

Preparation and Properties of PC/SAN Alloy Modified with Styrene-Ethylene-Butylene-Styrene Block Copolymer

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ABSTRACT: A polycarbonate (PC)/ poly (styrene-*co*-acrylonitrile) (SAN) alloy modified with styrene-ethylene-butylene-styrene (SEBS) block copolymer was prepared and the influence of SEBS content, PC content, and types of modifier on Izod notched impact strength, tensile strength, flexural strength, and Vicat softening temperature was studied. The results showed that the addition of SEBS could obviously increase the Izod notched impact strength and the elongation at break and decrease the tensile and flexural strength and Vicat softening temperature. PC/SAN alloy modified with SEBS had better mechanical

properties than the PC/SAN alloy modified with ABS. DSC analysis and SEM photographs revealed that the SEBS was not only distributed in the SAN phase but also distributed in PC phase in a PC/SAN/SEBS alloy while the ABS was mainly distributed in SAN phase in a PC/SAN/ABS alloy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 637–643, 2007

Key words: polycarbonate; styrene-ethylene-butylene-styrene block copolymer; poly (styrene-*co*-acrylonitrile); alloy

INTRODUCTION

Polycarbonate (PC) is used in a wide variety of applications because of its excellent balance of properties.^{1–3} However, deficient characteristics of PC, such as thickness dependence of notched impact strength and poor radiation, solvent and hydrolysis resistance, deter its application in some areas.

Blends of PC and poly (styrene-*co*-acrylonitrile) (SAN) show co-continuous structure with PC contents between 40 and 70 wt %, ^{4,5} a wide range of additivity in the temperature dependent rheological values,⁶ and a positive deviation from the additivity of the frequency dependence of the storage and loss moduli. The main problem of PC/SAN alloys is their tendency to coalesce during processing, which can result in coarse structure and inferior material properties.^{7–11} Even short downtimes at a processing temperature of 270°C (e.g., in injection molding machines) can cause a significant deterioration of the morphology.¹²

Moreover, the toughness of PC/SAN alloy is too poor and its notched impact strength is only about 100–200 J/m. So PC/SAN alloy was gradually substituted by PC/acrylonitrile-butadiene-styrene copolymer (ABS) alloy that had better mechanical properties. ABS was produced by the grafting

copolymerization of styrene and acrylonitrile into PB (Polybutadiene) latex, resulting in a mixture of PB, PB grafted with acrylonitrile and styrene, and Styrene-Acrylonitrile copolymer. Although this makes the production of ABS very complex, it allows a great flexibility in the product property design.

Because of this reason, blends of PC with ABS materials have been commercially available for many years.^{13–19} In a PC/ABS blend, in which all the rubber particles are in the SAN phase, PC and SAN that form the matrix in the blend exhibit phase-separated structure, regardless of the AN content in the SAN copolymers. However, these blends have two main drawbacks. Because PC blends with SAN are not miscible, the interfacial adhesion is not strong enough. The application of blends with phase-separated structure is often limited because of their poor adhesion at the weld.^{20–23} The other problem stems from the physical (or chemical) aging of butadiene rubber. 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. Improvements in the interfacial adhesion and the reduction of aging are essential for broadening the applications of PC/ABS blends.

For overcoming above two main drawbacks, many compatibilizers were used into the PC/ABS alloy, such as ABS-*g*-MAH,^{24,25} SMA (Styrene Maleic anhy-

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drude copolymer),²⁶ SAM (Styrene-Acrylonitrile-Maleic anhydride copolymer),²⁷ PMMA (polymethyl methacrylate),^{28,29} SAN-amine,^{30,31} etc. These compatibilizers could increase the compatibility and interaction between PC and SAN phase to increase the properties of a PC/ABS alloy. Moreover, new kinds of modifying PC/SAN alloy, in which there were no double bond, were also produced, such as PC/AES (Acrylonitrile-Ethylene propylene rubber-Styrene) alloy, where EPDM (ethylene-propylene-diene monomer) was grafted with Styrene and Acrylonitrile instead of polybutadiene in ABS.

In the present work, a PC/SAN alloy modified with SEBS was prepared and the influence of SEBS content, PC content and types of modifier on Izod notched impact strength, tensile strength, flexural strength and vicat softening temperature were studied. Moreover, DSC analysis and SEM photographs were used to study SEBS distribution in PC and SAN phase.

EXPERIMENTAL

Materials

Polycarbonate (PC201-15) and SAN copolymer (80HF), where styrene content is about 77 wt %, were purchased from LG DOW Polycarbonate and Ningbo LG Yongxing Chemical, respectively. SEBS and styrene-ethylene-ethylene-propylene-styrene block copolymer (SEEPS), where styrene content is both about 33 wt %, were kindly supplied by Kuraray, and their trademark are SEPTON8006 and SEPTON4055, respectively. ABS, which is a core-shell particle ABS and PB content is about 70 wt %, is supplied by U.S. Crompton Corp. and the trademark is Blendex338. Styrene Maleic anhydride copolymer (SMA) was kindly supplied by Shanghai Research Institute of Petrochemical Technology, and its trademark is SMA218. Irganox 1010 and 168 was selected as an antioxidant agent, which was supplied by Ciba Specialty Chemicals, and the additive content was 0.03 wt %.

