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Polymer 40 (1999) 3353–3365

polymer

Fracture behavior of PBT–ABS blends compatibilized by methyl methacrylate–glycidyl methacrylate–ethyl acrylate terpolymers

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Received 29 June 1998; accepted 28 July 1998

Abstract

The fracture properties of blends of poly(butylene terephthalate), PBT, with acrylonitrile-butadiene-styrene materials, ABS, compatibilized by a methyl methacrylate–glycidyl methacrylate–ethyl acrylate terpolymer, MGE, have been characterized by Izod impact and single-edge notch, three-point bend (SEN3PB) type tests. The impact properties have been shown to be very sensitive to specimen thickness and mildly sensitive to notch sharpness. Blends containing 30 wt% ABS and molded into 3.18 mm samples are super tough in the absence of a compatibilizer; however, 6.35 mm specimens require higher ABS contents and compatibilization to achieve significant toughness. Low quantities of MGE (1 wt%) are required to produce super tough blends of 6.35 mm thickness; whereas, higher quantities of MGE result in a decrease in the impact strength. A dual mode of deformation during Izod impact testing has been observed for uncompatibilized blends molded into 6.35 mm samples where brittle failure occurs in the region of fracture initiation and ductile failure occurs in the region of crack termination. Similarly, a more brittle mode of failure occurs for SEN3PB samples with long ligament lengths and ductile failure for samples with short ligament lengths. The distance a crack can propagate and the size of the stress whitened zone created during Izod impact testing have been shown to be related to the impact properties determined by Izod and SEN3PB tests. © 1999 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Poly(butylene terephthalate), PBT, can be blended with elastomeric materials to increase toughness, while retaining excellent tensile and thermal properties, as well as chemical resistance [1–29]. A series of papers from this laboratory have explored the morphology and toughness of blends of PBT with acrylonitrile-butadiene-styrene, ABS, materials. These PBT–ABS blends have been successfully compatibilized by methyl methacrylate (MMA), glycidyl methacrylate (GMA), ethyl acrylate (EA) terpolymers, MGE. The formation of an MGE–g-PBT graft copolymer at the PBT–ABS interface via reaction of epoxide rings in the GMA repeat units with the carboxyl endgroups of PBT permit optimization of the morphology generation and stabilization and impact toughness at low temperatures, within an acceptable processing temperature range for the production of these blends [2,3].

The effects of PBT molecular weight, ABS type and content, and MGE content and composition on PBT–ABS blend properties have been thoroughly explored [2–5]. In these previous reports, Izod impact testing has been the only method used to characterize material toughness. This technique, although widely used and beneficial, provides only limited information for characterizing the fracture behavior of ductile materials. The purpose of this paper is to examine in more detail the fracture behavior of PBT–ABS blends using notched Izod and instrumented Dynatup single-edge notch, three-point bend (SEN3PB) impact tests. The effects of specimen and notch geometry, ABS content, and reactive compatibilization are examined to better understand their influence on the fracture properties of PBT–ABS blends.

2. Background

The common method of characterizing the fracture resistance is by notched Izod and Charpy impact tests. The results from these methods are specific to the sample and notch geometry and a given fracture area, which may limit their use in identifying differences between tough materials under other high speed impact situations. In addition to

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PII: S0032-3861(98)00575-8

simply noting the energy dissipated in the tests, other useful information can be obtained by close examination of fractured test specimens. The materials examined here show interesting relationships between the Izod impact strength, the distance that the crack propagated during fracture, and the size of the process (stress whitened) zone.

One of the goals of fracture mechanics is to characterize toughness in terms of parameters that are properties of the material itself. Linear elastic fracture mechanics (LEFM) was developed to describe materials that undergo primarily elastic deformation and fail in a brittle manner [30,31]. Those techniques have been applied to brittle polymers, under plane-strain conditions, for determination of the critical stress-intensity factor, K_{1c}, which is a measure of the stress conditions at the crack tip [32]. These tests are valid only when the specimen thickness is large enough to ensure plane-strain conditions. In order to meet this criterion for super tough polymers, the specimens would have to be thicker than is practical for most fabrication procedures. Alternate techniques have been devised for tough polymers, such as the now accepted J-integral method [33] which has been used to characterize many ductile polymer systems such as HDPE, toughened polyamides, etc. [34–42]. However, this technique requires specialized equipment and specimens that are still often thicker than can be conveniently injection molded.

Mai and Williams [43] and Vu-Khanh [44] have suggested new approaches for characterizing the fracture behavior of ductile polymers. They have shown that the relationship between the fracture energy, U, and the size of the ligament (or fracture area) to be broken can be described by two parameter models that provide a more detailed characterization of ductile polymers than Izod or Charpy impact tests, but are simpler to implement than conventional fracture mechanics techniques. Their methodologies are based on ideas introduced by Broberg [45] which state that the region around the crack tip consists of an elastic region where fracture initiation occurs, and a plastic region where energy is absorbed during crack propagation. Mai and Williams measure the energy to fracture thin specimens in a double-edge notch tensile testing procedure at low strain rates; whereas, the Vu-Khanh method employs a single-edge notch, three-point bend sample configuration in an instrumented Dynatup drop tower at velocities typical of the Izod or Charpy impact tests. These methods have been used to characterize many ductile polymers such as polycarbonate, polyethylene, polyesters, and toughened nylons [16,24, 46–64]. Detailed descriptions and comparisons of these two techniques have been given recently [52,65].

The current work is based on a method that is mathematically similar to the essential work of fracture model used by Mai and Williams; however, the test configurations (thick samples and high speed impact tests) are similar to those used by Vu-Khanh. Previous work from this laboratory has shown for polycarbonate–ABS blends that it is more useful to relate the fracture behavior of samples with different thicknesses to the length rather than the area of the ligament to be broken [65]. The model divides the total fracture energy per unit area (U/A) determined by instrumented Dynatup impact testing into two separate contributions as follows

$$U/A = u_o + u_d \ell \tag{1}$$

where ℓ is the ligament length, u_o is defined as the specific limiting fracture energy (the units are energy per unit area), and u_d is called the dissipative energy density since it relates to the plastic deformation in the process zone (the units are energy per unit volume). A plot of U/A vs ℓ, should give a linear relationship where u_o is the intercept and u_d is the slope.

3. Experimental

The PBT material used here, Valox 315, was obtained from the General Electric Co. An emulsion-made SAN-grafted rubber concentrate, or ABS, material containing 45 wt% rubber was obtained from Cheil Industries. Detailed characterization of these materials is found in previous papers [1,2]. The reactive compatibilizer, MGE-10, is a bulk-made methyl methacrylate (MMA) rich terpolymer containing 10 wt% glycidyl methacrylate (GMA) to provide reactive functionality and 2 wt% ethyl acrylate (EA) to prevent unzipping. This material is completely miscible with the SAN phase of the current ABS material [66]. A detailed description of the synthesis and characterization of MGE terpolymers has been reported previously [2].

Pellets of PBT were cryogenically ground to powder and, along with MGE-10 powder, dried for 16 h at 65°C in a vacuum oven. As received ABS powder was dried for 16 h at 70°C in a convection oven. All blend components were mixed together in powder form prior to extrusion. A twin screw extruder operated at 220°C was used for processing all blends prior to injection molding at 240°C into 3.18 or 6.35 mm thick impact test bars; further description of the processing is given elsewhere [1,2].

Notched Izod impact tests were conducted according to ASTM D256 using 3.18 or 6.35 mm thick injection molded bars for standard and sharp notch specimens. Sharp notch test bars were produced by tapping a fresh razor blade into the bottom of a standard notch. At least five samples each from the gate- and far-end of the injected molded Izod bars were tested at room temperature and in the region of the ductile–brittle transition temperature; at other temperatures fewer samples were used, the exact number being dictated by the consistency observed. Only gate-end information is reported here, since the difference between gate- and far-end specimens was typically insignificant.

Instrumented impact testing was performed using a Dynatup Drop Tower Model 8200 with a 10 kg weight and a fracture velocity of 3.5 m s^{-1} (same as Izod test). Between 24 and 36 samples (half gate-end and half far-end) of the single-edge notch three-point bend (SEN3PB) specimens were tested; a sharp notch was made by tapping a fresh razor blade into the root of the notch leaving a ligament ranging from 2 to 10 mm in length. Fracture energy was calculated from the integrated area under the load–deflection curves. Izod impact testing resulted in partial breaks of these ductile materials; however, tests performed in the Dynatup with the SEN3PB configuration generally lead to almost complete or hinge type breaks. Descriptions of the test apparatus, sample geometry and preparation, and test procedure have been given previously [63].

