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Effect of a reactive-type flame retardant on rheological and mechanical properties of PC/ABS blends

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The effects of a flame retardant (FR; reactive-type: brominated epoxy resin) on the mechanical and rheological characteristics of polycarbonate(PC)/acrylonitrile-butadiene-styrene (ABS) blends were investigated at various conditions. A series of PC/ABS blends with and without the FR were prepared using a twin-screw extruder. The tensile yield strength and flexural strength of the blends increased with PC content, and the blends containing FR showed higher values than that of the blends without FR primarily due to the reactive nature of the FR. Furthermore, gradual increases in heat distortion temperature were observed over the broad range of PC content. The system without FR showed higher impact strength especially at high PC content. The temperature drastically affected the shear viscosity of the ABS matrix, but little changes in shear viscosity were observed for the PC matrix. This temperature dependence provided a characteristic viscosity change with respect to composition ratio in the blends. The relationship between shear viscosity and shear rate was analyzed using the Carreau model. The morphologies of the blends were also examined as a function of PC content.

1. Introduction

Polycarbonate (PC) is commonly used as a high-performance amorphous engineering thermoplastic due to its distinct properties, including exceptionally high impact strength, transparency, heat resistance, dimensional stability, and excellent electrical properties. PC also possesses other properties such as excellent colorability, high gloss, sterilizability, flame retardancy, biocompatibility, high heat distortion temperature (HDT), and strain resistance. The PCs do not possess a unique melting point, as exhibited by typical crystalline polymers, but have a high glass transition temperature of approximately 150°C [1]. Moreover, it is rather difficult to process PC, since its high melt viscosity hinders the fluidity and the residual stress resulting from the process could cause fractures. Although PC exhibits "tough" behavior in stress-strain and unnotched impact tests, this toughness is not retained under sharp notches and thick specimens [2]. To improve this, efforts have been made to develop polymer blends and alloys [3–5].

Acrylonitrile-butadiene-styrene (ABS) copolymer is the most popular rubber-toughened thermoplastic with several advantages, including low cost, good processability, and low notch sensitivity [6]. In general, ABS plastics consist of two phases; the styrene-acrylonitrile (SAN) forms a continuous matrix phase, and the other phase is composed of dispersed polybutadiene particles, which have layers of SAN grafted onto their surface. The SAN layers make these two phases compatible [7]. Therefore, the properties of ABS are affected by both the ratio of the monomers and the molecular structures of these two phases.

To improve its mechanical properties, ABS needs to be blended with other high performance engineering plastics, such as PC [8]. The PC/ABS blends are known to possess high impact strength and many other desirable properties. Furthermore, since it can be easily processed, PC/ABS blends has been widely utilized as an engineering thermoplastic [9, 10]. Because polymer blends allow the production of a synergistic balance of properties between the constituents, hybridization of the best properties can be easily accomplished [11]. Iinvestigations on the mechanical, thermal, rheological, and dielectric properties of PC/ABS systems have been performed [12–14].

Because thermoplastics, including PC/ABS blends, are easily combustible, flame-retarding formulations are desirable to reduce the probability of burning in

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the initial phase of a fire. Contrary to additive-type flame retardants (FRs), which are present as fillers, reactive-type FRs are introduced into the resin system via a chemical reaction [15–18]. However, the addition of large amounts of FRs could produce undesirable products and result in difficulties with processability. Reactive-type FRs have functional groups that bond with the matrix polymer. It can also be noted that reactive compatibilizers have been found to increase the mechanical strength of polymer blends [2, 19, 20].

We investigated the mechanical, thermal, and rheological properties of PC/ABS blend systems with brominated epoxy resin (BER) used as a reactive-type FR. Compounding was performed by a twin-screw extruder. In order to investigate the effect of the FR in PC/ABS blends, the morphology of the blend was also examined.

2. Experimental

2.1. Materials and sample preparation

PC (molecular weight (Mw) of 5.26×10^4 g/mol, Teijin Co., Japan) and ABS (Mw of 1.28×10^5 g/mol, Cheil Industries Inc., Korea) with 27% acrylonitrile (AN) in powder form were chosen to prepare the PC/ABS blends. The ABS used in our experiment is in powder form suitable for dispersion and processing, and consists of SAN and graft-ABS (g-ABS) at a blend ratio of 75/25 in blend form. Here, the g-ABS is composed of butadiene (BD) and SAN. Those two components (SAN and g-ABS), which makes up the consisting ABS portion of the PC/ABS blend, contain 14.4 and 31.7% of AN, respectively. Accordingly, the resultant AN content for the ABS component is 27% based on the blending ratio of SAN and g-ABS. BD and styrene monomer contents in ABS were 12 and 61%, respectively. Note that the 22% AN content in ABS has been studied recently [21].

