Toughening of Glassy Polystyrene Through Ternary Blending That Combines Low Molecular Weight Polybutadiene Diluents and ABS or HIPS-Type Composite Particles

J. QIN, A. S. ARGON, R. E. COHEN

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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ABSTRACT: The effectiveness of toughening brittle glassy polymers such as polystyrene (PS) through deformation-induced plasticization by low molecular weight diluents of polybutadiene (PB) was amply demonstrated in earlier studies. In those applications, surface-initiated crazes of unusual growth kinetics and stability could produce effective toughening in sheet samples of millimeter thicknesses, but would have been ineffective in more massive parts where crazes could not be initiated in the interiors to promote a plastic response of the entire volume. This shortcoming has now been rectified through the development of ternary blends incorporating into the previous PS/PB blends a critical small volume fraction of ABS- or HIPS-type composite particles that serve to initiate crazes throughout the volume. Thus, we demonstrated in the present study that incorporation of 10% commercial ABS or 20% commercial HIPS into the most effective PS/PB-3K blend results in tensile toughnesses equal to or exceeding those of commercial ABS or HIPS in full concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2319–2328, 1999

Key words: touch PS/PB blends; toughening with diluents; craze plasticity

INTRODUCTION

Many otherwise attractive structural polymers including, for example, the glassy thermoplastics of polystyrene (PS) and PMMA and the thermoset epoxies tend to be brittle in tension, well below their glass transition temperatures. Even some semicrystalline polymers such as polyamides (ny-

Correspondence to: A. S. Argon.

lon 6 or 66) and high-density polyethylene that are usually quite tough in slow tension become brittle under high strain rates or in the presence of notches. The inelastic response mechanisms of these polymers in tension can be quite different. While the glassy polymers show tensile extensibility by crazing, the semicrystalline polymers undergo large strain distortional plasticity by a combination of plasticity in their amorphous components and crystal plasticity in the crystalline fraction. The heavily crosslinked epoxies tend to fracture in a brittle manner in tension without exhibiting a significant plastic response.

In their brittle mode of response, the critical stress intensity factors $K_{\rm IC}$ for the fracture of such polymers are typically in the range of 0.25 MPa \sqrt{m} . These fracture toughnesses increase markedly if

Present address: J. Qin, Kimberly Clark Corp., 2100 Winchester Rd., Neenah, WI 54956.

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a widespread plastic response in whatever form can be promoted around the propagating cracks at appropriate rates.

The common denominator of the fracture response of polymers of the above description is that, in practice, fracture is initiated nearly always from adventitious inorganic inclusion particles of roughly 10–25 μ m in size, with relatively poor adhesion to the surrounding matrix. With the above levels of fracture toughness, this results in a brittle strength of around 40 MPa. Experiments on diluent-toughened PS presented in the companion communication,¹ which will be referred to here as I, indicated that the terminal fracture process discussed above is time-dependent, resulting in an increase in time to fracture with decreasing stress. The specific mechanism and the time-dependent nature of the fracture process has generally remained obscure beyond the functional dependencies presented in I. Attempts to improve the strength and the toughness of such polymers by removing the offending particles through clean-processing techniques have been proven to be impractical.² Thus, most of the successful procedures to improve the toughness of brittle polymers have centered on lowering the flow stress below the short-term brittle strength.³

In the well-known conventional cases of the HIPS and ABS polymers, this is accomplished by promoting the development of larger volume concentrations of active crazes, initiated from the compliant composite HIPS or ABS particles, above an appropriate size. In I, and in the earlier investigations⁴⁻⁶ that have led to I, it was demonstrated that an even more attractive method of toughening through the reduction of the flow stress consists of dispersing, on a fine scale, submicron size pools of diluent low molecular weight liquid rubber. When such diluents wet the surfaces of craze matter after the pools are tapped by the crazes, they result in deformation-induced plasticization of the craze matter with an attendant significant reduction of the craze flow stress.

In earlier work⁴⁻⁶ and in I, the toughening effectiveness of this mechanism was demonstrated in relatively thin sheets where crazes nucleated from free surfaces penetrate into the interior of samples of millimeter thickness to result in toughening. It is clear, however, that if craze nucleation remains only on the free surfaces, more massive parts cannot be toughened by this method. To rectify this limitation, we have now developed ternary blends in which a certain small volume fraction of HIPS- or ABS-type heterogeneous particles are incorporated into the polymer together with the main plasticizing agent of the low molecular weight diluent to disperse craze initiation over the entire volume as is the case in HIPS or ABS, but to rely primarily still on the diluent plasticization mechanism. In the present communication, we report on the successful development of this technique that broadens the range of applicability of the diluent-toughening mechanism. In this new approach, we continue to make use of the *precipitation molding* process that we introduced in I. Some preliminary observations similar to the results presented here were reported by us⁷ and also by Okamoto et al.⁸