The morphology of post-mortem fracture specimens was examined by either a JEOL JSM-35 scanning electron microscope (SEM) or a JEOL JEM 200cx transmission electron microscope (TEM). Fractured surfaces resulting from Izod impact testing at room temperature were used for SEM observations. 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. The deformation around the tip of arrested cracks parallel to both the injection flow and the crack extension directions was investigated using TEM at an accelerating rate of 120 kV. A more detailed description of the techniques used to generate these arrested cracks and obtain thin sections from fracture specimens around the region of the crack tip is found elsewhere [62,63]. Ultrathin sections were obtained by cryomicrotoming at − 45°C using a Riechert–Jung Ultracut E microtome. The sections were stained in OsO_4 vapor for 24 h which selectively stains the rubber phase in ABS and appear as dark domains in the TEM photomicrographs.

4. Izod results

4.1. Effect of ABS content and specimen geometry

ASTM D256 specifies the sample geometry and notch radius to be used in the Izod impact test; for some materials, very different fracture behavior may be observed when these conditions are changed. For example, neat polycarbonate (PC) is found to be very tough when 3.18 mm thick specimens are notched according to this standard; however, when a sharp notch or thicker specimen is used, PC fails in a brittle manner [15,67].

Fig. 1 shows the Izod impact strength as a function of ABS content in PBT–ABS blends with and without compatibilizer for various notch and specimen geometries. For the uncompatibilized blends shown in Fig. 1(a), the fracture strength is very sensitive to sample thickness and only mildly sensitive to notch sharpness. A minimum of

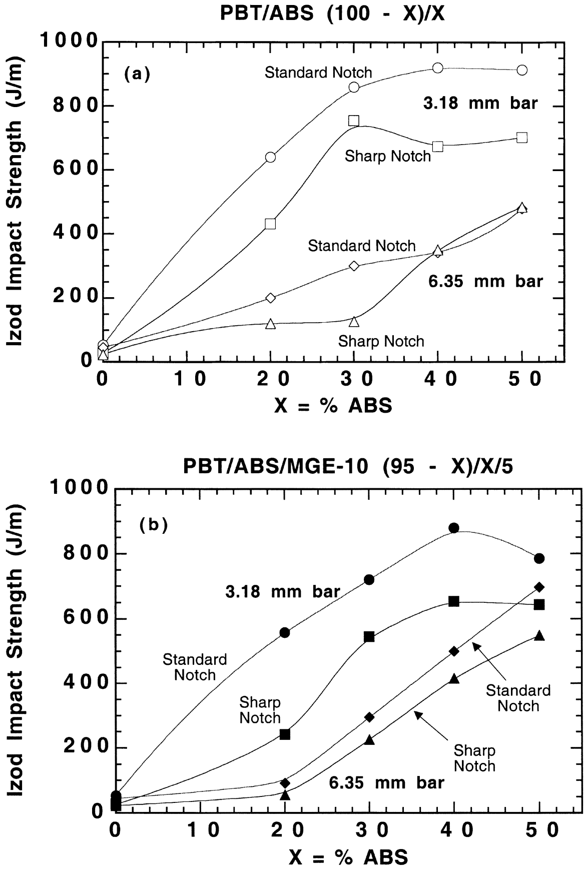


Fig. 1. Izod impact strength (standard and sharp notch) as a function of ABS content of: (a) PBT–ABS (100 – X)/X; and (b) PBT–ABS–MGE-10 (95 – X)/X/5 blends for 3.18 and 6.35 mm thick samples.

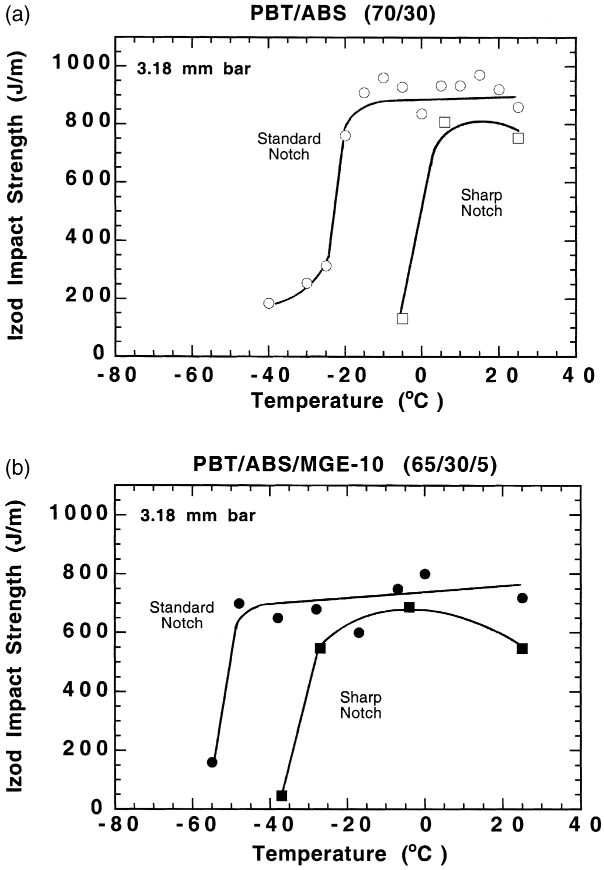


Fig. 2. Effect of temperature on standard and sharp notched Izod impact strength of: (a) PBT–ABS 70/30; and (b) PBT–ABS–MGE-10 65/30/5 blends for 3.18 mm thick samples.

30 wt% ABS is required to generate very tough 3.18 mm (thin) specimens; however, up to 50 wt% ABS is required to produce significant toughening in 6.35 mm (thick) specimens. The blends containing 5 wt% of the MGE-10 compatibilizer shown in Fig. 1(b) exhibit similar behavior in response to thickness and notch sharpness, but significant toughness (500 J m^{-1}) is achieved for thick specimens of blends containing 40 wt% ABS.

Fig. 2 shows the Izod impact strength as a function of temperature for PBT–ABS–MGE-10 blends containing 30 wt% ABS. When the notch is sharpened, there is a reduction in impact strength (10%–20%) and an increase in the ductile–brittle transition temperature (20°C) for both compatibilized and uncompatibilized blends. The presence of MGE-10 significantly improves the low temperature toughness for samples with both standard and sharp notches.

The effect of sample thickness on the impact properties vs temperature for PBT–ABS 70/30 blends is shown in Fig. 3(a). Thin specimens are super tough above − 20°C while thick specimens are much less tough resulting in nearly complete breaks at temperatures up to 45°C. Fig. 3(b) shows the extent of improvement that results from reactive compatibilization of blends containing 30 wt% ABS. An earlier paper has shown that residual acidic material in the emulsion-made ABS materials used here, may also cause crosslinking reactions involving the epoxide functionality of MGE-10 which has a deleterious effects on the impact properties of ABS and PBT–ABS–MGE blends [3]. It was also shown that the mixing sequence of the blend components can be used to minimize the effects of these unwanted reactions to produce compatibilized blends with superior impact properties. Two mixing sequences were used here to prepare the compatibilized blends containing 5 wt% MGE-10 that were molded into thick samples. In one, all components were mixed together in one extrusion step, denoted as 65/30/5 (single-pass). In the other, PBT and MGE-10 were first mixed together followed by the addition of ABS in a second extrusion step, denoted as (65/5)/30 (two-pass). The later procedure selectively allows the grafting reaction to occur while decreasing the potential for the unwanted crosslinking reaction. The impact strength of thin PBT–ABS–MGE-10, 65/30/5, specimens is very high at temperatures above − 50°C when the single pass method is used; however, when this method is used to prepare thick samples the impact strength is much lower. When the two-pass mixing protocol is used, thick specimens have superior impact properties when compared with the single-pass method although at about −10°C both mixing protocols result in relatively brittle blends (300 J m^{-1}). As seen in Fig. 4, PBT--ABS 60/40 blends that

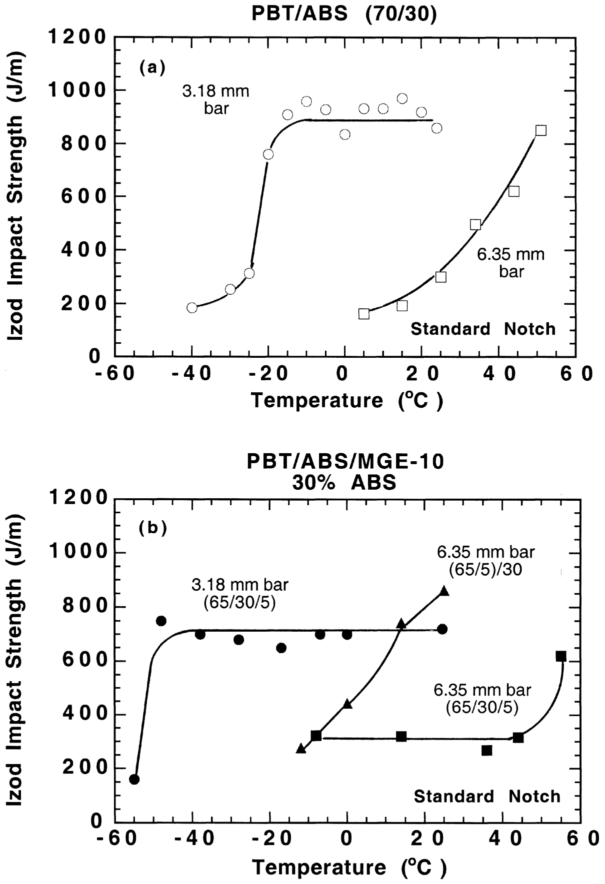


Fig. 3. Effect of temperature on standard notched Izod impact strength of: (a) uncompatibilized; and (b) compatibilized blends containing 30 wt% ABS prepared by two mixing protocols for 3.18 and 6.35 mm thick samples.

