Effect of the Compatibilizers on Flame-Retardant Polycarbonate (PC)/Acrylonitrile–Butadiene–Styrene (ABS) Alloy

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ABSTRACT: Polycarbonate (PC) blended with acrylonitrile–butadiene–styrene (ABS) has the maximum notched Izod impact strength, which is 58 kg cm cm^{-1} for PC/ABS1 and 66 kg cm cm^{-1} for PC/ABS2, at a ratio of 80/20 in this study. We selected the ratio of 80/20 to prepare flame-retardant PC/ABS alloys. The compatibility of flame-retardant PC/ABS alloy was examined by differential scanning calorimetry (DSC). The flame-retardant PC/ABS alloy had two values of the glass transition temperature (T_g), indicating that the alloy was not compatible. Three kinds of compatibilizers, methacrylate–butadiene–styrene (MBS), ethylene–vinyl acetate (EVA), and styrene–maleic anhydride (SMA) were used to improve the phenomenon. DSC measurement revealed that after compatibilization the alloy had only one value of T_g, meaning that the alloy became more compatible. Samples were frozen in liquid nitrogen to look at their morphology. We found that the domain sizes were reduced and the surface boundaries were closed and blurred, a feature that could promote the mechanical properties of the alloy. In this study, we also compared the effects of mechanical properties on differential compatibilizers for the flame-retardant PC/ABS alloy. Cycoloy 2800 is a commercial-grade flame-retardant product and was chosen to compare it with our prepared alloys in this study. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 795–805, 1997

INTRODUCTION

Plastics have become more widely applicable in our lives. With the expanding applications, there has arisen a serious concern about their threat to public safety in case of fire. So, it is important to pay attention to the flammability of plastics.

In the last decade, much attention has been paid to the development of polymeric blends. Blends offer the possibility of combining the unique properties of available materials and, thus, are in a position to produce materials with tailor-made properties. This characteristic has advantages over the development of a completely new polymeric material. However, compatibility of the materials is a problem. This problem has been solved in many cases by adding a small amount of additives known as compatibilizers.[1–3] These are generally block and graft copolymers or chemically reactive species which are concentrated at the interface and which act as emulsifiers. The function of the *in situ* (or *in vivo*)-formed compatibilizers have been reported to reduce interfacial tension and to improve the size of dispersed phases[4–8] and the adhesion between two immiscible

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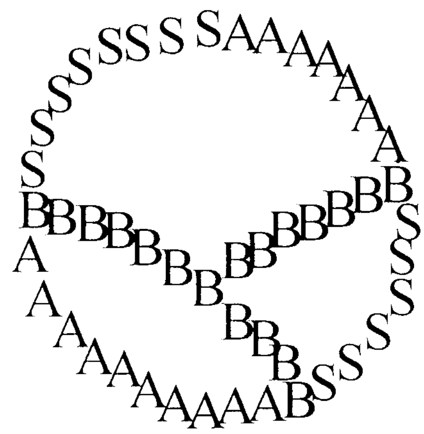
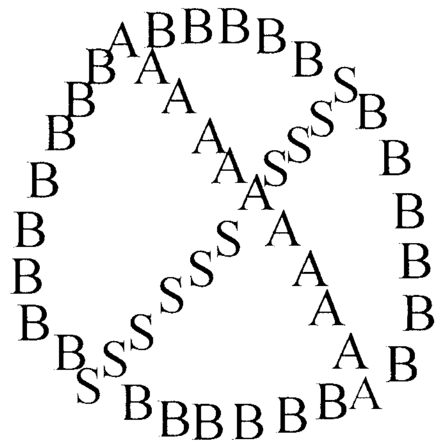
polymers. Compatibilizing reactions should be fast and irreversible and compatibilizers can bear high processing temperatures. Compatibilization can also be done through the addition of low molecular weight components to promote copolymer formation or crosslinking reactions.[9–11]

Acrylonitrile–butadiene–styrene (ABS) is widely used as a thermoplastic with good physical properties. However, the overall mechanical properties of ABS are lower than those of other engineering plastics and the heat-distortion temperature (HDT) of general-grade ABS is lower than 100°C. These deficiencies have limited its application in many fields. By improving its applications, ABS can be blended with other high-performance engineering plastics such as polycarbonate (PC).[12–14] Alloys or blends of PC/ABS have been commercially available for many years. They are reported to provide a useful balance of toughness, heat resistance, and ease of processing at a lower cost.

Meanwhile, thermoplastics are more or less easily combustible. Therefore, efforts to develop flame-retarding plastic materials have been proceeding with the increasing use of thermoplastics. However, addition of large amounts of flame retardants decreases the properties of thermoplastics and poses some problems on processability. Flame-retardant plasticizing polymers generally decrease the thermomechanical properties, and a nonsoluble solid-state flame retardant in a polymer significantly decreases the impact strength. As a result, special treatment is required. In this study, we added compatibilizers for special treatment.



