Toughening of Glassy Polymers by Prepackaged Deformation-Activated Diluents

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

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

ABSTRACT: The use of low molecular weight liquid rubber diluents in concentrations of $\sim$ 1%, dispersed finely in the form of submicron-sized pools, had been demonstrated in the past by Gebizlioglu and colleagues (*Macromolecules* 1990, 23, 3968) to be an effective source of toughening of brittle glassy polystyrene through deformation-accentuated plasticization effects of craze matter during the development of craze plasticity. Herein, we present results of a study extending the range of this plasticization effect through the development of a new "precipitation-molding" process that can routinely incorporate diluent pools of up to 4–5% by volume and can increase the tensile toughness by about a factor of 3 over what was achieved before. The experiments demonstrate that the toughening mechanism operates primarily through a substantial reduction of the craze flow stress that promotes an increase in craze plasticity that renders inactive adventitious inclusions that normally initiate fracture. Experiments with all blends at different temperatures and strain rates indicate that the fracture response can be represented by a universal behavior pattern of a single thermally assisted process of fracture of craze matter where the diluent merely modulates the plastic resistance. However, the experimental results show that the sorption of the diluent that controls the plasticization effect during straining competes against the time-dependent fracture process and that the toughening effect decreases monotonically with increasing strain rate and decreasing temperature that limits the effectiveness of the process to a range considerably below what is required for impact response. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1469–1490, 1999

Key words: toughening; diluents; craze plasticity

INTRODUCTION

There has been considerable awareness for some time that low molecular weight diluents can result in quite considerable toughening of brittle glassy polymers through craze plasticity by a mechanism different from those known to be effective in the heterogeneous blends of high-impact-polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS). Thus, for example, Kambour

and Bernier[1] have reported greatly improved ductile behavior by craze plasticity in polystyrene (PS) subjected for prolonged periods to acetone vapors, and Kruse[2] has reported the beneficial toughening effects achievable by blending a variety of low molecular weight diluents into HIPS and ABS. More recently, Dettenmaier and Leberger[3] have reviewed plasticization effects of the esters of phthalic acid on polycarbonate, where two separate forms of action were identified. The more dramatic and direct observations of the toughening effects of low molecular weight rubber diluents on PS, however, have come from a series of blending experiments of Gebizlioglu and colleagues[4,5] first in ternary blends of KRO-1/PS

with PB-3K [1,4-polybutadiene (PB) of 3 kg mol^{-1} molecular weight][†] and, more recently, in binary blends of PS with PB-3K. In those experiments, it was found that the addition of small volume fractions of PB-3K to both binary blends of KRO-1/PS and homo-PS resulted in considerable reduction in the craze flow stress (from 40 MPa in homo-PS down to 20 MPa or lower in the PB-3K containing blends) and in a dramatic accompanying increase in the strain to fracture. Through fundamental small angle X-ray scattering (SAXS) measurements of Brown and colleagues[6] of crazed binary blends of PS/PB-3K, it was established that the toughening could only be explained by an autocatalytic, deformation-induced plasticization effect of liquid PB-3K on the craze matter when crazes tap into the submicron size, phase-separated pools of PB-3K.

A theoretical model of this behavior, based on the presence of deformation-induced negative pressures in the craze flanks and craze matter tufts, proposed by Argon and colleagues[7] has provided a general framework for the basic mechanism of this toughening process. According to this model, the craze flow stress is governed by the plasticization effect resulting from the suddenly increased solubility of the free rubber in the presence of the substantial negative pressures present on the surfaces of the stems and root regions of the drawing craze matter tufts. It was considered that this occurs when the low molecular weight liquid rubber wets these surfaces upon being released by the growing craze that taps into the submicron size liquid rubber pools which, by themselves, are too small to initiate crazes.[8] It was assumed that the ductility of the blend is still limited by the various extrinsic or intrinsic craze matter defects that eventually initiate fracture, but that such fracture is substantially delayed under the reduced level of the craze flow stresses. This then permits the development of greatly increased levels of craze strain prior to fracture, provided that the pools of liquid rubber are small enough so as not to act as supercritical flaws to initiate fracture under the prevailing stress, once they have drained their contents onto craze matter. Thus, the monotonic sharp increase of the