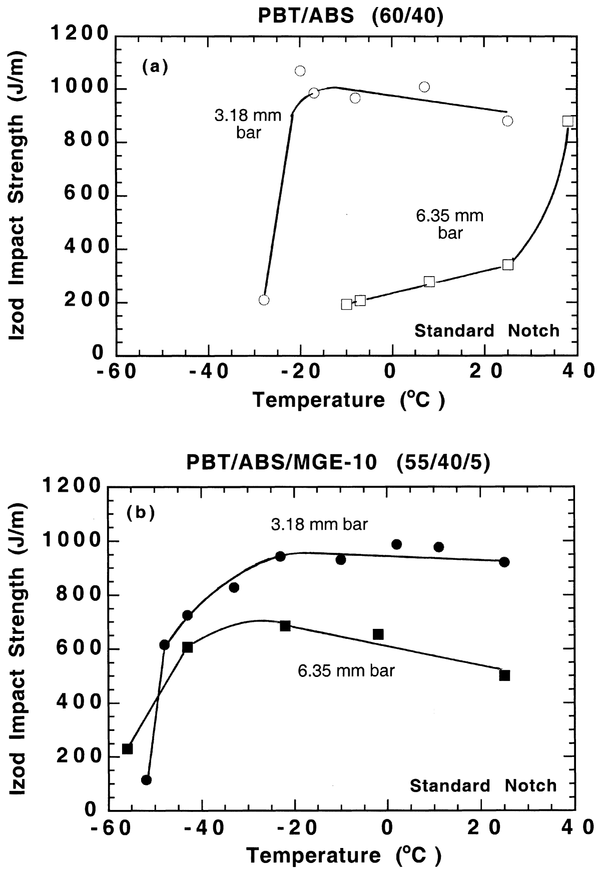


Fig. 4. Effect of temperature on standard notched Izod impact strength of: (a) PBT–ABS 60/40 and (b) PBT–ABS–MGE-10 55/40/5 blends for 3.18 and 6.35 mm thick samples.

are molded into thick samples are not very tough when compared with thin samples. When 5 wt% MGE-10 is added to this blend, thick samples have substantially higher impact strength and equivalent ductile–brittle transition temperatures as thin specimens. This result indicates that a compatibilizer is necessary to toughen PBT–ABS blends that are to be molded into thick parts.

The SEM photomicrographs of fracture surfaces generated during the Izod impact testing of selected blends containing 40 wt% ABS (Fig. 4) are shown in Fig. 5. It is clear that a large amount of yielding and deformation occurs in thin samples containing no compatibilizer. A more complex behavior is observed for uncompatibilized blends that are molded into thick samples (lower impact strength). These specimens have a smooth fracture surface, characteristic of brittle failure near the notch location where fracture is initiated during impact; as the crack propagates further away from the notch, there is a transition to a stress whitened surface, typically associated with ductile failure. This suggests that two modes of fracture (ductile–brittle) prevails in these uncompatibilized thick samples depending on the location of the crack front as it moves through the sample. A similar type of behavior has been seen in toughened nylon 6 blends, i.e. the mode of deformation (ductile–brittle) depends on the sample ligament length, and as a result the dependence of the specific fracture energy, U/A, vs ligament length, ℓ, is not described by Eq. (1) [61,64]. By adding 5 wt% MGE-10 to these thick samples, entirely ductile failure occurs and the fracture surface is more similar to that of the thin specimens.

4.2. Examination of fracture region

As mentioned earlier, additional information can be derived from Izod impact type testing by observing the fracture region of broken Izod bars. Fig. 6 schematically shows a typical fracture region generated during impact testing; here C is the crack propagation length, S denotes the size of the outer stress whitened zone (process zone) as seen on the exterior surface of the bar, while S' denotes the size of the stress whitened zone in the center of the sample. The interior dimension S' was observed by cryofracturing away the surface of the impact bar to view the center of the fracture region. There is little difference in the shape of the

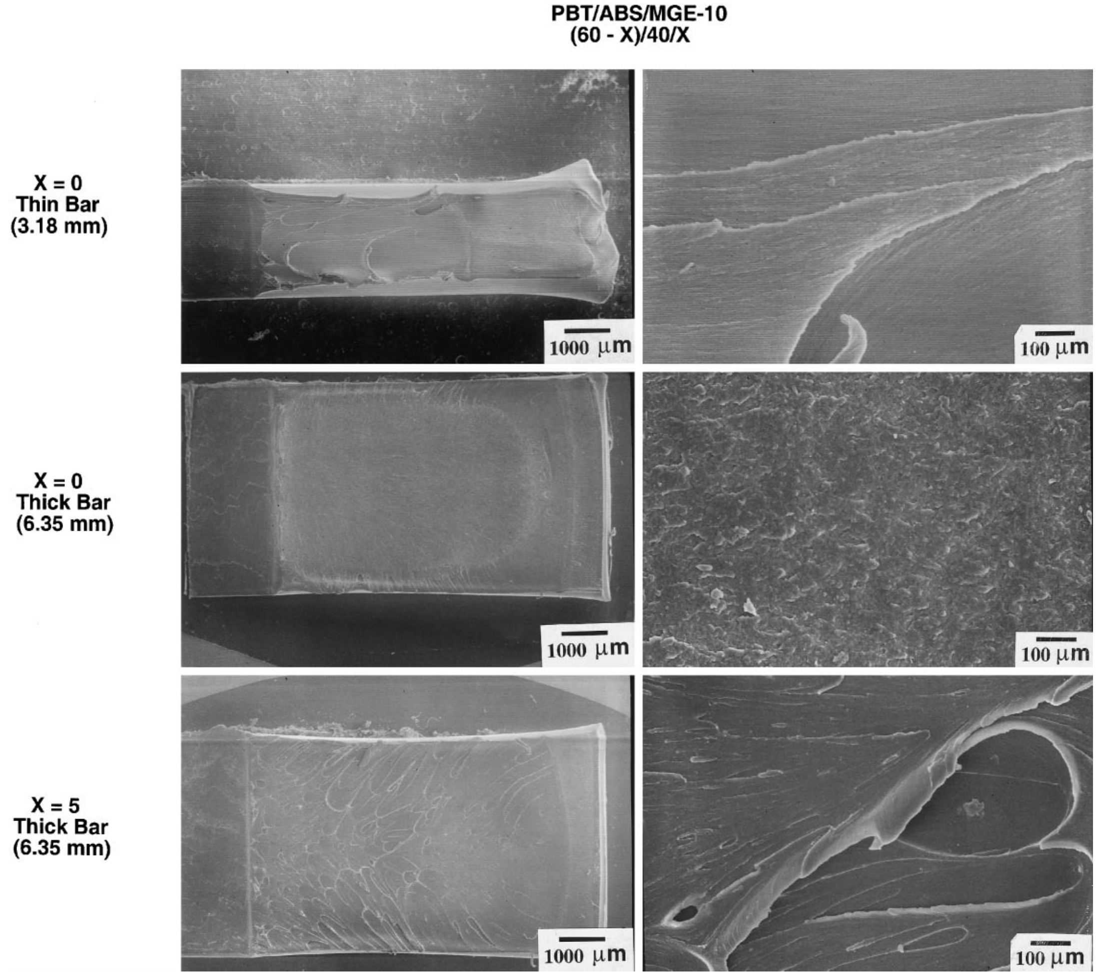


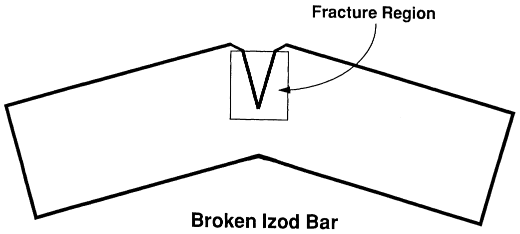
Fig. 5. SEM photomicrographs of fracture surfaces generated during Izod impact testing of PBT–ABS–MGE-10 (60 − X)/40/X blends for 3.18 and 6.35 mm thick samples.

outer and inner process zones for thin samples; however, the outer process zone is typically larger than the inner one (i.e. $S > S'$) for thick samples which may account for the fact that thick bars have lower fracture strength than thin ones. The parameters *S* and *C* reported here represent the averages of measurements made using calipers for at least five samples.