Model A



Model B

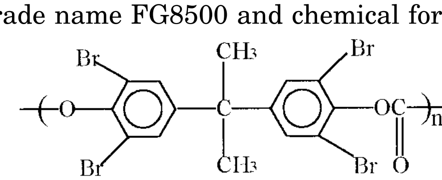
Figure 1 The models of ABS morphologies.

EXPERIMENTAL

Materials

The PC resin was supplied by GE Plastics Japan; meltflow index (MFI) = 9.5 at 300°C/1.2 kg. Its density was 1.2 g/cm^3 and the HDT = 132–138°C. The ABS resin was ABS1 (Taitalac GP-1000 made by Taita Chemicals Co., composition: 22% acrylonitrile, 19% butadiene, 59% styrene, MFI = 1.2–2.0 at 200°C/5 kg) and ABS2 (Taitalac GP-3000H made by Taita Chemicals Co., composition: 27% acrylonitrile, 24% butadiene, 49% styrene, MFI = 0.5–0.8 at 200°C/5 kg).

The flame retardant used was a tetrabromobisphenol A carbonate oligomer containing 58% aromatic bromine made by Teijin Chemicals, with the trade name FG8500 and chemical formula



The flame assistant used was commercial-grade antimony trioxide (Sb_2O_3) made by Gider Chemical Co. The compatibilizers used were methacrylate–butadiene–styrene (MBS), KCA-102, made

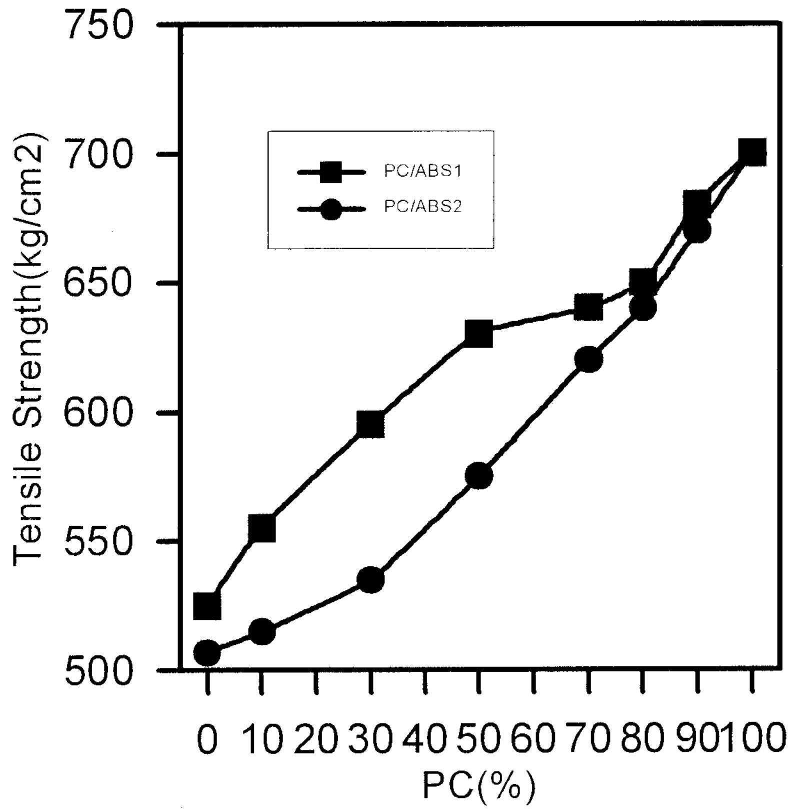


Figure 2 Tensile strength versus PC contents of PC/ABS blends with various rubber contents in ABS.

by Gin Wen Enterprise Co.; ethylene–vinyl acetate (EVA), UE659 made by USI Far East Co., having a 25% VA content; and styrene–maleic anhydride (SMA), Cat. #457, powder, styrene content 67%, made by Scientific Polymer Products.

Melt Blending and Specimen Preparation

PC pellets and ABS pellets were dried separately at 120 and 80°C in a vacuum for 4 h. The samples were then blended in a twin-screw extruder, ZSK-30, Werner and Pfleiderer, $L/D = 31$. The machine maintained the following conditions: 240–260°C and screw speed of 110 rpm. After extrusion, the pellets were loaded into the injection machine to prepare standard test specimens. The temperatures of injection were adjusted to give the optimized processing conditions according to the blending compositions.

Mechanical Properties

Tensile properties were measured by the ASTM D638 test method using an Instron universal testing machine Model 1130. The speed was 50 mm/min, and the chart speed was 100 cm/min. The cross-head load was 500 kg. The modulus was determined from the slope of the initial part of the stress–strain curve within the linear trend. Notched Izod impact strength was measured according to the ASTM D256 test method using the Izod type. The thickness was $\frac{1}{8}$ in.

Melting Flow Index (MFI)

The MFI of each blend was measured by the ASTM D1238 test method at 250°C with a 2160 kg load.