strain to fracture with increasing volume fraction of pooled liquid rubber in the binary blends of PS/PB-3K studied by Gebizlioglu and colleagues[5] could be attributed to the increasing availability of plasticizing diluent that lowered the craze flow stress. On the other hand, the eventual sharp decrease of the strain to fracture for PB-3K concentration exceeding 1.1% could be directly attributed to the appearance of larger, micron-size agglomerated pools of liquid rubber that were unavoidable in the spin casting technique of film preparation from dilute solutions. Evidently, these larger pools acted as supercritical flaws from which craze fracture initiated, even at the lowered levels of flow stress. Clearly, if larger volume fractions of free liquid rubber could be packaged into the blends in the form of submicron size pools, without agglomeration into larger size pools, the trend of monotonic increase in strain to fracture could be prolonged, leading to increasing toughness. Because the agglomeration of the pools of rubber, results most likely of Brownian migration of the emulsified rubber in the solution during solvent extraction, it was necessary to develop new and more rapid techniques of film preparation that prevent such agglomeration. Herein, we will describe such a new technique that has not only permitted preparation of blend morphologies in which the agglomeration threshold is displaced to significantly larger volume fractions of rubber, but has also permitted the systematic exploration of the conditions for achieving the most desirable morphologies in blends. In this method that has been called the *precipitation-molding technique,* the sizes of liquid rubber pools have been controlled to range between 0.05–0.5 μm, when the liquid rubber concentrations remained below 4%.

EXPERIMENTAL

The Precipitation-Molding Technique

To overcome the objectionable agglomeration of the phase-separated liquid rubber in the polymer solutions used in the spin casting method of film production, two stage casting schedules were tried. In the first of these stages, partial solvent removal was accomplished at relatively low temperature where the high viscosity of the solutions reduces agglomeration. This was followed by a second stage at higher temperature where the solvent extraction could be completed without much Brownian motion of the phase-separated

---

[†] In the experiments of Gebizlioglu, the PB had a predominantly 1,4 content ($\sim$ 85%) and a molecular weight of 2.96 kg mol^{-1}. This diluent was labeled as PB-3K. In the present study, much of the exploratory blending was conducted with a PB of only 16% 1,4 content, but with a molecular weight of 3 kg mol^{-1}. Therefore, we have referred to these diluents collectively as PB-3K to indicate the molecular weight, but have also given the 1,4 content for each case.

Table I Polymer Samples Used

Polymer	M_w	M_n	M_w/M_n	Vinyl-1,2 (%)	*Trans-* or *Cis*-1,4 (%)
PS[a]	268.00	112.00	2.39	—	—
PS	150.00	35.50	4.23	—	—
PB[b]	3.00	2.42	1.24	84	16
Standard PB	0.44	0.41	1.07	—	—
Standard PB	1.00	0.93	1.08	—	—
Standard PB	2.98	2.76	1.08	15	85
Standard PB	182.00	100.00	1.82	—	—
Standard PB	233.00	139.50	1.67	—	—
PB	—	2.60	—	35	65
PB	—	3.40	—	26	74

[a] This is labeled as HH101.
[b] PB-3K, used in most processing studies.
[c] M_w and M_n are in kg mol^{-1}.

rubber pools. This technique, however, was only marginally more successful than the one stage spin casting process used before.

In the new technique, agglomeration is drastically minimized by increasing the rate of solvent extraction quite substantially. This new precipitation-molding technique, to be discussed in greater detail in the Appendix, consists of three steps. In the first step, dilute solutions of PS and low molecular weight rubbers (primarily PB-3K) are prepared. In the second step, these are added dropwise into baths of certain nonsolvents at controlled temperatures to achieve nearly instantaneous precipitation of the polymer blends into small flocules. Finally, in the third step, the precipitated flocules are vacuum-dried and compression-molded into films or thin plates. As will be presented herein, the rapid precipitation process stifles agglomeration of the liquid rubber phase and achieves rubber pool sizes of the order of 0.2 μm or smaller. In addition, the technique lends itself to the preparation of relatively larger batches of material and with greater ease than what is possible with spin casting.

Materials Used in the Study

Two commercial PSs—with molecular weight (M_w) near 300 kg mol^{-1} and 150 kg mol^{-1} manufactured by Monsanto Plastics & Resins Company (Springfield, MA) (labeled as HH101) and Polysciences, Inc. (Warrington, PA), respectively—and one low molecular weight PB (with M_w = 3 kg mol^{-1} obtained from Polysciences, Inc.) were chosen as the basic polymers to prepare blend films. The molecular weight distribution of the PSs were quite different. For HH101, the

polydispersity ratio M_w/M_n was 2.39 and 4.23 for the other. Five other standard PBs (with narrow molecular weight distributions and manufactured by Polysciences, Inc.) and two other PBs (with different 1,4 content and manufactured by Scientific Polymer Products, Inc.) were also used to blend with PS to investigate the effects of PB molecular weight and molecular microstructure on the morphology and toughness of the PS/PB blend films. Four PB polymers with average molecular weights of $\sim$ 3 kg mol^{-1} were dissolved in d-chloroform at room temperature and filled into capped tubes for 1H NMR measurements. The 1,4 content in the PBs was calculated from the 1H NMR spectra. Table I lists all the polymers that were used in this study. The shear viscosities of the PBs were measured by a RMS-800 Rheometrics Mechanical Spectrometer at a shear rate of $\dot{\gamma}$ = 0.1 s^{-1} at room temperature.

