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Effect of crosslinking reactions and order of mixing on properties of compatibilized PBT/ABS blends

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Abstract

The low-temperature notched Izod impact strength of poly(butylene terephthalate), PBT, blends with acrylonitrile–butadiene–styrene terpolymers, ABS, can be improved by incorporating methyl methacrylate, glycidyl methacrylate, ethyl acrylate terpolymers, MGE, as a reactive compatibilizer. However, fracture properties depend on the order of mixing of the blend components. When all components of compatibilized blends are melt mixed together in a single-pass extrusion, the low-temperature toughness is improved; however, the room-temperature impact strength is reduced relative to uncompatibilized blends. Using a two-pass extrusion method where PBT and MGE are melt mixed together in a first extrusion prior to incorporating ABS in a second extrusion, the room-temperature impact strength is superior to that of blends prepared by the single-pass method. When a two-pass method is used where ABS and MGE are combined prior to extrusion with PBT, the impact properties at all temperatures are inferior to those of uncompatibilized blends. Evidence is presented which suggests that residual acids present in emulsion-made ABS material may cause a crosslinking reaction involving the epoxide functionality of MGE terpolymers resulting in a deleterious effect on the ABS mechanical properties and its blends with PBT. By changing the order of mixing, the sequence of chemical reactions which occur can be controlled to optimize blend properties. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Methyl methacrylate–glycidyl methacrylate; Poly(butylene terephthalate); Styrene–acrylonitrile

1. Introduction

Poly(butylene terephthalate), PBT, is an important engineering polymer because of its excellent tensile properties, heat resistance, and chemical resistance [1–15]. Because PBT is brittle under certain conditions such as notched Izod impact testing, several studies have described schemes for incorporating various impact modifiers into PBT to achieve toughening [1–38]. Recently PBT has been successfully toughened by acrylonitrile–butadiene–styrene, ABS, materials using a series of methyl methacrylate, glycidyl methacrylate, ethyl acrylate, MGE, terpolymers as the reactive compatibilizer [12].

The various components of such toughened alloys including a reactive compatibilizer can be combined using any one of several mixing protocols. Investigations have shown that the order of mixing of systems like nylon 6/ABS/imidized acrylic and nylon 6/rubber/maleated rubber has little or no effect on the toughness of these ternary blends [39,40]; however, ternary blends of nylon 6 with core–shell type impact modifiers compatibilized by a styrene/maleic anhydride copolymer do show substantial differences in the ductile–brittle transition temperature depending on the mixing sequence used [41]. Differences in impact performance stemming from alternate mixing protocols have many possible causes; the sequence of mixing may influence the course of the chemical reactions that occur or the location of the graft or block copolymer formed which in turn can affect the blend morphology and other factors that govern toughness.

An earlier paper showed that the ductile–brittle transition temperature of PBT/ABS blends was substantially reduced by incorporation of the MGE terpolymer as a reactive compatibilizer; on the other hand, the room-temperature Izod impact strength was observed to be noticeably lower than that of the corresponding uncompatibilized blend. One purpose of this work is to examine the effect of the order of mixing of blend components on the toughness characteristics of PBT/ABS/MGE blends with particular emphasis on the reduction in room-temperature fracture energy caused by this compatibilizer. It will be shown that the mixing sequence used significantly affects the mechanical properties, and rheological behavior of these blends. Considerable evidence suggests a chemical origin for these effects.

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Table 1
Materials used in this study

Designation used here	Supplier designation	Molecular and structural characteristics					Brabender torque[a] (N.m)	Izod impact strength[b] (J/m)	Source
		Rubber content (wt%)	SAN (free) mol. wt (g/mole)	AN content (wt%)	Graft ratio	Rubber particle size (μm)			
ABS-16[c]	Magnum 541	16	$\bar{M}_n = 59\,000$ $\bar{M}_w = 140\,000$	25	–	0.5–1.0[d]	6.8	250	Dow Chemical
ABS-45	Starex	45	$\bar{M}_n = 35\,000$ $\bar{M}_w = 90\,000$	25	0.45	0.30	16.5	550	Cheil Industries
SAN	Tyril 25	0	$\bar{M}_n = 77\,000$ $\bar{M}_w = 152\,000$	25			6.5	30	Dow Chemical
PBT	Valox 315						5.8	50	General Electric
PMMA	Plexiglass V811 (100)		$\bar{M}_n = 63\,000$ $\bar{M}_w = 158\,000$				6.7	–	Rohm and Haas
EGMA	EGMA Ingetabond 2C			[GMA] = 0.42 eq/kg			3.8	–	Sumitomo Naugatuck

[a] Values taken at 250°C and 50 rpm, after 10 min.

[b] Room-temperature notched Izod impact.

[c] ABS grades were designated by their wt% rubber.

[d] Polydisperse particle size distribution.

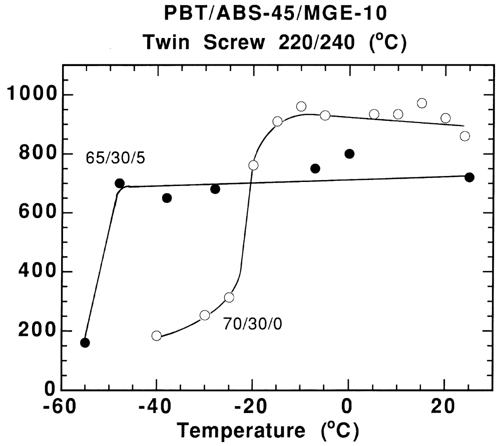
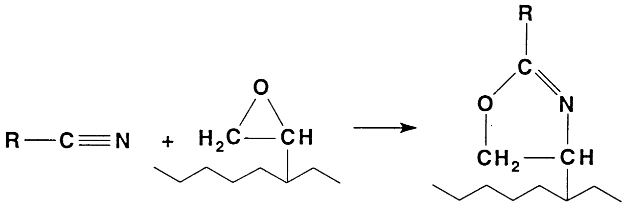


Fig. 1. Effect of temperature on notched Izod impact strength of PBT/ABS-45/MGE-10 $(70 - x)/30/x$ blends prepared in a twin-screw extruder at 220°C and molded at 240°C.