Heat-Distortion Temperature (HDT)

The HDT of each blend was measured by the ASTM D648 test method (264 psi load).

Thermal Properties

A DuPont Instrument 1090B analyzer equipped with a 910 differential scanning calorimeter

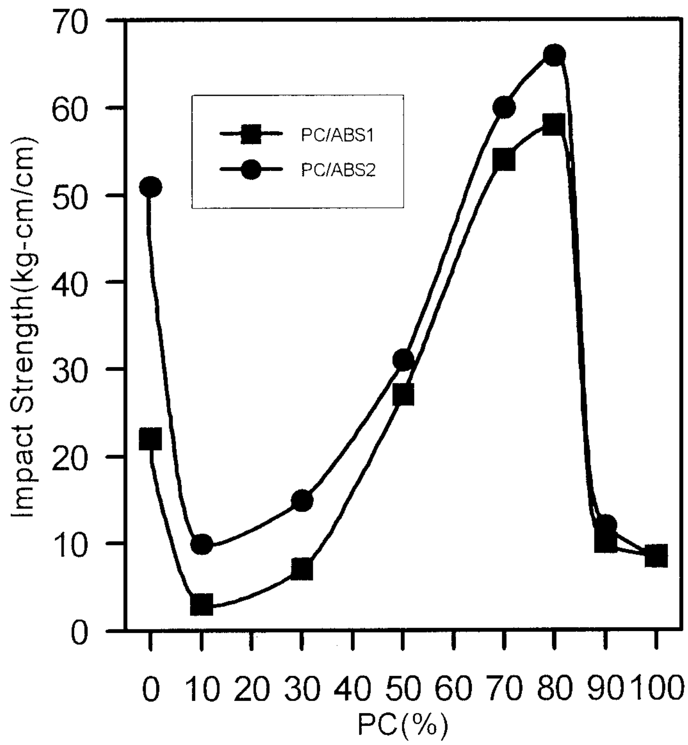


Figure 3 Notched Izod impact strength versus PC contents of PC/ABS blends with various rubber contents in ABS.

(DSC) was used at a heating rate of 10°C/min to measure the glass transition temperature (T_g).

Scan Electron Microscopy (SEM)

Specimens were frozen in liquid nitrogen for 10 min and broken. The fracture surfaces were coated with a thin layer of gold under a vacuum and measured by SEM with ABT-55. The morphology was studied through the SEM photographs.

Limiting Oxygen Index (LOI)

The limiting oxygen index (LOI) was measured in accordance with ASTM D2863-70. The sample, consisting of a bar of 6 mm wide, 3 mm thick, and 150 mm in length, was placed vertically at the center of a glass chimney which is 75 mm in diameter and has a minimum height of 450 mm. Thereafter, a mixture of oxygen and nitrogen of known composition was passed through the chimney at a rate of about 11.3 L/min. When the sample continued to burn for 3 min or when the flame propagated at a length of 50 mm, the oxygen content of the gaseous mixture corresponded to the LOI of the sample:

$$\text{LOI\%} = \frac{O_2}{N_2 + O_2} \times 100\%$$

RESULTS AND DISCUSSION

Mechanical Properties of PC/ABS Alloy

Paul et al. reported that the PC/SAN system[15] is partially miscible but that PC/polybutadiene (PB)[13] is an immiscible one. Therefore, ABS blended with PC will be a partially miscible system, because ABS is a terpolymer which is grafted acrylonitrile and styrene onto PB to form a two-phase rigid matrix toughened with rubber. We suppose that ABS with lower rubber contents will have an ABS matrix rich with the SAN phase in the outside (Model A), thus bringing about a better compatibility in PC/ABS1 blends. In contrast, ABS with higher rubber contents will have an ABS matrix rich with rubber in the outside (Model B) and, consequently, cause the incompatibility in PC/ABS2. For that reason, the compati-

Table I The Properties of Flame-Retardant (10 phr) PC/ABS Alloy with Various Compatibilizers Added