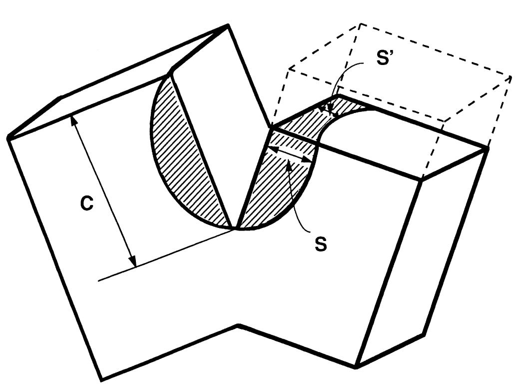
Fig. 7(a) shows the distance a crack propagates during Izod impact testing, *C*, as a function of the ABS content in PBT–ABS–MGE-10 blends. A high ABS content results in a shorter crack propagation length during impact testing for both thin and thick samples. Thick specimens, however, have a longer crack length than thin samples due to the more brittle nature of the fracture caused by the greater tendency for plane-strain conditions. The presence of compatibilizer has a different effect on the impact characteristics of thin and thick samples. As mentioned previously, crosslinking reactions lead to lower fracture energies of ductile PBT–ABS–MGE blends. This effect can also be seen by a slight increase in crack length in thin samples. As shown in Figs. 3 and 4, compatibilizer is necessary to produce toughened blends that are molded into thick samples; hence, most compatibilized blends that are molded into thick bars have shorter crack lengths in the Izod test, because of their improved toughness, than uncompatibilized blends.

Fig. 7(b) shows the size of the stress whitened zone, *S*, as a function of the crack propagation distance, *C*. As the fracture resistance of the material becomes less, the crack length is longer and the process zone is smaller. For a given process zone size, thick samples have longer crack lengths than do thin specimens because of the greater tendency for plain-strain conditions in these thicker samples that decreases their fracture resistance. The effect of reactive compatibilization on the process zone size can be seen by comparing Fig. 7(a) and (b). Compatibilization increases the crack propagation length of thin samples for a given composition and, therefore, a corresponding decrease in process zone size is observed. There is evidence that this counter intuitive trend is the result of the crosslinking reactions mentioned earlier [3]. As shown earlier, for blends molded into thick samples compatibilization significantly improves toughness resulting in a reduced crack propagation length and, thus, a larger process zone size is produced by adding MGE-10.

Fig. 8 shows the Izod impact strength for thin and thick samples of PBT–ABS–MGE-10 as a function of process zone size and crack propagation length. Larger process zone sizes and shorter crack lengths suggest increased toughness as seen here by a higher Izod impact strength. Again, thicker specimens are less tough as seen by longer crack lengths and smaller stress whitened zones for a given value of the Izod impact strength.



Broken Izod Bar



Detail of Fracture Region

Fig. 6. Schematic of broken Izod specimen indicating the crack propagation length, *C*, outer stress whitened zone, *S*, and inner stress whitened zone size, S'.

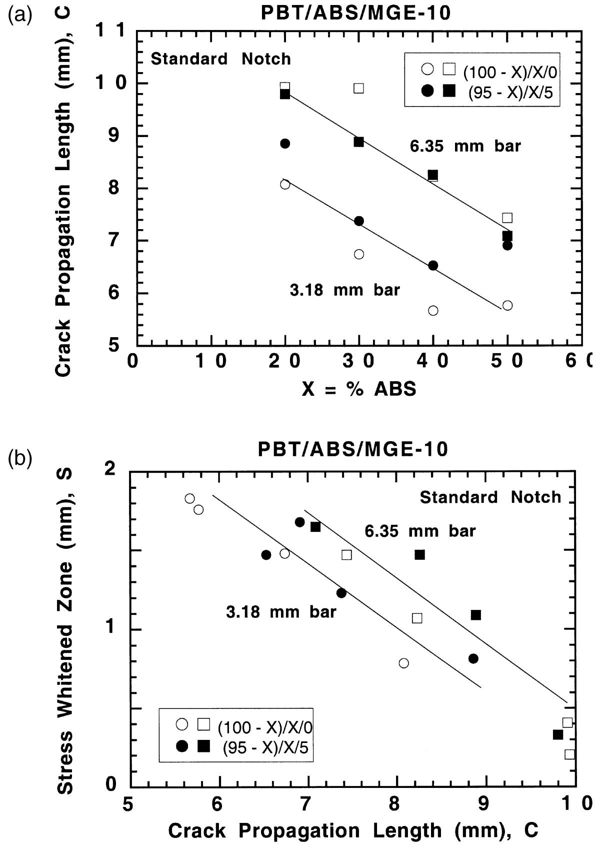


Fig. 7. Effect of ABS content on: (a) the crack propagation length, *C*; and (b) the outer stress whitened zone, *S*, generated during standard notched Izod impact testing of PBT–ABS $(100 - X)/X$ and PBT–ABS–MGE-10 $(95 - X)/X/5$ blends for 3.18 mm (○,●) and 6.35 mm (□,■) thick samples.

5. Single-edge notch, three-point bend results

5.1. Effect of ABS content and specimen geometry

To gain more insight into the fracture behavior of PBT–ABS blends, it is useful to measure the fracture energy as a function of ligament size (i.e. length) and to interpret the results in terms of the two parameter model discussed earlier. This type of analysis provides more insight into the fracture properties of ductile polymers than does typical Izod or Charpy impact tests. To enhance plane-strain conditions, the notches in all samples were razor sharpened. The fracture energy per unit area (*U*/*A*) was measured as a function of ligament length for thin (3.18 mm) and thick (6.35 mm) specimens of neat components used in the preparation of the current blends, e.g. PBT and ABS, and the results are shown in Fig. 9. The fracture response is independent of ligament length, i.e. $u_d = 0$, for both thin and thick samples of PBT and appears to be relatively independent of thickness. ABS, however, has a higher intercept than PBT and the slope is positive and depends on sample thickness; thin ABS samples have a higher u_d and lower u_o than do thicker specimens.

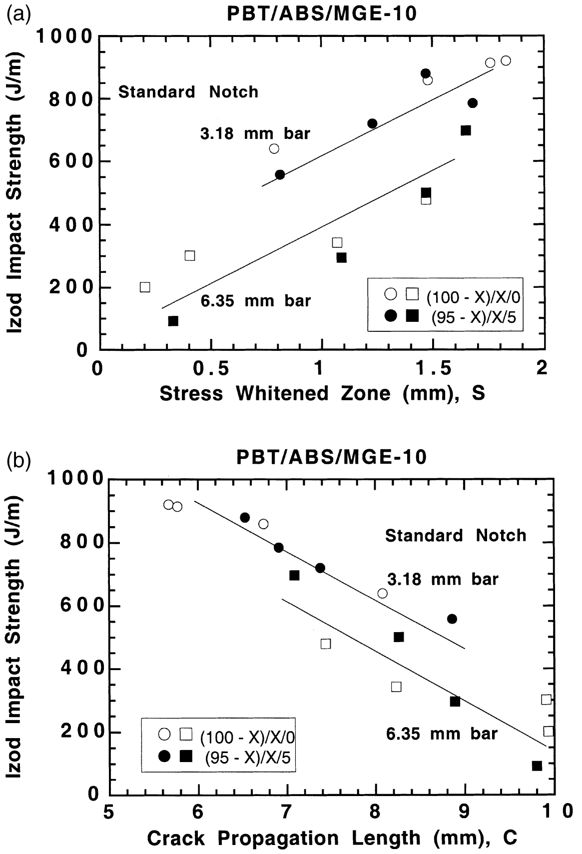


Fig. 8. Standard notched Izod impact strength vs: (a) the outer stress whitened zone size, *S*; and (b) crack propagation length, *C*, for PBT–ABS (100 − *X*)/*X* and PBT–ABS–MGE-10 (95 − *X*)/*X*/5 blends for 3.18 mm (○,●) and 6.35 mm (□,■) thick samples.

