Impact Strength in ABS–PPO Blends Compatibilized with Styrene–Acrylonitrile–Glycidil Methacrylate Terpolymers

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ABSTRACT: The impact strength of the acrylonitrile-co-butadiene-co-styrene terpolymer-poly(2,6-dimethyl-1,4-phenylene oxide (ABS-PPO) blends compatibilized with styrene-acrylonitrile modified with glycidil methacrylate (SAN-GMA) terpolymer can be significantly enhanced by the various processing conditions in reaction extrusion. Four different ABS terpolymers are used depending on the composition of acrylonitrile, styrene, and butadiene. The morphology of polybutadiene latex in ABS-1, ABS-3, and ABS-4 is an agglomerated type, while that of ABS-2 is a bimodal one. The three different methods in *in situ* compatibilizing extrusion are employed; the simple mixing of ABS and PPO, the simultaneous mixing of ABS and PPO, the reactive compatibilizer SAN-GMA, maleic anhydride (MA; designated A-series), and then the stepwise mixing of the mixtures of ABS-SAN-GMA in the MA-modified PPO (designated B-series). Although the ABS-4-PPO blend depicted the highest impact strength in the simple mixing, the ABS-3B-PPO blend showed the best impact strength in the stepwise mixing. The former behavior may be arisen from the high content of BR, whereas the latter may be due to the agglomerated rubber phase with SAN-GMA. The highest impact strength (47 kg·cm·cm⁻¹) was observed in ABS-3B-PPO at 50/50 with an inclusion of 10 wt % GMA (2) and 1 wt % MA. Thus, the proposed reaction mechanism is an existence of the compatibility between ABS and SAN-GMA and the reactivity between the MA-modified PPO and SAN-GMA. Phase morphology of the ABS-2-PPO and ABS-3-PPO blends were compared, and more efficient dispersion of ABS was observed in the B-series than in the A-series. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 841-852, 1999

Key words: impact strength; morphology; reaction extrusion; compatibilizer; styrene–acrylonitrile–glycidil methacrylate; acrylonitrile-*co*-butadiene-*co*-styrene terpolymer; poly(2,6-dimethyl-1,4-phenyl oxide; reactivity; compatibility

INTRODUCTION

Recently, research for compatible polymer blends by using various processing conditions is in demand rather than searching a new synthetic method for highly functionalized polymeric materials due to the high cost of research expenses. Reaction extrusion is one of the more interesting processing conditions, which can enhance the desired properties by grafting or compatibilization using an appropriate processing conditions.¹ By using a reaction extrusion technique, mechanical properties of a multiphase polymer blend can be significantly improved by the size and shape of the phase generated during its preparation.^{2–4}

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	Compositions (Wt %) ^a	Tensile Strength (MPa)	HDT (°C)	Melt Flow Index (200°C, 21.6 kg)	Impact Strength kg·cm·cm ⁻¹	$\begin{array}{c} \text{DMTA} \\ T_g \\ (^\circ\text{C}) \end{array}$
ABS-1	AN:20, SM:60, BR:20 (agglomerated BR)	480	85	50	18	129
ABS-2	AN:15, SM:45, BR:40 (bimodal BR)	360	75	15	22	125
ABS-3	AN:15, SM:45, BR:40 (agglomerated BR)	350	77	9	23	120
ABS-4	AN:15, SM:35, BR:50 (agglomerated BR)	320	73	6	27	116
PPO	Brand name: X-0101	840	145	0.52	5	225

Table I Characteristics of the Used Chemicals

^a AN is the abbreviation for acrylonitrile, BR for butadiene rubber, and SM for styrene monomer.

