Effects of Acrylonitrile Content on PC/ABS Alloy Systems with a Flame Retardant

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ABSTRACT: To investigate the effect of a flame retardant on PC/ABS alloy systems, a reactive-type brominated epoxy resin was used as a flame retardant, and mixed with PC/ABS at various amount using a twin-screw extruder. The rheological, morphological, mechanical, and thermal properties were investigated as a function of acrylonitrile (AN) content in ABS. The shear viscosity of the PC/ABS blend increased as the AN content in ABS increased. Temperature drastically affected the shear viscosity in the ABS matrix, but not as much in the PC matrix. A blend of PC 50% containing AN 22% is suitable to process because its shear viscosity is low in the high shear rate region and its mechanical properties drastically increase in the beginning of the PC matrix. In addition, gradual increases of heat distortion temperature were observed in the entire range of the PC content. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 417–423, 2000

Key words: PC; ABS; flame retardant; polymer alloy; rheological property

INTRODUCTION

Polymer blending and alloy systems allow the production of a synergistic balance of properties by the combination of the best properties of the constituents, with relative ease. The PC/ABS alloy chosen in this study has a high impact strength, a high mechanical strength, and many other desirable properties. Furthermore, because it can be easily processed, it has become highly utilized in engineering thermoplastics for many applications.[1,2] Thus, there have been many studies performed on the mechanical, thermal, rheological, and dielectric properties of PC/ABS systems.[3–6]

Polycarbonate (PC) is a resin in which groups of dihydric or polyhydric phenols are linked through carbonate groups. Virtually all general-purpose PCs are based on bisphenol A. PC is a high-performance amorphous engineering thermoplastics with an exceptionally high impact strength, clarity, heat resistance, dimensional stability, and a good electric property. Other properties include excellent colorability, high gloss, sterilizability, flame retardancy, biocompatibility, and strain resistance.[7] However, PC does not have a true melting point, as is the case for crystalline polymers, but does have a high glass transition temperature of approximately 150°C.[8] Therefore, processability of PC is rather difficult because its high melt viscosity hinders the fluidity of PC, and the residual stress resulting from processing causes fractures. To improve these problems, new polymer blends and alloys have been developed.[9,10]

ABS (acrylonitrile–butadiene–styrene terpolymer) resins, a blending component of PC, belong

to a very versatile family of engineering thermoplastics. Acrylonitrile contributes heat resistance, chemical resistance, and surface hardness to the system. In addition, the styrene component contributes processibility, rigidity, and strength. On the other hand, butadiene contributes toughness and impact resistance.

ABS plastics are two-phase systems. Styrene–acrylonitrile (SAN) forms the continuous matrix phase, and the second phase is composed of dispersed polybutadiene particles, which have a layer of SAN grafted onto their surface. This SAN layer makes the two phases compatible.[11] Therefore, the property balance of ABS is affected by both the ratio of the monomers and the molecular structure of the two phases. Although this makes the production of ABS very complex, it allows a great flexibility in the product property design. As a result of the unique morphology of ABS, hundreds of different commercially available products have been developed.

Despite several classes of ABS products with different impact strengths and special purposes, the mechanical properties of ABS are lower than those of engineering plastics, so the applications of ABS are limited. Thus, to expand its applications, ABS can be blended with other high-performance engineering plastics, such as PC.[12,13]

However, thermoplastics are easily combustible. Therefore, with the increasing use of thermoplastics, there have been numerous efforts to develop flame-retarding plastic materials. As a result, flame-retarding formulations are available for most thermoplastics, which reduce the probability of burning in the initial phase of a fire. Flame-retardant plastics thus secure the utilization for thermoplastics by increasing their range of applications.[14]

Flame retardants are classified as additive type and reactive type. Additive-type flame retardants are present as fillers, while reactive-type flame retardants are introduced into the resin system through a chemical reaction. However, the addition of large amounts of flame retardants decreases the properties of thermoplastics, and results in some problems with processability. Flame-retardant plasticizing polymers generally decrease thermomechanical properties, and a nonsoluble solid-state flame retardant in polymers significantly decreases the impact strength, so special treatment is required.[15] In addition, the flame retardant must be able to withstand the extreme processing conditions without degrading or adversely affecting the other components.

