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ORIGINAL PAPER

Influence of blend composition on the mechanical properties and morphology of PC/ASA/SAN ternary blends

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Abstract Bisphenol A polycarbonate/acrylonitrile–styrene–acrylic/styrene–acrylonitrile copolymer (PC/ASA/SAN) ternary blends were prepared over a range of compositions via mixing PC, SAN, and ASA copolymer by melt blending. An analysis was made on the mechanical properties and morphology of the blends. Special care was taken to make comparisons of the morphologies and properties of blends with different SAN content. When a small amount SAN was introduced to PC/ASA blends, the dispersion condition of ASA in the matrix was improved and a better integrated mechanical properties was realized. Further increasing the SAN content led to a decrease of impact strength, which was due to the changing of the morphology of the blends and the inherent brittleness of matrix. The study about the effect of ASA content on the properties of PC/ASA/SAN blends showed that the blend with 20 wt% ASA had good mechanical properties.

Keywords PC · SAN · ASA · Morphology · Mechanical property

Introduction

Polymer blending is an effective method to obtain a new material system with the desirable features of its constituents by combining two or more different polymers. The properties and morphology of polymer blends depended on a variety of factors: molecular characteristics of the components blend composition, rheological properties, processing conditions, thermal treatments [1–6].

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Bisphenol A polycarbonate (PC) is used in a wide variety of applications because of its excellent balance of properties, including optical clarity, high heat deformation temperature, toughness and electrical properties [7]. However, deficient characteristics of PC deter its application in some areas. A number of approaches have been used to enhance its poor characteristics, such as the thickness dependence of the notched impact strength and the poor radiation, solvent, and hydrolysis resistance [8–12]. Blends of bisphenol-A-polycarbonate (PC) with acrylonitrile–butadiene–styrene (ABS) materials represent one of the most important classes of commercial polymer blends [13–15]. Polymer mixture obtained from melt processing always exhibits a separated phase structure when its interaction energy is positive at processing temperature and pressure. And often multiphase blends require some form of compatibilization to obtain useful properties; however, the relatively favorable interactions between PC and the styrene/acrylonitrile (SAN) matrix of ABS apparently makes it possible in this case to produce commercially useful materials without any compatibilizer in PC/ABS blends[16–18]. However, PC/ABS blends have a main drawback stem from the physical (or chemical) aging of butadiene rubber in ABS. Butadiene rubber, containing a double bond in its repeat unit, undergoes physical (or chemical) aging caused by ultraviolet (UV) radiation in outdoor applications. The aging of butadiene rubber results in a continuous decline in the mechanical strength and color changes. ASA (acrylonitrile–styrene–acrylic) terpolymer prepared by grafting copolymerization of styrene and acrylonitrile monomers onto acrylic rubber particles has a similar structure compared with ABS terpolymer expect the butadiene rubber was replaced by acrylic rubber, which can resolve the physical (or chemical) aging of butadiene rubber. Blend of bisphenol A polycarbonate (PC) and acrylonitrile–styrene–acrylic elastomer (ASA) terpolymer with excellent properties have been developed for automobile applications [18]. However, due to the poor compatibility of PC and ASA copolymer, some compatibilizer, such as PC-b-PMMA, PC-g-SAN, are combined into the system [7, 19].

The miscibility of SAN and PC has been studied widely, and it is well recognized that the interactions between PC and SAN copolymers containing various amounts of AN are not favorable enough to produce complete miscibility, but a PC blend with SAN containing about 24 wt% AN shows optimum interfacial adhesion, regardless of the blend compositions [20]. And as pointed by researches, the PC/ABS blend with a PC, graft rubber particle and SAN can obtain good morphology and properties [21]. In our study, SAN with AN content of 24% was combined into the PC/ASA system to prepare a ternary blend system of PC/ASA/SAN. An analysis was made on the relationship of structure and properties of the ternary blends.

Experimental

Materials

Bisphenal A polycarbonate, purchased from Bayer, was a commercial grade of 2805 with MFR of 25 g/10 min and M_n and M_w is 33,000 and 51,000, respectively;

Acrylonitrile–styrene–acrylic copolymer(ASA) were purchased from Compton with a rubber content of 60%. SAN with AN content of 24 wt% was kindly supplied by Jilin Chemistry Company (China), and the M_n and M_w is 32,000 and 74, 000, respectively.