One of the more successful systems in multiphase polymer blend is bisphenol A polycarbonate-acrylonitrile-co-butadiene-co-styrene terpolymer (PC-ABS). In this blend, the modulus and the tensile strength followed a simple rule of mixtures, while the elongation at break showed the minimum at 50% of PC.⁴ Notched Izod impact strength is nearly constant at the level of pure ABS up to 50% PC, then increases rapidly upon further incorporation of PC.⁴ In addition, a different degree of orientation of the ABS phase was observed at the AB-S-PC sample edges.⁵ The effect of processing variances, such as blending conditions or annealing treatment on the phase morphology of PC-ABS, was studied.⁶ Some success was attained in generating nylon 6-ABS blends using a SMA copolymer containing 25% maleic anhydride (SMA 25). It was found that the impact strength of this compatibilized blend was extremely sensitive to the amount of SMA 25 copolymer that was added.^{7,8} Phase morphologies of Nylon 6-ABS blend compatibilized with an imidized acrylic polymer and the commercially available Triax material were also examined by using a transmission (TEM) technique. An optimum level of SMA 25 was reported to achieve maximum toughness.

Some attempts were made to develop the compatibilized ABS terpolymer–poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blend by reaction extrusion to examine the possibility of replacing the role of Noryl resin (PS–PPO blend). Although Noryl resin has been widely used for various applications, it has a deficiency of low impact strength.^{9–12} ABS, owing to high impact strength, and PPO, owing to high deflection temperature, can be designed to develop the ABS–PPO blend by choosing an appropriate compatibilizer or modifier in compatibilizing extrusion.

The aim of this work is to study the effect of various processing conditions on the impact strength and the morphology of ABS-PPO blend by using *in situ* reaction extrusion. ABS and PPO are immiscible by showing two different T_g 's at 121 and 225°C, respectively, using dynamic mechanical thermal analysis (DMTA). Four different ABS terpolymers are used, which are designated



Figure 1 Comparison of the phase morphology of polybutadiene rubber latex in ABS-2 and ABS-3 by a TEM technique.



Figure 2 Heat deflection temperature of various ABS-PPO blends by simple mixing.

by ABS-1, ABS-2, ABS-3, and ABS-4 according to the contents of each component of acrylonitrile (AN), styrene (SM), and butadiene latex rubber (BR). Three processing conditions are employed for reaction extrusion: the first is the simple mixing of ABS and PPO; the second is the simultaneous mixing of ABS, PPO, the reactive compatibilizer SAN–GMA, and the modifier maleic anhydride (MA), and the third is the stepwise mixing of the mixtures between the MA-modified PPO and the mixture of ABS and SAN–GMA. A subsequent article will be reporting, in more detail, the specific interaction between the modified PPO and the ABS–SAN–GMA using Fourier transform infrared (FTIR), Torque rheometer, and transmission electron microscopy (TEM) techniques.

EXPERIMENTAL

Materials

ABS terpolymers are obtained from Kumho Chemicals Inc., Yochun, Chun-La-Nam-Do. Four



Figure 3 Impact strength of ABS-PPO blends by simple mixing.



Figure 4 MA dependence of impact strength of ABS-2B–PPO = 50/50 with a different amount of SAN–GMA (2) and SAN–GMA (10).

different grades of ABS materials are used, and the compositions of each terpolymer are listed in Table I. Each ABS is synthesized by the following procedures. For ABS-1, ABS-3, and ABS-4, polybutadiene (PB) latex is synthesized by emulsion polymerization in the water phase with an addition of catalyst and molecular controller to form 1000 Å of latex particle. Then the size of PB latex is agglomerated to as large as 3000 Å. SM and AN (3 : 1 ratio) are fed for grafting to the PB latex, then the grafted ABS terpolymer is slugged and dried. On the other hand, for ABS-2, PB latex is formed as large as 2000–3000 Å, then SM and AN are added to make the ABS terpolymer using the same procedure as described before. The melt flow index of ABS is also listed in Table I. PPO is purchased from Asahi Chemicals, Japan, with a brand name of X-0101. The number- and weight-average molecu-



Figure 5 SAN–GMA (2) dependence of impact strength in ABS-2B–PPO and ABS-3B–PPO with compositions of 60/40, 50/50, and 40/60.



Figure 6 Impact strength of ABS-2B–PPO and ABS-3B–PPO as a function of MA content with 10 wt % SAN–GMA (2).

lar weights of PPO are 8934 and 21,895, respectively, and the polydispersity (PDI) is 2.45.