2. Background

An earlier paper showed that the epoxy functionality of MGE terpolymers reacts with the carboxyl endgroups of PBT [12]; however, other reactions are possible for the PBT/ABS/MGE system. For example, nitrile groups have been shown to react with epoxides in the presence of acid catalysts to form oxazoline linkages as follows [42–45]:



(1)

Nitriles can also undergo hydrolysis to carboxyl groups

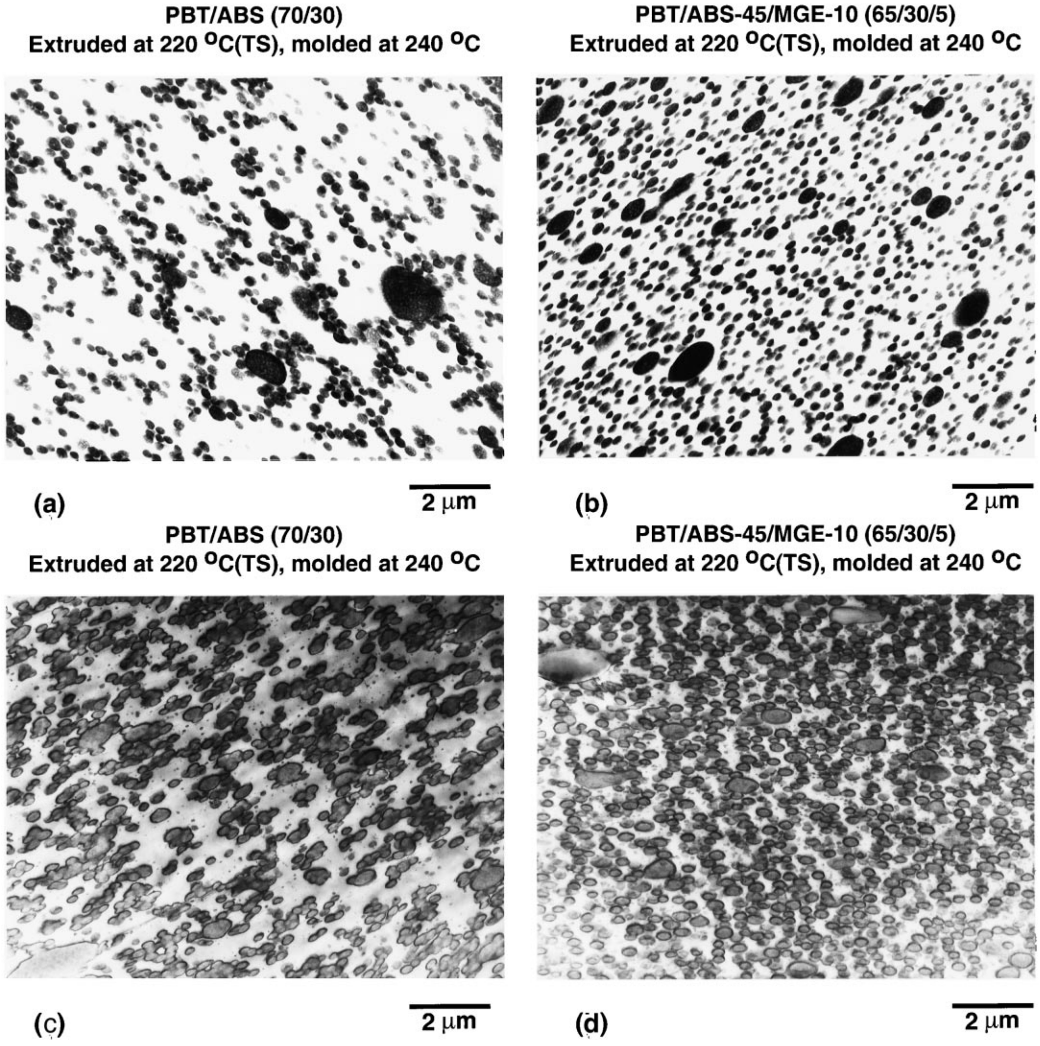


Fig. 2. TEM photomicrographs of PBT/ABS-45/MGE-10 $(70 - x)/30/x$ blends prepared in a twin-screw extruder at 220°C and molded at 240°C: (a) and (c) $x = 0$, uncompatibilized blend; (b) and (d) $x = 5$, compatibilized blend. The rubber particles of the ABS phase are stained dark by OsO_4 in (a) and (b) while the SAN of the ABS is stained dark by RuO_4 in (c) and (d).

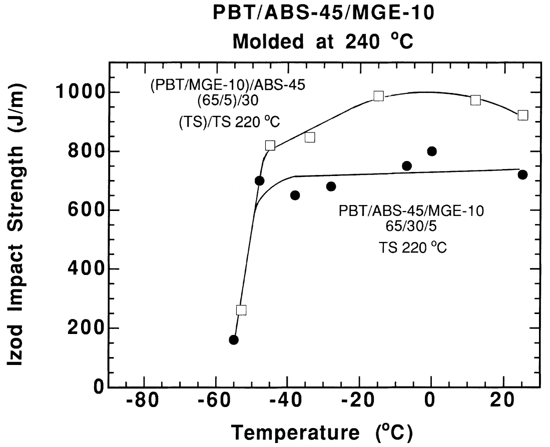
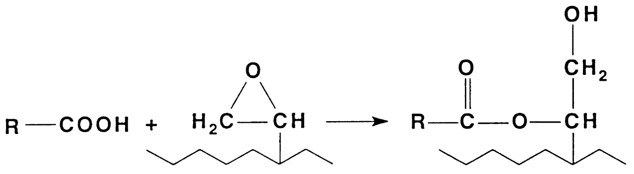


Fig. 3. Effect of temperature on notched Izod impact strength of PBT/ABS-45/MGE-10 blends containing 30 wt% ABS and 5 wt% MGE-10 prepared by a single-step extrusion method, 65/30/5, and a two-step extrusion method, (65/5)/30. Blends were prepared in a twin-screw extruder at 220°C and molded at 240°C.

[46] which in turn can react with the epoxide groups:

$$R{-}C{\equiv}N + 2H_2O \xrightarrow{\text{acid or base}} R{-}COOH + NH_3 \qquad (2)$$



(3)

Trace metals from polyester polymerization catalysis, e.g. antimony, titanium, etc., have been shown to have a large effect on the extent of reactions, as indicated by torque rheometry, that occur in polyester blends with GMA-containing copolymers [47].