EXPERIMENTAL

Materials and Specimen Preparation

The resins that were used in the present ternary blends are given in Table I. Of these, the PS, ABS, and HIPS polymers were conventional. The PB resins were all close to the optimum molecular weight range of 3 kg/mol as determined from our earlier study I. The PBs with the designated different molecular microstructure reported in Table I influence strongly the viscosity and the resulting wetting and the spreading rates of the diluents on the interfaces of the craze matter and their deformation-induced sorption into the craze borders.

The component polymers were dissolved in reagent-grade toluene with a typical proportion of 10 g polymer to 300 mL solvent. The solutions, left overnight in a flask, were slowly added, in a dropwise manner, to the nonsolvent bath which contained 1500 mL methanol to form precipitate flakes nearly instantaneously. The precipitated blend flakes or flocules were dried in a vacuum oven for more than 24 h at 60°C and were then compression-molded into sheets of about 0.5–1.0-mm thickness at 170°C in a laboratory press. The details of this so-called precipitation molding technique of material production were discussed in somewhat greater detail in I.

The molded sheets or films were trimmed into "dog-bone"-shaped tensile specimens of 6.35-mm gauge length and 3.18-mm gauge width with fresh surgical blades on a template. To prevent nucleation of unwanted crazes at surface imperfections, all four surfaces of the specimens were

	Molecular Weight	PB Molecular	
Material	(kg/mol)	Microstructure	Manufacturer
\mathbf{PS}	300		Polysar, Monsanto Plastics
	$(M_w/M_n = 2.4)$		Resins Co. (Springfield, MA)
ABS			Polysciences, Inc.
HIPS			Mobil Corp. (Edison, NJ)
PB	$M_{w} = 3.0$	16%:1,4	Polysciences Inc.
			(Warrington, PA)
PB	$M_{w} = 3.0$	85%:1,4	Polysciences Inc.
PB	$M_{n}^{"} = 2.6$	71%:1,4	Scientific Polymer Products, Inc.
PB	$M_n^{''} = 3.4$	74%:1,4	Scientific Polymer Products, Inc.

 Table I
 Materials Used in the Ternary Blends

polished with 0.3 μ m alumina slurry. The polished specimens were washed in a dilute detergent solution, rinsed thoroughly, hung vertically in a vacuum oven, and dried for 48 h at 80°C.

TEM Observation of Microstructure

The TEM study of the microstructure of the compression-molded thin films was performed using a Phillips 300 transmission electron microscope, operating at an accelerating voltage of 100 kV. The specimens were stained by immersing them for 7 days in a 1% aqueous solution of OsO_4 to enhance the absorption contrast between the PB pools and the PS background, followed by thorough washing. This staining could be performed either before or after deformation. Ultrathin sections were cut on an LKB-8800 ultramicrotome fitted with freshly prepared glass knives and then transferred to a copper grid suitable for TEM observations. Section thicknesses were kept in a range of 20-40 nm. For the TEM observation of the craze microstructure, the crazed specimens cut from the whitened zone of the fractured specimens after tensile tests were stained in the same 1% aqueous solution of OsO_4 for 5 days. The cuts in the ultra microtome were made in a direction approximately 45° to the principal tensile axis. The sections were taken across the thickness of the specimens at right angles to the craze planes to produce the minimum number of artifacts on the craze microstructure.

Tensile Tests

The tensile tests were performed on an Instron machine Model 4201. The imposed strain rates were all $2.6 \times 10^{-4} \text{ s}^{-1}$. The experiments were

conducted at room temperature $(23^{\circ}C)$ and around 50% RH. The load-elongation curves were used to determine the following four quantities: (1) maximum load at yield or fracture; (2) strain to fracture; (3) fracture energy indicated by the area under the curves to be referred to in what follows as the "tensile toughness," and (4) the modulus of elasticity.