The reactive compatibilizer is a terpolymer comprised with glycidil-methacrylate-modified SAN copolymer and designated SAN–GMA. Two different SAN–GMA terpolymers are used; one designated SAN–GMA (2) contains 2 wt % of GMA, while another SAN–GMA (10) is comprised with 10 wt % of GMA. These two compatibilizers are the products of Kumho Chemicals Inc, Yochun, Korea, which are synthesized by bulk polymerization. The weight-average molecular weights are 170,000–180,000 with 2.5 of polydispersity (PDI), and their T_{g} 's are between 100 and 110°C.

Reaction extrusion is carried out by using a Haake Rheocord 9000 mixer at 270°C and 70 rpm,



Figure 7 Impact strength of ABS-PPO with 10 wt % SAN-GMA (2) and 1 wt % MA.

and the employed processing conditions are as follows: the first is the simple mixing of ABS and PPO without an addition of any materials; the second is the simultaneous mixing of ABS, PPO, and the reactive compatibilizer SAN–GMA (2) or SAN–GMA (10); and the modifier MA for PPO (called A-series); the third is the stepwise mixing of the mixtures of ABS–SAN–GMA into the MA-modified PPO.

Instruments

JOEL JSM-840-A scanning electron microscopy (SEM) was used for the phase morphology and JEOL JEM-1220 transmission electron microscopy (TEM) was also used. All specimens were prepared by fracturing molded plates in liquid nitrogen. Then, all the samples were previously coated with gold before being used for SEM. Haake Rheocord 9000 reaction extruder with W&P 25 φ twin screw was operated at 270°C and at 70 rpm, and, sometimes, a single screw with 32 φ was used.

Polymeric viscoelasticity and thermal properties were investigated by means of DMTA Mk III of Polymer Laboratories. Bar type of specimens with dimensions of $2 \times 8 \times 30$ mm was prepared by compression molding, and the experiments were carried out by bending motion with 4°C/min of heating rate under cryogenic conditions. The T_g was observed in the second heating process after the first heating, then followed by the quench cooling.

Impact strength was obtained by using the POE 2000 TM Notched Izod Impact Strength Tester of Dynatup made in the USA. Bar type of 3 \times 10 \times 64 mm specimen was prepared by ASTM D256, and the experiment was carried out at room temperature.

Heat deflection temperature (HDT) was measured by using the Yasuda Seiki Thermal Tester with a bar type specimen of $6.4 \times 12.5 \times 120$ mm under the road of 18.6 Kg.

RESULTS AND DISCUSSION

Some information for the materials used in this study are listed in Table I: the composition of AN is almost the same; however, the contents of SM and BR are various. In particular, for both the ABS-2 and ABS-3 terpolymers, the contents of AN, SM, and BR are the same with 12, 45, and 40 wt %, respectively. TEM photographs of ABS-2 and ABS-3 are compared in Figure 1, where the phase morphology of butadiene rubber in ABS-2 is bimodal type, while the BR in ABS-3 is an agglomerated shape. Although the TEM morphologies of ABS-1 and ABS-4 are not shown in this figure, they exhibit all agglomerated types as likely seen in ABS-3. The tensile strength is the highest in ABS-1 (480 MPa) owing to the high content of AN, while that of PPO is 840 MPa. ABS-1 also reveals the highest HDT value (85°C) among four ABS terpolymers, while that of PPO is 145°C. The impact strength of ABS-4 is the highest (27 kg·cm·cm⁻¹) due to not only the high content of BR but also to the agglomerated BR type, while that of PPO is very poor (5 kg·cm·cm⁻¹).

The measured HDT of each ABS-PPO blend prepared by the simple mixing was drawn in Figure 2. HDT for the whole blends raised with the content of PPO, following a simple rule of mixtures. ABS-1-PPO showed the highest HDT due to the high content of acrylonitrile.