Common additive-type flame retardants are the halogenated aliphatics, brominated aromatics, halogenated, and nonhalogenated organophosphates, and the oxides of aluminum and antimony. Also, reactive flame retardants have functional groups that can react with other monomers, which bond to the polymer. They commonly include epoxies, rigid polyurethane foams, and unsaturated polyesters. Antimony oxide is also frequently used as a synergist with various reactive flame retardants in addition to its wide use as an additives.[16]

In this study, reactive-type brominated epoxy resins were examined as flame retardants in PC/ABS blend systems. The blending ratios of PC/ABS were 10/90, 30/70, 50/50, 70/30, and 90/10 (%). In each case, 15 phr of flame retardant, 5 phr of antimony oxide, and 0.3 phr of antioxidant were added. Compounding was performed by a twin-screw extruder with an L/D ratio of 34.5 : 1. The mechanical, thermal, and rheological properties of the samples were then studied. To investigate the effects of AN content in ABS on PC/ABS alloy systems, the morphology of the blend was also observed.

EXPERIMENTAL

Materials

Powder forms of PC and ABS were selected in this study, because powder forms were suitable for dispersion and processing. Bisphenol A PC ($M_w = 5.26 \times 10^4$) was obtained from Teijin Co., Japan, because of the specific grade viscosity. ABS was obtained from Cheil Industries Inc., Korea, at three different acrylonitrile (AN) contents (22, 24, and 27%). The ABS commercially used in the market is a blend of SAN (styrene–acrylonitrile copolymer) with graft-ABS at a ratio of 75/25 (%). Graft-ABS is composed of butadiene and SAN. The AN content was fixed at 14.4% in graft-ABS. However, it was varied in SAN at 25.0, 26.6, and 31.7%. Therefore, the overall AN contents in ABS were 22, 24, and 27%. These values are summarized in Table I.

The compositions and molecular weights of the various ABSs are listed in Table II. The butadiene (BD) content in ABS was fixed at 12% to observe the effects of AN content in ABS. Styrene monomer (SM) content in ABS was decreased as AN content increased.

Table I   AN Content in ABS

Code	g-ABS (25%)	SAN (ABS)	Overall AN Content
AN22	25% × 0.144	75% × 0.250	22%
AN24	25% × 0.144	75% × 0.266	24%
AN27	25% × 0.144	75% × 0.317	27%

The flame retardant (FR) used in this study was a reactive-type brominated epoxy resin (BER) (shown below) that was obtained from the Makhtshim Co. The molecular weight is 4×10^4, the density is 1.8 g/cm^3, and the bromine content is 53–54 (%).

CH$_3$(CH$_2$)—[Br—⬡—Br—CH$_2$—⬡—Br—Br]$_n$—(CH$_2$)$_4$—CH—CH$_2$ (with epoxide O)
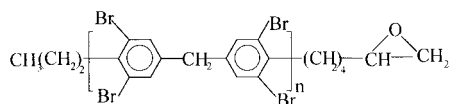
In addition, Sb$_2$O$_3$ ($M_w = 292$) was introduced as a flame-retarding additive. A 0.3 phr of an antioxidant (from Adeka Arbus Co.) was also added.

Specimen Preparation

Both PC and ABS were dried at 120°C for 4 h before processing to remove moisture, because moisture causes hydrolysis during processing.[8] The melt blending method was adopted by using a twin-screw extruder with a L/D ratio of 34.5 : 1. Test bars were made by injection molding. The compositions of the PC/ABS alloy systems are listed in Table III.

Measurements

Rheology

The investigation of shear viscosity as a function of shear rate is essential to estimate the processing condition and mechanical properties of the final product of the polymer alloy system. A cap-

Table II   Molecular Weight and Composition of ABS

Code	AN (%)	BD (%)	SM (%)	Molecular Weight
AN22	22	12	66	$M_w = 1.05 \times 10^5$
AN24	24	12	64	$M_w = 1.54 \times 10^5$
AN27	27	12	61	$M_w = 1.28 \times 10^5$

Table III   Composition of PC/ABS Alloy Systems

PC (%)	ABS (%)	g-ABS (%)	SAN (%)	FR (phr)	Sb$_2$O$_3$ (phr)	Antioxidant (phr)
10	90	25	75	15	5	0.3
30	70	25	75	15	5	0.3
50	50	25	75	15	5	0.3
70	30	25	75	15	5	0.3
90	10	25	75	15	5	0.3

illary rheometer (Rosand Inc., UK) was used for this experiment. The L/D ratio (long die length/short die length) was 32/1. Various piston speeds were used [166.60, 133.30, 66.66, 33.33, 16.66, 6.67, and 3.33 (mm/min)] at various temperatures (240, 260, and 280°C). Results were then calculated using the Rabinowitsch correction.