Blend preparation

PC/ASA/SAN blends with different composition were produced by compounding ASA copolymer with SAN and PC in a twin screw extruder (*D*=30 mm, *L*/*D*=32) at 240–260 °C. Prior to mixing, the PC pellets were dried for a minimum of 12 h under vacuum at 100 °C. ASA was dried at 65 °C and SAN pellets at 85 °C. The extruded grand was pelletized in-line, dried at 90 °C for 24 h under vacuum, and then injection molded into bars for mechanical testing at 260 °C. The mold temperature was set at 60 °C.

Examination of mechanical properties of PC/ASA/SAN blends

The dimensions of all the specimens obtained by injection molding for notched Izod impact strength test were 63.5 × 12.7 × 6 mm, according to ASTM D256. The test was conducted on XJU-22 Impact tester at 23 °C. All tensile specimens were injection molded into dumbbell shape, whose dimensions of the parallel part were 60 mm in length with a cross-section of about 12.90 × 2.90 mm^2. Tensile tests were conducted on AGS-H 5 kN electrical testing machine at constant crosshead speed of 50 mm/min at 23 °C, according to ASTM D638. MFR (melting flow rate) was collected using a Mpxrz-400C MFR machine with a loading of 5 kg at 260 °C.

Morphology

A scanning electron microscope (JSM-5600) was used to examine the morphology of blends. All samples were etched by a mixture of 120 ml H_2SO_4, 30 ml H_2O and 5 g GrO_3 for 5 min to remove the ASA and SAN phase and then were coated with a thin gold layer in a sputter coater before examination.

Results and discussion

Effect of SAN content on the mechanical property of PC/ASA/SAN blends

In order to investigate the influence of SAN content on the morphology and property of PC/ASA/SAN blends, a series of blends were obtained by melt blending with a constant ASA content of 20 wt%, while varying the ratio of SAN and PC in matrix. In Fig. 1 the curve showed that the impact strength of the blends increased firstly when a small amount of SAN was introduced into the system. However, with the content of SAN increasing further, the impact strength of the blends decreased. The blend with 5 wt% SAN had a maximum impact strength of about 600 J/m, but the impact strength dropped to 100 J/m when the SAN content was 30 wt%.

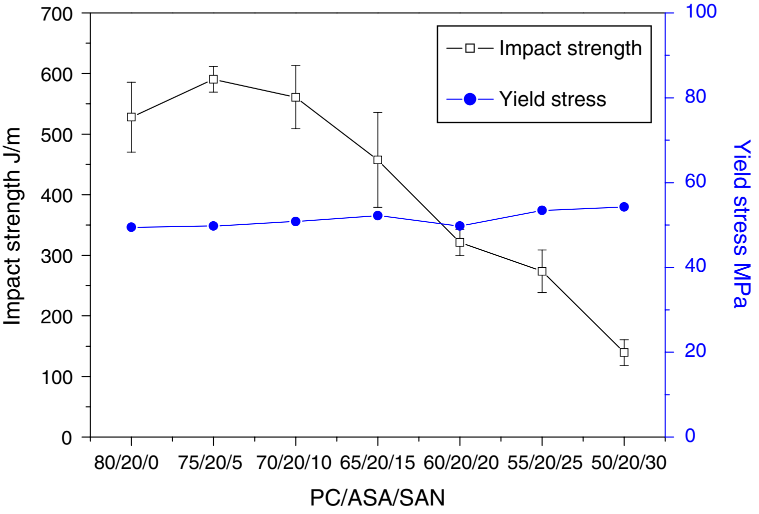


Fig. 1 Effect of SAN content on impact strength and yield stress of PC/ASA/SAN blends

Since ASA is a core-shell structure particles with a -g-SAN shell, it will have a good interfacial adhesion to SAN matrix. As pointed by researches, PC blends with SAN containing about 24 wt% AN showed optimum interfacial adhesion. So in our study the small amount SAN acted as the compatibilizer and the maximum value of impact strength can be obtained with a SAN content of 5 wt%. As the increasing of the SAN content up to 15%, a drop of impact strength may be attributed to the variation of matrix composition. In rubber modified polymer blends, the mechanical property is affected by many structural variables including the volume fraction, the size and size distribution of the rubber phase, the properties of the matrix and the interfacial adhesion of between dispersed phase and matrix. During the failure process of a rubber-toughened polymer, most of the energy is absorbed by the deformation of the rigid matrix. So the properties and composition of the matrix are therefore of paramount importance in determining the mechanical properties of blends [22, 23]. Since in our study SAN is a relative brittle matrix compared with ductile PC, so more SAN introduced into the system must lead to the decrease of the impact strength of blends.