All microstructure observations and mechanical property tests have been conducted on compression-molded films with a thickness between 0.4 to 0.6 mm prepared as outlined in the section on "The Precipitation-Molding Technique."

Microtoming and Microscopy

The morphology of dispersions of the liquid PB pools in the PS films was investigated using a Phillips 300 transmission electron microscope, which was operated at an accelerating voltage of 100 kV. A small triangular piece cut from the molded blend films was stained in a 1% aqueous solution of OsO_4 for 7 days to enhance absorption contrast between the PB and PS phases.[9] Ultrathin sections suitable for transmission electron microscopy were cut on an LKB-8800 ultramicrotome fitted with freshly pre-

pared glass knives. Section thicknesses were kept in a range of 20–40 nm.

Stereological measurements of the fixed particles of PB in the micrographs were made with a Magiscan Image Analyzing Computer (no longer in existence), manufactured by the Joyce-Loebl Company.

Specimen Polishing and Tensile Testing

Specimens for tensile tests were prepared by trimming the molded films with surgical blades on a "dog-bone" template with a 6.35 mm gauge length and a 3.18 mm gauge width. To eliminate unwanted craze clustering at surface imperfections, all four surfaces of each specimen were polished with 0.3 μm alumina slurry. Two side surfaces were polished by Dremel Moto-Tools, and two large surfaces were polished on a Microcloth-covered polishing wheel. Polished samples were washed in a dilute detergent solution, rinsed thoroughly, hung vertically in a vacuum oven, and annealed for 48 h at 80°C. The majority of tensile tests were conducted at a strain rate of 2.6×10^{-4} s^{-1} using specially prepared grips on a Model 4201 Instron Machine that has a temperature-controlling chamber with a range from −75°C to 200°C. However, other tests with strain rates up to 0.1 s^{-1} were also performed at room temperature.

EFFECTS OF PROCESSING CONDITIONS ON MORPHOLOGY

Effect of Concentration of Polymer Solution

Because the primary goal for the development of the new precipitation-molding process was control of the size and dispersion of the entrapped pools of liquid rubber, a special processing study was conducted using different concentrations of polymer components with the same PS/PB ratio in the starting polymer solutions. The final morphology of the molded films containing 2% PB-3K (with 16% 1,4 content) prepared by using different concentrations of total polymer in toluene as a solvent showed that, as the concentration became more dilute, the PB pool size in the molded films tended to decrease and the distribution of the "particle" sizes became narrower.[‡] Figure 1 (for a similar blend with 3% PB-

---

‡ Throughout this article, we will use the description *particle* and *pool* somewhat interchangeably. The first will be used in a stereological sense, whereas the second will be reserved for mechanistic discussions where the high fluidity of the rubber (with a low molecular weight species of PB) is well

Figure 1   Stress-strain curves of the PS/2% PB-3K blend films prepared from precipitates obtained from the different concentrations of polymer solutions in toluene.

3K, 16% 1,4 content) and Table II summarizes the results of tensile properties and particle size measurements of these molded films containing 2% PB-3K (with 16% 1,4 content). The performance of the films made from the higher concentrations (5–15%) of the polymer solution was roughly the same as that of pure PS films. In these blends, made from concentrated solutions, most rubber particles were larger than 0.5 μm in diameter and had relatively large interparticle spacing. Thus, the combination of the relatively high viscosity of the high vinyl PB-3K of this particular study (see the section on "Effect of Blend Morphology on Properties") that must result in poor spreading properties of the rubber, together with the large interparticle spacing, must have been responsible for the low plasticization efficiency and the high yield strengths of these blends. In addition, the large particle sizes must then also have acted as supercritical flaws in craze matter under the prevailing flow stress and have been responsible for premature fracture of the blends. Thus, the large particles of relatively viscous rubber have resulted in no important improvement of behavior over homo-PS. In polymer solutions with initial rubber concentrations of 1.6% or lower, the particle sizes and interparticle spacings have become sufficiently small to permit the plasticization effect to lower the craze flow stress significantly and thereby also prevent premature craze fracture. Hence, these blends show lower yield stresses and quite markedly increased strains to fracture to result in much tougher material. The fracture strain of the film prepared from 1% concen-

---

established. The films produced from the various blends in this research were typically of a thickness of 0.5 mm.