The FR used in our study was reactive-type BER, (Mw of 4×10^4 g/mol, Makhteshim Co., Israel). The density was 1.8 g/cm^3, and the bromine content was 54%. In addition, antimony oxide (Sb_2O_3) was introduced as a flame retarding additive [22]. The content of anti-oxidant (Adeka Argus Co., Japan) was 0.3 parts per hundred of resin by weight (PHR) for each PC/ABS blend system.

Both PC and ABS were dried at 120°C for 4 h before processing, since moisture causes hydrolysis during processing [1]. The sample codes defined as PC10, PC30, PC50, PC70, and PC90 represent the blend ratios of PC/ABS 10/90, 30/70, 50/50, 70/30, and 90/10, respectively. In each case, 15 PHR of FR, 5 PHR of antimony oxide, and 0.3 PHR of antioxidant are added. A twin-screw extruder with a die length/die diameter (L/D) ratio of 34.5 was used to mix the blends. The compositions of the PC/ABS systems are listed in Table I.

2.2. Characterization of the blends

A capillary rheometer (Rosand Inc., UK) was used to measure the shear viscosity as a function of shear rate. The L/D ratio was 32. Various piston speeds (166.60, 133.30, 66.66, 33.33, 16.66, 6.67, and 3.33 mm/min) were used at three different temperatures (240, 260, and 280°C). The flow rate of the polymer is measured from the weight of polymer exiting the capillary die per unit time [23]. The shear rate varies across the capillary and the Rabinowitsch correction was made to obtain the accurate apparent viscosity.

To obtain the tensile and flexural properties, a universal testing machine (UTM; Instron Inc., USA) was used [24]. The cross head speed in the tensile strength test was 5 mm/min and the flexural strength test was 2.8 mm/min. An Izod impact tester (Toyoseiki Inc., Japan) was used to measure the impact strength [25].

A scanning electron microscope (SEM; JSM-840A, Jeol Inc., Japan) with a magnification of 5,000 at 20 kV was used to investigate the morphology. After the sample was dried, it was immersed in liquid nitrogen so that its surface was not affected by any external stresses. It was then fractured using an Izod impact tester. The sample was coated with gold to make the surface to be conducting.

The heat distortion temperature (HDT) was measured as the temperature at which the deformation length was 10^{-2} inches using a HDT tester (Toyoseiki Inc., Japan). The specimen was immersed in a silicone oil bath and loaded at a constant pressure of 18.6 kg/cm^2. The temperature was increased from 50 to 200°C at a constant heating rate of 2°C/min.

3. Results and discussion

The shear viscosity, which can be used as a measure of the processability, was obtained as a function of shear rate. Fig. 1 illustrates shear viscosity versus shear rate for the various blend ratios of PC/ABS with BER. In these measurements, we fixed the FR content to examine the effect of PC/ABS composition on the shear viscosities under various conditions. Despite the crucial role of the FR in the flow behavior of the PC/ABS system, we found that the change of flow behavior was not significantly affected due to the fixed quantity of FR. In a later part of this section, we will discuss about the effect of FR on rheological properties. In Fig. 1, shear viscosity decreased as the shear rate increased,

TABLE I Composition of PC/ABS blends

PC(%)	ABS(%)	g-ABS(%)	SAN(%)	FR(PHR)	Sb_2O_3(PHR)	Anti-oxidant(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