Specimen preparation

PC, SAN, and SEBS were dried in a vacuum oven at 120, 90, and 80°C for at least 8 h before melt processing. The mixture of PC, SAN, SEBS, and antioxidant was then extruded in a corotating intermeshing twin-screw extruder with L/D = 41, which was produced by Germany Berstoff. From hopper to die, the barrel temperature was set at 30°C/250°C/250°C/255°C/255°C/255°C/260°C/260°C/255°C for PC content 70 wt %. The screw speed was 200 rpm. Extruded pellets of the alloy were vacuum-dried at 80°C for 10 h and injection-molded to give all the

required test specimens with a melt temperature of 250°C and a mold temperature of 70°C.

Measurements

The notched Izod impact strength was measured according to the ASTM D256 test standard method using an impact test machine Model 2500 from RAY-RAN at room temperature (23°C) and -20°C. The dimension of the specimens was 63.5 × 12.7 × 3.18 mm³ with a V-shape notch of 0.25-mm depth. The swaying velocity of the hammer was 3.5 m/s. Each datum of impact strength represents the average value of impact strengths for a minimum of five specimens.

Tensile and flexural strength were measured according to ASTM D638 and ASTM D790, respectively, by using a tensile machine Instron Model 4465 at room temperature. The crosshead speeds were 50 and 1.26 mm/min, respectively. The support span was 49.6 mm for the flexural strength measurement. Each datum represents the average value for a minimum of five specimens.

The Vicat Softening point Test (VST) was measured according to ASTM D1525 in a VST equipment Model 1700 from the RAY-RAN at heating rate of 50°C/h and 49 N loads. Each VST datum represents the average value of the VST for a minimum of three specimens.

A differential scanning calorimeter (DSC) Model Perkin-Elmer Pyris 1 was used to measure the glass transition temperature (T_g) of PC, SAN, and their alloy at a scanning speed of 10°C/min from 0 to 250°C under a nitrogen atmosphere. The weight of the specimens was about 5 mg.

A JSM-7401F field scanning electron microscope (SEM) was used to observe the morphology of PC/SAN alloy modified with SEBS. The specimens were cryogenic in liquid nitrogen at least 4 h and broken. The fractured surfaces were exposed into a 10 wt % NaOH aqueous solution for 4 h at 80°C to remove PC phase or exposed into a boiling cyclohexane for 4 h to remove SEBS phase.

RESULTS AND DISCUSSION

Influence of SEBS content on mechanical properties of PC/SAN alloy modified with SEBS

Improving the impact strength of a rigid material such as PC/SAN alloy is the most important purpose of modifying this kind of material with elastomer. Figure 1(a) shows the influence of the SEBS content on Izod notched impact strength of PC/SAN alloy modified with SEBS at 23°C and -20°C, respectively, in which PC content is 70 wt %. It shows that the impact strength at 23°C initially increases with