Table II   Mechanical Properties of the Molded Films Made from Different Concentrations of Polymer Solutions

Concentration (%)	Craze Yield Stress (MPa)	Strain to Fracture (%)	Toughness (MJ m^{-3})	$\bar{d}^a$ Average Particle Size (μm)
15.0	23.6	1.26	0.30	0.422
10.0	32.8	0.79	0.26	0.186
5.0	32.7	1.10	0.36	0.213
2.5	34.6	1.32	0.46	0.116
1.6	33.6	4.41	1.48	0.088
1.0	22.0	11.18	2.46	0.054

Note—PS: 150.00 M_w; PB: 3.00 M_w (kg mol^{-1}); content 2% PB; solvent: toluene; temperature: 25°C (16% 1,4 PB-3K).
[a] $\bar{d}$ = 1.12 $(4\bar{A}/\pi)^{1/2}$, where 1.12 is a statistical sectioning factor.

tration of polymer in solution was 10 times larger than that of the 15% polymer solution. This effect of increasing strain to fracture with increasing dilution of the starting solutions is summarized in Figure 2.[§] This improvement is attributed directly to the uniformity of particle sizes obtained from dilute solutions and to the absence of any supercritical size PB pools in these blends, all having the same volume fraction of 0.02 of free rubber.

A superficial indication of the precipitation rate of the rubber in the initial solution was obtained from observations of the time of change of the appearance of the polymer solution from transparent to opaque when dropped into the nonsolvent bath. As the concentration became more dilute, the precipitation time appeared to decrease. This observation indicated that the less concentrated the initial solution, the more quickly the nonsolvent penetrates into the drops of polymer solution, and the more profuse the nucleation rate of rubber particles becomes in the remaining solution. Such increased precipitation rate of the rubber and the decreasing time available for agglomeration achieve the ideal conditions of finely dispersed liquid rubber pools of diameters <0.2 μm.

Effect of Type of Solvent and Precipitation Temperature

The net diffusive exchange of the solvent with the nonsolvent in the droplets of polymer solution during the precipitation process significantly affects dispersion of the PB particles in the final blends.

Because such interdiffusion should depend on the types of both the solvent and nonsolvent, as well as the temperature of the precipitation of the blend particles, these effects were studied to some extent to relate them to the morphology achievable in the precipitated polymer blends and in the eventual molded polymer films. Toward this goal, three kinds of solvent were studied: xylene, toluene, and tetrahydrofuran (THF). The films precipitated from the xylene solutions yielded the smallest PB particles and the most uniform dispersion with the smallest interparticle spacing. The yield stresses and the strain to fracture that have been obtained for these blends are given in Table III, which shows that the xylene-precipitated film has the largest strain to fracture and the lowest yield stress, whereas the blends prepared from toluene and THF were only marginally better than homo-PS. Clearly, the results herein must be subject to the same explanation given in the section on the "Effect of Concentration of Polymer Solution" for the effect of concentration of initial polymer solution. Once again, the

Figure 2   Effect of concentration of polymer solutions on the strain to fracture of films of PS/2% PB-3K (with 16% 1,4 content), deformed at a strain rate of 2.6 × 10^{-4} s^{-1}.

[§] Each data point in Figure 2 corresponds to the single set of stress-strain curves in Figure 1. Because there can be considerable scatter in strains to fracture due to variability in surface preparation in seemingly identical experiments, Figure 2 must not be viewed as a definitive ductile to brittle transition occurring at the diluent concentration of ~ 3%.

Table III Mechanical Properties of the Molded Films Made from Different Solvents

Solvent	δ^a (cal cm^{-3})$^{1/2}$	Craze Yield Stress (MPa)	Strain to Fracture (%)	Toughness as MJ m^{-3}	Average Particle Size (μm)
Xylene	8.8	22.5	7.11	1.60	0.087
Toluene	8.9	31.8	0.71	0.23	0.186
THF	9.1	35.7	0.86	0.32	0.192

Note—PS: 150.00 M_w; PB: 3.00 M_w (kg mol^{-1}); content 2% PB (16% 1,4); concentration: 10%; temperature: 25°C.
[a] Obtained from ref. 21, neglecting hydrogen—bonding effects; δ of PB and PS: 8.5 and 9.1.

key is the relatively poor fluidity behavior of the PB-3K with a high 1,2 vinyl content. The blends in which the interparticle spacings of rubber are large show poor plasticization behavior because of inadequate spreading rate and evidently the associated poor sorption of the diluent rubber into the craze borders. Thus, the resulting high flow stress creates adverse conditions that promote premature craze fracture, wherein the drained large rubber pools also act as supercritical flaws.