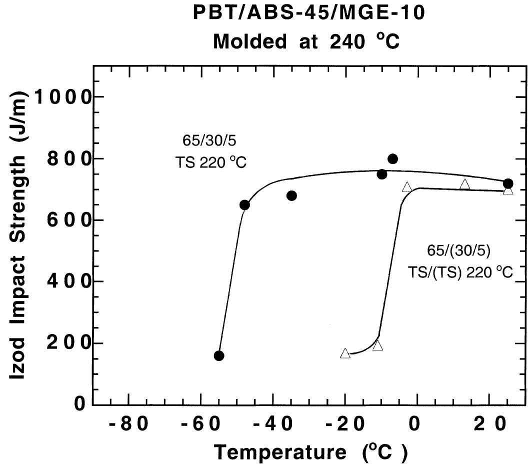
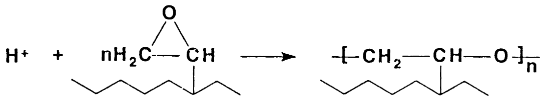


Fig. 4. Effect of temperature on notched Izod impact strength of PBT/ABS-45/MGE-10 blends containing 30 wt% ABS and 5 wt% MGE-10 prepared by a single-step extrusion method, 65/30/5, and a two-step extrusion method, 65/(30/5). Blends were prepared in a twin-screw extruder at 220°C and molded at 240°C.

Epoxides have the potential to react with strong nucleophiles, many of which may be present in emulsion-made ABS materials such as surfactants, coagulants, pH controllers, residual initiators, and post-polymerization additives [48]. It is beyond the scope of this work to analyze for all of these possible trace components in the ABS materials used here. The pH of the current emulsion-made ABS material is shown to be acidic. The patent literature reveals that strong proton donors, e.g. sulfuric acid, are commonly used as coagulants in the emulsion process to recover ABS powder from the latex [4,49–51]. Strong acids may catalyze the above-mentioned nitrile/epoxide reaction or initiate ring opening polymerization of the oxirane functionality, i.e.



(4)

This work will show evidence that the presence of a strong acid in ABS during processing these reactive blends greatly influences the impact performance of ABS/MGE and PBT/ABS/MGE blends because of such reactions and provides a basis for understanding the order of mixing effects noted. It would be useful to determine the chemical structure of the products produced from these reactions using an analytical method such as NMR; however, as will be shown, these techniques are impractical due to the fact that the resulting product is crosslinked and insoluble. Because of these limitations, mechanical and rheological testing will be used in conjunction with electron microscopy to develop inferences about the types of reactions that occur.

3. Experimental

Table 1 summarizes the materials used in this work. A detailed description of these materials is found elsewhere [4,49–51]. The styrene/acrylonitrile copolymer, SAN, and the ABS-16 material were made by bulk polymerization processes, i.e. mass-made; however, the ABS-45 was made by an emulsion process and may contain many residual chemical species. The current emulsion-made ABS material was dispersed in neutral water and stirred for 24 h, the pH of the water was then measured and found to be 6, indicating the presence of some acid in the ABS powder.

The reactive compatibilizer used in this work, MGE-10, is a methyl methacrylate, MMA, terpolymer containing 10 wt% glycidyl methacrylate for reactive functionality, and 2 wt% ethyl acrylate to prevent unzipping. This material is miscible with the SAN matrix of the ABS materials used here [52] because of the predominance of the MMA units and was designed to have similar rheological

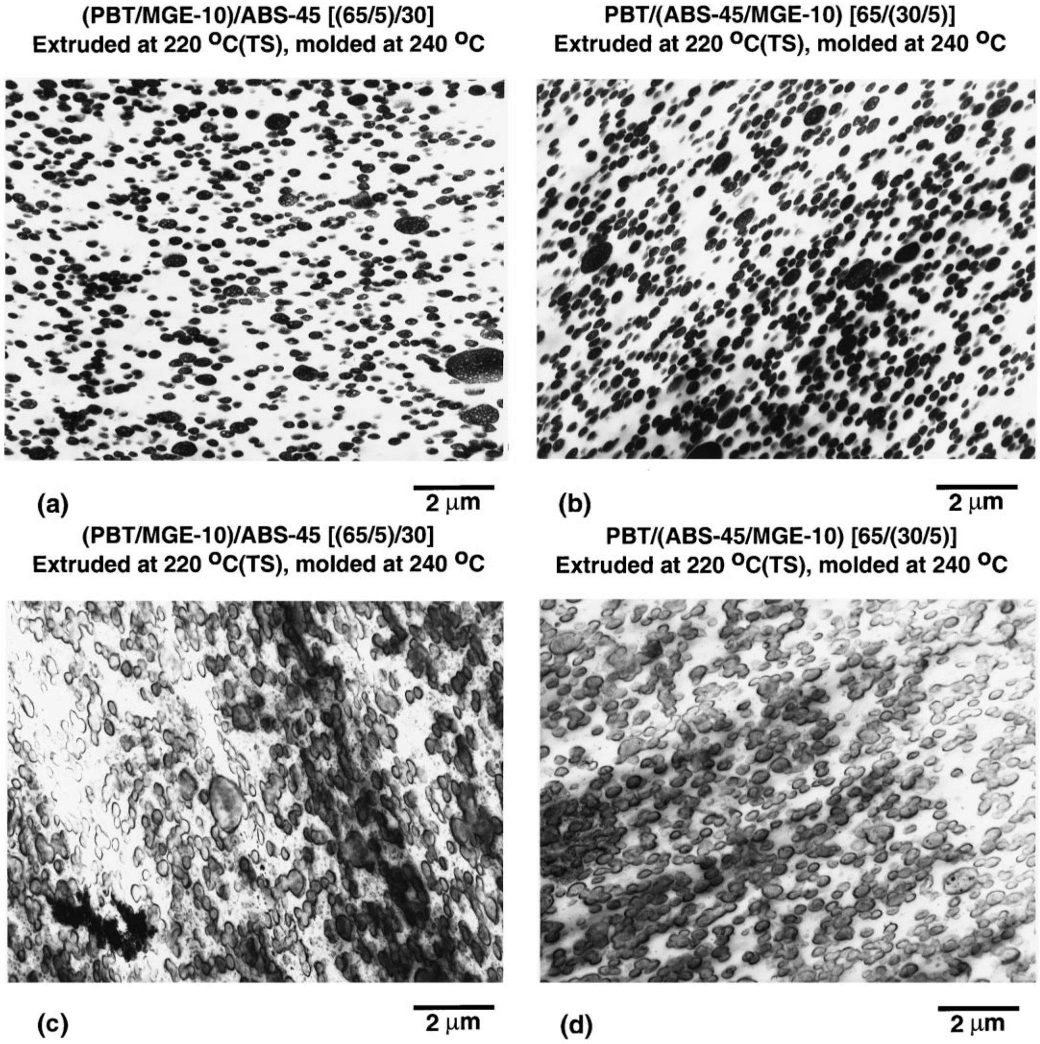


Fig. 5. TEM photomicrographs of blends prepared by different two-step extrusion methods in a twin-screw extruder at 220°C and molded at 240°C: (a) and (c) (PBT/MGE-10)/ABS-45 (65/5)/30; (b) and (d) (PBT/ABS-45)/MGE-10 (65/30)/5. The rubber particles of the ABS phase are stained dark by OsO_4 in (a) and (b) while the SAN of the ABS is stained dark by RuO_4 in (c) and (d).

characteristics as the PMMA listed in Table 1. The synthesis and characterization of MGE-10 is described elsewhere [12]. EGMA, a commercial ethylene/glycidyl methacrylate copolymer containing 6 wt% GMA is used in some experiments to conserve the use of MGE-10 compatibilizer. The strong organic acid *p*-toluene sulfonic acid, *p*-tsa, used in this work was obtained from Aldrich.