Morphology

A scanning electron microscopy (SEM) (JSM-840A, JEOL Inc., Japan) was used to investigate the morphology. The magnification was 5000 at a 20-kV light voltage. After the sample was dried, it was immerged in liquid nitrogen so that its surface was not affected by the external stress. It was then fractured using an Izod impact tester. The sample was coated with gold to make the surface conductible.

Mechanical Test

To obtain the tensile property, a universial testing machine (UTM) (Instron Inc., USA) was used, as suggested by ASTM standards. The crosshead speed of the tensile strength test was 5 mm/min. An Izod impact tester (Toyoseiki Inc., Japan) was further used to measure the Izod impact strength. The angle that was denoted by a pointer was converted to energy.

Thermal Test

A heat distortion temperature (HDT) tester (Toyoseiki Inc., Japan) was used to measure the HDT. The specimen was immersed in a silicone oil bath, whose temperature was increased at a constant rate of 2°C/min, from 50 to 200°C. The specimen was then loaded at a constant stress (or pressure) of 18.6 kg/cm^2, and then deformed as the temperature was increased. The HDT was
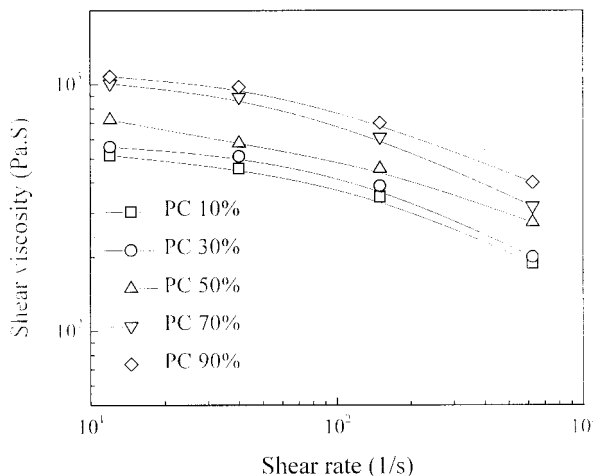
Figure 1 Shear viscosity vs. shear rate for various ratios of the PC/ABS blend with AN 22% in ABS at 240°C.

chosen as the temperature at which the deformation length was 10^{-2} inches.

RESULTS AND DISCUSSION

Rheological Property

In this study, shear viscosity was obtained as a function of shear rate. The apparent shear viscosity is used as a measure of the processability. The polymer melt has a high viscosity that is difficult to process. A low viscosity is required for processing, and in general, viscosity decreases as temperature increases. However, because higher temperatures degrade the polymer chain, a compromise must be made.

Figure 1 shows shear viscosity vs. shear rate for the various blending ratios of PC/ABS blends at 240°C. Shear viscosity decreases as shear rate increases. This is a general characteristic of polymer melts. As the PC content is increased in the PC/ABS blends, the shear viscosity is increased because the shear viscosity of pure PC is much higher than that of pure ABS. Furthermore, the shear viscosity increased as the AN content in ABS increased, and the styrene-block content in ABS decreased. In addition, styrene-block shows a glass transition behavior near 100°C, and acrylonitrile-block has a higher processing temperature. So, styrene-block degrades faster as the temperature increases. Usually, styrene-block in ABS is used as an adjusting agent for the processability by lowering the viscosity.[17]

The shear viscosity and shear rate were also measured for various blending ratios of PC/ABS blends at temperatures of 260 and 280°C. Similar shear viscosity behavior was observed at 260 and 280°C.