The interdiffusion rate of the solvent with the nonsolvent is strongly dependent on temperature. Experiments conducted at −30°C, 23°C, and 40°C showed that a higher temperature of precipitation produces a finer dispersion of PB. Figure 3(a,b) and Table IV summarize the mechanical properties that have resulted from these precipitation studies. The same phenomenon encountered in the section on the "Effect of Concentration of Polymer Solution" seems to be governing again such that the blends in which particle sizes and interparticle spacings are large show poor plasticization behavior with associated brittleness due to premature craze fracture emanating from the larger particles and poor diluent spreading properties on craze surfaces. These blends have properties not much different from those of homo-PS. Only the blends with the finest particle size and interparticle spacing show adequate plasticization behavior and strains to fracture leading to improved toughness as shown in Fig. 3(b).[¶] Further improvements in particle disper-

sion by going to higher precipitation temperatures was not possible, because the nonsolvent (methanol) has a boiling point at 60°C.

EFFECT OF BLEND MORPHOLOGY ON PROPERTIES

Effect of Diluent PB Content on Properties

In the spin casting technique of blend preparation used previously by Gebizlioglu and colleagues,[5] ef-

Figure 3 (a) Stress-strain curves and (b) tensile toughness of films of PS/2% PB-3K (with 16% 1,4 content) produced by compression molding of powder precipitated from 10% xylene solutions at the three different temperatures.

[¶] In this entire study, "toughness" refers to "tensile toughness" of the area under the stress-strain curve and not fracture toughness. For quasi-homogeneous extension of a tension bar (as was often the case herein), the tensile toughness, in units of MJ m^{-3}, represents the deformation work to fracture per unit volume, dissipated in the gage section of the bar. Clearly, this differs fundamentally from fracture toughness that is taken to be either the critical stress intensity factor K_c required to drive a mode I crack in semibrittle fracture, or more appropriately the specific fracture work (or energy release rate) G_c ($= K_c^2(1 - \nu^2)/E$), where ν is Poisson's ratio and E is Young's modulus.

Table IV   Mechanical Properties of the Molded Films Containing 2% PB-3K Made from Powder Precipitated at Different Temperatures from a 10% Xylene Solution

Temperature (°C)	Craze Yield Stress (MPa)	Strain to Fracture (%)	Toughness (MJ m^{-3})	Average Particle Size (μm)
40	22.0	3.78	0.81	0.101
25	31.8	0.71	0.23	0.186
−30	29.0	0.39	0.11	0.241

Note—PS: 150.00 M_w; PB: 3.00 M_w (kg mol^{-1}); content: 2% PB; concentration: 10%; solvent: xylene (16% 1,4 PB-3K).

fective toughening of homo-PS was limited to PB-3K concentrations of <1.1%, because agglomeration of liquid rubber into supercritical size pools could not be prevented. With the precipitation-molding technique discussed herein, fine particle dispersions with particle size <0.2 μm could be readily achieved for much larger concentrations of rubber. This, and the other degrees of freedom available through the use of diluents with different molecular microstructure through the use of different concentrations of PB 1,4 component, has expanded the range of toughening available by this mechanism of stress (or deformation)-induced local plasticization at the craze level.

Figure 4(A–F) shows transmission electron microscopy (TEM) micrographs of six blend morphologies with PB-3K 16% 1,4 content ranging from 1.0% to 10%, prepared from initial xylene solutions at 10% PB concentration. Clearly, with the exception of the PB blends of 5 and 10% [shown in Fig. 4(E,F) that had rubber particles close to and exceeding 1 μm in diameter and were relatively brittle], all other blends maintained an average particle size of <0.3 μm. The mechanical properties of these blends tested at room temperature are given in Figure 5, and are summarized in Figure 6 and Table V. They show the characteristic monotonic decrease of the craze flow stress with increasing PB content reported previously by Gebizlioglu and colleagues,[5] but also a continued increase in strain to fracture up to PB-3K concentrations of 4%. The decrease in the strain to fracture >4% of PB is again due to the appearance of larger rubber agglomerations that act as supercritical flaws when incorporated into crazes. This results in the peaking of the tensile toughness at 4% of PB-3K.

Effect of Molecular Weight of PB Diluents on Properties

The mechanism of toughening by the local plasticization effect proposed by Argon and colleagues[7]

requires that the diluent be present on the craze surfaces in liquid form, at full concentration, to produce the maximum plasticization effect when in contact with the deforming craze surfaces. In the context of this mechanism, it is clear that the molecular weight of the diluent and its molecular microstructure will be very important. Herein, we report first on the effect of molecular weight of the PB diluent, whereas in the section on the "Effect of Molecular Microstructure of Diluent on Properties," we report on the effect of the molecular microstructure of the diluent rubber.