RESULTS

Deformation-induced Sorption of Liquid PB into PS in Binary Blends

There is now conclusive evidence that the introduction of liquid PB effectively toughens brittle PS. The finely dispersed pools of liquid PB in the PS matrix act as a deformation-assisted diluent to plasticize the PS at the base of the craze fibrils, resulting in a lowered craze flow stress, delaying the formation of cracks in crazes to prevent early craze fracture. The experimental evidence for this phenomenon was presented in detail in our pre-vious communications.^{1,4-6} As shown in Figure 1, the stress-strain curve of the pure PS shows a very brittle behavior in tension, with a high yield stress and a nearly negligible strain to fracture. Less than 1% PB, with 3 kg/mol M_w , and 85% of the 1,4 component blended into the PS reduces the yield stress somewhat, with no improvement in the fracture strain. In comparison, the stressstrain curve for the film with 2% PB indicated a significantly increased strain to fracture at around 25% and a substantial decrease in the craze flow stress. As the liquid PB content increased from 3 to 4%, the flow stresses gradually



Figure 1 Stress–strain curves of PS/PB-3K blends with 85% PB 1,4, for different volume fractions of PB diluents, carried out at a strain rate of $2.6 \times 10^{-4} \text{ s}^{-1}$ at 23°C.

decreased to about 11 MPa and the fracture strains increased to about 50%. These changes resulted in an increase of the tensile toughness shown in Figure 2 by the open circles. When the blend contained about 4% PB, the tensile toughness reached a maximum value of 6.25 MJ/m³, which is more than 28 times larger than that of homo-PS. When the added PB exceeded 4%, the strain to fracture and the tensile toughness decreased sharply. These undesirable decreases could be attributed to the appearance of PB pools with a size larger than 1 μ m, acting as supercritical flaws to initiate fracture, as discussed in I.



Figure 2 Effect of PB molecular microstructure on tensile toughness in PS/PB-3K blends at a strain rate of $2.6 \times 10^{-4} \text{ s}^{-1}$ at 23°C: (open circles) with 85% 1,4 and (filled circles) with 16% 1,4 fraction.

Figure 2 shows also the effect of a complementary blend (filled circles) with only 16% 1,4 content having a much higher viscosity (and presumably lower diffusivity in PS) that is only about one-third as effective as the blend with 85% 1,4 content. The systematic decrease of the toughening effectiveness of the diluents with decreasing 1,4 content is shown in the stress–strain curves of Figure 9 in I. The cause for this dependence through increased viscosity of the diluent and resulting partly from the poorer wetting and spreading effectiveness on the craze matter interfaces was discussed in greater detail in I.

Indirect evidence of the mechanism of plasticization through the draining of liquid PB onto the craze surfaces is given in the micrographs of Figure 3(a,b). The figures show a change in the visual appearance of the dispersion of PB pools between the undeformed case of (a) and the deformed case of (b) of PS films containing 3% of the diluent PB. The unstretched film contains a higher concentration of rubber pools than do the stretched films, while the latter shows many long and wavy crazes which apparently collected a certain amount of diluent upon contact. The reduced craze flow stress and the significantly increased strain to fracture has apparently resulted in the extended range of growth of crazes to greater lengths without initiating overall fracture. Supporting evidence for this scenario could be obtained from the number density of the observable diluent rubber pools in micrographs such as those of Figure 3 comparing the state before and after deformation. There was a definite reduction in the number



Figure 3 Morphology of PS/PB-3K with 3% PB: (a) before and (b) after deformation, showing an apparent depletion of intact PB pools by being incorporated into crazes.

density of intact pools of all sizes in the deformed samples.

Blends of PS with ABS and HIPS Particles

Prior to exploring the properties of ternary blends containing PS, PB diluents, and certain volume fractions of ABS and HIPS particles, a series of experiments was carried out with binary blends of PS containing only different volume fractions of ABS or HIPS particles. Figure 4(a,b) shows the morphology of the two commercial ABS and HIPS materials purchased to provide composite ABSand HIPS-type particles for incorporation into the blends. The figures show the well-known ABS and HIPS composite particles of roughly $1-2 \mu m$ size and at a particle volume fraction of typically 0.5. The toughness characteristics of these commercial materials are well known. They were not studied further.

Binary blends of PS and ABS and of PS and HIPS were prepared by a slight variant of the precipitation molding technique in which initially solutions of PS and ABS or HIPS were prepared, followed by the precipitation step and compression molding. In this manner, reference binary



Figure 4 TEM micrographs of commercial (a) ABS and (b) HIPS, manufactured by Polysciences Inc. and Mobil Co., respectively, used to provide particles in constructing ternary blends.



Figure 5 Stress-strain curves of binary PS/ABS blends used for comparison with the behavior of ternary blends at strain rates of 10^{-4} s⁻¹ at 23°C.

blends were prepared of PS with ABS (or HIPS) with volume fractions of 0.05, 0.1, 0.2, and 0.3 (containing composite particle volume fractions of roughly 0.025, 0.05, 0.1, and 0.15). Compression-molded sheets of these blends of about 0.5–1.0-mm thickness were prepared as before and were tested in tension. The resulting stress–strain curves for the PS/ABS blends are shown in Figure 5. They show that at these relatively low

volume fractions the composite particles are quite ineffective in producing toughening.