Figure 2 plots the shear viscosity vs. the blending ratios of PC/ABS at a low shear rate and at various temperatures. A low shear rate corresponds to 10 s^{-1} from the capillary rheometer. For a concentration up to 50% of PC, the resulting ABS forms the ABS matrix with a continuous phase structure. The shear viscosity of the ABS matrix is highly dependent on the PC content. Because ABS has poor thermal property compared to PC, the ABS matrix is rather easily affected by heat. Therefore, at a PC content greater than 50%, the shear viscosity of the PC matrix is hardly affected by heat. These results are consistent with the case of a high shear rate, as shown in Figure 3. The high shear rate was 5 $\times 10^2$ s^{-1} using a capillary rheometer. Therefore, from the economical point of view, PC 50% is very suitable for the application, because PC is more expensive than ABS. At a PC 90% blend, the shear viscosities are the same at both 240 and 260°C. This indicates that the blends having a rich PC content are hardly affected by heat, because PC has a higher processing temperature.[7] However, the shear viscosity of PC decreased at 280°C. In addition, the shear viscosity of blend in a high shear rate was less affected than that in a low shear rate at 280°C.
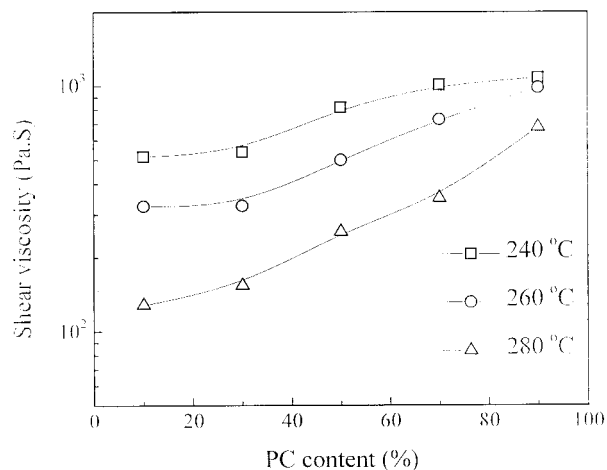

Figure 2 Shear viscosity vs. a blending ratio of PC/ABS with AN 22% in ABS for various temperatures at a low shear rate.
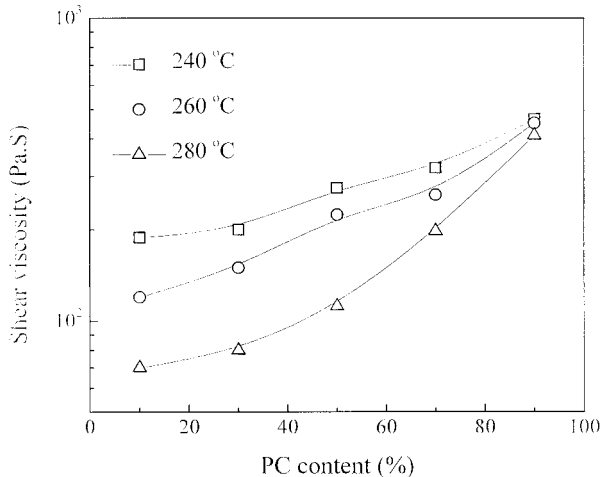
Figure 3 Shear viscosity vs. blending ratios of PC/ABS with AN 22% in ABS for various temperatures at a high shear rate.

Morphology

Figure 4 shows the morphology of blends for 22% AN contents for three different blending ratios of PC/ABS. A PC/ABS blend with a flame retardant has four different phase structures. The first phase is the SAN phase, the second is the buta-diene–rubber particle on the SAN phase, the third is the PC phase, and the fourth is an insoluble solid additive flame retardant. The white particle in the figure is the flame retardant, which was well dispersed in both the PC phase and ABS phase. The component with the higher content becomes the continuous phase structure, and the minor component becomes dispersed particles. Spherical domains of minor components are formed according to the weight fraction of PC and ABS. When the weight fractions of PC and ABS phase are equal, the PC and ABS form a continuous phase structure with a physical adhesion.[18] So it is anticipated that the mechanical properties were improved. In Figure 4, the fracture surface shows the ductile property, suggesting that PC and ABS have a partial interaction. Blends with an interaction between the two components have a higher impact strength and are made ductile at the surface. In blends with AN 24% and AN 27% for 50% PC, the morphology shows the brittle characteristics, in comparison to the higher impact strength of AN 22%, as shown in Figure 5. Thus, blends with AN 22% have a greater interaction than blends with AN 24% or AN 27%. This is due to the content of styrene, which, in general, increases the impact strength. A lower content of

AN means a larger content of styrene, hence, a higher impact strength. Figure 6 illustrates these results.