Five standard PB diluents with narrow molecular weight distribution ranging in molecular weight from 0.44 to 233 kg mol^{-1} (see Table I) were used. These PB blends contained ∼ 85% 1,4 repeat units and, thus, were rather different from the high vinyl PB-3K. Figure 7(A–D) shows TEM micrographs of the morphology of four of these five PS/PB molded films, each containing a total PB concentration of 2.0%. The micrographs for the PS/PB films with PB of molecular weights 0.44 (not shown) and 1.0 kg mol^{-1} appear completely homogeneous. No phase separation has taken place in these blends, because apparently the solubility limit is within 2% PB concentration. For this wt %, when the molecular weight of the PB exceeds 1.0 kg mol^{-1}, phase separation of PB was found. As Figure 7(B) shows, PB with 2.98 kg mol^{-1} molecular weight ($\approx$ PB-3K) has the finest dispersion of particles in the PS. The responses of these samples are illustrated in Figure 8(a,b) and are summarized in Table VI. The stress-strain curves change dramatically. Both very low (<1K) and very high ($\geq$4K) (kg mol^{-1}) molecular weights of PB are all unfavorable to improve toughness. The molded film with 2% PB of 2.98 kg mol^{-1} M_w ($\approx$ PB-3K), however, possesses the best toughness properties. Very low molecular weight PB (<1K) is compatible with the PS and does not phase separate to form pools in the PS matrix and cannot locally plasticize the crazes.

Figure 4 TEM micrographs of compression-molded films of PS/2% PB-3K (with 16% 1,4 content) produced by compression molding of powder precipitated at 23°C from xylene solutions of different initial concentrations ranging from 1% to 10%.

On the other hand, very high molecular weight PB is very viscous and, as a result, it neither disperses finely in the PS nor does it have the required spreading or diffusion properties on or into PS surfaces at the craze borders. Clearly, the beneficial toughening effect of PB diluents is limited to only a narrow range of molecular weights of PB, ~ 3.0 kg mol^{-1}.

Effect of Molecular Microstructure of Diluent on Properties

The molecular microstructure of the PB diluent also plays a very important role in affecting toughness in PS/PB blends. This was investigated by studying the effects of PBs containing different proportions of 1,2 and 1,4 repeat units along the chain at the most effective molecular weight of 3K. These two isomers of PB have quite substantially different T_g's and temperature-dependent viscosities. Whereas the T_g of PB-1,2 is around −30°C that of *trans-* or *cis*-PB-1,4 is within −100°C to −60°C. Moreover, PB-1,2 has a much larger viscosity than the linear PB-1,4 at any temperature above their respective T_g's.

The effect of different ratios of PB-1,4/PB-1,2 on the overall toughness of the PS/PB-3K blends was investigated. Figure 9 shows the effect of the PB molecular microstructure on the stress-strain behavior of PS/PB-3K blends of 3% PB-3K tested at room temperature. Clearly, as the concentration of PB-1,4 units in the PB component increases, there is a dramatic monotonic decrease in the craze flow stress and a corresponding monotonic increase in the strain to fracture, resulting in a steady increase of toughness as shown in Figure 10(b). This is a direct result of the rather sharp decrease in viscosity of the PB-3K as the more flexible PB-1,4 repeat units replace the PB-1,2 units, as shown in Figure 10(a), making the less viscous PB blends spread more effectively on the craze surfaces and, most likely, also diffuse much more readily into the craze borders where plasticization has its major effect and accentuated plastic drawing out of craze tufts takes place.

Figure 6   Effect of PB-3K (with 16% 1,4 content) diluent on: (A) the flow stress; (B) the strain to fracture; and (C) the tensile toughness of films strained at a rate of 2.6×10^{-4} s^{-1} at room temperature.

Effect of Test Temperature and Strain Rate on the Toughness of PS/PB-3K Blends

Finally, the important effect of the test temperature and strain rate on the toughness of PS/PB blends governed by the spreading mobility of liquid PB on PS craze borders and the accentuated diffusion into the PS was investigated by means of stress-strain experiments over a wide temperature and strain rate range in blends containing 3% PB-3K with three different types of PB, having 1,4 contents of: 16%, 74%, and 85%. Figure 10(a) shows that, for PB-3K the viscosity decreases over this range of isomer fraction in the PB chains by more than 2 orders of magnitude with increasing PB-1,4 content. Figure 11(a–c)

Figure 5   Stress-strain curves of PS/2% PB-3K films (with 16% 1,4 content) produced by compression molding of powder precipitated from different initial concentrations ranging from 1% to 5%.