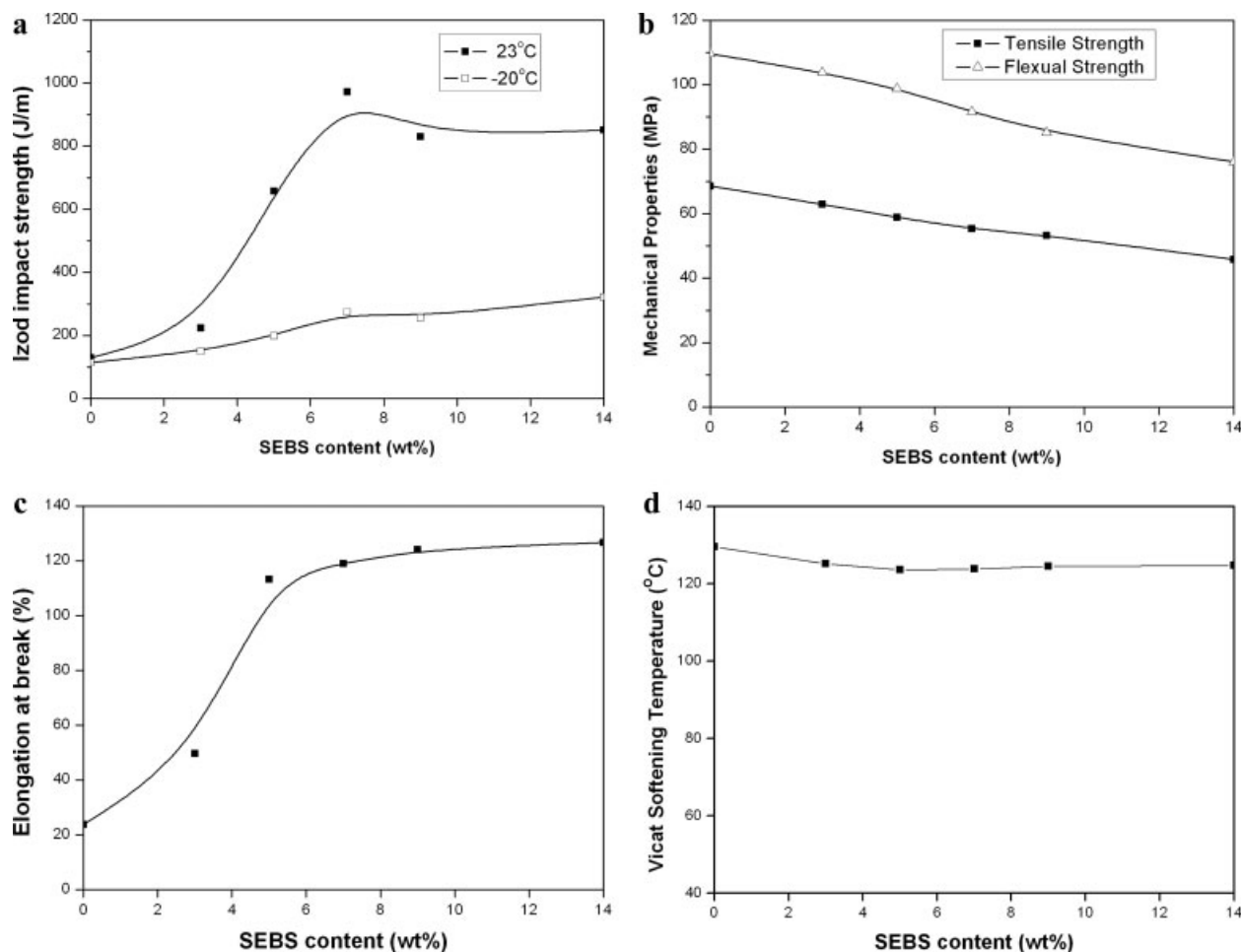


Figure 1 Influence of SEBS content on (a) Izod impact strength at 23°C and -20°C, respectively, (b) tensile and flexural strength, (c) elongation at break and (d) Vicat Softening Temperature, of PC/SAN alloy modified with SEBS, where PC content is 70 wt %.

the increase of the SEBS content. The impact strength increases from 130 J/m without SEBS to 970 J/m with 7 wt % SEBS. When the SEBS content is larger than 7 wt %, the impact strength has a little decrease and then maintains a constant value about 850 J/m. However, SEBS has no obvious affection on impact strength at -20°C according to Figure 1(a). The impact strength at -20°C also increases with the increase of SEBS content, however, the variety of impact strength is only about 200 J/m.

Figure 1(b) shows the influence of the SEBS content on tensile and flexural strength of PC/SAN alloy modified with SEBS. The tensile and flexural strength decreases with the increase of the SEBS content. Moreover, as shown in Figure 1(c), the elongation at break firstly increases with the increase of the SEBS content and then almost maintains a constant value. The elongation at break of the modifying PC/SAN alloy containing 7 wt % SEBS is about 120% while the elongation at break of PC/ABS alloy about 24-50%.³² Figure 1(d) shows the SEBS content on the

Vicat Softening Temperature (VST) of PC/SAN alloy modified with SEBS. The results show that the VST of PC/SAN alloy has a little decrease after the addition of SEBS. Moreover, the VST is almost not influenced by SEBS content.

Influence of PC content on mechanical properties of PC/SAN alloy modified with SEBS

The influence of PC content on Izod notched impact strength of PC/SAN alloy with SEBS at 23°C and -20°C is shown in Figure 2(a), where the proportion of SAN/SEBS is fixed to 70/30. It shows that impact strength at 23°C increases with the increase of PC content, especially while PC content is between 60 wt % and 70 wt %. Then impact strength is little change when PC content is more than 70 wt %. The impact strength at -20°C also increases with the increase of PC content, but the max impact strength appears at PC content 90 wt % instead of PC content 70 wt % at 23°C. Figure 2(b)