The specific fracture energy vs ligament length for PBT–ABS–MGE-10 blends of different compositions and specimen thickness are shown in Fig. 10. The fracture properties of blends containing 20 wt% ABS are shown in Fig. 10(a). The fracture energy of the thin bars is substantially greater than that for thick bars. Addition of compatibilizer reduces the fracture energy somewhat (recall crosslinking effects mentioned earlier); this effect is most significant for thin bars. For thick samples the specific fracture energy is lower at long ligament lengths than at short ligament lengths, i.e. the slope (u_d) appears to be negative. Fig. 10(b) shows the fracture energy vs ligament length for PBT–ABS–MGE-10 blends containing 30 wt% ABS. Again, thin samples have higher specific fracture energies than thick samples at long ligament lengths; however, they have similar values at short ligament lengths. A combined brittle–ductile mode of failure is observed for uncompatibilized thick specimens, i.e. samples with longer ligament lengths are less tough than those having shorter ligament lengths. The presence of compatibilizer shifts this dual fracture process to a more ductile mode of failure for the thick bars; nevertheless, the thick bars still have lower specific fracture energies than the thin ones. Fig. 10(c) and (d) show similar plots for blends containing 40 and 50 wt% ABS, respectively. The trends are qualitatively similar to those shown in Fig. 10(b) in terms of thickness and compatibilizer effects; however, the fracture properties of thicker samples

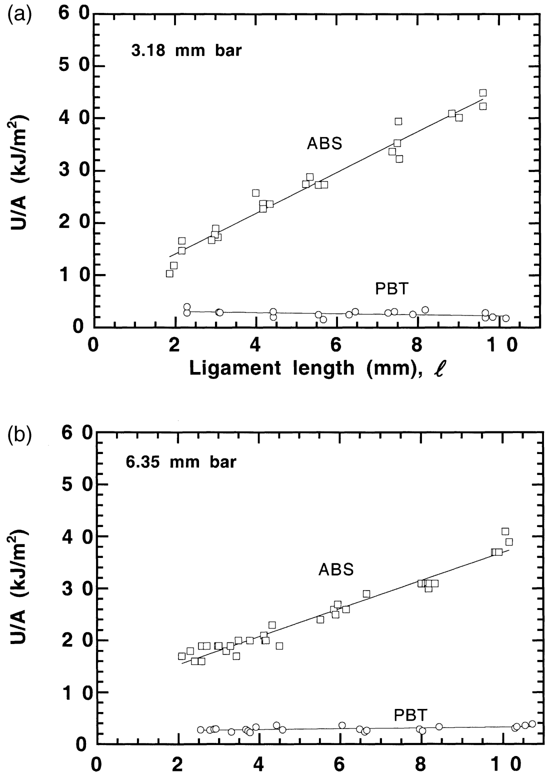


Fig. 9. Fracture energy as a function of ligament length of neat PBT and ABS materials for: (a) 3.18 mm; and (b) 6.35 mm thick samples with a sharp notch.

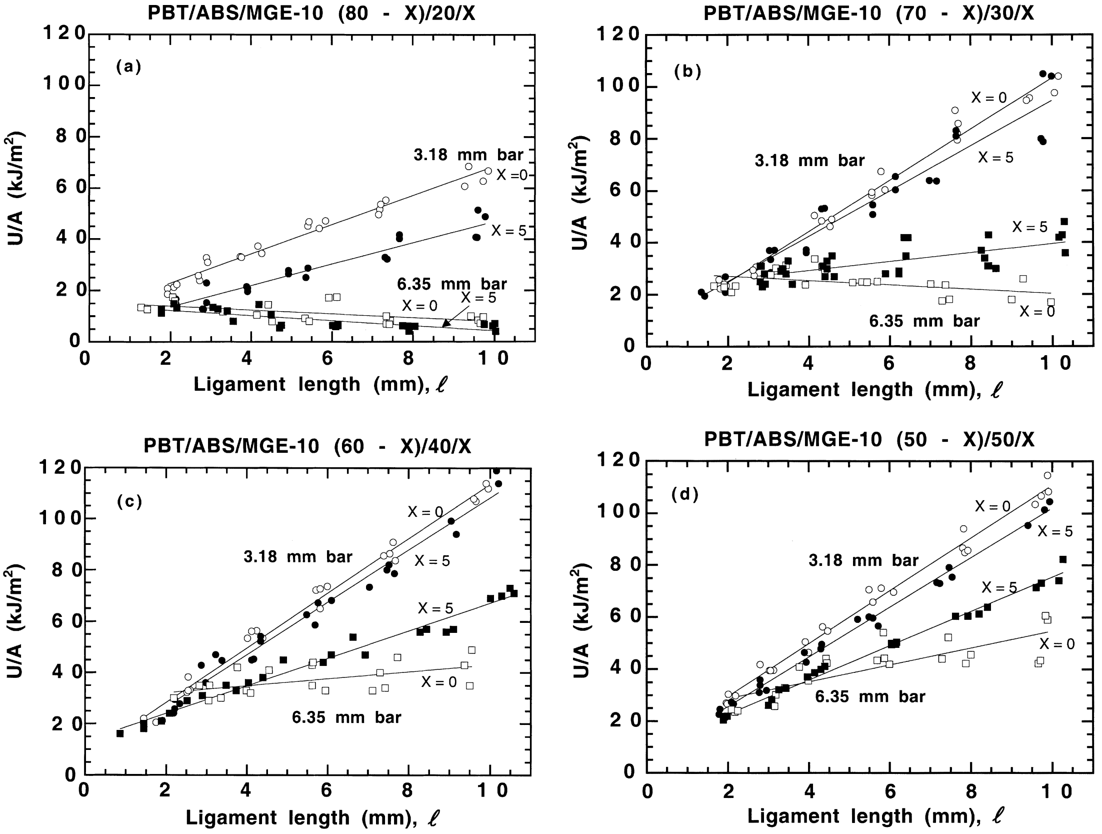


Fig. 10. Fracture energy as a function of ligament length for compatibilized (5 wt% MGE-10) and uncompatibilized PBT–ABS blends containing: (a) 20 wt% ABS; (b) 30 wt% ABS; (c) 40 wt% ABS; and (d) 40 wt% ABS for 3.18 and 6.35 mm thick samples with a sharp notch.

containing compatibilizer are much closer to those of thinner specimens, i.e. thick samples require more ABS to achieve toughening.

To further clarify the complex failure of thick samples of uncompatibilized blends, Fig. 11 shows the data for thick specimens of the binary PBT–ABS 70/30 blend shown in Fig. 10(b) segregated into two regions according to the primary mode of failure. Samples fail in a ductile manner for ligament lengths less than 4 mm and the specific fracture energy appears to increase with ligament length, while at longer ligament lengths the failure is brittle and the specific fracture energy appears to decrease with ligament length. Such behavior has been observed in other systems [61,64] and is consistent with the dual mode of fracture noted in the SEM photomicrographs shown in Fig. 5, e.g. brittle failure at the onset of crack growth (long ligament length) and ductile failure in the crack termination region (short ligament length).

The TEM photomicrographs shown in Fig. 12 illustrate the effect of sample thickness on the deformation zone ahead of the crack tip of PBT–ABS 70/30 blends. It is clear that a higher degree of shear yielding occurs in thin samples than do thick samples. The rubber particles in thin samples are much more elongated and the deformation zone extends further away from the crack tip than observed for the thick specimen. This difference in the degree of shear yielding most likely accounts for the large differences in observed impact strength of uncompatibilized blends molded into different thicknesses.

A summary of the extrapolated values of the specific limiting fracture energy (u_o) and the dissipative energy density (u_d) for the PBT–ABS–MGE blends shown in Figs. 9 and 10 is given in Fig. 13 and Table 1. The slopes (u_d) for thin specimens are higher and the intercepts are lower than those for thick samples. For both thin and thick bars, higher

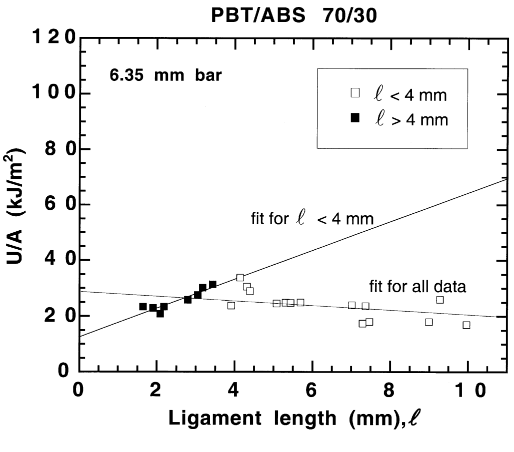


Fig. 11. Fracture energy as a function of ligament length of PBT–ABS 70/30 blends for 6.35 mm thick samples with a sharp notch.

