends, respectively, and studied that the phase morphology and phase inversion behavior cover the complete range of compositions.[4–10] Liu et al.[11] converted the nitrile groups of the SAN into oxazoline groups by condensation reaction with aminoethanol, both in a Brabender batch mixer and in a twin-screw extruder, and the morphological studies indicated that such modified SAN copolymers could be used as compatibilizers for PA/SAN and PA/ABS blends. Ohishi and Nishi[12] investigated the phase morphology and the compatibilization mechanism of PA-6/ABS blends compatibilized with SAN and polyarylate (PAr) block copolymer (SAN–PAr) and showed how effective the SAN–PAr block copolymer was on their impact energy absorption control. Cho et al.[13] reported the effects of reactive reinforced interface on the morphology and tensile properties of amorphous polyamide and SAN blend have been investigated using SANMA copolymer as a reactive compatibilizer.
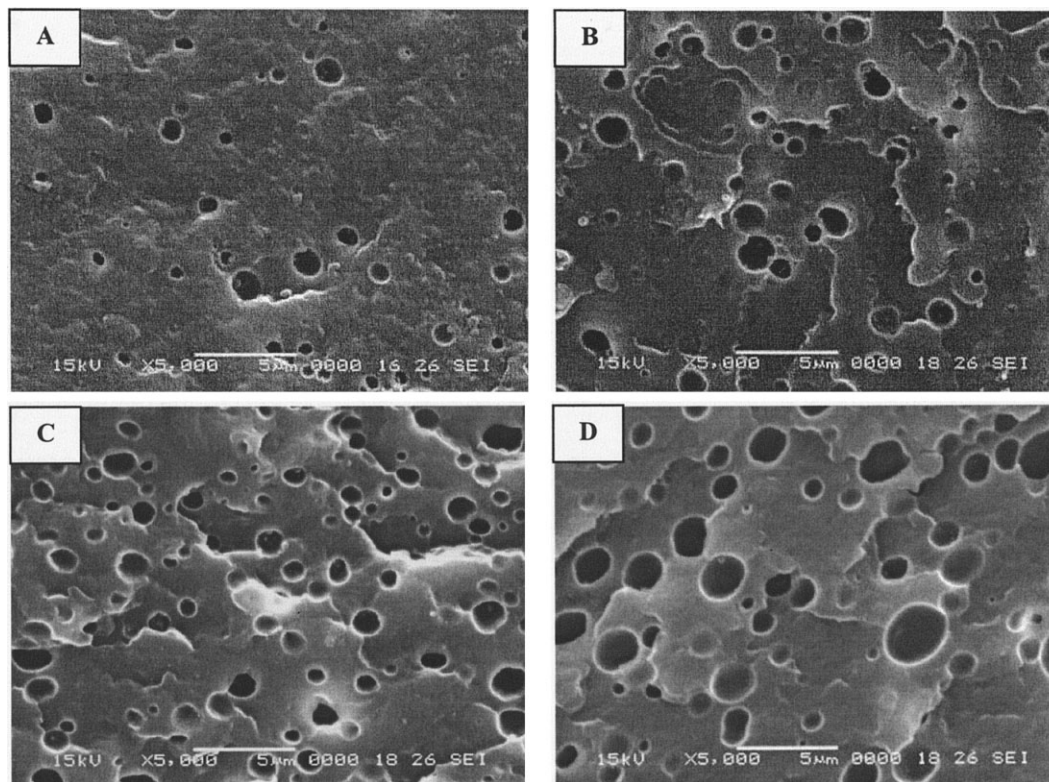

Figure 1 SEM micrograph of the fractured surface of the PA6/SAN blends containing different SAN content (at magnifications of ×5000). A: 2.5% SAN; B: 5% SAN; C: 10% SAN; D: 15% SAN.