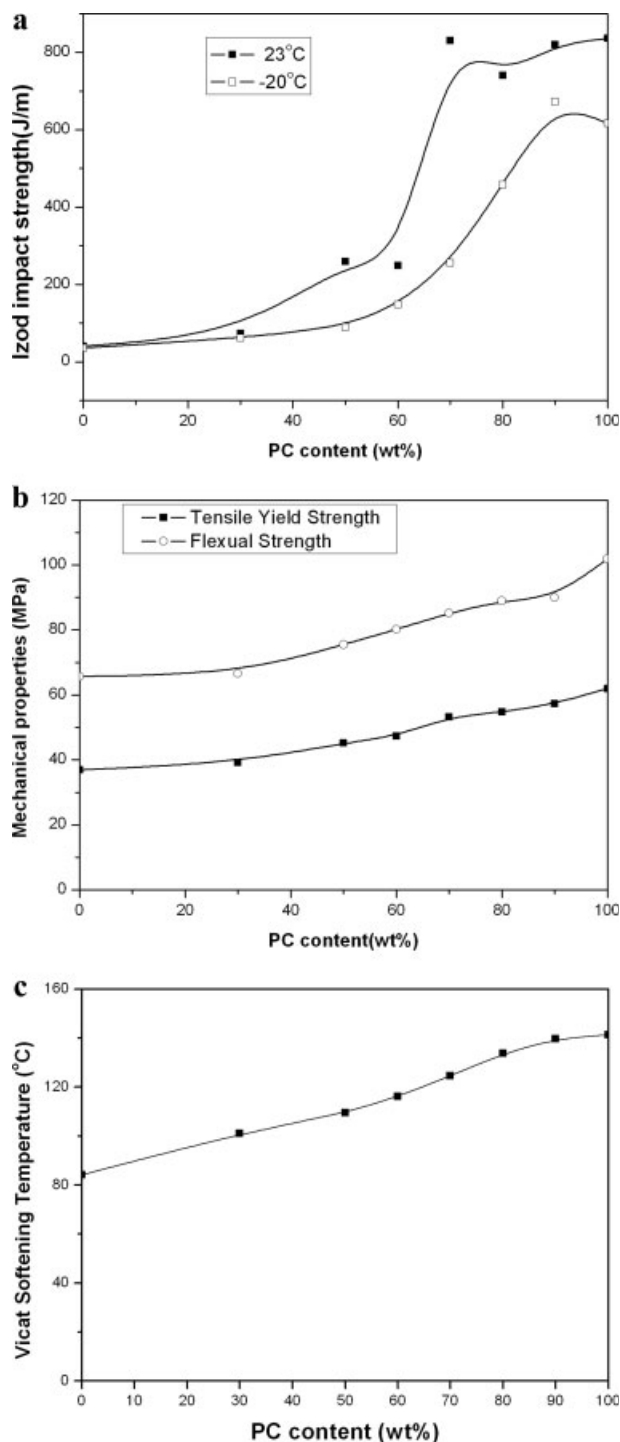


Figure 2 Influence of PC content on (a) Izod impact strength at 23°C and -20°C, (b) tensile and flexural strength and (c) Vicat Softening Temperature, of PC/SAN alloy modified with SEBS, where SAN/SEBS is fixed to 70/30.

shows that influence of PC content on tensile and flexural strength of PC/SAN alloy modified with SEBS. The tensile and flexural strength almost linearly increase with the increase of PC content. Moreover, as shown in Figure 2(c), VST of PC/SAN alloy

modified with SEBS is remarkably influenced by PC content. It almost linearly increases with the increase of PC content.

Influence of types of modifier on mechanical properties of PC/SAN alloy

Except for the SEBS and PC content, the influence of modifier type on impact strength of PC/SAN alloy at 23°C and -20°C was studied and shown in Figure 3(a), in which three kinds of modifier SEBS, SEEPS, and ABS were used and the modifier content was 9 wt %.

Figure 3(a) shows that the SEBS has the highest value of impact strength about 830 J/m at 23°C while the ABS has the lowest impact strength about 580 J/m at 23°C. Moreover, because there was no double bond in SEBS molecular segment, the PC/SAN alloy modified with SEBS must have better weatherability than PC/ABS alloy. Figure 3(a) also shows that SEEPS, which has similar segments with SEBS, has a lower impact strength about 587 J/m at 23°C compared to SEBS. Though the SEBS has the highest impact strength at 23°C, the ABS has the highest impact strength 520 J/m at -20°C. The impact strength of PC/SAN alloy modified with SEBS at -20°C is only 256 J/m and SEEPS modifying PC/SAN alloy has the lowest impact strength 188 J/m.

The influence of modifier types on the tensile and flexural strength are shown in Figure 3(b), in which the modifier content is 9 wt %. It shows that three kinds of modifier have the similar influence on the tensile and flexural strength. The influence of modifier types on elongation at break is shown in Figure 3(c). It shows that SEBS and SEEPS have the similar elongation at break about 120% while ABS has the lowest elongation at break about 22%. Moreover, the influence of three kinds of modifier SEBS, SEEPS and ABS on VST also were studied. The VST of above three kinds of modifier were 124.5°C, 125.7°C, and 126.5°C, respectively. The results indicated that PC was the main factor to influence VST of alloy instead of modifier type and content.