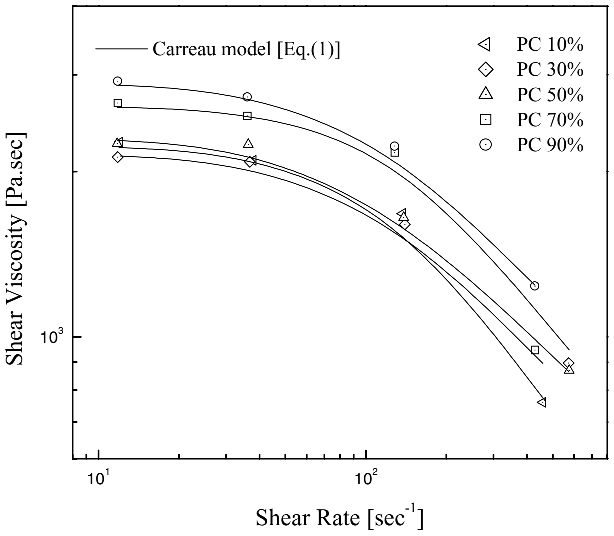


Figure 1 Shear viscosity versus shear rate for various blend ratios of PC/ABS with 27% AN in ABS at 240°C. The solid lines represent Carreau model (Equation 1) fit.

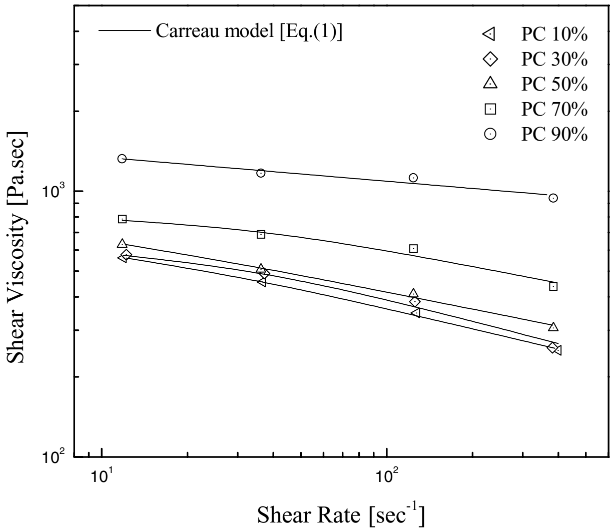


Figure 2 Shear viscosity versus shear rate for various blend ratios of PC/ABS with 27% AN in ABS at 260°C. The solid lines represent the Carreau model (Equation 1) fit.

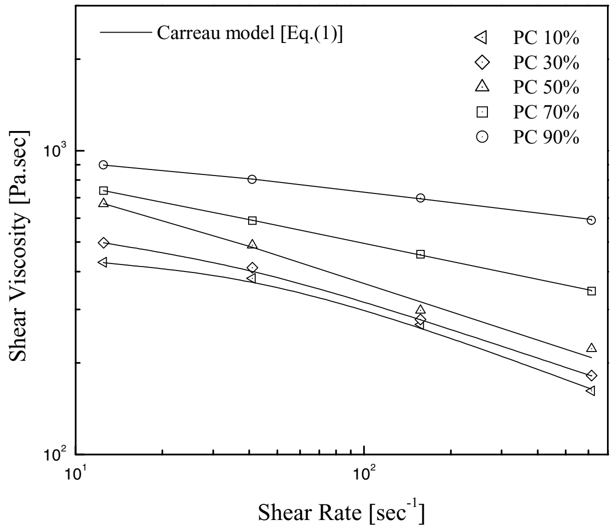


Figure 3 Shear viscosity versus shear rate for various blend ratios of PC/ABS with 27% AN in ABS at 280°C. The solid lines represent the Carreau model (Equation 1) fit.

exhibiting the characteristic shear thinning behavior of polymer blends, for all different PC contents. On the other hand, the shear viscosity of the blends monotonically increased with the increase in PC content over the entire range of shear rate. Here, the enhancement of shear viscosity due to the PC very small for the broad range of PC content. This is because the shear viscosity of pure PC is much higher than that of pure ABS [26]. In other words, only 10% of PC content in the blend could alter the overall flow properties of pure ABS, and the resultant values of viscosities in the system are slightly lower than that of the high PC content case. Styrene-block in ABS is known to decrease the viscosity of blend. Since styrene-block has a glass transition temperature of approximately 100°C and acrylonitrile-block has a higher melting temperature, styrene-block degrades first as temperature increases. Usually styrene-block in ABS was used as an adjusting agent for the processability by lowering the sheer viscosity [27]. The shear viscosity as a function of shear rate at temperatures of 260 and 280°C are also shown in Figs 2 and 3, respectively. By comparing the results with Fig. 1, we found that the degree of shear thinning reduced with the increase in temperature, due to the increase in mobility and fast relaxation of each component.