The tensile properties of the PC/ASA/SAN blends were examined in a uniaxial tensile test at a strain rate of 50 mm/min. The effect of SAN content on the yield stress of PC/ASA/SAN blends was also shown in Fig. 1. It was found that the yield stress of the blends were nearly slightly steady increased and had no strong fluctuate, which implied that SAN content had slight effect on the yield stress of PC/ASA/SAN blends. Actually PC/ASA/SAN blends contained three phases: ASA rubber phase, SAN phase, and PC phase. The rubber phase was surrounded by the SAN phase. The SAN phase and the PC phase formed the overall phase structure. The rubber phase had the lowest yield strength compared with other two phases. Since all the rubber content in the blends was constant, which was a main factor controlling the stress yield of PC/ASA/SAN blends, so the slight increase of the stress yield with the increase of SAN content should be attributed to the higher stress strength of SAN than PC matrix.

Modulus of resilience (U_r) was defined as the energy that can be absorbed per unit volume without creating a permanent distortion. As shown in Fig. 2, the area up to the yield point is termed the modulus of resilience; the term “modulus” is used because the units of strain energy per unit volume are N-m/m^3 or N/m^2, which is the same as stress or modulus of elasticity. The term “resilience” alludes to the concept that up to the point of yielding the material is unaffected by the applied stress and upon unloading will return to its original shape. The modulus of resilience is then the quantity of energy the material can absorb without suffering damage and can be calculated using the following formula,

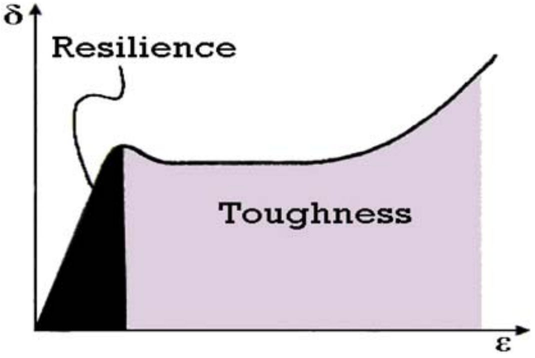
$$U_r = \frac{\sigma^2}{2E} = 0.5\sigma\varepsilon = 0.5\sigma\left(\frac{\sigma}{E}\right),$$

Where σ is yield stress, E is Young’s modulus, and ε is strain. The effect of SAN content on the resilience modulus of PC/ASA/SAN blends was illustrated in Fig. 3. It was found that the modulus of resilience increased first and then decreased with increasing content SAN.

Melt flow rate (MFR) is a measure of the ease of the melt flowing of a thermoplastic polymer. It is defined as the mass of polymer in grams flowing in 10 min through a capillary of specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperature. MFR is inversely proportional to viscosity of the melt at the conditions of the test, so it is an important parameter to character the rheological behavior and processability of thermoplastic polymers. The effect of the SAN content on the MFR of PC/ASA/SAN blends was shown in Fig. 4. It was found the combination of SAN to PC/ASA blend increased the flow ability of polymer blends, and the MFR of blends increased proportional to the SAN content. The more SAN the blends contained, the greater the extent increase of MFR was.

Combining the data of mechanical properties of PC/ASA/SAN blends with different SAN content, a conclusion can be drawn that the blends with 5 and 10 wt% SAN had higher impact strength, yield strength, modulus and suitable processability, and showed better integrated properties.