Many researchers²⁴⁻²⁸ found that if a compatibilizer was introduced into a PC/ABS alloy, the impact strength would be remarkably increased. These compatibilizers include ABS-*g*-MAH,^{24,25} SMA,²⁶ SAM,²⁷ PMMA,^{28,29} SAN-amine,^{30,31} etc. In the present work, the influence of a compatibilizer on PC/SAN alloy modified with SEBS was also studied. SMA was selected as a compatibilizer and its content was 5 wt %. However, the experimental results showed that the impact strength of PC/SAN alloy modified with SEBS and SMA was only about 650 J/m at 23°C that was lower than the impact strength of alloy without SMA about 830 J/m.

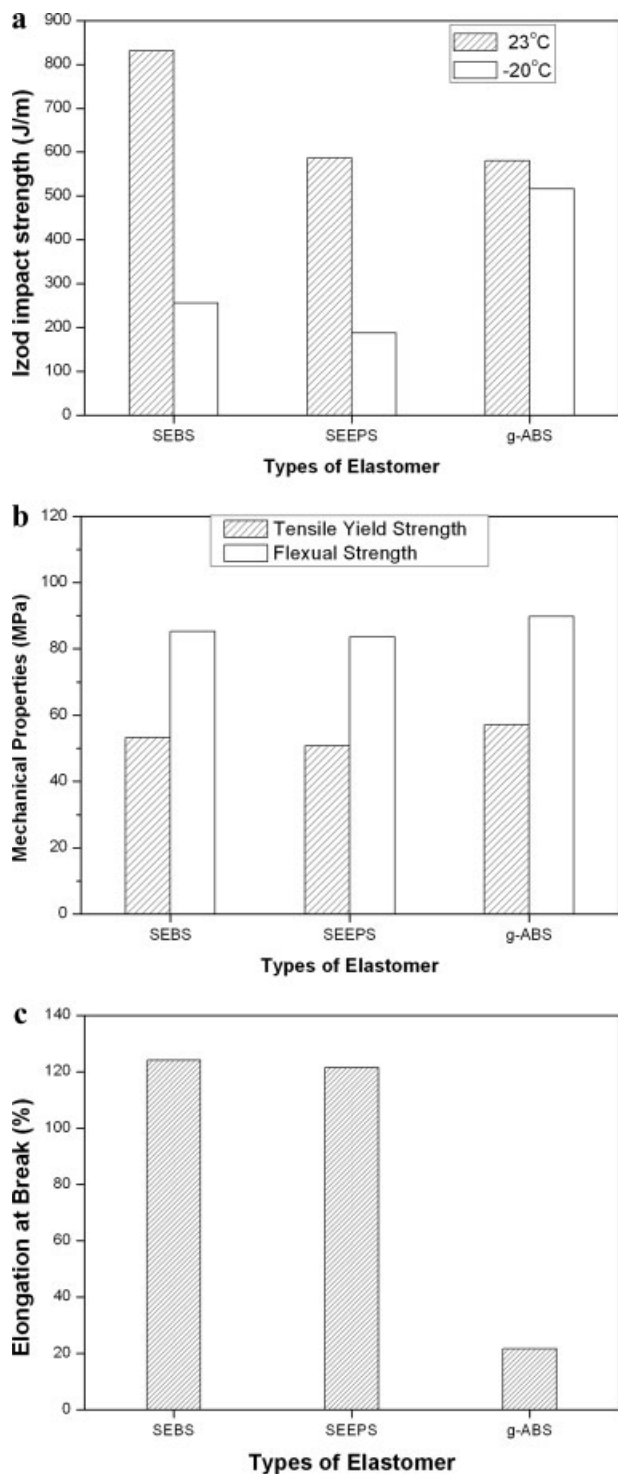


Figure 3 Influence of types of modifier on (a) Izod impact strength at 23°C and -20°C, respectively, (b) tensile and flexural strength and (c) elongation at break, of PC/SAN alloy modified with SEBS, where PC/SAN/Modifier = 70/21/9.

DSC analysis and morphology observation

The varieties of Glass Transition Temperature (T_g) of PC phase and SAN phase were detected by DSC analysis. Because the SEBS content was small and

the range of testing temperature was from 0 to 200°C, the T_g of the EB part in SEBS was not included in here. And the T_g of the St part in SEBS was overlapped by the T_g of SAN. Table I shows the varieties of T_g of PC, SAN and their alloys. The T_g of PC and SAN are 148.0°C and 110.7°C, respectively. However, as SEBS was added into PC and SAN, their T_g changed to 150.4°C and 110.6°C, respectively. Two T_g 's occurred in the PC/SAN alloy, namely, a T_{g1} of 110.8°C for SAN phase and the other T_{g2} of 144.3°C for PC phase. There were also two T_g 's in PC/SAN/SEBS alloy, however, their value also changed, 111.8°C for SAN phase and 152.0°C for PC phase. Generally speaking, the decrease in the difference of the T_g of the two phases implies an improved compatibility in the polymer alloy. The T_g difference ($T_{g2} - T_{g1}$) of 40.2°C in PC/SAN/SEBS alloy is larger than that of 33.5°C in PC/SAN alloy, which confirm that SEBS has a bad effect to the compatibility of PC and SAN. The same result also occurred in PC/SAN/ABS alloy.