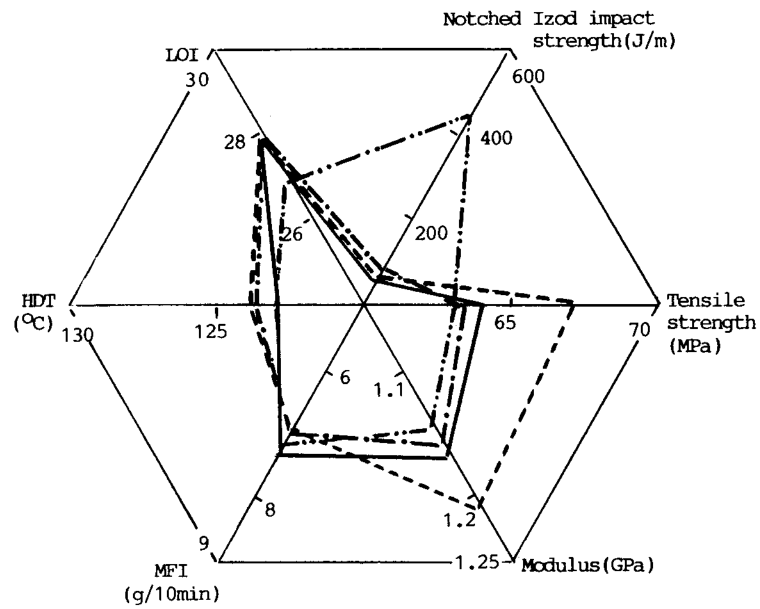
	Notched Izod Impact Strength (J/m)	Tensile Strength (MPa)	Modulus (GPa)	HDT (°C)	MFI (g/10 min)	LOI
FR (10 phr)	62.7	64.2	1.17	122.7	7.30	28
+MBS (1 phr)	67.6	63.7	1.16	123.5	7.00	28.0
+MBS (3 phr)	470.4	63.7	1.16	124.1	6.80	28.0
+MBS (5 phr)	519.4	62.7	1.13	125.3	6.60	28.0
+EVA (1 phr)	460.6	63.3	1.14	122.8	7.15	27.0
+EVA (3 phr)	578.2	62.8	1.14	123.0	6.99	26.5
+EVA (5 phr)	89.1	62.7	1.12	124.2	6.84	26.0
+SMA (1 phr)	63.9	67.4	1.21	123.6	6.86	28.0
+SMA (3 phr)	65.6	68.0	1.23	126.4	6.76	28.0
+SMA (5 phr)	67.5	68.8	1.25	127.7	6.71	27.5
FR (15 phr)	57.8	63.0	1.15	124.6	8.50	30
+MBS (1 phr)	62.7	62.7	1.13	126.4	8.30	30
+MBS (3 phr)	456.7	61.8	1.12	126.7	7.10	30
+MBS (5 phr)	473.3	61.2	1.11	127.7	6.60	30
+EVA (1 phr)	58.4	62.7	1.13	126.2	8.40	30
+EVA (3 phr)	64.7	62.4	1.12	126.4	7.60	29.5
+EVA (5 phr)	79.3	62.1	1.11	127.0	7.10	28.5
+SMA (1 phr)	54.1	66.4	1.20	126.9	7.32	30
+SMA (3 phr)	48.9	67.3	1.22	128.0	7.28	30
+SMA (5 phr)	39.5	68.0	1.25	128.8	7.08	30
Cycoloy 2800	452.8	55.1	1.81	80.0	18.00	29

bility of PC and ABS will be decided by the amount of butadiene (B) contained in ABS. The schematic models are shown as Figure 1. Hence, when ABS with a high B content is blended with PC, there will be a low tensile strength. However, the notched Izod impact strength will be higher than that of ABS with a low B content blended with PC. Figure 2 presents the behavior of tensile strength vs. various ABS contents for PC/ABS alloys. The tensile strength decreased with the amount of the ABS system. When ABS with a high B content is blended with PC, there will be a low tensile strength. The tensile strength of ABS with a high rubber content shows a lower value than does the ABS with a lower rubber content.

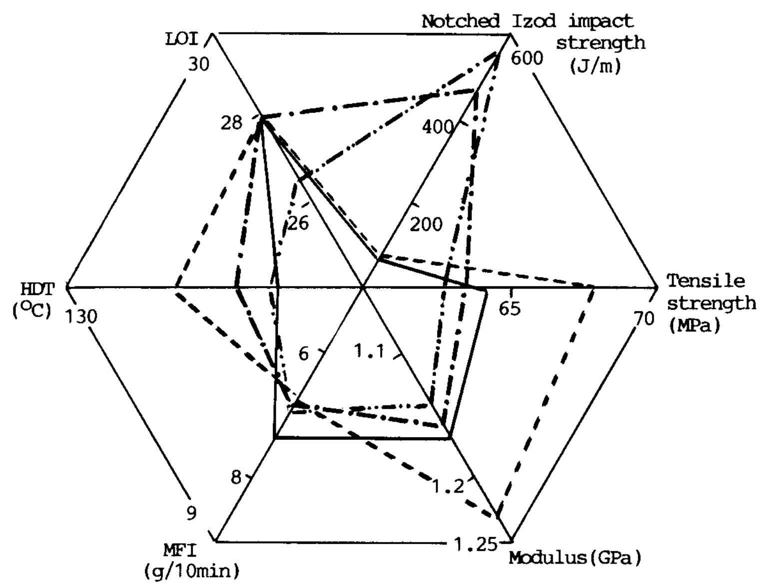
The notched Izod impact strength vs. various ABS contents for PC/ABS alloys is shown in Figure 3. While PC has the notch and thickness sensitivity in unmodified commercial engineering plastics, blending with ABS can improve this phenomenon. When the PC content is raised to 80%, the impact strength increases significantly. The result may be attributed to the 20% ABS that exists in a dispersed phase. The phase provides only slight phase separation and uniform dispersion, which can absorb a certain amount of energy. The notched Izod impact strength of ABS with a high B content was higher than that of ABS with a low B content blended with PC.