In addition, *in situ* polymerization was another effective way to control morphologies of polymer blends to improve the dispersion. In this method, much attention had mainly focused on rubber- or thermoplastic-modified thermoset polymer, e.g., epoxy resins/thermoplastics systems.[17–20] It had been shown that the blend morphologies could be controlled by both dissolution/diffusion of thermoplastics in the polymerizable monomer and thermodynamics combined with reaction kinetics.[21]

In our laboratory, a novel approach for improving toughness of PA 6 had been explored.[22] The approach was that another polyamide, i.e., polyamide 66 (PA66), was used to toughen MCPA6. By *in situ* anionic polymerization of ε-caprolactam with PA66 dissolved in it, a small content of PA66 could dramatically improve the toughness of MCPA6/PA66 blends. According to this way, we attempted to add the SAN content to MCPA6. The purpose of this study was to explore the phase morphology and the thermal behavior of MCPA6/SAN blends prepared by *in situ* anionic ring-opening polymerization. The two-phase nature of ABS materials plus their high melt viscosity/elasticity complicated the morphological and the thermal behavioral study of MCPA6/ABS blends.[7] Thus, the MCPA6/SAN blends were useful for the better understanding of the morphology development and thermal behavior. It was of particular interest to show that the

reactive compatibility between MCPA6 and SAN by the possible side reaction of SAN content occurred under alkaline condition in the anionic ring-opening polymerization of ε-caprolactam. Both the reactive compatibility and the polymerization process were carried out simultaneously. In addition, polyamide 6 was directly melt-blended with SAN copolymer according to the same composition as MCPA6/SAN, which was designated as PA6/SAN.

EXPERIMENTAL

Materials

Styrene–acrylonitrile copolymer (SAN, AS-127H) was supplied by Chimei Corp. (Taiwan, Republic of China), and it contains 34 wt % acrylonitrile. PA6 (YH-600) was provided by Baling Shihua Chemical and Synthetic Fiber Co., Ltd (Yueyang, Hunan, People's Republic of China). Prior to each processing step, all polyamide-containing materials were dried in a vacuum oven for at least 24 h at 80°C to remove absorbed water. ε-Caprolactam was obtained from Joint Stock Company, Republic of Belarus. Sodium hydroxide (NaOH) and 2,4-toluene diisocyanate (TDI) (analysis purity) used in this work were purchased from Shanghai Chemical Reagents Company without further treatment.
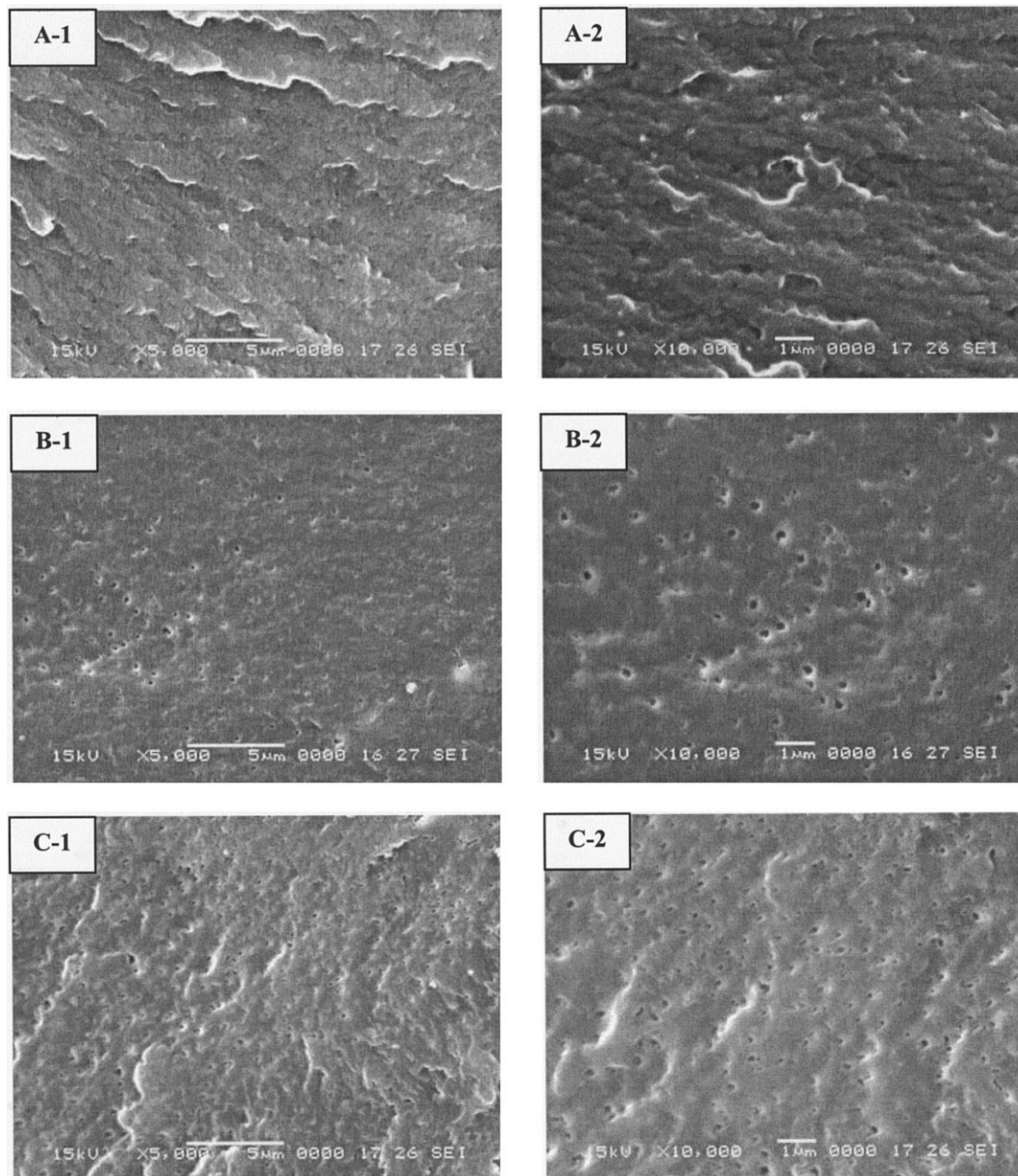
Figure 2 SEM micrograph of the fractured surface of the MCPA6/SAN blends containing different SAN content (at magnifications of ×5000 and ×10,000). A: 2.5% SAN; B: 10% SAN; C: 15% SAN.