Moreover, the T_g of PC phase in a PC/SAN/SEBS alloy increased from 148.0°C to 152.0°C while the T_g of SAN phase only increased from 110.7°C to 111.8°C. However, in a PC/SAN/ABS alloy, the T_g of SAN phase decreased from 110.7°C to 106.2°C and the T_g of PC phase only decreased from 148.0°C to 147.0°C. It was well-known that the polybutadiene in a PC/ABS alloy was mainly distributed in SAN phase.^{33,34} This might be the reason that the ABS had more influence to T_g of SAN phase than that of PC phase. Because SEBS had more influence to PC phase than SAN phase in a PC/SAN/SEBS alloy. So, it could imply that SEBS was not only distributed in SAN phase but also distributed in PC phase. This implication could be proved by morphology observation as follows.

Scanning electron micrographs (SEMs) for the cyclohexane-etched surfaces of PC/SEBS, SAN/SEBS, and PC/SAN/SEBS alloys are shown in Figure 4, where the holes are the SEBS phase etched by cyclohexane. Figure 4(a) shows that the diameter of SEBS particles dispersed in PC phase is about 0.2–

TABLE I
Glass Transition Temperatures (T_g) of PC, SAN, and their alloys

Recipe	Ratio	T_{g1} (°C)	T_{g2} (°C)	$T_{g2} - T_{g1}$ (°C)
PC	–		148.0	
SAN	–	110.7		
PC/SAN	70/30	110.8	144.3	33.5
SAN/SEBS	70/30	110.6		
PC/SEBS	70/30		150.4	
PC/SAN/SEBS	70/21/9	111.8	152.0	40.2
PC/SAN/ABS	70/21/9	106.2	147.0	40.8

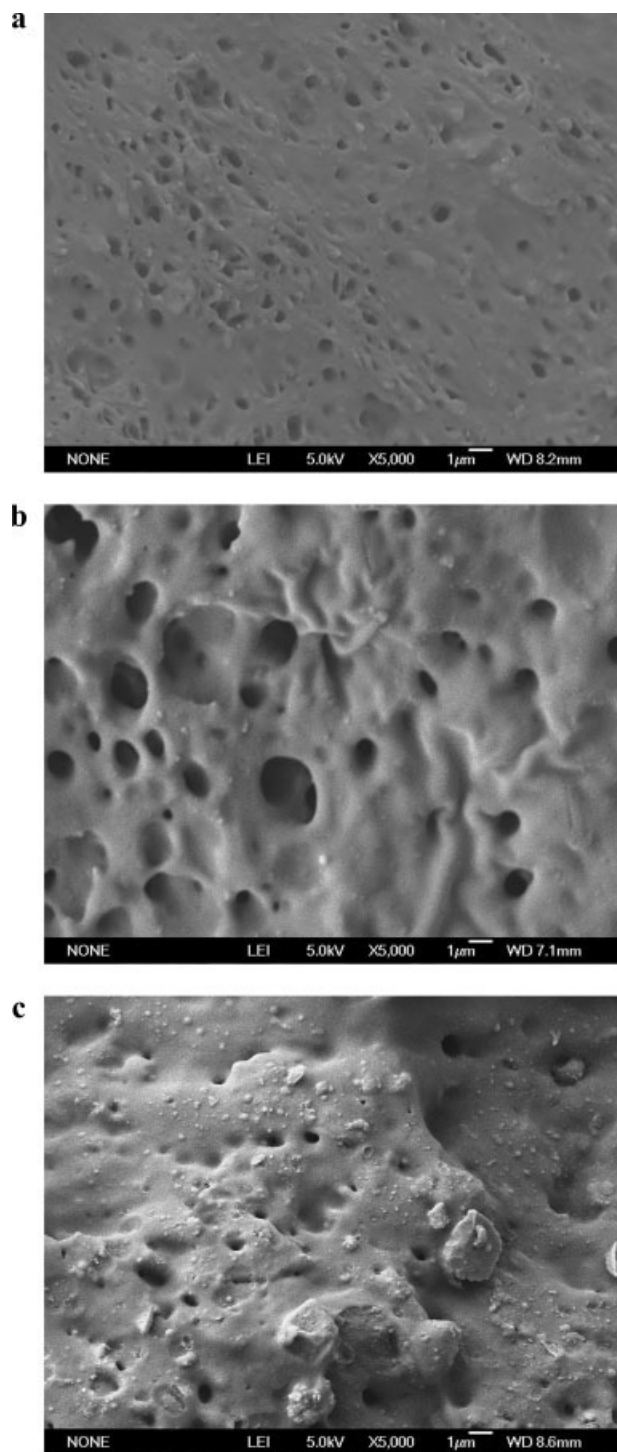


Figure 4 SEM photographs of (a) PC/SEBS, (b) SAN/SEBS and (c) PC/SAN/SEBS after 4 h in boiling cyclohexane.