Compatibilizers for Flame-Retardant PC/ABS Alloy

Flame retardants were added into the PC/ABS alloy and the mechanical properties were weakened. MBS, EVA, and SMA were added into the flame-retardant PC/ABS alloy to strengthen the properties. By utilizing compatibilizers with a chemical structure of similar to PC or ABS, they will dissolve into the PC/ABS alloy. They all have the —COO— carbonyl group that can dissolve into PC. We know that the compatibilizers concentrate at the interface, just as a thin molecular layer which will show its function. Suppose that there are two situations that may take place after fracture: If the content of the compatibilizer is inadequate, fracture will take place between the two phases, because the interfacial adhesion is not formed perfectly to improve the interface of the two polymers. If the content of the compatibilizer is excessive, fracture will take place between



(a)

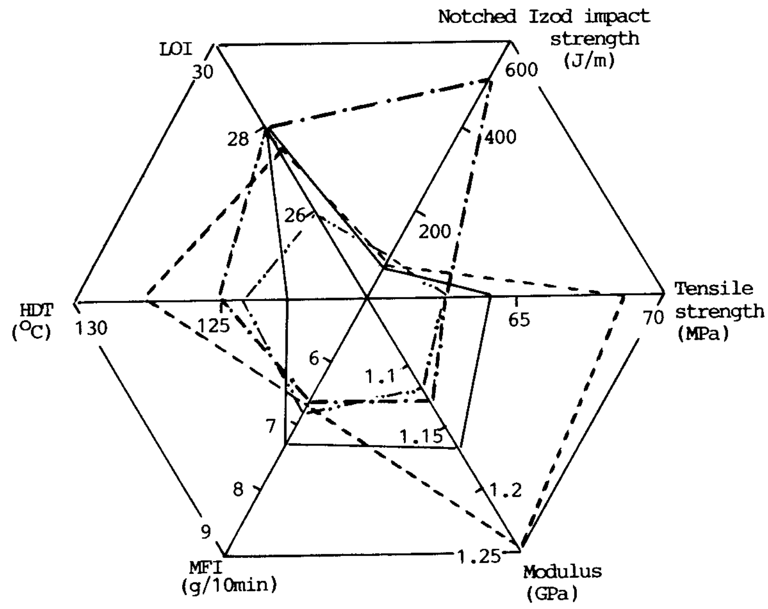


(b)

Figure 4 (a) The properties of flame-retardant (10 phr) PC/ABS alloy with compatibilizers for 1 phr: (——) without compatibilizer; (– • –) MBS; (– • • –) EVA; (----) SMA. (b) The properties of flame-retardant (10 phr) PC/ABS alloy with compatibilizers for 3 phr: (——) without compatibilizer; (– • –) MBS; (– • • –) EVA; (----) SMA. (c) The properties of flame-retardant (10 phr) PC/ABS alloy with compatibilizers for 5 phr: (——) without compatibilizer; (– • –) MBS; (– • • –) EVA; (----) SMA.

two layers, because as a compatibilizer layer is formed between two polymers, no special interaction comes into being between two polymers.

Table I shows all the properties of flame-retardant PC/ABS alloy with and without compatibilization. We also list the commercial-grade flame-retardant product Cycoloy 2800 for reference. Figure 4 shows the properties of various contents of compatibilizers added into the PC/ABS alloy containing 10 phr of the flame retardant.



(c)

Figure 4 (*Continued from the previous page*)

Figure 5 shows the properties of various contents of compatibilizers added into the PC/ABS alloy containing 15 phr of the flame retardant. Just by adding 1 phr of EVA into the PC/ABS alloy containing the 10 phr flame retardant, the notched Izod impact strength increased significantly. Adding the same content of MBS did not have as much effect as EVA did, because the content of MBS is inadequate to form a perfect interface between PC and ABS. When the content of MBS exceeds 3 phr, the amount is enough to form the perfect interfacial adhesion to raise the impact strength. In the case when 5 phr of EVA was added, the content was found to be too much and the EVA did not form a thin layer. EVA did not have any special interactions between PC and ABS. Increasing the content of the flame retardant will destroy the interfacial adhesion of the alloy as the mechanical properties are weakened. However, adding SMA does not help the notched Izod impact strength because SMA does not have the soft-chain segment as MBS and EVA do to improve the impact strength. SMA is a brittle copolymer. Adding SMA increases the tensile strength and modulus for the flame-retardant PC/ABS alloy. By contrast, adding MBS and EVA to the alloys would show only a slight decrease.

When the content of compatibilizers is increased, the MFI is decreased. This is due to intermolecular actions. Adding the compatibilizer into the alloy makes the material interforce much stronger but retards the processability of the alloys. In this study, there are many factors affecting the MFI, such as temperature, interactions of molecules, contents of the compatibilizers' components, and kinds of compatibilizers. All these factors must be taken into consideration. The LOI is the standard of a material's flammability. Adding compatibilizers does not affect the LOI very much.