Table 1
Summary of fracture parameters for PBT–ABS–MGE-10 blends

PBT–ABS–MGE-10	3.18 mm samples		6.35 mm samples	
	u_o (kJ m^{-2})	u_d (MJ m^{-3})	u_o (kJ m^{-2})	u_d (MJ m^{-3})
$(100 - X)/X/0$				
$X = 0$	3.3	-0.1	2.5	-0.1
20	11.5	5.7	15.4	-0.7
30	5.1	9.8	28.9	-0.8
40	7.0	10.7	29.4	1.4
50	9.2	10.2	22.2	3.3
100	6.4	3.9	10.0	2.7
$(95 - X)/X/5$				
$X = 20$	5.4	4.2	14.3	-1.0
30	7.7	8.7	22.5	1.7
40	6.2	10.2	13.2	5.4
50	6.6	9.6	9.5	6.6

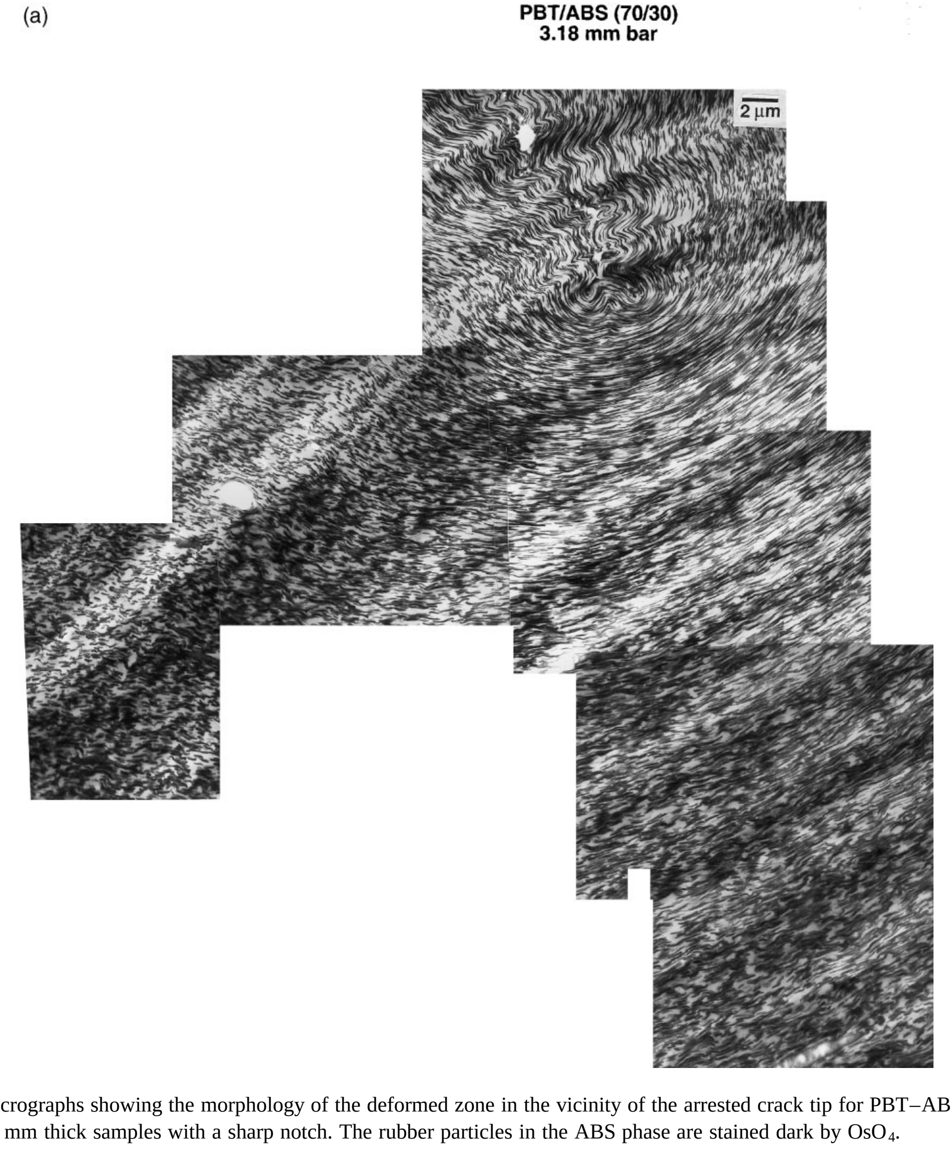


Fig. 12. TEM photomicrographs showing the morphology of the deformed zone in the vicinity of the arrested crack tip for PBT–ABS 70/30 blends for: (a) 3.18 mm; and (b) 6.35 mm thick samples with a sharp notch. The rubber particles in the ABS phase are stained dark by OsO_4.

Table 2
Effect of ligament length range on apparent value of u_o for PBT–ABS blends molded into 6.35 mm bars

PBT–ABS–MGE-10 (100 − X)/X/0	Ligament lengths under 4 mm u_o (kJ m^{-2})	All ligament lengths used u_o (kJ m^{-2})
$X = 20$	15.4	15.2
30	12.6	28.9
40	16.8	29.4
50	4.7	22.2

ABS contents leads to an increase in the dissipative energy density; thin samples have a relatively constant u_d at an ABS contents of 30 wt% and higher. Addition of the MGE-10 compatibilizer reduces u_d for thin samples; however, for thick specimens, compatibilization ensures a more ductile mode of failure and leads to an increase in u_d. The intercept, u_o, is relatively constant for compatibilized and uncompatibilized blends molded into thin (3.18 mm) samples for all ABS concentrations, as seen in Fig. 13(b); however, for 6.35 mm thick samples, the intercepts for uncompatibilized blends are much higher than those for compatibilized blends. This suggests that more energy is required to initiate fracture in thick uncompatibilized samples; however, because the mode of failure (ductile vs brittle) depends on the ligament length in these thick specimens, samples with a large ligament length fail in a more brittle manner (lower impact strength) and the resulting intercept is overestimated. Table 2 shows u_o values obtained from fracture of samples with short ligament lengths (< 4 mm) (see Fig. 11); these intercepts are closer to those of the compatibilized thick samples shown in Table 1.

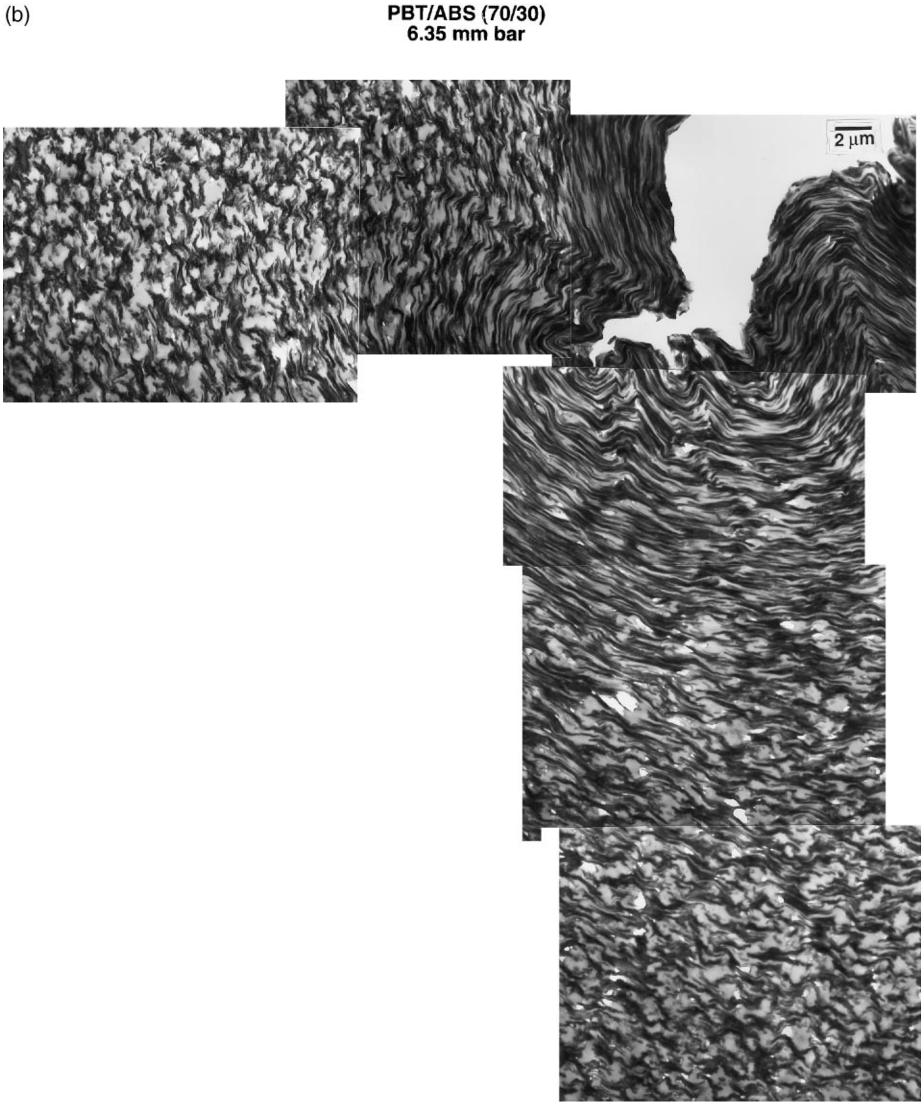


Fig. 12. Continued.

5.2. Relationships between impact testing techniques

A linear relationship exists between the slope of specific fracture energy vs ligament length, i.e. u_d, determined from Dynatup type tests and the Izod impact strength of the blends reported here as seen in Fig. 14(a). Such relationships have been reported previously for PC–ABS and nylon 6–polypropylene blend systems [47,65]. Blends with high values of u_d (thin samples) have been shown to have a higher impact strength and, hence, the data for thin samples lie in the upper range of this relationship. The thicker samples have a lower Izod impact strength (see Fig. 1) than thin samples and have u_d values in the lower range. In Fig. 8(b), the Izod impact strength appears to be related to the crack propagation length, C; shorter cracks are formed in blends with higher fracture toughness. A similar relationship is observed between u_d and C as seen in Fig. 14(b) where blends with higher u_d have a higher impact strength (thin bars) resulting in shorter crack propagation lengths; whereas, thick bars (low u_d) have longer crack propagation lengths.