Pellets of PBT were cryogenically ground to a powder form and, along with the reactive compatibilizer powder, dried for 16 h in a vacuum oven at 65°C. SAN pellets, ABS-16 pellets, and as-received ABS-45 powder were dried for 16 h in a convection oven at 70°C. For blends containing PBT, all components were thoroughly mixed prior to processing in a twin-screw extruder. However, since SAN is miscible with both PMMA and MGE-10, blends containing no PBT were processed in a single-

Table 2
Room-temperature tensile properties of PBT/ABS-45/MGE-10 blends[a]

Blend	Yield stress (MPa)	Modulus (GPa)	Elongation (%)
PBT/ABS-45 70/30	1.7 ± 0.10	36 ± 0.1	110 ± 15
PBT/ABS-45/MGE-10 65/30/5	1.8 ± 0.07	37 ± 0.2	50 ± 6
(PBT/MGE-10)/ABS-45 (65/5)/30	1.7 ± 0.07	36 ± 0.4	55 ± 10
PBT/(ABS-45/MGE-10) 65/(30/5)	1.7 ± 0.04	37 ± 0.1	35 ± 17

[a] All blends were prepared in the twin-screw extruder at 220°C and molded at 240°C. Five specimens of each sample were tested at 5.08 cm/min.

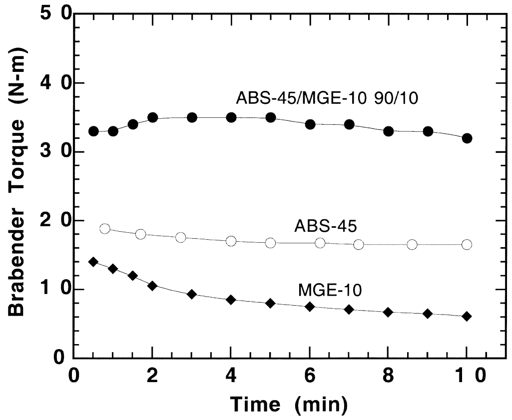


Fig. 6. Brabender torque response at 250°C of ABS-45/MGE-10 (90/10) blend and its components.

screw extruder because intensive mixing was not needed to achieve complete homogeneity. All blends were extruded at 220°C and then injection molded at 240°C. A more detailed description of the processing steps used here can be found elsewhere [1,12].

Notched Izod impact tests were conducted according to ASTM D256 as a function of temperature to determine ductile–brittle transition temperatures. At least five samples each from the gate- and far-ends of the injection-molded Izod bars were tested at room temperature and in the region of the ductile–brittle transition; at other temperatures fewer samples were tested, the exact number being dictated by the consistency observed. Only gate-end results are reported here; the differences in fracture properties between gate- and far-end specimens were typically insignificant. An Instron was used to determine the tensile properties of selected blends in accordance with ASTM D638 at a cross-head speed of 5.08 cm/min. An extensometer strain gage with a 5.08 cm gap was used to obtain the modulus and yield stress values.

The morphology of the blends were examined by a JEOL JEM 200cx transmission electron microscope (TEM) at an acceleration rate of 120 kV. Ultra-thin sections taken from the center of injection-molded Izod bars, perpendicular to the direction of flow, were obtained by cryo microtoming at $-$ 45°C using a Riechert–Jung Ultracut E microtome. OsO_4 or RuO_4 was used to stain either the rubber particles or the SAN phase of the ABS, respectively, which appear as dark domains in TEM photomicrographs. The weight average ABS domain size of PBT/ABS blends was determined using NIH Image software. Non-round domains are assigned the diameter of a circle with equivalent area. No attempt was made to account for the fact that the microtome does not cut each domain at its equator. A JEOL JSM-35 scanning electron microscope (SEM) was used to observe fracture surfaces created during Izod impact testing at room temperature. Prior to SEM examination, fracture surfaces were coated with gold using a Pelco Model 3 Sputter Coater and then viewed at a beam voltage of 25 kV.

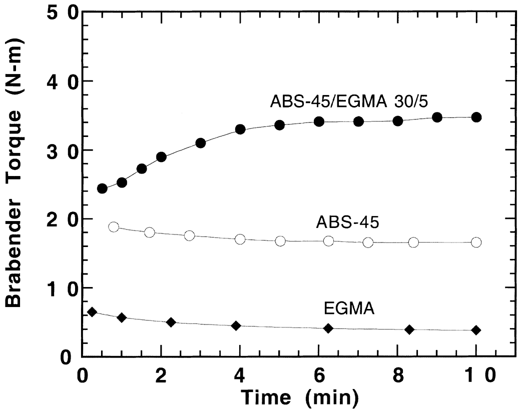


Fig. 7. Brabender torque response at 250°C of ABS-45/EGMA (30/5) blend and its components.

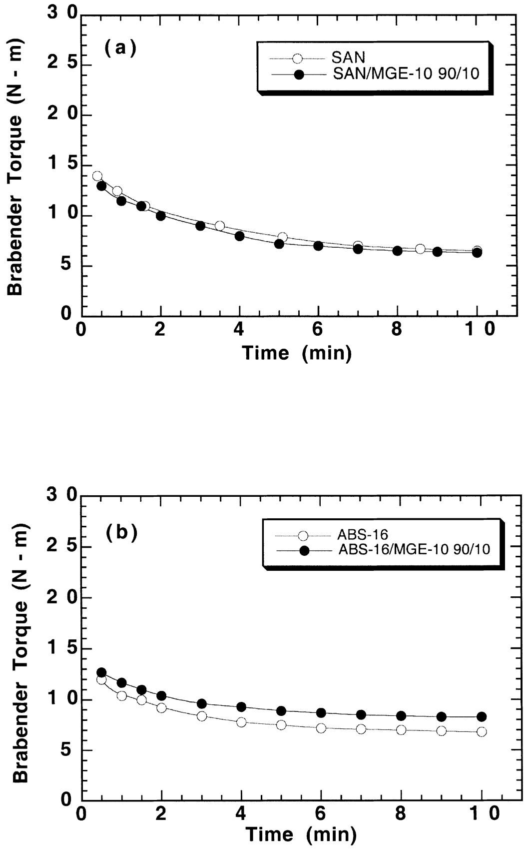


Fig. 8. Brabender torque response at 250°C of SAN/MGE-10 (90/10) blend and SAN (a); and ABS-16/MGE-10 (90/10) blend and ABS-16 (b).