Figures 6–8 show the DSC measurement. Without adding compatibilizers, the flame-retardant PC/ABS alloy is a partially miscible system that has two values of T_g. After adding compatibilizers, the alloys had only one value of T_g; in addition, the compatibilizers were effective in improving the compatibility of the flame-retardant PC/ABS alloy.

To observe the fractured surfaces of the alloys, SEM is used to study the morphology. The morphologies of the flame-retardant PC/ABS alloy without compatibilizers are shown in Figure 9. At the interface, there is not any adhesion among PC, ABS, and the flame retardant; thus, in the fracturing procedure, many spherical shapes are pulled away from their original positions to create holes in the surface of the resins. By adding compatibilizers, a significant difference in the morphology between binary alloys is expected. We found

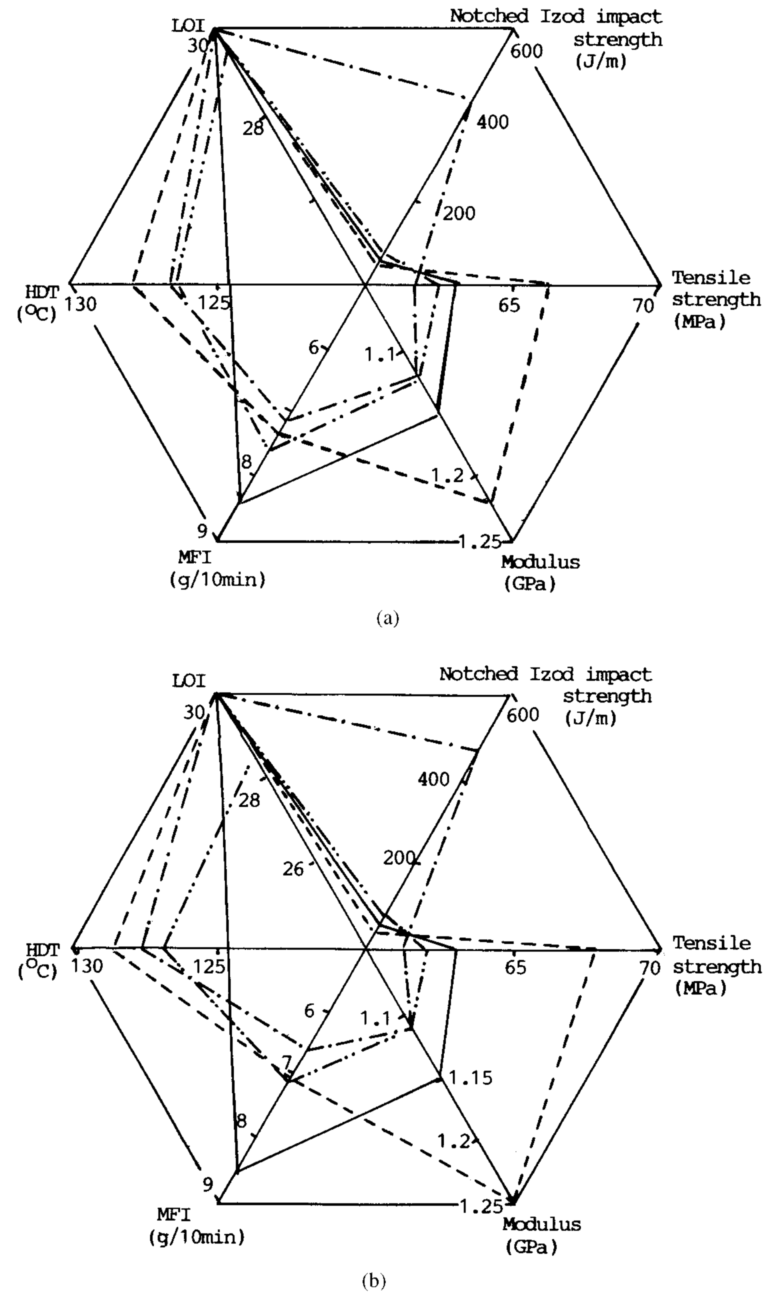


Figure 5 (a) The properties of flame-retardant (15 phr) PC/ABS alloy with compatibilizers for 3 phr: (——) without compatibilizer; (– · –) MBS; (– · · –) EVA; (----) SMA. (b) The properties of flame-retardant (15 phr) PC/ABS alloy with compatibilizers for 5 phr: (——) without compatibilizer; (– · –) MBS; (– · · –) EVA; (----) SMA.

that the domain sizes were reduced and the surface boundaries were closed and blurred. This effect will promote the mechanical properties of the flame-retardant PC/ABS alloy. Figure 10 shows the morphology of the flame-retardant (10 phr) PC/ABS alloy after adding 3 phr of compatibilizers.