Fig. 2 Resilience and toughness



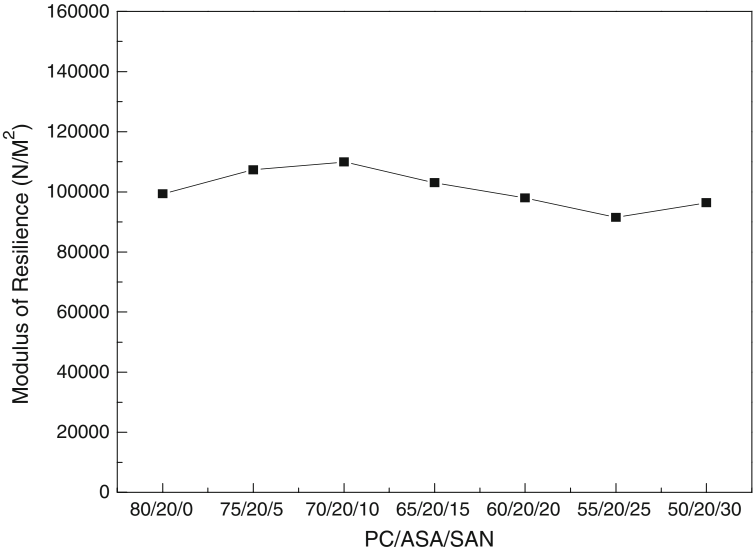


Fig. 3 Effect of SAN content on resilience modulus of PC/ASA/SAN blends

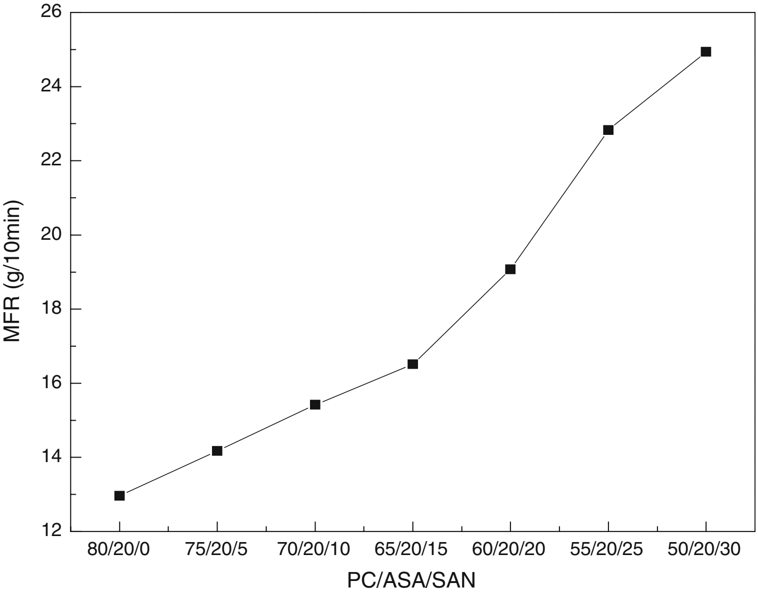


Fig. 4 Effect of SAN content on MFR of PC/ASA/SAN blends

Effect of ASA content on the mechanical property of PC/ASA/SAN blends

As shown in Fig. 5 the effect of the ASA content on the impact strength of PC/ASA/SAN blends was investigated by keeping the PC content of 70 wt% and changing

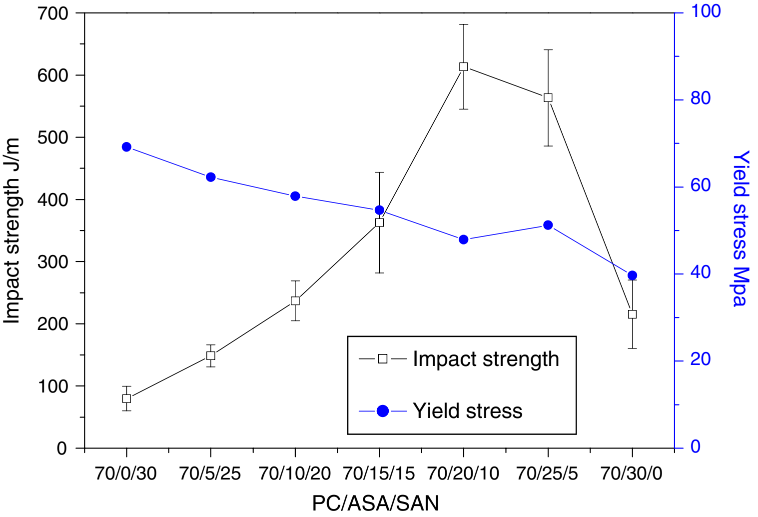


Fig. 5 Effect of ASA content on impact strength and yield stress of PC/ASA/SAN blends