Figure 6(a–d) shows the morphology of these PS/ABS blends. The dispersion of the composite ABS particles in the two lowest volume fraction blends is not uniform but becomes more uniform in the two higher-volume fraction blends. Clearly, due to the relatively low volume fractions of the particles, the active craze front densities per unit volume in these materials were not high enough in the tension tests, resulting in only marginal reductions in the craze flow stress, and early fractures of craze matter at these relatively high craze flow stresses followed. The results obtained with PS and HIPS blends were very similar and will not be presented.

Ternary Blends of PS with Diluent PB and ABS- and HIPS-type Particles

As stated in the Introduction, the toughening that results from the plasticization effect of the PB diluents on the actively deforming craze matter is very attractive in thin films where the surfacenucleated crazes can effectively penetrate into the interior portions of the thin films sufficiently readily. In the more massive parts, this may no



Figure 6 TEM micrographs of the morphologies of the binary PS/ABS blends used for comparison with the ternary blends: (a) PS/5% ABS; (b) PS/10% ABS; (c) PS/20% ABS; (d) PS/30% ABS.



Figure 7 TEM micrograph of a ternary blend of PB-3K containing a volume fraction of 0.1 of ABS that resulted in maximum tensile toughness.

longer be possible and would result in the elevation of flow stress due to the undeforming core regions of such thicker samples and leads to brittle behavior. Incorporation of a critical volume fraction of ABS- or HIPS-type composite particles into the blends promotes craze nucleation thoughout the entire material and therefore prevents the retention of an elastic core. It is for this purpose that a series of ternary blends were prepared where increasing volume fractions of ABS and HIPS were added into the diluent plasticized binary PS/PB blends. Thus, in all of these ternary blends, the base material consisted of a binary blend of PS containing 3% of the PB diluent of M_n = 3.4 kg/mol molecular weight and 74% of the 1,4 component in the molecular microstructure. In the ABS-containing blends, the ABS fractions were 0.02, 0.05, 0.1, and 0.2 (introducing composite particle volume fractions of roughly 0.01, 0.025, 0.05, and 0.1, respectively). In the corresponding HIPS-containing blends, the HIPS fractions consisted of 0.05, 0.10, 0.20, and 0.30 (introducing composite particle volume fractions of roughly 0.025, 0.05, 0.10, and 0.15, respectively).

Figure 7 shows the morphology of a blend of PB-3K containing a volume fraction of 0.1 ABS. The morphology of the PB-3K blend containing a volume fraction of 0.2 HIPS was very similar. The micrographs show clearly the familiar composite particles of ABS and HIPS and the much smaller diluent pools dispersed into the homo-PS background. Very similar morphologies were obtained and studied by Okamoto et al.,⁸ placing emphasis

on cavitation in composite particles, which in our model is of little relevance.

The stress-strain curves of the four ternary blends containing ABS and those containing HIPS are shown in Figure 8(a,b), respectively. The order of the effects on the blends containing different fractions of HIPS is largely systematic. As the HIPS content increases, the flow stresses first decrease and the strains to fracture increase until a concentration of 30% of HIPS is reached. Following this, there is a monotonic decrease in the strain to fracture. For the ABS-containing blends, a similar reversal is seen. The flow stresses first decrease as the strain to fracture increases. With the blends with ABS fractions of 0.1 and 0.2, however, the flow stresses begin to increase again and the strains to fracture begin to decrease in an inexplicable way. The exact cause of these reversals of the beneficial toughening



Figure 8 Stress-strain curves of ternary blends of PS/PB-3K with (a) different volume fractions of ABS and (b) different volume fractions of HIPS tested at 10^{-4} s⁻¹ at 23°C.

effects with increasing ABS and HIPS fractions is not clear at these high volume fractions but could be a result of an interference of the PB diluent and the ABS particles such as, for example, a scavenging action of the ABS particles for the PB diluent that would reduce the free PB diluents in the finely dispersed pools and thereby results in the lessening of the diluent-induced toughening effect through plasticization.

Circumstantial evidence of this possibility is given in the micrographs of Figure 9(a,b) of a PS/PB-3K blend with 20% of ABS where the toughness reduction is marked. Figure 9(a) shows a field of large ABS particles in a field of PB pools. Two of the particles have a significantly darker appearence. Figure 9(b), which gives a larger magnification of a typical case, shows that the dark particle is a conventional ABS particle with one entire dome trapped in the microtomed slice while the other ABS particles which are most probably central slices show merely a signifi-



Figure 9 TEM micrographs of PS/PB-3K containing 20% ABS, where tensile toughness is markedly reduced: (a) two dark particles of ABS; (b) a dark particle of ABS and other ABS particles with thick PB rubber layers at their borders.