Mechanical Properties

Figure 6 shows the tensile yield strength vs. the blending ratio of PC/ABS at 25°C. For AN 22%, the tensile yield strength increases as the PC content increases. For a PC content less than 50%, the tensile yield strength increases linearly in the ABS matrix. At a PC content greater than 50%, the tensile yield strength had a constant value in the PC matrix. Therefore, PC particles in an ABS matrix increase the tensile yield strength,
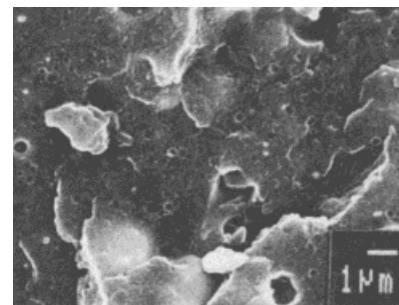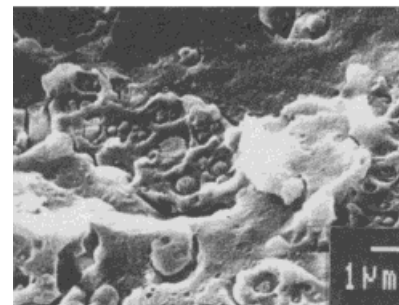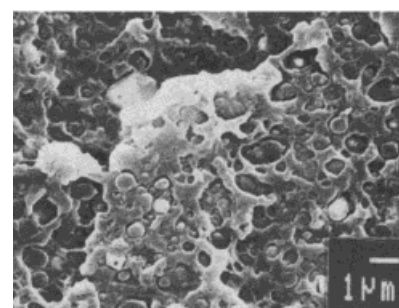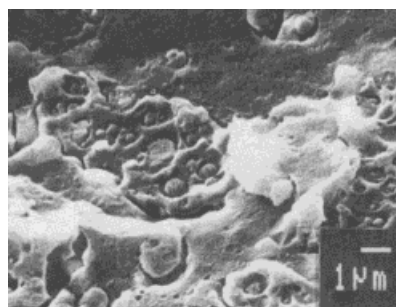

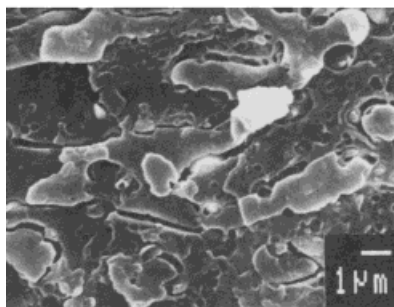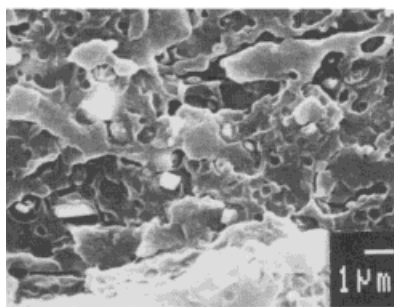**Figure 4** SEM micrographs of impact fracture surface of PC/ABS with AN 22%.

(a) AN 22%

(b) AN 24%

(c) AN 27%

Figure 5 SEM micrographs of impact fracture surfaces of PC/ABS with PC 50% for various AN contents.

Figure 6 Izod Impact strength vs. blending ratios of PC/ABS for various AN contents at 25°C.

other). A ring opening occurs in the epoxide group of the flame retardant, which reacts (along with BER) with the carbonyl part of the ester group in PC.

Figure 7 shows the Izod impact strength vs. the blending ratio of PC/ABS at 25°C. Influential factors on the impact resistance of rubber-toughened polymers are the strength of each component, the adhesion between the components, and the size and state of the dispersion of the rubber phase.[19,20] Though both PC and ABS have a high impact strength, the impact strength of PC is higher than that of ABS. While the impact strength of PC/ABS blends do not increase in the ABS matrix, they do drastically increase in the