Table V   Mechanical Properties of the Molded Films with Different PB Content

PB (wt %)	Craze Yield Stress (MPa)	Strain to Fracture (%)	Toughness (MJ m^{-3})	Average Particle Particle Diameter (μm)
0	39.5	0.63	0.25	—
0.5	34.3	0.79	0.27	0.110
0.7	34.0	1.89	0.77	0.113
1.0	34.3	4.09	1.38	0.159
1.2	34.3	3.78	1.26	0.135
1.5	32.1	4.72	1.52	0.148
2.0	31.4	7.24	2.27	0.176
2.5	29.8	7.87	2.31	0.160
3.0	31.4	9.13	2.69	0.173
3.5	23.3	11.97	2.61	0.182
4.0	19.7	13.23	2.73	0.242
5.0	12.2	8.53	1.64	0.267
10.0	12.6	5.67	0.65	0.278

Note—PS: 268.00 M_w; PB: 3.00 M_w (kg mol^{-1}) (16% 1,4 content). Powder prepared from xylene solutions with 10% PB concentration, precipitated at 25°C.

shows the stress-strain curves of these blends of PB-3K, with increasing 1,4 content over a temperature range from -40°C to nearly the T_g of PS, all at a given strain rate of 2.6×10^{-4} s^{-1}. The figures indicate clearly the already well-established trend of an increase in the strain to fracture as the flow stress decreases with increasing temperatures. They show, moreover, that the blend with the largest PB-1,4 content [Fig. 11(c)] has the best low temperature behavior, because it has the lowest low temperature craze flow stresses for a given strain rate. The effect of the temperature on the toughness of these blends is summarized in Figure 12, which shows a combination of two limiting effects on the toughness. First, as the PB-1,4 content in the PB diluent increases and the T_g of the diluent decreases (giving an increase in $T - T_{gPB}$ with increasing T), the toughness of the blends increases. This is the range of behavior where the increase in the strain to fracture more than compensates for the decrease in flow stress. Second, however, as the test temperature nears the T_g of the PS matrix, resulting in an overall decrease of the plastic resistance of homo-PS, this becomes the dominant effect and the additional decreases in the flow stress of the matrix due to PB-induced plasticization is of lesser importance. This behavior suggests that the plasticizing effect of the blends can be viewed as being based on changes in free volume coming alternatively from sorption of PB or from elevation of temperature. This correlation can be stated as a function of the geometrical mean of the difference between the test tempera-

ture and the two glass transition temperatures: T_{gPB} and T_{gPS}; it is shown in Figure 13 to demonstrate that this consideration has considerable merit.

The corresponding effect of strain rate on the craze flow stress at room temperature was explored for the two blends with the most viscous and least viscous PB diluents of 16% 1,4 and 85% 1,4 content in Figure 14(a,b). Figure 15 shows the monotonic decrease of tensile toughness with strain rate for the three PS/PB blends with different 1,4 isomer content. Clearly, as might be expected, an increase in strain rate, having the same effect as a decrease in temperature, produces a decrease in toughness. In parallel with the decreased surface mobility and diffusivity of the PB diluents with decreasing 1,4 isomer content (that is implied in Figs. 12 and 14), Figure 15 shows that the decrease in toughness with increasing strain rate is steeper in the blends with diluents of lower PB-1,4 isomer content. Even for the case of the 85% 1,4 content in the PB-3K, the trend in Figure 15 shows that, at a strain rate of 10 s^{-1} at room temperature, the toughness will have dropped to the background level. This is close to the estimate for strain rates made by Argon and colleagues[7] for loss of toughness in these blends.

DISCUSSION

Rate Mechanisms of Diluent-Induced Toughening

As is well known, toughness is a measure of a competition between continued inelastic deforma-

Figure 7 TEM micrographs of the particle morphologies of compression-molded films of PS/2% PB (with 16% 1,4 content) with different molecular weights: (A) M_w = 0.44 kg mol^{-1}; (B) M_w = 2.98 kg mol^{-1}; (C) M_w = 182 kg mol^{-1}; and (D) M_w = 233 kg mol^{-1}.

tion and the associated development of fracture that can more or less abruptly terminate the deformation process. Fracture, whether brittle or ductile, in engineering solids is normally initiated from flaws or morphological imperfections. Whereas intrinsic heterogeneties characteristic of the morphology or of the molecular level microstructure can initiate fracture by deformation-induced local stress concentrations,[10,11] it is more often a consequence of adventitious inclusions entrapped during processing. In glassy polymers exhibiting craze plasticity, fracture is usually initiated when a widening craze encounters at its border a poorly adhered or weak inclusion. This can then result in unstable tearing of the craze structure or separation of the latter along its border with the polymer matrix.[12,13] In the blends investigated in the present study, an uncharacteristically large rubbery domain or a diluent pool can serve as such an inclusion if its size is in