Preparation of MCPA6/SAN and PA6/SAN blends

SAN was first dissolved in ε-caprolactam monomer at 170°C under nitrogen until a homogeneous transparent solution was obtained. The resulting mixture was vacuumed at 170°C for 20 min to remove water, followed by the addition of 1.2 wt % NaOH under stirring. Afterwards, vacuum was kept for another 20 min and then 1.2 wt % TDI was added. Immediately, the mixture was poured into a mold preheated at 180°C, polymerized in the oven at 180°C for 30 min, and subsequently cooled at 35°C. After being extracted for 5 h with boiling water to eliminate the residual monomer, the MCPA6/SAN blends were dried in a vacuum oven for 24 h at 80°C, then directly carved into standard testing specimens according to ASTM.

For comparison, another series of PA6/SAN blends were prepared by melt extrusion in a corotating twin-screw extruder (Φ = 35 mm, SHJ-30) at 240 rpm. The barrel temperatures are 230–250°C. The pellets were dried in a vacuum oven for 24 h at 80°C and then injection molded into standard Izod impact specimens in an injection-molding machine (SZ-160/80 NB) at 230°C.

Measurement

The MCPA6/SAN blends were directly carved into standard testing specimens according to ASTM. The Izod notched impact strength was measured according to ASTM D 256, using an IZOD machine Model
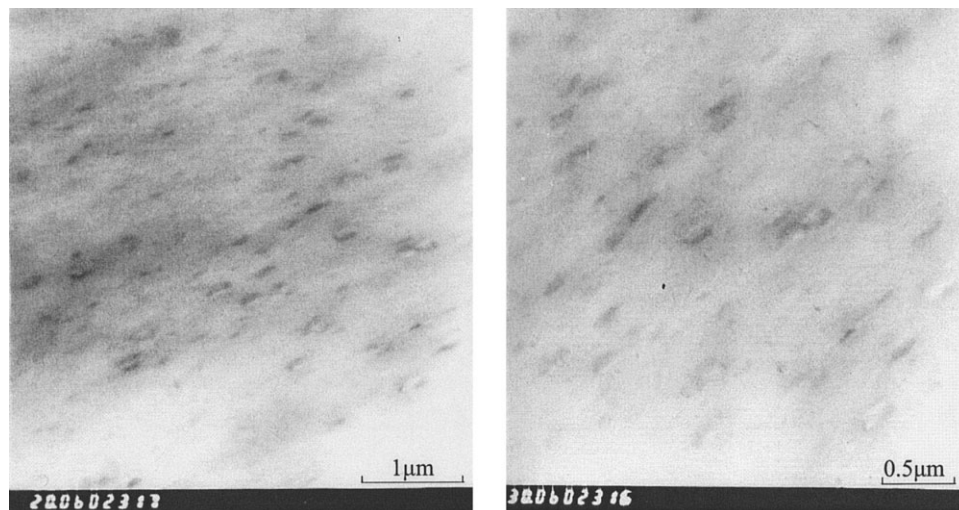
Figure 3 TEM photomicrographs showing the morphology of 100/10 MCPA6/SAN blends (at magnifications of ×20,000 and ×30,000).

CSI-137D by the pendulum method at 23°C. The tensile tests were performed on an Instron machine series 1122 according to ASTM D 638 at crosshead speed of 50 mm/min for the type of specimen I. The test results reported are the average values of at least five specimens tested in each case to obtain a reliable value.

The cryo-fractured surface of samples in liquid nitrogen was etched in tetrahydrofuran (THF) for 24 h at ambient temperature to remove SAN domains, followed by sputtering with gold prior to scanning electron microscope (SEM, JSM-6360LV, JEOL) examinations. In addition, the morphology of selected blends was examined by transmission electron microscopy (TEM). The samples were ultramicrotomed at −80°C and stained with a 0.2% ruthenium tetroxide for a period of 40 min. TEM imaging was carried out on a HITACHIH 600 microscope operating at an accelerating voltage of 75 keV.

After extracted in THF for 72 h, the MCPA6/SAN blends were recovered directly by the evaporation of the solvent. Fourier transform infrared spectroscopy in its attenuated total reflectance mode (ATR-FTIR) was recorded with a Nicolet AVATAR 360 apparatus. The scan time was 32 scans with a resolution of 4 cm^{-1}.

Differential scanning calorimeter (DSC) measurements were carried out on a NETZSCH DSC 200 PC under nitrogen atmosphere at a heating/cooling rate of 10°C/min. The samples were first heated to 250°C and maintained for 2 min to erase any previous thermal history. The crystallization and melting thermograms were taken from the subsequent cooling and the second heating cycles.

The wide-angle X-ray diffraction (WAXD) was performed on a X-ray diffraction analyzer (Rigaku D/Max-III, Japan) equipped with a rotating Cu anode

generator system using Cu Kα1 (λ = 1.540 Å) radiation. The diffraction angles (2θ) were from 5° to 50°. The data were accumulated for 6 s at angular intervals of 2θ = 0.1°.