The impact strength of ABS–PPO blends prepared by the simple mixing is depicted in Figure 3. The ABS-1–PPO and ABS-2–PPO blends show no enhancement in impact strength regardless of the blend compositions, while the ABS-3–PPO and ABS-4–PPO blends show enhanced impact properties. The agglomerated butadiene rubber shape and the relatively high content of BR in ABS-3–PPO and ABS-4–PPO would be the factors for influencing the impact properties.

Since we are interested in designing a blend system that represents high impact strength and high HDT for supplement of Noryl, two different processing procedures are employed for further study. Each blend system is specified by ABS-2A– PPO or ABS-2B–PPO, with an inclusion of *A* or *B* according to the processing conditions. *A* represents the simultaneous mixing of all materials (ABS, PPO, SAN–GMA, and MA), and *B* represents the stepwise mixing of the ABS–SAN–GMA mixtures into the MA-modified PPO.

Appropriate amounts of GMA in a SAN–GMA terpolymer are verified to achieve maximum toughness. In Figure 4, the impact strength of ABS-2B–PPO 50/50 with 10 wt % of SAN–GMA (2) and SAN–GMA (10) is measured in terms of the contents of MA (0–4 wt %). As seen in this figure, no improvement is observed for 10 wt % of SAN–GMA (10), while 10 wt % SAN–GMA (2) shows an enhancement as follows: in particular, 10 wt % SAN–GMA (2) with 1 wt % of MA gives the highest impact strength in this blend. The optimum level of GMA in a SAN–GMA terpolymer is 2 wt %; thereby, SAN–GMA (2) is chosen for further investigation.

Since ABS-2B–PPO 50/50 showed the highest impact strength with SAN–GMA (2), the optimum content of MA for achieving the maximum



Figure 8 DCP dependence of ABS-2B–PPO and ABS-3B–PPO with 10 wt % SAN–GMA (2), 1 wt % of MA, and 0.1 wt % of DCP.

impact strength in the ABS-2–PPO and ABS-3– PPO blends was examined using 10 wt % SAN– GMA (2). As seen in Figure 5, ABS-3B–PPO showed higher impact strength with an incorporation of 1 wt % MA.

Again, the optimum level of SAN–GMA (2) for giving high impact strength in the ABS-2B–PPO and ABS-3B–PPO blends was verified under the fixed MA content (1 wt %). As seen in Figure 6, relatively high impact strength was observed when 10 wt % SAN–GMA (2) was used in the ABS-3B system. From the results in Figures 5 and 6, the optimum contents of the reactive compatibilizer and the modifier are 10 wt % SAN–GMA (2) and 1 wt % MA, respectively. This result proposes that not only a certain amount of compatibilizer with a certain level of GMA, but also a certain amount of maleic anhydride, is needed to achieve an optimum compatibilization and reactivity between ABS and PPO.

The impact strength of whole range of blend compositions in ABS–PPO compatibilized with 10 wt % SAN–GMA (2) and 1 wt % MA are drawn in Figure 7. As pointed out before, the impact strength of the blends prepared by the B-series was higher than that by the A-series. This may be evidence of higher reactivity and compatibility in the B-series than in the A-series in the existence of a certain amount of SAN–GMA (2) and MA. In addition, although the constituents and the contents between ABS-2 and ABS-3 are exactly the same, the impact strength of ABS-3B–PPO in the stepwise reaction extrusion (B-series) is highly improved. This enhancement is certainly arisen from the agglomerated butadiene rubber in ABS-3B and the existence of appropriate reactive sites between the compatibilizer and the modifier MA as well. In addition, ABS-3B–PPO 50/50 shows the highest impact strength (47 kg·cm·cm⁻¹), then 60/40 of ABS-3B–PPO is the next high (38 kg·cm·cm⁻¹).

From the above experimental results, the following possible mechanism in the ABS–PPO blend compatibilized with SAN–GMA and MA is proposed: there is an existence of reactivity between the reactive compatibilizer SAN–GMA (2) and the MA-modified PPO, and compatibility between the SAN–GMA and ABS. In particular, because the specimens prepared with 10 wt % of SAN–GMA (2) gives higher impact strength than with 10 wt % of SAN–GMA (10), the modified PPO with 1 wt % MA reacts with a certain amount of reactive compatibilizer. The proposed mechanism is depicted in the following.