To examine the relationship between shear viscosity (η) and shear rate ($\dot{\gamma}$), we fitted the measured viscosities at three different temperatures (240, 260, and 280°C) using the Carreau model [28]:

$$\eta = \frac{\eta_0}{[1+(\dot{\gamma}t_1)^2]^{(1-n)/2}}. \qquad (1)$$

Here, η_0 is the zero shear rate viscosity, which can be directly obtained from the plateau value (i.e., $\dot{\gamma} \rightarrow 0$), t_1 is a characteristic time, and n is a dimensionless parameter, where the slope in the power law region is given by $(n-1)$. Equation 1 reduces to the Newtonian assumption when $n = 1$ and describes shear-thinning behavior for $n < 1$. The shear-thinning behavior of many polymer blends [29] and polymer/clay nanocomposite systems [30–32] are well described by the Carreau model. Choi *et al.* [31] determined that the shear-thinning occurs at the critical shear rate ($\dot{\gamma}_c$), in the vicinity of t_1^{-1}. Here, t_1 is roughly related to the longest relaxation time (λ) required for the elastic structures to relax. [33, 35] The results obtained at 240°C are summarized in Table II. Despite the incompleteness of the raw data (which is not sufficient to estimate the critical shear rate accurately due to the pressure transducer limits of the capillary rheometer to measure the viscosity), it is possible to predict the critical shear rate from the characteristic time using the Carreau model. The monotonic slight increase of shear viscosities over the entire range of shear rates could be explained by the little change in the characteristic time, t_1 and other physical parameters. For example, the critical shear rates at which the shear thinning behavior starts are not distinguishable when plotted in the log scale (horizontal

TABLE II Carreau model (Equation 1) parameters for PC/ABS blend systems at 240°C

PC content	η_0 ($\times 10^2$ Pa sec)	t_1 ($\times 10^{-3}$ sec)	n	$\dot{\gamma}_c$ (sec^{-1})
PC10	22.20	7.21	0.15	138.70
PC30	21.43	9.46	0.41	105.71
PC50	22.90	11.09	0.48	90.17
PC70	26.23	5.51	0.15	181.49
PC90	28.84	9.41	0.41	106.27

axes). This implies that the general behavior of different PC/ABS compositions are almost identical, except the slight change in zero-shear-rate viscosities. As mentioned previously, the measured shear viscosity (Fig. 1) at 240°C was found to fit the Carreau model well, however, the Carreau model in Figs 2 and 3 at the higher temperatures were inadequate for the data. As temperature increases, the shear viscosity data appears to obey a power law relationship [35, 36].

With respect to the effect of FR on rheological behavior, it is not difficult to conjecture the role of FR on the shear viscosities. Lee *et al.* [37] investigated the ternary PC/ABS blends (similar to our system) using thermal, mechanical and rheological properties. They showed the shear viscosity data for different PC/ABS compositions as a function of shear rate at 250°C. When we compare the results with those of our PC/ABS systems containing FR additives at 260°C, we can find that the viscosities of PC/ABS-FR systems at higher temperature are similar or somewhat higher than those of the PC/ABS blend systems at 250°C [37]. Considering the temperature effect on melt viscosity, it is certain that the reactive FR component might increase the overall viscosities over the entire range of composition ratio.

Fig. 4 represents the shear viscosity versus the blend ratios of PC/ABS at a relatively low shear rate ($\dot{\gamma} = 10$ sec^{-1}) at three different temperatures. For a concentration up to 50% of PC, the ABS matrix forms a continuous phase structure. The shear viscosity of the ABS matrix depends on the PC content. Since ABS has poor thermal properties compared to PC, the ABS matrix is rather easily affected by heat. For PC content greater than 50%, the shear viscosity of the PC matrix is hardly affected by additional heat. These results are consistent with the case for a high shear rate ($\dot{\gamma} = 5 \times 10^2$ s^{-1}), as shown in Fig. 5. Therefore, from the economic point of view, PC50 is regarded to be the optimal choice since PC is more expensive than ABS. For PC90, the shear viscosities are almost the same at both 240 and 260°C, indicating that the blends having a rich PC content are hardly affected by heat. However, the shear viscosity of PC decreased at 280°C. In addition, the shear viscosity of the blend at 280°C was less affected for a high shear rate case than for a low shear rate case.