RESULTS AND DISCUSSION

SEM analysis

To make the dispersed domain clearly visible, the SAN content was selectively etched with THF. Figures [1(A–D)] showed the etched SEM micrographs of PA6/SAN blends with different SAN content, respectively. As expected, the PA6/SAN blend exhibited a
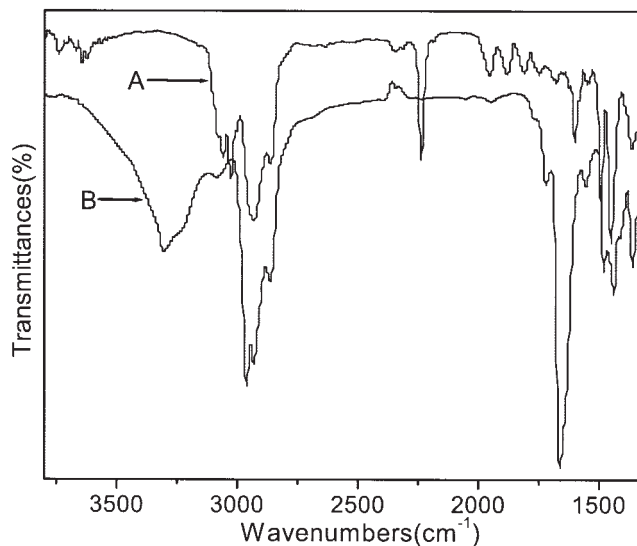

Figure 4 FTIR spectra of SAN in different blends. A: PA6/SAN; B: MCPA6/SAN.
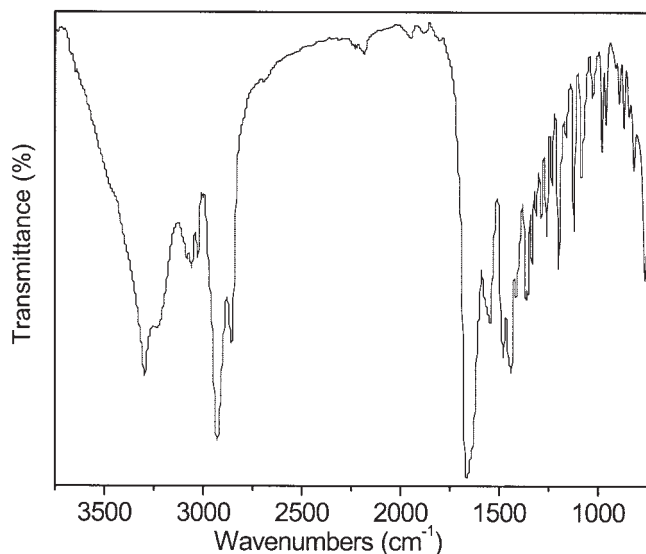
Figure 5 FTIR spectra of the products after hydrolysis in ε-caprolactam and purification.

3 clearly demonstrate that the coalescence of SAN domains was prevented efficiently. The above observation suggested that a finer dispersion of the SAN phase in the matrix be achieved in terms of *in situ* anionic ring-opening polymerization of ε-caprolactam.

According to our knowledge, the improved dispersion might be attributed to the following two factors in the MCPA6/SAN system. First, it was expected that phase separation would be impeded effectively, because of high rate of anionic ring-opening polymerization that usually fulfilled within a few minutes. Second, the hydrolysis reaction occurred for CN groups of SAN under sodium hydroxide solution. The SAN hydrolysis resulted in similar structures, such as amide, amidine, glutarimide, etc.[23–25] As a result, the forming groups might improve the compatibility between MCPA6 and SAN.

FTIR analysis

To confirm the above hydrolysis reaction, the SAN component in the above blends was first extracted by THF. After evaporating the THF solvent, the product was analyzed by means of ATR-FTIR. Figure 4 shows the infrared spectra of both PA6/SAN and MCPA6/SAN blends, respectively. In the PA6/SAN blend, the vibration peak of CN group at 2237 cm^{-1} could be clearly observed, whereas for the MCPA6/SAN blend, no peak was observed at the corresponding wavenumber. However, the two additional peaks at 3300 and 1650 cm^{-1} occurred, which corresponded to the amide group.[26] That was to say, the hydrolytic reaction of SAN did occur under alkaline condition, and the resulting groups, similar to those of the MCPA6 matrix, might improve the compatibility of MCPA6/SAN blends and the dispersion of SAN. To further confirm the side reaction, the dried SAN was first dissolved in ε-caprolactam at 170°C, after the ε-caprolactam monomer was vacuumed at that temperature

distinctly two-phase structure because of their poor compatibility. The domain size increased from 1–1.5 to 3 μm in diameter with the addition of SAN content up to 15%. This might be attributed to coalescence of SAN domains at higher concentration.