0.8 μm , which is less than the diameter of SEBS particles about 0.6–2 μm in SAN phase shown as Figure 4(b). This indicates that SEBS has better compatibility with PC than SAN. Moreover, because the diameter of many SEBS particles in PC/SAN/SEBS alloy, as shown in the Figure 4(c), is less than 0.8 μm , it

suggests that quite a number of SEBS is dispersed in PC phase.

It is difficult to find a solvent only etching SAN phase but not etching SEBS phase. So we used alkali to etch PC phase as SAN was continuous phase to further study the dispersion of SEBS phase in PC and SAN phase. Figure 5 is the SEM photographs of

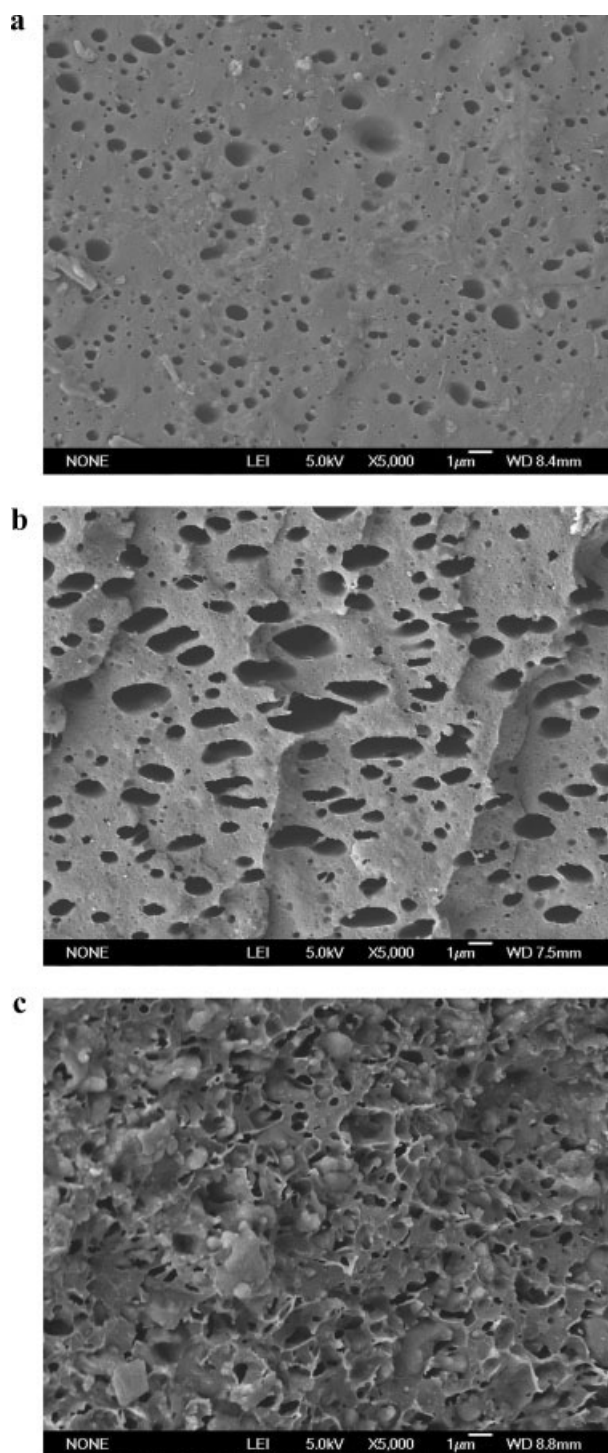


Figure 5 SEM photographs of (a) PC/SAN alloy, (b) PC/SAN/ABS and (c) PC/SAN/SEBS etched by NaOH solution, where PC is 30 wt %.

the alkali-etched surfaces of PC/SAN alloy, PC/SAN/ABS alloy, and PC/SAN/SEBS alloy, where the black holes are the PC phase alkali-etched. Figure 5(a) shows that the holes formed by PC phase are evenly distributed in SAN phase and indicates that PC phase has good compatibility with SAN phase. However, when ABS was added into PC/SAN alloy, shown in Figure 5(b), larger and distortional holes were formed. This indicates that ABS phase mainly existed in SAN phase affects the compatibility of PC and SAN phase and the same conclusion is also acquired from DSC analysis. Singularly, shown as Figure 5(c), many gray particles about 0.3–0.5 μm and little holes about 0.2–0.6 μm are formed in PC/SAN/SEBS alloy. The gray particles should be SEBS particles that early existed in PC phase but now were exposed when PC phase were etched by alkali. This indicates that SEBS phase has good compatibility with PC phase and cocontinuous structure is formed by SAN phase and PC-SEBS phase. As SEBS was used to modify PC/SAN alloy, SEBS was distributed not only in SAN phase but also in PC phase. This might be the reason that impact strength and elongation at break of PC/SAN/SEBS were better than those of PC/SAN/ABS.