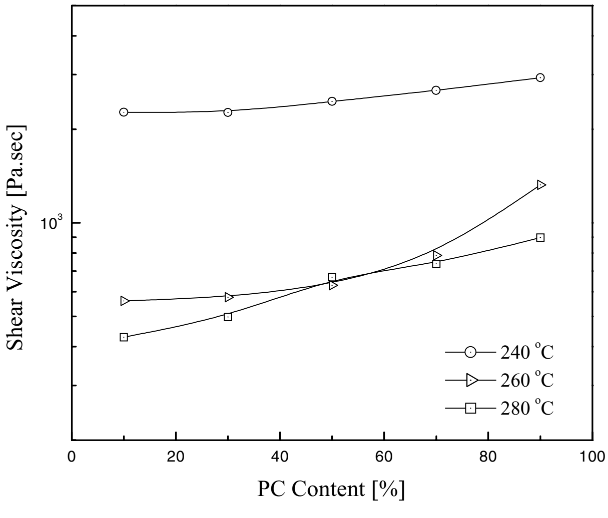


Figure 4 Shear viscosity versus blend ratios of PC/ABS contained 27% AN in ABS with various temperatures at low shear rate (10 sec^{-1}). The solid lines represent the Carreau model (Equation 1) fit.

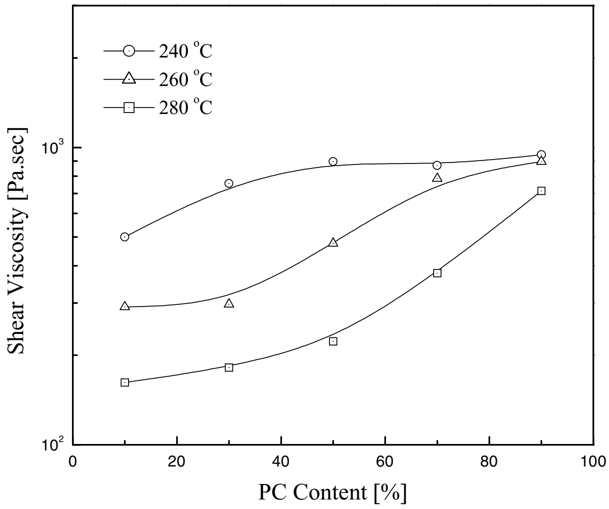
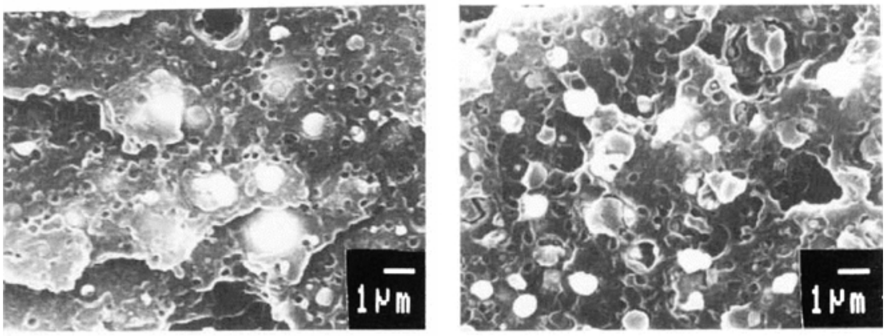


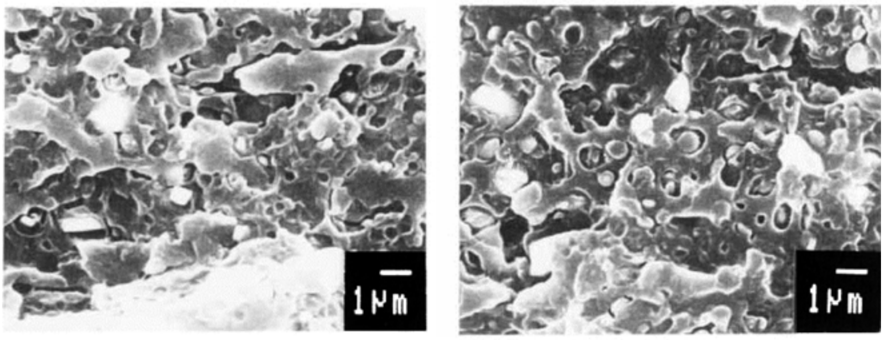
Figure 5 Shear viscosity versus blend ratios of PC/ABS contained 27% AN in ABS with various temperatures at high shear rate (500 sec^{-1}). The solid lines represent the Carreau model (Equation 1) fit.