Figure 10 Effect of ABS and HIPS content on the tensile toughness levels of ternary blends tested at 10^{-4} s⁻¹ at 23°C. A clear loss of toughness at high ABS and HIPS concentrations is discernible.

cantly thicker black border, supporting the possibility of scavenging of the liquid PB by the particles at their borders. The overall decrease in the toughening for both the ABS and the HIPS is summarized in Figure 10.

Figure 11 shows the morphology of crazes in these ternary blends at the compositions where the maximum toughness levels are reached. As expected, the crazes are initiated by the composite particles and are, however, rather wavy and long, indicative of the diluent-induced accentuated mechanism of craze growth.

The effectiveness of the ternary blends in combining the role of craze initiation by the composite particles of ABS and HIPS and the powerful process of toughening by diluent-induced plasticization is demonstrated in Figure 12(a,b), respectively. These figures show that the combined effect is fully as effective at the toughness maximum as is the toughening achieved by pure ABS [Fig. 12(a)] and HIPS [Fig. 12(b)], where, in fact, the toughening achieved with the ternary blend containing HIPS particles is about 40% higher than the corresponding pure HIPS.

DISCUSSION

In the present investigation, we demonstrated that the principal drawback of the diluent-induced toughening effect arising from surface nucleation of crazes can be rectified by creating ternary blends where craze nucleation in the interiors of more massive parts can be achieved by incorporation of roughly 10% ABS and 20% HIPS in the base PS/PB-3K blends with 3% PB diluent. The roughly 5% ABS or 10% HIPS particles by volume then achieve toughness levels equal to or even exceeding those achieved by a full concentration of ABS and HIPS.

In I, which explored a wide range of variables in the base blends of PS/PB, it was shown that the diluent-induced toughening with the PB blends of maximum fluidity (85% 1,4 fraction) has limitations at high strain rates due to either the ratecontrolling processes of the diluent spreading on the craze surfaces or the rate of plasticization at the base of drawing tufts where toughening became lost at strain rates of about 10 s⁻¹. In ABS



Figure 11 TEM micrographs of craze morphologies in the ABS and HIPS containing ternary blends with PS/PB-3K, exhibiting maximum toughness levels at 10^{-4} s⁻¹ at 23°C.



Figure 12 Demonstration of the effectiveness in toughness achievable with ternary blends where (a) 10% ABS in PS/PB-3K achieves the same toughness of full strength ABS and (b) 20% HIPS in PS/PB-3K achieves higher toughness than in full strength HIPS.

and HIPS, a tough response at a considerably higher strain rate (of the order of 10^3 to 10^4 at notches) results, presumably, from the effectiveness of the composite particles in initiating a substantial craze front length per unit volume during the allotted short-time increments encountered in the Charpy or Izod impact experiments, permitting this vast craze front to propagate at relatively low velocities commensurate with the reduced flow stresses.

The introduction of composite particles into the ternary blends should serve to accomplish a similar goal and push the response of the diluent-toughened blends to higher strain rates than those achieved in I. This possibility was already explored by Piorkowska et al.⁹ in both ABS and HIPS particle-containing ternary blends. The blends, however, were unsatisfactory in their toughness behavior, apparently because the composite particle volume fractions at approximately

the 10-20% level were inadequate in producing the required craze front concentrations, and that at these high strain rates, the sorption of the diluent was not fast enough to produce concurrent plasticization at the craze borders—a subject that we investigated in detail in the accompanying theoretical study.¹⁰ The evidence of the Piorkowska et al.9 study indicated clearly the enhanced production of crazes around the particles but also their inability to spread out. Apart from the less than satisfying response of the ternary blends at the impact strain rates, the means of toughening more massive parts by this technique with the diluent-induced plasticization over a very large range of experimental conditions makes this approach very attractive for glassy polymers in intermediate strain-rate applications.

CONCLUSIONS

In the present study, we demonstrated that the previously discovered toughening process based on the deformation-induced plasticization effect of glassy polymers by low molecular weight liquid diluents of PB can be effectively extended to massive parts by ternary blends of PS/PB-3K containing a key volume fraction of composite ABS or HIPS particles. Thus, incorporation of 10% of ABS or 20% HIPS into the binary blends of PS/PB-3K can result in toughness levels equaling or exceeding those of commercial ABS or HIPS ma-

terial in intermediate strain-rate-range applications.

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