the ASA content in the blends. The ASA content varied from 0 to 30 wt% and the SAN content decreased from 30 to 0 wt% accordingly in the blends. It was found that impact strength of blends increased with the ASA content varied from 0 to 20 wt %, and the impact strength had a maximum value of 600 J/m as the ASA content reached 20 wt%; when the ASA content was above 20 wt%, the impact strength of blends decreased and dropped to 200 J/m as ASA content reached 30 wt%. It is well known that the elastic rubber phase in brittle matrix acted as stress concentrators so that they can initiate crazes or shear yielding of matrix to absorb the impact energy [24]. So in our system, when more rubber particles were introduced into the PC/SAN matrix, an increase of energy absorption and subsequently an increase of impact strength were observed. However, when more ASA was introduced into the blends, the rubber phase may become agglomerated or interpenetrated, which destroyed the strength of matrix or made some rubber particles lose the ability to toughen the matrix and led to the decrease of impact strength. On the other hand, when the ASA content reached 30 wt%, and no SAN phase existed in the system, the poor interfacial adhesion would also lead to the decrease of impact strength.

Figure 5 showed the effect of ASA content on the yield strength of PC/ASA/SAN blends. It was found that the yield stress of the blends decreased with the increase of ASA content. Yield stress of composite materials is a combined property determined by the strength of each component and the bond between the components. In some case, it can be considered as a qualitative indication of stress transfer level between the components of a composite material. In the present case, the introduction of ASA copolymer with lower strength and modulus resulted in lower yield strength. Furthermore, the decrease of SAN in blends must lead to a decrease of the stress transfer from the rubber phase to the matrix, which may be another reason caused the decrease of yield stress.

The effect of ASA content on the resilience modulus of PC/ASA/SAN blends was illustrated in Fig. 6. It was found that the increase of ASA content led to a decrease of the resilience modulus of blends. But there is an outstanding data as the composition of PC/ASA/SAN was 70/25/5, the resilience modulus restored to 12,000 N/m^2.

It is well known that the rubber phase must be crosslinked to keep appropriate elastic during the syntheses of ASA. So as the more ASA copolymer was added to the blends, the viscosity of blends would increase and the blends were difficult to process. Figure 7 showed the effect of ASA content on MFR of PC/ASA/SAN blends. The melt flow rate of blends decreased with the increase of ASA content, which may be caused by Einstein model increase in viscosity due to particles. Since SAN is a resin with good fluidity, the increase of ASA content must lead to an accordingly decrease of SAN, which may be another reason caused the decrease of MFR of blends.

Morphological characterization

Scanning electron microscopy (SEM) was used to investigate the morphology of PC/ASA/SAN blends. It must be stated here that the ASA and SAN matrix were removed by etching processing, which was dark region in the microphotographs. Figure 8 showed the morphologies of PC/ASA blends with ASA content of 20 and 30 wt%, respectively, and no SAN was introduced to the blends. Since PC/ASA blend was an incompatible system and in the two blends the dispersed phase showed heterogeneous distribute. It was also found the dispersed phase morphology was strong affected by the ASA rubber content in the blends. Indeed, by increasing the