Fig. 6 shows SEM micrographs of samples with 5 different blend ratios of PC/ABS. A PC/ABS blend with a FR has four different phase structures including an SAN phase, butadiene rubber particles on the SAN phase, a PC phase, and insoluble solid additive FR [21]. The white particles in Fig. 6 are the FR, which were well dispersed in both PC and ABS phases. The component with the higher content is the continuous phase, and the minor component is dispersed particles [38, 39]. Spherical domains of minor components are formed based on the weight fraction of PC and ABS. On the other hand, for injection-molded PC/ABS blends, Lee *et al.* [40, 41] observed that in PC-rich blends, the ABS phase formed a bead-and-string structure oriented in the injection direction near the edge, while in the centre the ABS was dispersed as rubber domains and spherical particles of free SAN. The ABS-rich blends had a conventional blend morphology with PC domains dispersed in ABS. When PC and ABS possess equal weight fractions, they form a continuous phase structure with a physical adhesion [42], and they are expected to improve the mechanical properties. In Fig. 6, the fracture surface shows ductile behavior, suggesting that PC and ABS have a limited interaction. Blends with interaction between the two components have a higher impact strength and are made ductile at the surface.

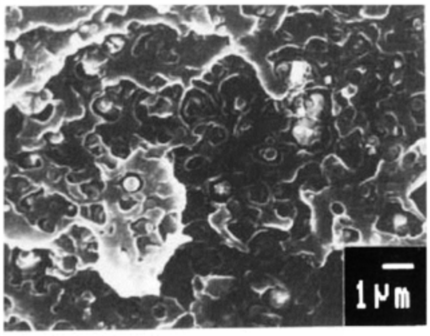
Fig. 7 shows the tensile yield strength and flexural strength versus the blend ratio of PC/ABS at 25°C. Without FR, the tensile yield strength increases with



(a) PC 10 (b) PC 30



(c) PC 50 (d) PC 70



(e) PC 90

Figure 6 SEM micrographs of the various blend ratios of impact fracture surface for PC/ABS at 27% AN.

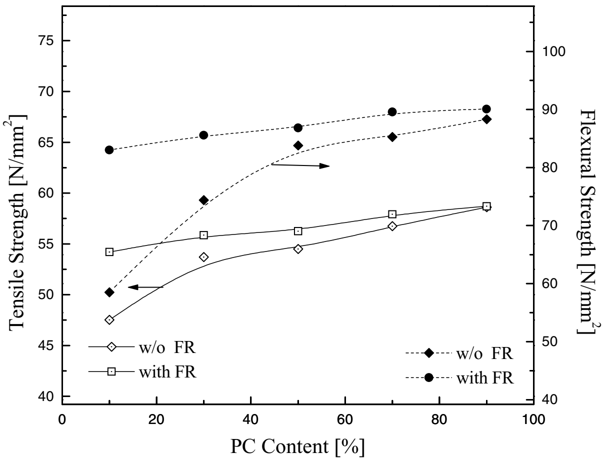


Figure 7 Tensile yield strength (open symbol) and flexural strength (filled symbol) versus blend ratios of PC/ABS at 25°C.

increasing PC content [43]. However, with FR, the tensile yield strength increases slightly with PC content. Therefore, the tensile yield strength exhibits a plateau value, i.e., independent of the PC content. However, the overall tensile yield strength of the blends with FR are greater than that of blends without FR, since the flame retardant is a reactive-type such that the epoxide group in the flame retardant and the ester group in the PC interact with each other. A ring opening occurs in the epoxide group of the FR, which reacts with the carbonyl part of the ester group in PC. The flexural strength with FR was not strongly affected by the increase of PC content either, contrary to the increase of systems without FR. The overall values are higher than those of the blend without FR, corresponding with the blend morphology, which shows brittle behavior. Based on the results from Fig. 7, we can see that the addition of FR to PC/ABS blend improves the tensile yield strength and the flexural strength. On the other hand, the enhancements of tensile strength and flexural strength were more distinct at low PC content by the incorporation of epoxy and PC component. But, this kind of reactive-type enhancement effect diminished over 50% of PC, and saturated to a certain degree. There exists only a filling effect of the hard component in the blend system due to the fixed quantity of the FR component.