CONCLUSIONS

With increasing content of ABS, the tensile strength of the PC/ABS alloy is reduced. The tensile strength of ABS with a higher B content is lower than that of ABS with a lower rubber content, because rubber can toughen the resins. How-

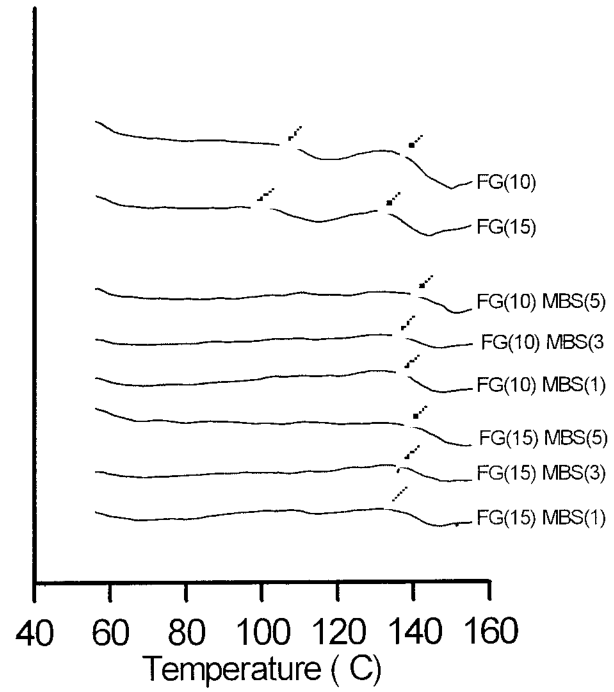


Figure 6 Glass transition temperature versus various MBS contents for flame-retardant PC/ABS alloy.

ever, the notched Izod impact strength reaches its maximum when the composition of PC/ABS stands at 80/20.

Adding the flame retardant raised the value of the LOI but lowered the mechanical properties of the PC/ABS alloy. Addition of MBS up to 3 phr increased the notched Izod impact strength significantly for the PC/ABS alloy containing a 10 and 15 phr flame retardant. Addition of 1 and 3 phr EVA into the alloys of the 10 phr flame retardant increased the impact strength markedly. By adding 5 phr of EVA, the impact strength decreased. Addition of SMA did not affect the impact strength of the flame-retardant PC/ABS alloy. However, for the tensile strength and modulus, adding SMA increases the properties. By contrast, by adding MBS or EVA to the alloy, the properties would show only a slight decrease.

For T_g, all three compatibilizers were effective. Without the compatibilizers, the flame-retardant PC/ABS alloys had two values of T_g. After compatibilization, the modified alloys had only one value of T_g, indicating that the alloy system became more compatible. SEM showed that the surface boundaries were blurred and closed, an effect

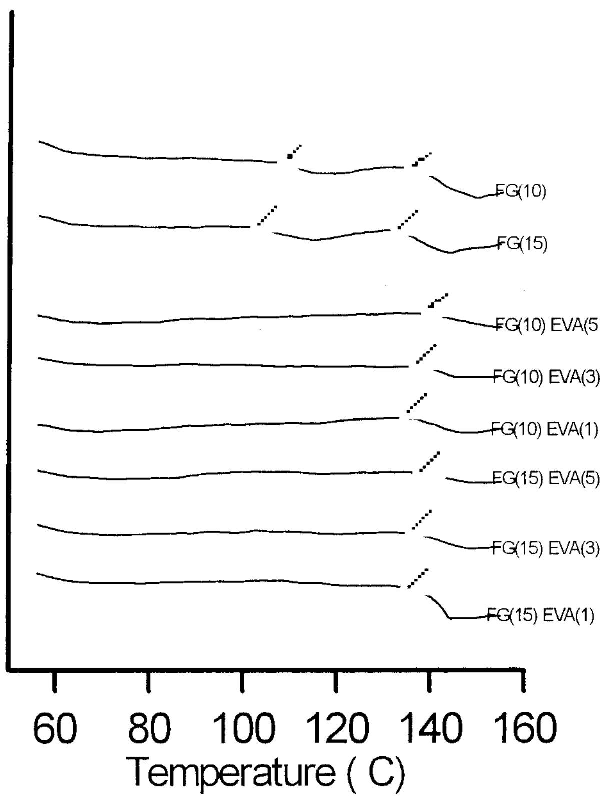


Figure 7 Glass transition temperature versus various EVA contents for flame-retardant PC/ABS alloy.