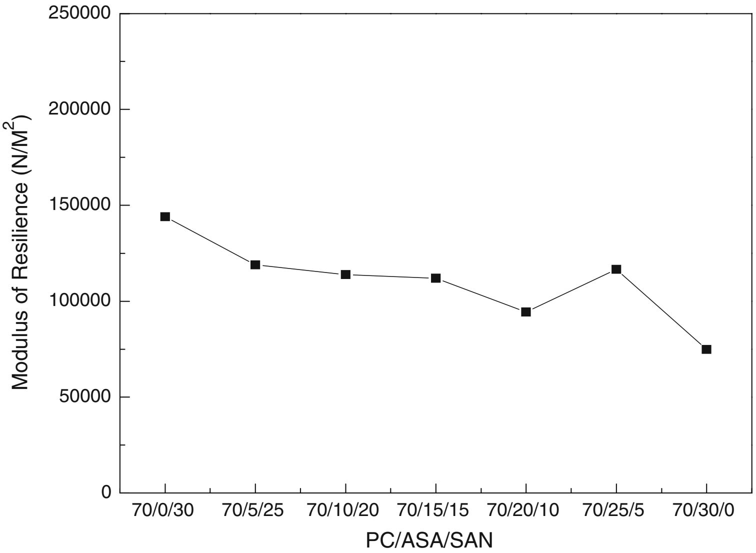


Fig. 6 Effect of SAN content on resilience modulus of PC/ASA/SAN blends

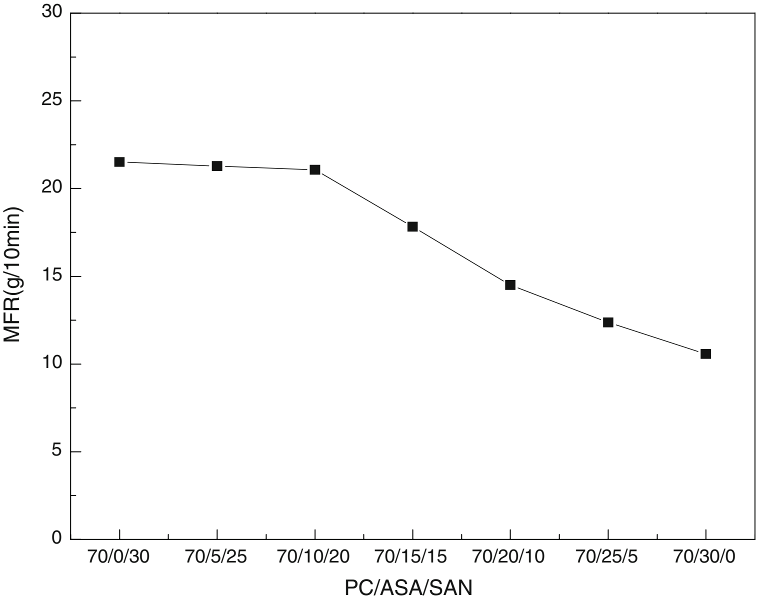
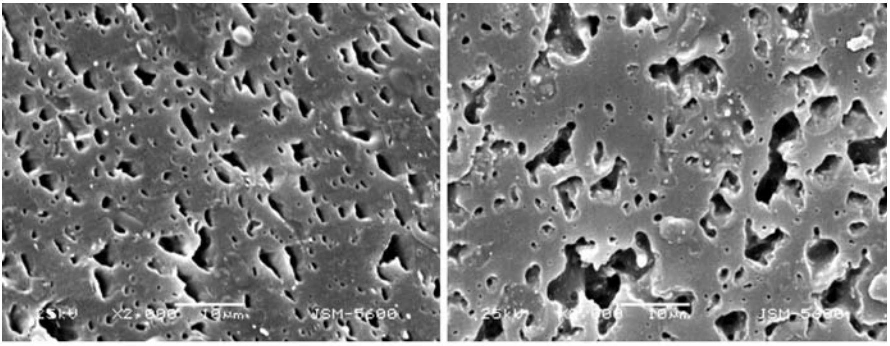


Fig. 7 Effect of ASA content on MFR of PC/ASA/SAN blends

concentration of the ASA rubber, the number of ASA rubber in the system increased, which led to an increased number of particle-particle collisions. So an increase of ASA content resulting in an increased size of coalescing could be observed in Fig. 8b.

It is well known that when two immiscible polymers are mixed, the size, shape and distribution of one phase into other depends on material parameters, i.e., blend composition, viscosity, elasticity ratio, shear stress, and interfacial tension [24–26]. However, from the point of view of a broader classification, multiphase polymer blends may be divided into two major categories: blends with a discrete phase



(a) (b)

Fig. 8 SEM photographs of PC/ASA blends with the composition of **a** PC/ASA_80/20 **b** PC/ASA_70/30 structure and blends with a co-continuous structure. In the blend, the component that occupies most space will most likely assume the role of continuous phase. However, the component with lower viscosity will tend to encapsulate the more viscous component, since this reduces the rate of energy dissipation by mixing. In a special system, there is the probability that the volume ratio favored component A to be the continuous phase, but the viscosity ratio favored component B to be the continuous phase. Thus either component A or B will be the continuous phase in this system, and then co-continuous structure is formed.

In our study, a third component SAN was introduced into the PC/ASA system, a ternary phase blends with PC and SAN as matrix, ASA as dispersed phase in SAN phase was formed. Figure 9 gave the morphologies of the PC/ASA/SAN blends with different SAN content. It was found that when the ASA content was fixed at 20%, the different fractions of SAN in blends had a great influence on the morphologies of PC/ASA/SAN blends. Since ASA and SAN phase were removed by etching processing, the strong acids solution leaves holes in the PC matrix, corresponding to ASA and SAN domains. As shown in Fig. 9a, it was found that the PC occupies most space and forms continuous phase, and ASA and SAN domains form the dispersed phase as 5 wt% SAN was introduced to the PC/ASA blends. Compared with poor and inhomogeneous dispersion morphology of PC/ASA