However, compared with PA6/SAN blends, a marked difference in the morphology could be observed for MCPA6/SAN blends. At a low SAN content [Fig. 2(A)], the domain size of SAN was too small to be almost observed at the present magnification. Although the size of dispersed phase increased with the addition of SAN, similar to the PA6/SAN blends, the diameter of dispersed particles was about 200 nm even at SAN content of 15%; the size distribution was more uniform. The TEM micrograph (Fig. 3) also shows the good dispersion of SAN dispersed phase in MCPA6 matrix. The average SAN particle size is as small as 150 nm in accord with the SEM results. Figure
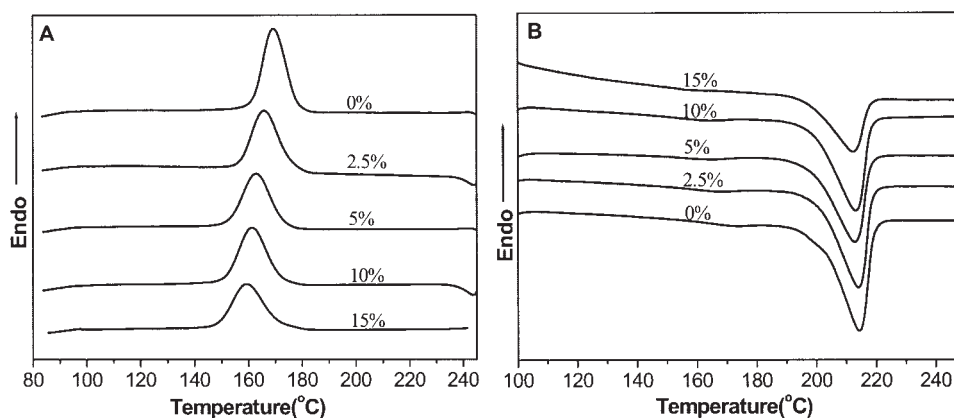

Figure 6 Thermograms of MCPA/SAN with various amounts SAN. A: cooling; B: heating.

TABLE I
Melting and Crystallization Parameters for MCPA6/SAN Blends

MCPA/SAN (w/w)	Heating (2nd)			Cooling		
	T_m (°C)	ΔH_m (J/g PA6)	X_{DSC} (%)	ΔH_c (J/g PA6)	T_c (°C)	ΔT_c (K)
100/0	214.3	−55.86	29.00	64.73	169.4	44.9
100/2.5	213.7	−50.76	26.72	55.68	165.9	47.8
100/5.0	212.8	−47.70	25.11	51.70	163.0	49.8
100/10	213.0	−46.30	24.53	57.11	161.3	51.9
100/15	212.3	−45.58	23.99	48.92	159.2	53.1

for 30 min, the resulting mixture was dissociated at 180°C for 300 min in order that the dissociation reaction of SAN was fulfilled to a greater extent. Water was used to scour off the residual ε-caprolactam monomers, and then the precipitate was dried in a vacuum oven at 100°C. Figure 5 is the IR spectra of the precipitate products. There is no obvious peak in about 2237 cm^{-1}, and it is said that the SAN degradation did occur in our condition. The peaks at 1650 and 1550 cm^{-1}was the characteristic absorbency of the carbonyl group existing in ε-caprolactam, which showed the reaction between SAN and CL.

DSC analysis

Figures 6(A,B) show the cooling and the second heating DSC scans of various MCPA6 blends. The melting and crystallization parameters for pure MCPA6 and MCPA6/SAN blends were summarized in Table I. As indicated from Figure 6 and Table I, ΔH_m, ΔH_c, and T_c decreased gradually in MCPA6/SAN blends, but the degree of super cooling ($\Delta T_c = T_m - T_c$) values showed the opposite trend. Additionally, the melting temperature (T_m) of MCPA6 portion for the MCPA6/SAN blends was almost independent of blend. Such above-mentioned results indicated that the SAN and/or the hydrolyzed SAN tended to interfere with the crystallization of the MCPA6 in various blends because of its fine dispersion and the hydrolysis of the SAN. But the SAN content had little effect on the crystalline structure. However, Jafari et al.[15] found that all the PA6/SAN melt blends showed a significant increase in nucleation ability, crystalline degree, and crystallization rate of PA6 because of the addition of SAN, and SAN played a more major role in controlling the crystallization behavior of PA6.