A Brabender Plasticorder with a 50 ml mixing head operated at 250°C and 50 rpm was used for rheological characterization of these materials. Dynamic mechanical properties were measured using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA Mark I) at a frequency of 1 Hz. Blends were cooled to $-$ 150°C using liquid nitrogen and heated at a rate of 2°C/min to 125°C.

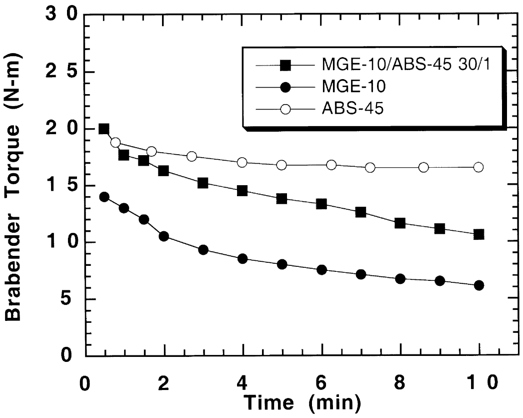


Fig. 9. Brabender torque response at 250°C of MGE-10/ABS-45 (30/1) blend and its components.

4. Effect of order of mixing

The Izod impact strength is shown in Fig. 1 as a function of temperature for compatibilized (5% MGE-10) and uncompatibilized PBT/ABS blends containing 30% ABS. All components were dry blended together prior to mixing via a single pass through the twin-screw extruder. As noted previously, the compatibilized blend exhibits superior low-temperature toughness; however, the room-temperature impact strength is lower than that of the uncompatibilized blend. This is an unexpected result and was a motivating factor for this study. The TEM photomicrographs in Fig. 2 show there is improved dispersion of ABS within the PBT matrix when the reactive compatibilizer is included in the blend. The rubber particles or the SAN within the ABS phase, which appear dark in these photomicrographs because of OsO_4 (stains rubber particles) and RuO_4 (stains SAN) staining, appear to be more well distributed in the compatibilized blend as a result of a reduction in the ABS domain size. The weight average particle size, $\bar{d}_W$, of the ABS domains is 0.80 μm in the uncompatibilized blend and 0.38 μm in the compatibilized blend prepared by this mixing protocol. The improved low-temperature ductility is attributed to this improved ABS dispersion which is the expected consequence of compatibilization. It does not follow, however, that the room-temperature fracture energy would be reduced; a variety of experiments described below was performed to better understand this issue.

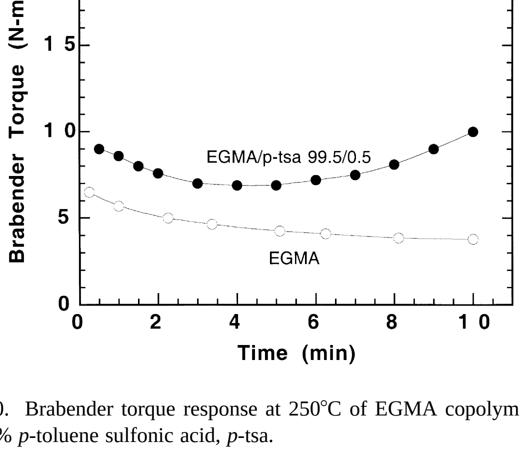


Fig. 10. Brabender torque response at 250°C of EGMA copolymer plus 0.5 wt% *p*-toluene sulfonic acid, *p*-tsa.

Fig. 3 shows the Izod impact strength as a function of temperature for compatibilized blends prepared by two different mixing procedures. In one, all of the components were mixed together and melt processed via a single-pass extrusion, as in Fig. 1; these blends are denoted here by the following designation of their composition, 65/30/5. In the other, a two-pass extrusion approach was employed for the blend denoted as (65/5)/30; PBT and MGE-10 were melt mixed together in a first extrusion step and then ABS-45 was combined with the PBT/MGE-10 blend in a second extrusion. There is no difference in the ductile–brittle transition temperatures of the blends prepared by these two mixing techniques; however, the Izod impact strength is higher at all temperatures above the ductile–brittle transition when PBT and MGE-10 were premixed prior to adding ABS-45.

Fig. 4 compares the single-pass extrusion technique, or the 65/30/5 composition, with another two-step procedure where ABS-45 and MGE-10 were melt mixed together in a first extrusion before adding PBT in a second extrusion, i.e. a blend designated as 65/(30/5). There is little difference in the room-temperature impact strength between these two mixing techniques; however, the ductile–brittle transition is over 40°C higher for blends made by the two-step extrusion method. This suggests that there is some fundamental difference in blends prepared by these methods. A first clue that signals a chemical origin for such differences is that the viscosity of the ABS-45/MGE-10 blend made in the first extrusion was very high relative to neat ABS-45. This suggests that a chemical reaction (e.g. grafting, crosslinking, etc.) takes place when ABS-45 and MGE-10 are melt mixed directly. The reaction evident in ABS/MGE-10 binary blends can occur during preparation of ternary PBT/ABS/MGE blends in addition to the desired carboxyl/epoxide reaction envisioned for formation of a graft copolymer that compatibilizes the blend. The TEM photomicrographs in Fig. 5 show that the two-pass extrusion employed in Fig. 3 leads to a slightly better ABS dispersion ($\bar{d}_W = 0.40$) than the two-pass technique used in Fig. 4 ($\bar{d}_W = 0.42$); however, the ABS dispersion for both two-pass techniques is superior to that of the uncompatibilized blend (see Fig. 2).

The tensile properties of PBT/ABS-45/MGE-10 blends prepared by different mixing protocols are shown in Table 2. There is little difference in the modulus and yield strength of these blends. However, the elongation at break of the PBT/(ABS-45/MGE-10) 65/(30/5) blend is lower than that of uncompatibilized or compatibilized blends prepared by different mixing protocols; this indicates a loss of ductility.