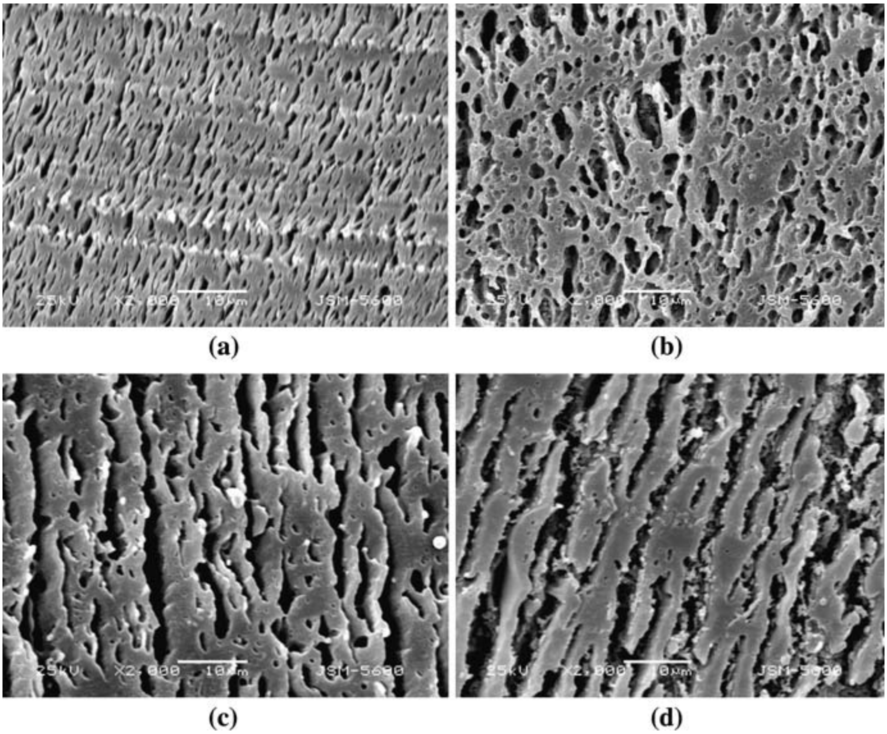


Fig. 9 SEM photographs of PC/ASA/SAN blends with the composition of PC/ASA/SAN: **a** 75/20/5, **b** 70/20/10, **c** 65/20/15 and **d** 50/20/30

blends, the PC/ASA/SAN blend with 5 wt% SAN had a relative well dispersed morphology and the dispersed domains were elongated and the structures became finer. With the continuous increase of the SAN content of PC/ASA/SAN blends, it was found that the shape of ASA and SAN domains becomes irregular, somewhat similar to the co-continuous structure and the size of ASA and SAN phase showed increasing trend and the shape of phase microstructure tended to be strip shown in Fig. 9b–d. Since SAN with 24 wt% AN and PC system are partially compatible, the introductions of a small amount of SAN into PC/ASA system can act as a compatibilizer and enhanced the interfacial adhesion of the ASA and PC matrix. However with the further increase of SAN content in the blend, the phase size of SAN increased correspondingly and co-continuous structure were formed due to its higher content of SAN. Combining the data of mechanical properties, better integrated properties of PC/ASA/SAN with 5% SAN should be attributed to the relative well dispersed morphology shown in Fig. 9a. The addition of a small amount SAN enhance the interfacial adhesion and minimize the size of rubber phase, which led to the better mechanical properties.

Conclusions

PC/ASA/SAN blends with different composition were prepared by melt blending. SAN and ASA content have great influence on the morphology and properties of PC/ASA/SAN blends. Addition of small amount SAN into PC/ASA blends can improve the rubber dispersion condition and result in higher impact strength. The blends with 5 wt% SAN showed good dispersed morphology and better integrated properties with higher impact strength, yield strength, modulus and suitable processability.