ABS-2A-PPO System AB

ABS-2B-PPO System



Figure 9 SEM photographs of the ABS-2/PPO blend.

Dicumyl peroxide (DCP) is often used to improve compatibility in reaction extrusion. In order to find the possibility of enhancing the impact strength, 0.1 wt % DCP was added in the ABS-2B–PPO and ABS-3B–PPO blends under the fixed amount of 10 wt % SAN–GMA (2) and 1 wt % MA. As seen in Figure 8, DCP does not improve the impact strength in any blend compositions but depresses it. Thus, DCP is not worth while for using in this blend system.

Figure 9 shows the SEM photographs of the series of the ABS-2B–PPO blend in A- and B-series. First of all, the morphological behavior between the domain and the continuous phase in



Figure 9 (*Continued from the previous page*)

ABS-3A-PPO System



Figure 10 SEM photographs of the ABS-3/PPO blend.

B-series is more wetted and finely dispersed than the A-series. Furthermore, when the ABS-rich phase (60–70% ABS) is reached, 2–3 μ m of the PPO domain formed in the ABS continuous phase. As the PPO content is increased up to 50%, the same continuous phase of ABS is formed with bigger size of PPO domain (5 μ m). However, in the PPO-rich phase (60-70% PPO), the co-continuous PPO and ABS phases are observed. In particular, in ABS-2B–PPO, 30/70, a network type of PPO is formed, and this is assumed to cause the previously observed high HDT and low impact strength.

In Figure 10, the same SEM photographs are



Figure 10 (Continued from the previous page)

shown for ABS-3-PPO. For ABS-3A-PPO, the phase morphologies are similar to those of ABS-2A-PPO. However, in ABS-3B-PPO, with 30-40% PPO, 2–3 μ m of the PPO domain is formed in the ABS continuous phase, then at 50/50, the fiber type of PPO is finely dispersed and embedded in the ABS matrix. When 60% is reached, PPO still remains as a small domain, and at 70/ 30, a network type of PPO is formed as a cocontinuous phase with ABS. Although PPO is better wetted and embedded in the ABS matrix in the ABS-2B and ABS-3B systems, no big difference is observed in the phase morphology between two systems, except for more finely dispersed PPO in ABS-3B-PPO than in ABS-2B-PPO. This difference may be influenced by the different phase morphology of PB latex.

CONCLUSIONS

Various processing conditions are employed to prepare the ABS-PPO blend in situ compatibilizing extrusion. They are the simple mixing of ABS and PPO; the simultaneous mixing of ABS, PPO, the reactive compatibilizer SAN-GMA, and the modifier MA (designated A series); and the stepwise mixing of the mixture of ABS and SAN-GMA into the MA-modified PPO (designated B series). The best method for showing the highest impact strength is the stepwise mixing (B-series). This is evidence of the compatibility or reactivity between ABS and PPO in the presence of a certain amount of SAN-GMA (2) and MA. The ABS-3B-PPO blend system is confirmed to reveal the highest impact strength with 10 wt % SAN-GMA (2) and 1 wt % MA in a reaction extrusion. In particular, the blend at 50/50 showed the highest impact strength, then 60/40 and 40/60 are the next order. This arises from not only the agglomerated rubber shape, which gives better wetting with PPO, but also the appropriate reactive sites between the compatibilizer SAN-GMA and the

modifier MA. The proposed reaction mechanism is an existence of the compatibility between ABS and the reactive compatibilizer SAN–GMA and the reactivity between the MA-modified PPO and SAN–GMA. In a morphological study, better dispersion or wetting is observed in the B-series blend. This is consistent result with the previously obtained impact properties. Thus, the best blend system for achieving the high heat deflection temperature and high impact strength is ABS-3B–PPO for replacing the Noryl.

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