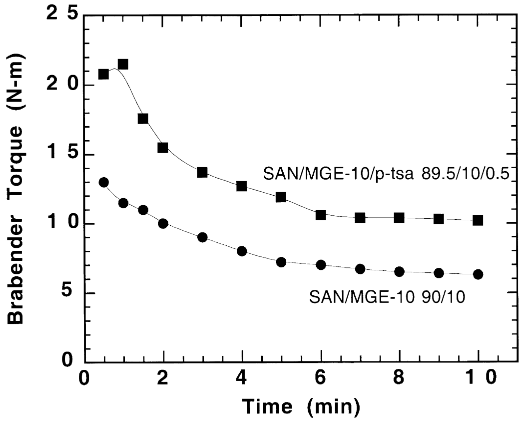


Fig. 11. Brabender torque response at 250°C of SAN/MGE-10 blend with and without 0.5 wt% *p*-toluene sulfonic acid, *p*-tsa.

5. Torque rheometry

The dispersion of ABS in PBT blends is improved when the reactive MGE compatibilizer is incorporated regardless of the mixing protocol used; however, the fracture toughness of these blends is very sensitive to the order in which the components are combined. The following experiments were performed to better understand the underlying reasons for this.

As mentioned earlier, a significant increase in melt viscosity on blending ABS-45 with MGE-10 was observed, and that lead is pursued here via various Brabender torque rheometry experiments. Plots of Brabender torque as a function of mixing time are shown in Fig. 6 for ABS-45/MGE-10 90/10 blends and each pure component. The blend viscosity is seen to be much higher than that of neat ABS-45 or MGE-10 which suggests that some reaction occurs during melt blending these components.

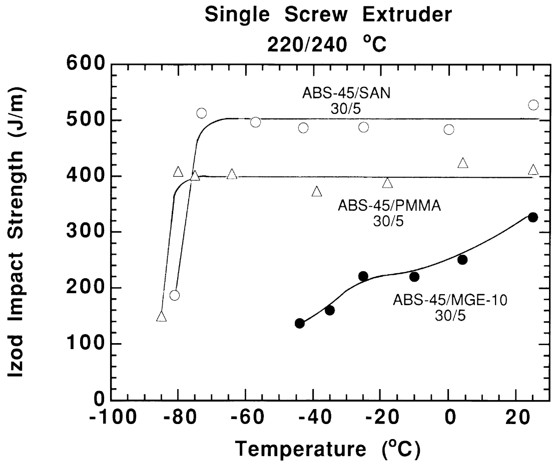


Fig. 12. Effect of temperature on the notched Izod impact strength of ABS-45/PMMA, ABS-45/SAN, and ABS-45/MGE-10 (30/5) blends prepared in a single-screw extruder at 220°C and molded at 240°C.

Fig. 7 shows Brabender torque plots for an ABS-45/EGMA 30/5 blend and the neat ABS-45 and EGMA materials. The blend viscosity is again much higher than that of the individual components indicating the possibility of chemical reaction. EGMA is not miscible with the SAN matrix of ABS unlike MGE-10; thus, it is clear that miscibility is not an important issue in these observations.

It is instructive to examine whether similar torque increases occur when MGE-10 is melt blended with SAN or ABS-16 materials made by a mass polymerization process rather than the emulsion polymerization process used to prepare materials like ABS-45. Brabender torque plots for SAN and an SAN/MGE-10 90/10 blend are shown in Fig. 8(a); the mixture resulting from this experiment was found to be completely soluble in methyl ethyl ketone (MEK) indicating that no significant gel-forming reactions occur during melt processing. Fig. 8(b) shows corresponding plots for an ABS-16 blend with MGE-10; the melt viscosity of the blend is not substantially increased relative to the pure ABS material. These experiments show a fundamental difference in rheological response when epoxy functional polymers are blended with emulsion-made versus mass-made ABS materials.

Plots of Brabender torque versus time for a MGE-10/ABS-45 30/1 blend and the two components are shown in Fig. 9. The viscosity of the blend approaches that of the neat ABS-45 even though only a small amount of ABS-45 is present, suggesting that very little of the contaminant present in ABS-45 is required to initiate a substantial viscosity increase, i.e. the ABS material seems to provide a catalytic effect. We postulate that such a catalytic effect may stem from residual acidity (recall pH measurement mentioned earlier) in the emulsion-made ABS material.

To test this possibility various experiments were performed in which *p*-toluene sulfonic acid, *p*-tsa, a strong organic acid, was added to the blend. Fig. 10 shows the Brabender torque response for EGMA and a mixture of EGMA with a small amount of *p*-tsa. The viscosity nearly doubles as a result of the addition of this small amount of *p*-tsa. This suggests that such a strong acid can cause polymerization of the epoxide groups of EGMA. A blend of SAN and MGE-10 was shown to be unreactive as indicated by the Brabender torque experiment shown in Fig. 8. By incorporating a small amount of *p*-tsa into this blend, the melt viscosity of this blend is nearly doubled as seen in Fig. 11. This viscosity increase could be the result of either the polymerization of the epoxide functionality [reaction (4)] of MGE-10 or the nitrile/epoxide reaction [reaction (1)] catalyzed by the presence of acid. A small quantity of the SAN/MGE-10/*p*-tsa blend was stirred for 24 h in MEK; an insoluble gel was seen to exist and was recovered by vacuum filtration and dried for 24 h at 100°C. The gel fraction of this sample was determined to be 25 wt%. On the other hand, SAN/MGE-10 blends containing no acid prepared in a similar manner are completely soluble in MEK.