References

1. Paul DR, Barlow JW (1980) Polymer blends (or alloys). J Macromol Sci Rev Macromol Chem 18:109–168
2. Kulshreshtha AK (1993) A Review of commercial polyblends based on PVC, ABS and PC. Polym Plast Technol Eng 32:551–578
3. Chen Q, Yu W, Zhou C (2008) Transient stresses and morphology of immiscible polymer blends under varying shear flow. Colloids Surf A Physicochem Eng Asp 326:175–183
4. Chiu F, Lee HY, Wang YH (2008) Thermal properties and phase morphology of melt-mixed poly (trimethylene terephthalate)/poly (hexamethylene isophthalamide) blends. J Appl Polym Sci 107:3831–3839
5. Wu JS, Shen SC, Chang FC (1993) Effect of polycarbonate molecular weight on polymer blends of polycarbonate and ABS. J Appl Polym Sci 50:1379–1389
6. Wildes G, Keskkula H, Paul DR (1999) Fracture characterization of PC/ABS blends: effect of reactive compatibilization, ABS type and rubber concentration. Polymer 40:7089–7107
7. Kamg EA, Kim JH, Oh SY, Rhee W (2000) The effects of PC-PMMA block copolymer on the compatibility and interfacial properties of PC/SAN blends. Polym Eng Sci 40:2374–2384
8. Tjong SC, Meng YZ (2000) Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly (acrylonitrile–butadiene–styrene) blends. Eur Polym J 36:123–129

9. Lu ML, Chang FC (1995) Fracture toughness of a polycarbonate/acrylonitrile–butadiene–styrene blend by the ASTM E813 and hysteresis energy *J* integral methods: effect of specimen thickness and side groove. Polymer 36:2541–2552
10. Elmaghor F, Zhang L, Fan R, Li H (2004) Recycling of polycarbonate by blending with maleic anhydride grafted ABS. Polymer 45:6719–6724
11. Ishikawa M (1995) Stability of plastic deformation and toughness of polycarbonate blended with poly (acrylonitrile–butadiene–styrene) copolymer. Polymer 36:2203–2210
12. Zong R, Hu Y, Wang S, Song L (2004) Thermogravimetric evaluation of PC/ABS/montmorillonite nanocomposite. Polym Degrad Stab 83:423–428
13. Greco R (1996) Polycarbonate toughening by ABS. In: Martuscelli E, Musto P, Ragosta G (eds) Advanced routes for polymer toughening, chap 9. Elsevier, Amsterdam
14. Lombardo BS, Keskkula H, Paul DR (1994) Influence of ABS type on morphology and mechanical properties of PC/ABS blends. J Appl Polym Sci 54:1697–1720
15. Wu JS, Shen SC, Chang FC (1994) Effect of rubber content in acrylonitrile–butadiene–styrene and additional rubber on the polymer blends of polycarbonate and acrylonitrile–butadiene–styrene. Polym J 26:33–42
16. Keitz JD, Barlow JW, Paul DR (1984) Polycarbonate blends with styrene/acrylonitrile copolymers. J Appl Polym Sci 29:3131–3145
17. Kim JH, Kim CK (2003) Changes in the interfacial properties of PC/SAN blends with compatibilizer. J Appl Polym Sci 89:2649–2656
18. Guest MJ, Daly JH (1990) Dynamic mechanical spectroscopy of blends of bisphenol-A polycarbonate with styrene–acrylonitrile copolymers. Eur Polym J 26:603–610
19. Kim WN, Burns CM (1988) Thermal behavior, morphology, and some melt properties of blends of polycarbonate with poly (styrene-co-acrylonitrile) and poly (acrylonitrile–butadiene–styrene). Polym Eng Sci 28:1115–1125
20. Callaghan TA, Takakuwa K, Paul DR, Padwa AR (1993) Polycarbonate–SAN copolymer interaction. Polymer 34:3796–3807
21. Tan ZY, Xu XF, Sun SL, Zhou C, Ao YH, Zhang HX (2006) Influence of rubber content in ABS in wide range on the mechanical properties and morphology of PC/ABS blends with different composition. Polym Eng Sci 46:1476–1484
22. Wu S (1992) Control of intrinsic brittleness and toughness of polymers and blends by chemical structure: a review. Polym Int 29:229–247
23. Zhou C, Bao XY, Tan ZY, Sun SL, Ao YH, Zhang HX (2006) Transition from crazing to shear deformation in ABS/PVC blends. J Polym Sci Part B Polym Phys 44:687–695
24. Lacroix C, Grmela M, Carreau PJ (1998) Relationships between rheology and morphology for immiscible molten blends of polypropylene and ethylene copolymers under shear flow. J Rheol 42:41–62
25. Petra P, Paul DR (2003) Formation of co-continuous structures in melt-mixed immiscible polymer blends. Polym Rev 43:87–141
26. Martin P, Carreau PJ, Favis BD (2000) Investigating the morphology/rheology interrelationships in immiscible polymer blends. J Rheol 44:569–583