WAXD analysis

WAXD spectra of MCPA6 and its blends with SAN are shown in Figure 7. It could be seen that all the MCPA6/SAN samples exhibited only α crystal form, which corresponded to the crystallographic planes (200) and (002 + 202).[27–29] The α structure was known to be more thermally stable and can be obtained by

slow cooling of the melt.[30] Otherwise, the α crystal form did not show any significant change with the different SAN content.

Mechanical properties

The mechanical tests (see Table I) indicated that the Izod notched impact strength of MCPA6/SAN was improved when a small amount of SAN was incorporated. The impact strength increased about one time at 2.5% MCPA6/SAN when compared with that of pure MCPA6. In addition, the blend samples showed a larger change in tensile strength and elongation at break with SAN content. But it must be noted that the content of SAN has a little effect on the mechanical properties. In general, the mechanical properties of polymer blends are also highly dependent on the morphology as well as the interfacial adhesion.[13] Since the possible copolymer improved the interfacial adhesion strength and the morphology of MCPA6/SAN blends, their properties were obviously improved. The results were in good agreement with the above FTIR analysis Table II.
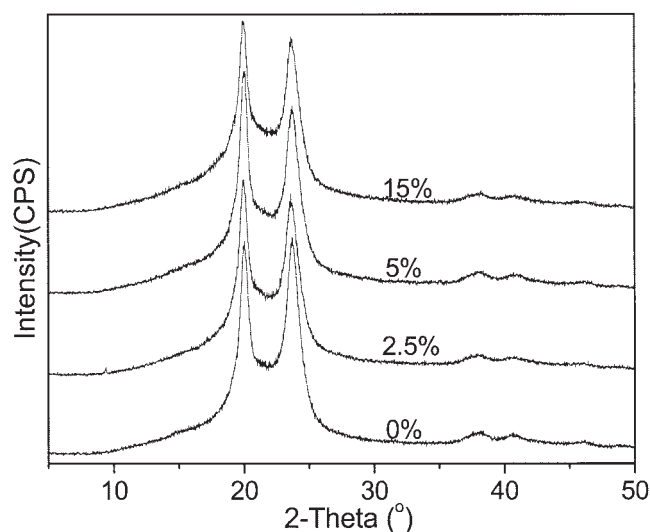

Figure 7 WAXD spectra of MCPA6/SAN with different SAN content.

TABLE II
Mechanical Properties of MCPA6/SAN with Different SAN Content

MCPA6/SAN (w/w)	Notched impact strength (J/m)	Elongation at break (%)	Tensile strength (MPa)
100/0	21	2.6	22.6
100/2.5	33	7.3	49.4
100/5	38	7.6	46.0
100/10	34	6.6	54.3
100/15	32	4.3	41.3

CONCLUSIONS

In this study, MCPA6/SAN blends were prepared by *in situ* anionic ring-opening polymerization technique. SEM micrographs of the blends showed that SAN had a finer dispersion in the MCPA6/SAN blends than that in the PA6/SAN blends prepared by direct melt blending of PA6 and SAN. This could be attributed to rapid anionic polymerization and hydrolysis of CN groups of SAN. This hydrolysis product increased the compatibility between SAN and MCPA6. FTIR results confirmed the hydrolysis reaction. The results of the DSC cooling process showed that the ΔH_m, ΔH_c, and T_c decreased gradually in the MCPA6/SAN blends. The crystallization of MCPA6 was inhibited by the presence of SAN. But, the T_m of MCPA6 portion for the MCPA6/SAN blends was almost independent of blend. Only α crystal form of the MCPA6 existed in the blends by means of WAXD.

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