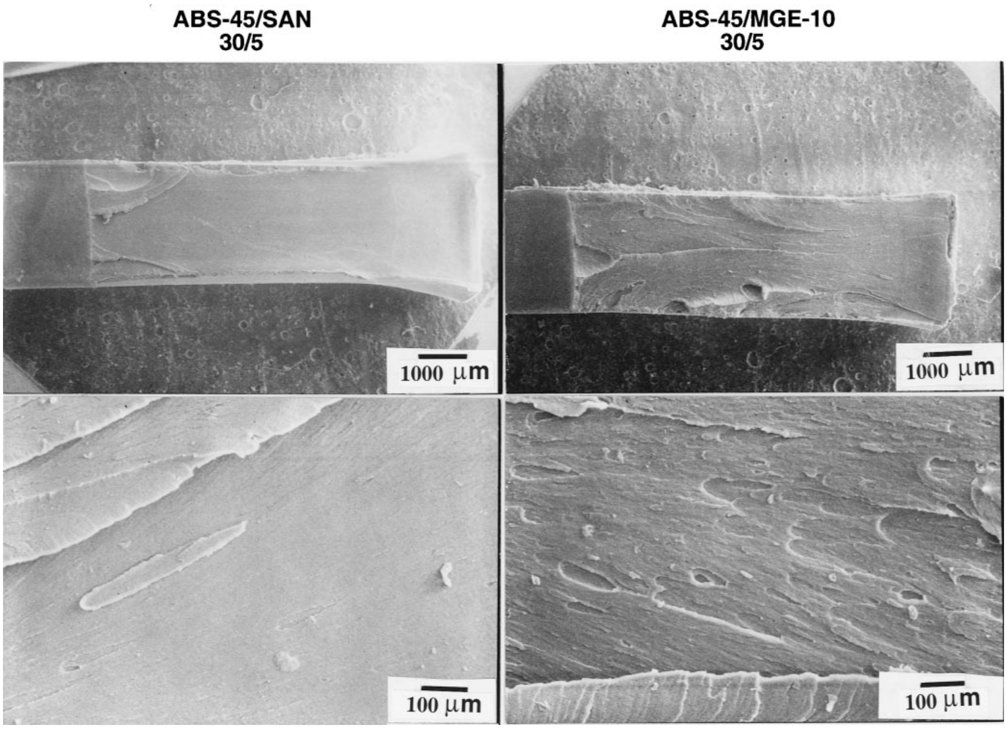


Fig. 13. SEM photomicrographs of the fracture surfaces of ABS-45/SAN and ABS-45/MGE-10 (30/5) blends prepared in a single-screw extruder at 220°C and molded at 240°C.

6. Effect of reactions on ABS properties

Blends of ABS-45, containing no PBT, with SAN, PMMA, and MGE-10 were prepared for evaluation of their morphology, impact, tensile, and dynamic mechanical properties. Fig. 12 shows the Izod impact strength as a function of temperature for blends of ABS-45 with these materials for comparison at the same rubber content. Blends containing PMMA were made in order to examine the effect of a nonreactive acrylic material on ABS-45 properties. The impact strength of ABS-45/PMMA 30/5 is slightly lower than ABS-45/SAN 30/5 blends, indicating that the presence of an acrylic polymer with no epoxide groups, which is miscible with the SAN matrix, does have a small effect on ABS impact properties. The blend of ABS-45 with MGE-10, however, shows a dramatic change in impact behavior; the impact strength is greatly reduced and the ductile–brittle transition temperature is increased by nearly 50°C. This change in ABS properties caused by reactions with MGE-10 could lead to poorer mechanical performance of toughened PBT blends; e.g. lower impact strength and higher ductile–brittle transition temperatures.

The fracture surfaces of the ABS-45/SAN and ABS-45/MGE-10 blends are compared in Fig. 13. ABS-45/SAN blends have a high degree of contraction perpendicular to the direction of crack propagation which is commonly seen in ductile systems; however, blends containing MGE-10 show very little lateral contraction and have a rough and pitted surface indicating a more brittle mode of failure. Table 3 shows the tensile properties of ABS-45 blends with SAN, PMMA, and MGE-10. There is little difference in the modulus and yield strength between these materials; however, the elongation at break is much lower in blends containing MGE-10 indicating a loss of ductility.

The morphology of the ABS-45/SAN and ABS/MGE-10 blends are compared in the TEM photomicrographs of Fig. 14. It is clear that the presence of the compatibilizer has no significant effect on the spatial distribution of the rubber particles within the ABS material, i.e. the poor mechanical performance of ABS-45/MGE-10 and

Table 3
Room-temperature tensile properties of ABS-45 blends[a]

Blend	Yield stress (MPa)	Modulus (GPa)	Elongation (%)
ABS-45/SAN 30/5	0.83 ± 0.02	19 ± 0.2	116 ± 7
ABS-45/PMMA 30/5	0.84 ± 0.03	19 ± 0.1	99 ± 6
ABS-45/MGE-10 30/5	0.83 ± 0.03	19 ± 0.1	51 ± 3

[a] All blends were prepared in the single-screw extruder at 220°C and molded at 240°C. Five specimens of each sample were tested at 5.08 cm/min.

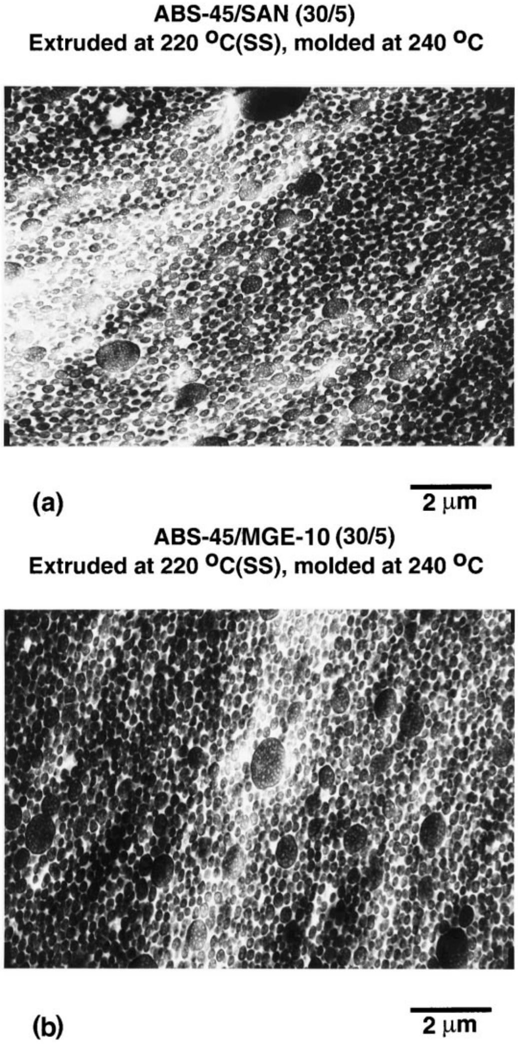


Fig. 14. TEM photomicrographs of ABS-45/SAN and ABS-45/MGE-10 (30/5) blends prepared in a single-screw extruder at 220°C and molded at 240°C. The rubber particles of ABS are stained dark by OsO_4.