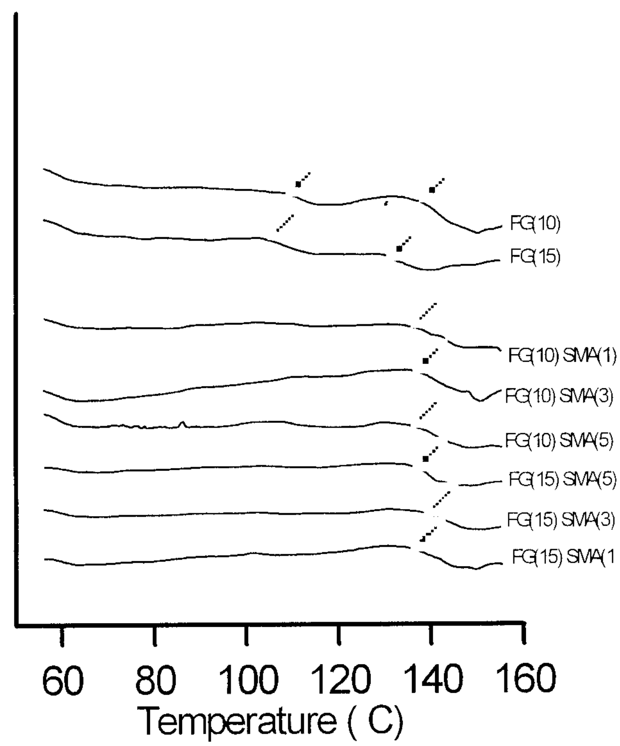
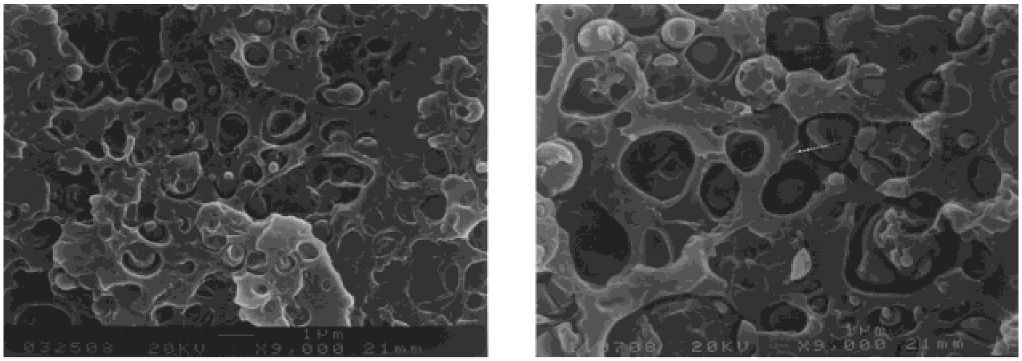


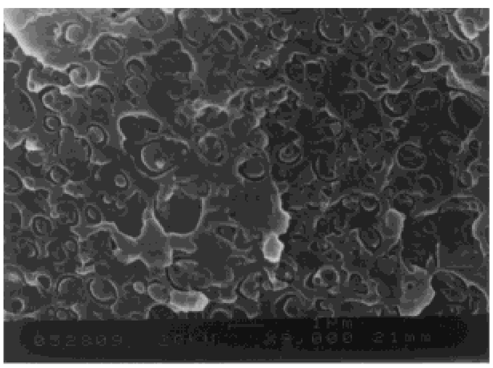
Figure 8 Glass transition temperature versus various SMA contents for flame-retardant PC/ABS alloy.

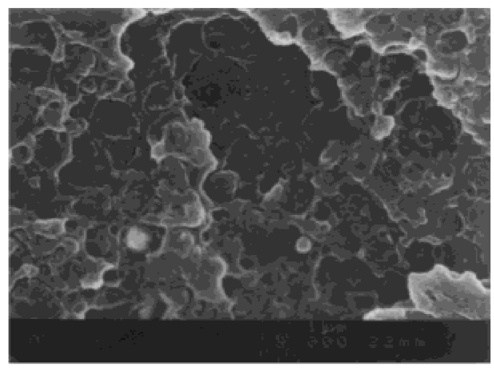


(a) FR (10phr) (b) FR (15phr)

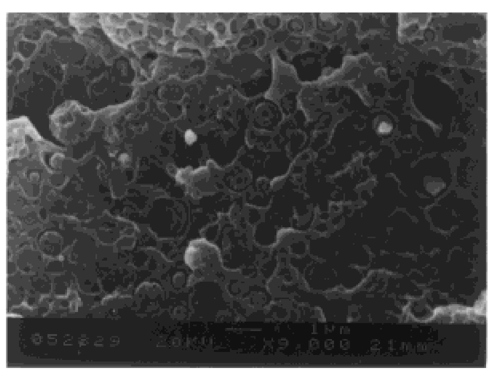
Figure 9 Morphologies of flame retardant PC/ABS without compatibilizers.

helpful to mechanical properties. Compared with the commercial flame-retardant products, Cycoloy 2800, we found that adding 3 and 5 phr of MBS to the PC/ABS alloy of the 15 phr flame retardant gave better results than did C2800 in terms of impact strength, tensile strength, HDT, and LOI.





(a) MBS (b)EVA



(c) SMA

Figure 10 Morphologies of flame-retardant (10 phr) PC/ABS alloys after adding 3 phr of compatibilizers.

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