but ABS particles in a PC matrix do not affect the tensile yield strength. So the morphology has a ductile behavior. In AN 24% and AN 27%, the tensile yield strength does not increase with PC content. This corresponds to the fact that their morphology shows a brittle behavior. Therefore, the tensile yield strength shows a nearly constant value, which is independent of the PC content. However, the overall tensile yield strength of the blends with a flame retardant are greater than that of blends without a flame retardant. This results from the flame retardant being a reactive type (the epoxide group in the flame-retardant and the ester group in the PC interact with each
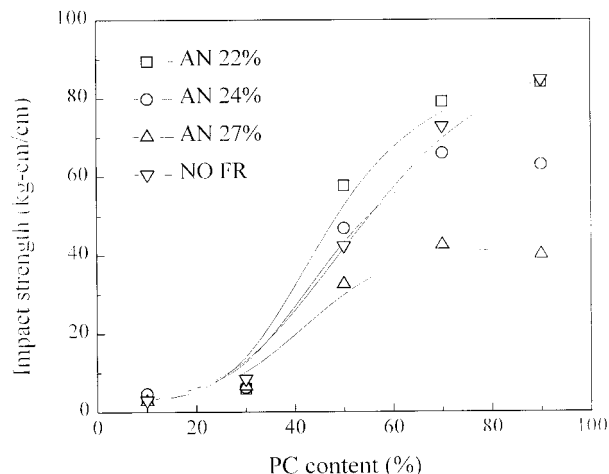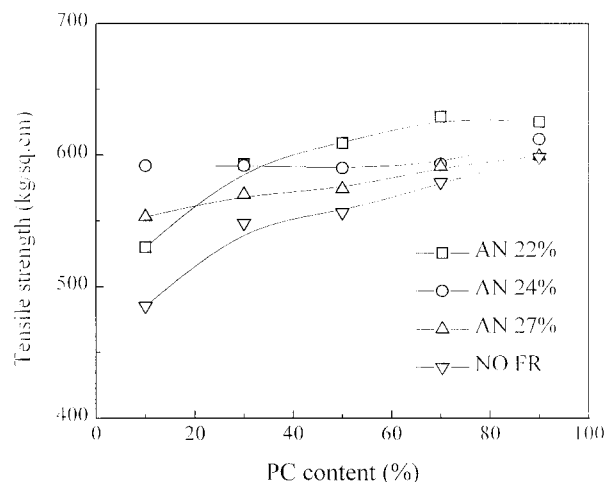

Figure 7 Tensile yield strength vs. blending ratios of PC/ABS for various AN contents at 25°C.
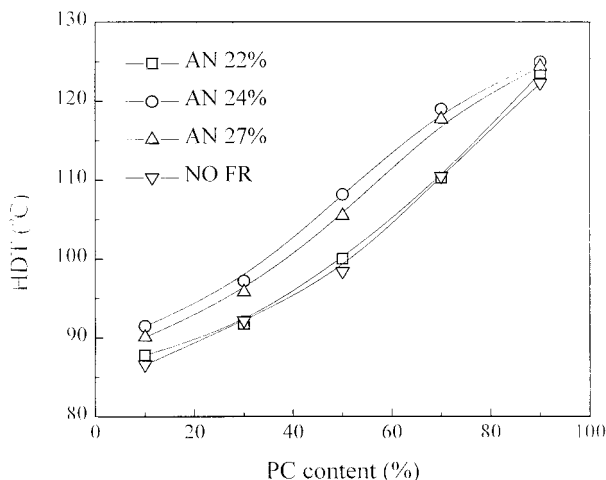
Figure 8 HDT vs. blending ratios for blends of PC/ABS.

PC matrix. This implies that PC particles do not contribute to the impact strength in the ABS matrix. The PC/ABS blend has a high mechanical adhesion in PC 50% and in PC 70%. This was shown in morphological studies. Because styrene-block increases the impact strength of rubber-toughened polymers and the content of styrene in ABS decreases as AN content increases, the impact strength of the blend decreases as AN content increases. The butadiene content was fixed as a constant in this study.

Thermal Properties

Figure 8 shows the HDT vs. the blending ratio. HDT is one of the most important factors in estimating the efficiency of engineering plastics. PC has a HDT at around 130°C, which is much higher than that of most thermoplastics. Therefore, PC improves the thermal properties in both PC and ABS matrices. The HDT is higher in AN 27% than in AN 22%, because AN has a high thermal resistance. This can be interpreted with the effect of molecular weights. The HDT of blends with a flame retardant is higher than blends without a flame retardant because flame retardants are the reactive type. In addition, gradual increases of the HDT is observed as the PC content is increased.

CONCLUSIONS

The effect of AN content in ABS on PC/ABS alloy systems was investigated in the presence of a flame retardant. The shear viscosity of PC/ABS

blends increases as the AN content in ABS increases. In addition, the shear viscosity of the PC/ABS blend is affected by temperature in the ABS matrix, but not in the PC matrix. The tensile yield strength of AN 24% and AN 27% do not increase because its morphology is brittle. Nonetheless, the tensile yield strength of blends containing the flame retardant is higher than that of blend without the flame retardant because the flame retardant used in this study is a reactive type. The Izod impact strength rapidly increases in a PC matrix due to its morphology of a continuous phase structure. For commercial use, ABS with AN 22% is the most suitable because it has a low shear viscosity and a high impact strength.

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