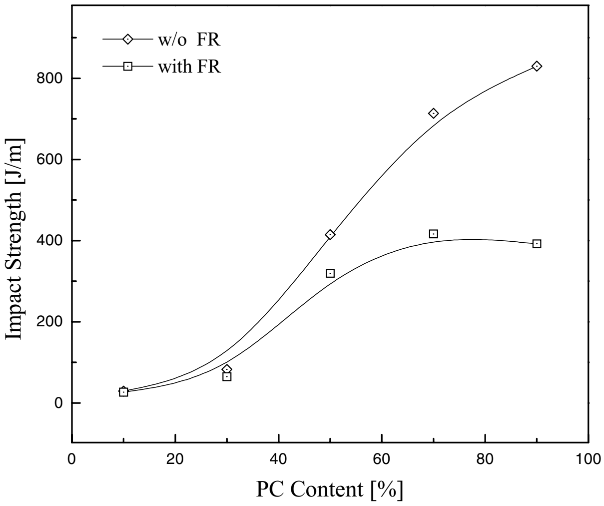


Figure 8 Notched Izod impact strength versus blend ratios of PC/ABS with and without FR at 25°C.

At higher PC content, there are small changes of mechanical properties caused by filler effect of FR.

Fig. 8 shows the notched Izod impact strength versus the blend 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 [44]. The impact strength of PC is higher than that of ABS. The impact strength of PC/ABS blends does not increase in the ABS matrix, while it drastically increases in the PC matrix. This implies that PC particles do not contribute to the impact strength of the ABS matrix. PC/ABS blend has a high mechanical adhesion in PC50 and in PC70. With respect to the existence of FR, it is noticeable that the impact strength is much lower in FR adopted system at high PC content. As mentioned above, the PC component could trigger the increase of impact strength with the increase of PC content. But the reactive incorporation of FR with the blend reduced to a certain degree with PC content. In other words, it is reasonable to conclude that the enhancements of impact strength over 50% are dominantly affected by PC, not by the reactive interaction of FR part with PC. It means that the impact strength of the blend containing FR component at a specific PC content would be inferior to a non-FR system, because the FR portion does not participate in the increase of impact strength, which are mainly originated from the rubbery part.

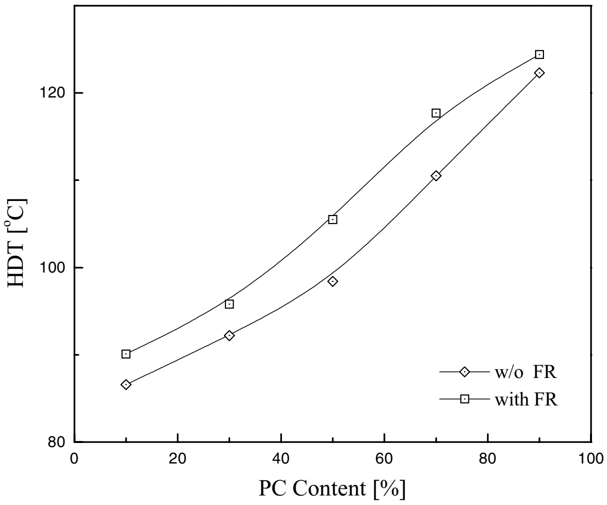


Figure 9 HDT versus blend ratios of PC/ABS with and without FR.

Fig. 9 shows the HDT versus the blend ratio. Since PC has a HDT approximately 130°C, which is much higher than most thermoplastics, PC improves the thermal properties. The HDT of blends with a reactive-type FR is higher than blends without FR. In addition, a gradual increase in the HDT is observed with increasing PC content.

4. Conclusions

The effects of reactive-type FR (BER) on the mechanical properties of PC/ABS blends were investigated, and rheological characterizations of the blends were also performed at various conditions. The reactive nature of the FR with PC increased the tensile yield strength and flexural strength, and the increase of PC portion also enhanced the mechanical properties of PC/ABS blends. Furthermore, gradual increases in HDT were observed over the broad range of the PC content. The system without FR showed higher impact strength especially in the high PC content. The different temperature sensitivity between PC and ABS caused the characteristic viscosity change with respect to composition ratio in the blends, and the relationship between viscosity and shear rate was analyzed with Carreau model. The reactive type FR caused the increase in viscosity for the PC/ABS system with the help of additive effect and reactive incorporation with PC in the overall matrix. The morphological investigation revealed the complex fractured surface of the blends having different composition ratio.

Acknowledgments

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