5.3. Effect of compatibilizer content

Previous studies have shown that adding 5 wt% MGE-10 is beneficial for improving the properties of PBT blends containing 30–40 wt% ABS molded into thin samples [4]. This compatibilizer content results in blends with excellent ABS dispersion, low temperature toughness, and blend processability. The optimum compatibilizer content for producing super tough blends containing 40 wt% ABS when

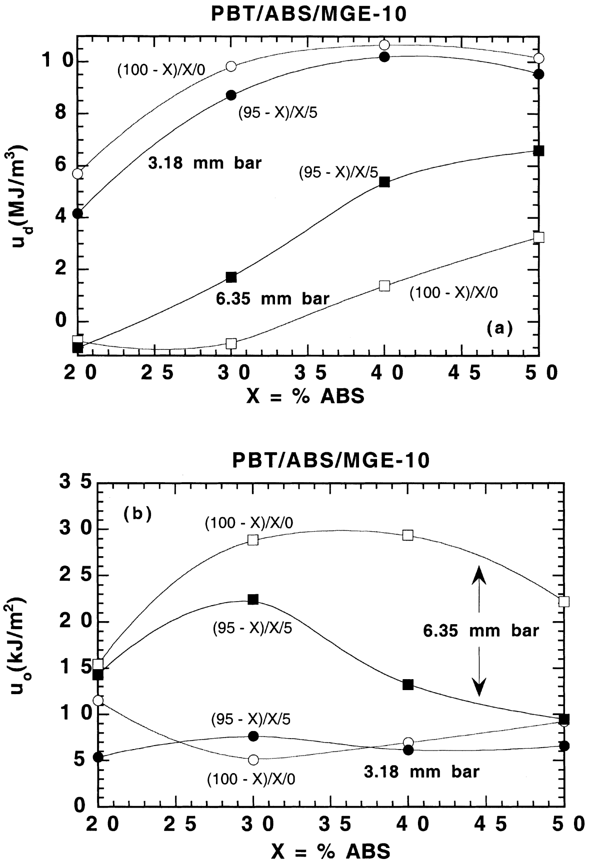


Fig. 13. Effect of ABS content on: (a) the dissipative energy density, u_d; and (b) specific limiting fracture energy, u_o, of PBT–ABS (100 − X)/X and PBT–ABS–MGE-10 (95 − X)/X/5 blends for 3.18 mm (○,●) and 6.35 mm (□,■) thick samples with a sharp notch.

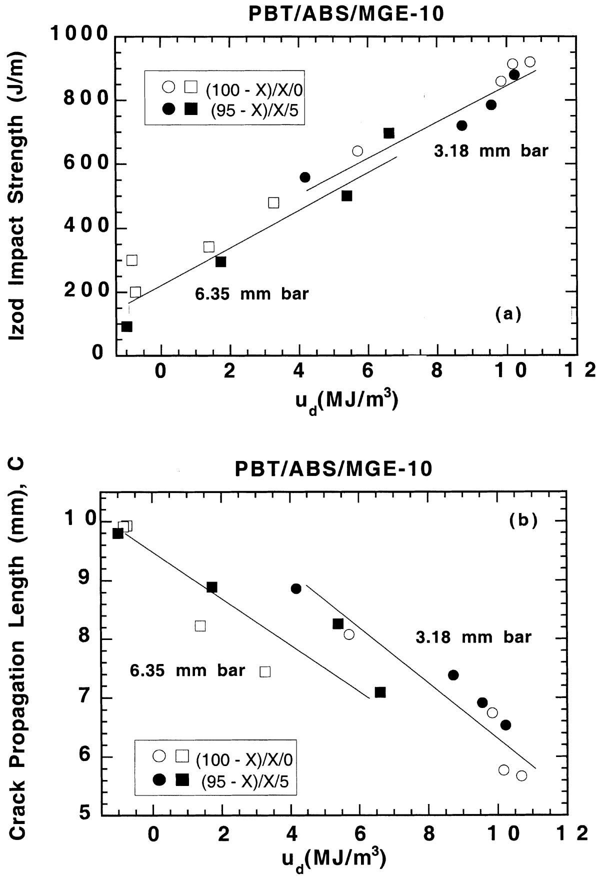


Fig. 14. (a) Standard notched Izod impact strength, and (b) crack propagation length, C, as a function of the dissipative energy density, u_d, for PBT–ABS (100 − X)/X and PBT–ABS–MGE-10 (95 − X)/X/5 blends for 3.18 mm (○,●) and 6.35 mm (□,■) thick samples.

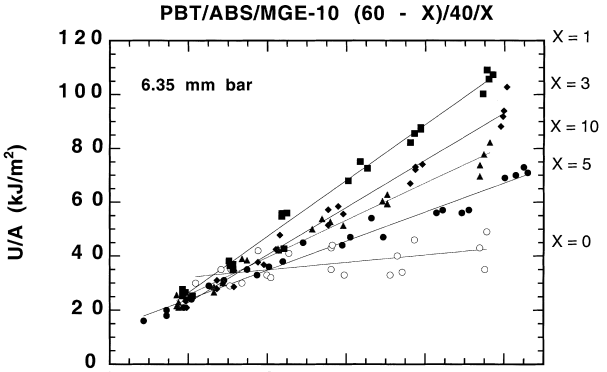


Fig. 15. Fracture energy as a function of ligament length for PBT–ABS–MGE-10 (60 − X)/40/X blends for 6.35 mm thick samples with a sharp notch.

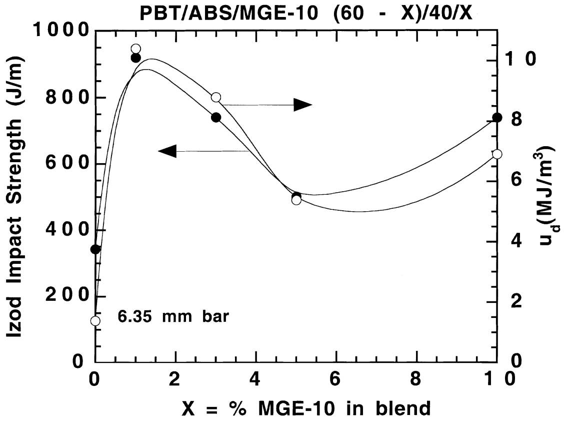


Fig. 16. Standard notched Izod impact strength and dissipative energy density, u_d, as a function of MGE-10 content in PBT–ABS–MGE-10 (60 − *X*)/40/*X* blends for 6.35 mm thick samples.

molded into thick bars is well below 5 wt%, as seen in Fig. 15. Only 1 wt% MGE-10 is needed to achieve maximum toughness. Compatibilizer contents above 1% result in lower impact strength for these blends possibly because of the greater potential for crosslinking reactions involving the epoxide units of MGE, which has been shown to have a deleterious effect on impact strength of blends molded into thick bars (see Fig. 3).

Fig. 16 shows the Izod impact strength and u_d determined from SEN3PB testing as a function of MGE-10 content in PBT/ABS/MGE-10 (60 − *X*)/40/*X* blends. A maximum Izod impact strength and u_d occur at 1 wt% MGE-10, and the minimum impact strength and u_d is observed for the uncompatibilized blend. Higher levels of compatibilizer result in blends with reduced impact strength and u_d. Fig. 17 shows the impact strength and crack propagation length from Izod impact testing as a function of u_d. Behavior similar to that observed in Fig. 14 is seen here where high values of u_d correspond to higher values of impact strength and shorter crack propagation lengths. The two extremes of these curves are for the uncompatibilized blend (minimum u_d) and the compatibilized blend containing 1 wt% MGE-10 (maximum u_d), again illustrating the need for some degree of compatibilization when blends are molded into thick bars.

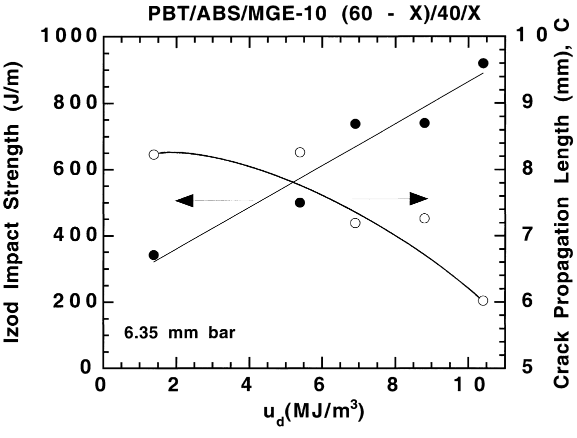


Fig. 17. Standard notched Izod impact strength and crack propagation length, *C*, as a function of the dissipative energy density, u_d, of PBT–ABS–MGE-10 (60 − *X*)/40/*X* blends for 6.35 mm thick samples.