CONCLUSIONS

SEBS is a good modifier for PC/SAN alloy and it can obviously increase the impact strength and elongation at break at room temperature of PC/SAN alloy while decrease its tensile and flexural strength and Vicat softening temperature. Especially, Only the addition of 7 wt % SEBS into PC/SAN alloy could obviously improve the PC/SAN alloy's Izod notched impact strength from 130 J/m to 970 J/m. Compared to PC/SAN alloy modified with SEBS, PC/SAN alloy modified with ABS had lower impact strength, which is about 580 J/m when ABS content is 9 wt %. The elongation at break of PC/SAN modified with SEBS was about 120% as SEBS content was 9 wt %. However, PC/SAN alloy modified with ABS had only about 22% elongation at break at similar content. DSC analysis showed that SEBS had more influence on T_g of PC phase than SAN phase in a PC/SAN/SEBS alloy while ABS had more influence on T_g of SAN phase in a PC/SAN/ABS alloy. SEM photographs revealed that the SEBS was distributed not only in SAN phase but also in PC phase. But the ABS was mainly distributed in SAN phase in a PC/SAN/ABS alloy, which was similar to polybutadiene distributed in SAN phase of PC/ABS alloy.

References

- Paul, D. R.; Barlow, J. W.; Keskkula, H. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1988; Vol. 12, p 399.
- Merfeld, G. D.; Paul, D. R. In *Polymer Blends*, Paul, D. R., Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 1. Chapter 3.
- Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1988; Vol. 11, p 48.
- Lee, M. P.; Hiltner, A.; Baer, E. *Polymer* 1992, 33, 685.
- Quintens, D.; Groeninckx, G.; Guest, M.; Aerts, L. *Polym Eng Sci* 1990, 30, 1474.
- Driscoll, S. B.; Benoit, W. P. *Int J Eng Plast* 1995, 8, 79.
- Kelnar, I.; Fortelny I. *J Polym Eng* 1985, 14, 269.
- Quintens, D.; Groeninckx, G. *Polym Eng Sci* 1990, 30, 1474.
- Quintens, D.; Groeninckx, G. *Polym Eng Sci* 1990, 30, 1484.
- Wildes, G.; Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 5609.
- Wildes, G.; Keskkula, H.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1999, 37, 71.
- Cheng, T. W.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1992, 45, 1245.
- Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1988; Vol. 11, p 648.
- Liu, P. Y. (to General Electric Co.) U.S. Pat. 4,390,657 (1983).
- Jalbert, R. L.; Smejkal, J. P. *Mod Plast Encycl* 1976, 53, 108.
- Keitz, J. D.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1984, 29, 3253.
- Quentens, D.; Groeninckx, G.; Guest, M.; Aerts, L. *Polym Eng Sci* 1991, 31, 1207.
- Quentens, D.; Groeninckx, G.; Guest, M.; Aerts, L. *Polym Eng Sci* 1991, 31, 1215.
- Callaghan, T. A.; Takakuwa, K.; Paul, D. R.; Padwa, A. R. *Polymer* 1993, 34, 3796.
- Kwei, T. K.; Frisch, H. L.; Radigan, W.; Vogel, S. *Macromolecules* 1977, 10, 157.
- Wool, R. P. *Polymer Interfaces, Structure and Strength*; Hanser: Munich, 1989; p 336.
- Kang, E. A.; Kim, J. H.; Kim, C. K.; Rhee, H. W.; Oh, S. Y. *Polym Eng Sci* 2000, 40, 2374.
- Kim, J. H.; Kim, C. K. *J Appl Polym Sci* 2003, 89, 2649.
- Zhang, X. F.; Chen, Y. S.; Zhang, Y.; Peng, Z.; Zhang, Y.; Zhou, W. *J Appl Polym Sci* 2001, 81, 831.
- Balakrishnan, S.; Neelakantan, N. R. *Polym Int* 1998, 45, 347.
- Huang, P. *Elastomer* 1997, 7, 24. Chinese.
- Parsons, C. F. *Eur. Pat. Appl. EP 331,970* (1989).
- Lim, J. C.; Park, J. K. *J Appl Polym Sci* 2005, 95, 689.
- Yang, K.; Lee, S. H.; Oh, J. M. *Polym Eng Sci* 1999, 39, 1667.
- Wildes, G.; Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 7089.
- Wildes, G. S.; Harada, T.; Keskkula, H.; et al. *Polymer* 1999, 40, 3069.
- Cao, M. G.; Pu, H. D.; Li, Y. H. *Plast Ind* 1997, 26, 119.
- Husaini, K.; Kishimoto, K.; Notomi, M.; et al. *Fatigue Fract Eng Mater Struct* 2001, 24, 895.
- Inberg, J. P. F.; Gaymans, R. J. *Polymer* 2002, 43, 2425.