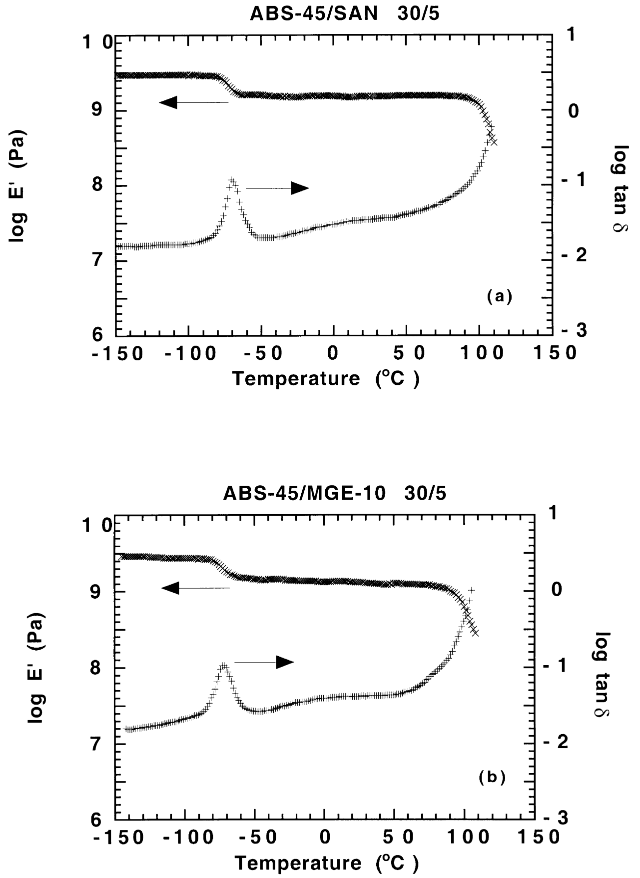


Fig. 15. Dynamic mechanical properties of ABS-45/SAN and ABS-45/MGE-10 (30/5) blends prepared in a single-screw extruder at 220°C and molded at 240°C.

PBT/ABS-45/MGE-10 blends is not a result of morphological changes. Dynamic mechanical properties for the ABS-45/SAN and ABS-45/MGE-10 blends are shown in Fig. 15. These results indicate that there is no significant change in the ABS rubber phase (e.g. modulus or glass transition temperature) as a result of reactions that occur with MGE-10; hardening of the rubber phase by some type of degradation or crosslinking reaction would embrittle the ABS [53].

To examine the effect of MGE-10 on the properties of a pH-neutral ABS material, blends of ABS-16 with SAN, PMMA, and MGE-10 were prepared and the impact strength measured (see Fig. 16). As seen in Fig. 12, the presence of PMMA in ABS-45 slightly reduces the impact strength relative to ABS-45 blended with SAN; however, the presence of MGE-10 in ABS-16 does not have a large effect on impact properties like that observed with the emulsion-made ABS-45. However, the addition of a small amount of *p*-tsa to the ABS-16/MGE-10 blend reduces the impact strength by over 50% and the ductile–brittle transition temperature is increased by over 60°C; clearly the presence of strong acid induces deleterious chemical reactions.

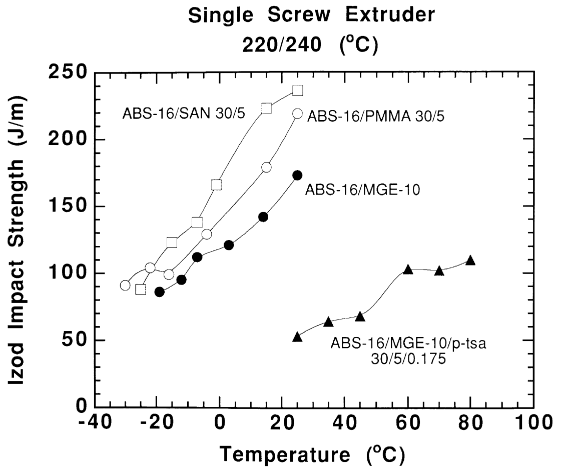


Fig. 16. Effect of temperature on the notched Izod impact strength of ABS-16/PMMA, ABS-16/SAN, and ABS-16/MGE-10 (30/5) blends and ABS-16/MGE-10/*p*-tsa (30/5/0.175) blends prepared in a single-screw extruder at 220°C and molded at 240°C.

We conclude that strong acids (or other contaminants in emulsion-made ABS materials) cause the formation of a gel or crosslinked network within the SAN matrix when the MGE compatibilizer is present. Regardless of their chemical structure, it is these crosslinked chains that reduce the impact strength of the ABS or its blends with PBT since, as shown in other studies [54,55], plastic deformation or ductility is suppressed when physical chain slippage or disentanglement is restricted by crosslinking. From the results shown here, it is not possible to positively identify the chemical mechanism of the crosslinking reactions; however, in our opinion ring opening polymerization of the epoxide groups, as shown in reaction (4), is the simplest and most likely possibility.

It appears that the order of mixing affects ternary blend properties in such cases because this governs in part the extent of the desired graft copolymer formation [reaction (3)] versus the undesirable crosslinking reaction and perhaps where the graft copolymer formed resides in the blend. The simple scheme of mixing all components simultaneously requires the graft reaction to compete with crosslinking; however, mixing PBT with MGE-10 without any ABS present (hence no contaminant to catalyze crosslinking) allows the graft reaction to occur preferentially. Thus, addition of the ABS (and its contaminant) in the last extrusion step appears to minimize the deleterious crosslinking reaction or, at least, its effects.

7. Conclusions

The degree of ABS dispersion in PBT/ABS blends is improved by incorporating MGE terpolymers; however, the low-temperature Izod impact strength and the room-temperature toughness are very sensitive to the order in which blend components are combined apparently due to the crosslinking reactions that occur when the epoxy functional polymer, MGE-10, and the emulsion-made ABS-45 are both present in the blend. When a two-step mixing method is used where PBT and reactive compatibilizer are combined prior to adding ABS, the room-temperature impact properties are superior to those for blends made by the single-step extrusion method; however, if a two-step method is used where ABS and MGE-10 are first extruded together before adding PBT, the impact strength is greatly reduced and the ductile–brittle transition temperature is increased relative to ternary blends made by the single-pass method or blends containing no compatibilizer at all. There is evidence that some residual chemical (probably an acid) in the emulsion-made ABS materials catalyzes reactions of the epoxy units of the compatibilizer; these reactions increase blend viscosity with no change in the morphology of the blend or the nature of the ABS rubber phase; however, there is a deleterious effect on the mechanical properties of the ABS and ultimately its blends with PBT. Mass-made ABS-16 and SAN do not cause such reactions of the MGE compatibilizer; however, separate addition of acid will cause the reaction to occur. This and other evidence suggests that acid from the ABS catalyzes or initiates reactions of the epoxy functionality; most likely the acid promotes ring opening polymerization of the epoxide units although other reaction pathways cannot be ruled out. By altering the order of mixing used, the sequence in which chemical reactions occur, i.e. grafting versus crosslinking, can be manipulated thereby optimizing blend properties.

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