6. Conclusions

The fracture toughness of PBT–ABS–MGE-10 blends has been examined by Izod and SEN3PB type tests. The SEN3PB tests were performed as a function of sample ligament length to determine the specific limiting fracture energy, u_o, and the dissipative energy density, u_d. The Izod impact properties of PBT–ABS–MGE-10 blends are very sensitive to specimen thickness, but only mildly sensitive to notch sharpness. Blends molded into thin samples (3.18 mm) were found to be tough by both test methods in the absence of compatibilizer when the ABS content is 30 wt%; however, thick samples (6.35 mm) require reactive compatibilization and higher ABS contents to achieve superior low temperature toughness. The Izod impact strength of compatibilized blends molded into thick specimens were found to be sensitive to the order of component mixing due to crosslinking reactions that involve the epoxide units of MGE-10 catalyzed by residual acids in emulsion-made ABS materials. The optimal MGE-10 content for room temperature toughness was found to be about 1 wt% to generate superior toughness in PBT–ABS–MGE-10 blends containing 40 wt% ABS and molded into thick samples.

A dual mode of deformation during Izod impact testing has been observed by SEM for uncompatibilized blends molded into thick samples. These specimens fail in a more brittle manner near the region of crack initiation and in a more ductile manner near the region of crack termination. Similarly, the observed mode of fracture during SEN3PB testing of uncompatibilized blends molded into thick bars has been shown to be sensitive to the sample ligament length. A more brittle mode of failure occurs for samples with long ligament lengths; whereas, samples with short ligament lengths deform in a more ductile manner.

The distance a crack can propagate during Izod impact testing and the size of the stress whitened zone (process zone) formed are related to the Izod impact strength; blends with a high impact strength have large process zones and short crack propagation lengths. Thicker samples generally have longer crack lengths and smaller process zones than do thin samples. A linear relationship exists between u_d and the Izod impact strength where high values of u_d exist for blends with high impact strength (low crack propagation length).

Acknowledgements

This work was supported by the Army Research Office. The authors would like to thank General Electric Co. and

Cheil Industries for the materials and various technical communications.

References

[1] Hage E, Hale W, Keskkula H, Paul DR. Polymer 1997;38:3237.
[2] Hale W, Keskkula H, Paul DR. Polymer (submitted).
[3] Hale W, Pessan LA, Keskkula H, Paul DR. Polymer (submitted).
[4] Hale W, Lee J-H, Keskkula H, Paul DR. Polymer (submitted).
[5] Hale W, Keskkula H, Paul DR. Polymer (submitted).
[6] Hourston DJ, Lane S. In: Collyer AA, editor. Rubber toughened engineering plastics. London: Chapman and Hall, 1994:243.
[7] Utracki LA. Polym Engng Sci 1995;35:2.
[8] Binsack R, Rempel D, Humme G, Ott K-H. (Bayer). US Patent no 4 292 233, 1981.
[9] Binsack R, Rempel D, Lindner C, Morbitzer L. (Bayer). US Patent no 4 535 124, 1985.
[10] Wang I-CW. (General Electric) US Patent no 4 753 986, 1988.
[11] Benson CM, Burford RP. J Mater Sci 1995;30:573.
[12] Okamoto M, Shimodu Y, Kojima T, Inoue T. Polymer 1993;34:4868.
[13] Hobbs SY, Dekkers MEJ, Watkins VH. J Mater Sci 1988;23:1219.
[14] Dekkers MEJ, Hobbs SY, Watkins VH. J Mater Sci 1988;23:1225.
[15] Brady AJ, Keskkula H, Paul DR. Polymer 1994;35:3665.
[16] Wu J, Yee AF, Mai Y-W. ACS Polym Prepr 1992;33:626.
[17] Wu J, Mai Y-W, Cotterel B. J Mater Sci 1993;28:3373.
[18] Wu J, Mai Y-W. J Mater Sci 1993;28:6167.
[19] Pratt CF, Phadke SV, Oliver E. (General Electric). US Patent no 4 965 111, 1990.
[20] Xanthos M, Dagli SS. Polym Engng Sci 1991;31:929.
[21] Kanai H, Sullivan V, Auerbach A. J Appl Polym Sci 1994;53:527.
[22] Kanai H, Auerbach A, Sullivan V. Soc Plast Engng, ANTEC 1994:2817.
[23] Hourston DJ, Lane S, Zhang HX, Bootsma JPC, Koetsier DW. Polymer 1991;32:1140.
[24] Hourston DJ, Lane S, Zhang H-X. Polymer 1991;32:2215.
[25] Flexman EA. Amer Chem Soc, Adv Chem Ser 1993;233:79.
[26] Cruz CA, Havriliak SJ, Slavin S. Proceedings of Additives ’95: Advances in additives and modifiers for polymers and blends, executive conference management, Clearwater Beach, FL, 22–24 Feb 1995.
[27] Hourston DJ, Lane S, Zhang HX. Polymer 1995;36:3051.
[28] Moffett AJ, Dekkers MEJ. Polym Engng Sci 1992;32:1.
[29] Lindner C, Binsack R, Rempel D, Ott K-H. (Bayer). US Patent no 4 417 026, 1983.
[30] Griffith AA. Phil Trans 1920;A221:163.
[31] Irwin GR. Appl Mater Res 1964;3:65.
[32] Kim H, Keskkula H, Paul DR. Polymer 1991;32:2372.
[33] E-813 Standard Test Method for J1c, a Measure of Fracture Toughness, Annual Book of ASTM Standards Philadelphia, PA: American Society for Testing and Materials, 1989.
[34] Chung WN, Williams JG. Determination of J_{1c} for polymers using the single specimen method, ASTM STP 1114. In: Joyce JA, editor Elastic–plastic fracture test methods: the users experience, vol 2. Philadelphia, PA: American Society for Testing and Materials, 1991:320.
[35] Hashemi J, Williams JG. J Mater Sci 1991;26:621.
[36] Hodgkinson JM, Williams JG. J Mater Sci 1981;16:50.
[37] Takemori MT, Narisawa I. Proceedings of Advances in Fracture Research 7th International Conference on Fracture (ICF7), 1989:2733.
[38] Lu M-L, Chang F-C. J Appl Polym Sci 1995;56:1065.
[39] Mai Y-W, Powell P. J Polym Sci, Polym Phys 1991;29:785.
[40] Crouch BA, Huang DD. J Mater Sci 1994;29:861.
[41] Zhou Z, Landes JD, Huang DD. Polym Engng Sci 1994;34:128.
[42] Huang DD, Williams JG. J Mater Sci 1987;22:2503.
[43] Mai Y, Williams JG. J Mater Sci 1977;12:1376.
[44] Vu-Khanh T. Polymer 1988;29:1979.
[45] Broberg KB. Int J Fract 1968;4:11.
[46] Wu J, Mai Y-W, Yee AF. J Mater Sci 1994;29:4510.
[47] Heino M, Hietaoja P, Seppala J, Harmia T, Friedrich K. J Appl Polym Sci 1997;66:2209.
[48] Santana OO, Maspoch MLL, Martinez AB. Polym Bull 1997;39:511.
[49] Karger-Kocsis J, Moskala EJ. Polym Bull 1997;39:503.
[50] Karger-Kocsis J, Czigany T, Moskala EJ. Polymer 1997;38:4587.
[51] Hashemi S. Polym Engng Sci 1997;37:912.
[52] Mai Y-W. Polym Comm 1989;30:330.
[53] Wu J, Mai Y-W. Polym Engng Sci 1996;36:2275.
[54] Mai Y. Int J Mech Sci 1993;35:995.
[55] Vu-Khanh T, De Charentenay FX. Polym Engng Sci 1985;25:841.
[56] Mai Y, Williams JG. J Mater Sci 1977;12:1376.
[57] Paton CA, Hashemi S. J Mater Sci 1992;27:2279.
[58] Mai Y-W, Cotterell B, Horlyck R, Vigna G. Polym Engng Sci 1987;27:804.
[59] Levita G, Parisi L, Marchetti A. J Mater Sci 1994;29:4545.
[60] Mamat A, Vu-Khanh T, Favis BD. J Polym Sci 1997;35:2583.
[61] Vu-Khanh T. Theor Appl Fract Mech 1994;21:83.
[62] Kayano Y, Keskkula H, Paul DR. Polymer 1997;38:1885.
[63] Kayano Y, Keskkula H, Paul DR. Polymer 1998;39:821.
[64] Okada O, Keskkula H, Paul DR. Polymer (submitted).
[65] Wildes G, Keskkula H, Paul DR. Polymer (submitted).
[66] Gan PP, Paul DR, Padwa AR. Polymer 1994;35:3513.
[67] Yee AF, Olszewski WV, Miller S. In: Deanin RD, Crugnola AM, editors. Toughness and brittleness of plastics, vol 154, Washington, DC: American Chemical Society, 1976:97.