excess of a critical magnitude for the prevailing craze flow stress and the fracture toughness of the craze structure. This scenario of fracture in crazable glassy polymers is well established through the experiments of Murray and Hull,[12] Doyle and colleagues,[13] and a large number of subsequent investigators who have studied the types of inclusions that are encountered in usual industrial practice.[14] Some have even considered possibilities of controlling adventitious inclusions by improved cleanliness in processing.[15] In addition, the fracture toughness of typical craze matter and its connection to the craze structure have also been a subject of study.[16] Whereas these considerations are all of importance, the most effective operational means of improving toughness has proved to be accepting a certain set of adventitious imperfections resulting from high-quality material processing practice and to lower the craze flow stress to render them subcritical in

Figure 9   Effect of PB molecular microstructure of the diluents at 3% concentration and molecular weight of 3 kg mol^{-1} on the stress-strain behavior of films tested at a strain rate of 2.6×10^{-4} s^{-1} at room temperature.

Figure 8   Effect of the molecular weight of PB diluent at 2% concentration on: (a) the stress-strain behavior and (b) tensile toughness of compression-molded films. (The PB of 0.44, 1.50, and 18.00 M_w had a 16% 1,4 content, whereas those of 2.6 and 2.98 M_w had 1,4 contents of 65% and 85%.)

dered harmless. Because substantial volume fractions of rubber (of the order of 0.2–0.25) are incorporated to produce the characteristic composite compliant particles of HIPS and ABS, the penalty in this practice is a substantial reduction in stiffness (typically 50%) and a loss of transparency. The low molecular weight liquid rubber-induced plasticization approach of Gebizlioglu and colleagues[5] follows the same ultimate approach of lowering the craze flow stress. However, it accomplishes the same result in a radically different manner by dispersal of liquid rubber pools having a volume fraction of only 0.01 and, in the process, pays a negligible penalty in stiffness reduction and compromises the transparency only very slightly. In the theoretical model of Argon and colleagues,[7] developed to explain the toughening, the mechanism is governed by the rate of deformation of the fully plasticized craze borders where the assumption was made that the time for wetting of the craze surfaces by the diluents and

relation to this lowered stress level. The well-known practices of rubber particle modification in *HIPS* and *ABS* are examples of this approach. Such high impact polymers have craze flow stresses typically at half the level of the homopolymer that they modify, so that all but the most extreme adventitious inclusions are ren-

Table VI   Mechanical Properties of the Molded PS/PB Films with a Different Molecular Weight of PB

M_w	Craze Yield Stress (MPa)	Strain to Fracture (%)	Toughness (MJ m^{-3})	Average Particle Size (μm)
0.44	34.1	0.63	0.21	Homogeneous
1.00	30.4	0.79	0.24	Homogeneous
2.98	17.1	18.58	2.86	0.057
182.00	27.7	1.26	0.34	0.092
233.00	24.7	0.95	0.23	0.226

Note—PS: 150.00 M_w (kg mol^{-1}); content: 2% PB with 16% 1,4 component. Polymer powder obtained from xylene solution with 10% PB concentration. Not all blends shown in Fig. 8(a,b) are summarized in this table.
M_w is in kg mol^{-1}.

Figure 10 Effect of the molecular microstructure of PB diluents with increasing 1,4 content at 3 kg mol^{-1} molecular weight on: (a) the viscosity of the diluent and (b) the tensile toughness, obtained in tests described in Figure 9.

their sorption into the craze borders is negligible in comparison with the drawing times of the plasticized tuft matter. The experimental findings presented in the present study where the effects of temperature, type of diluent, and rate of deformation were explored indicated that the previous model of Argon and colleagues[7] needed reexamination to account for these effects. The present experiments show clearly that the toughening effect decreases monotonically with decreasing temperature, with increasing strain rate of deformation, and with increasing viscosity of plasticizing diluent. What is required is a more comprehensive theoretical model for craze growth rate (extension and widening) to better explain the craze growth rate measurements of Spiegelberg and colleagues[17,18] in diluent-plasticized PS that is central to the toughening mechanism.

Such a model has been developed and is the subject of a separate communication.[19] Herein, we develop a general framework that demonstrates that the entire set of phenomena of toughening associated with the diluent plasticization is indeed explainable by a single time-dependent fracture process arising, most probably, from adventitious inclusions, but could also be a result of more intrinsic processes governing fracture of craze matter.

Universal Time-Temperature Characterization of Fracture of Glassy Polymers

The central premise of what is developed herein is that the fracture of a crazable glassy polymer is associated with a thermally governed, stress-dependent fracture process associated with craze matter that is central and is unmodified by either the composite compliant craze initiating particles or by the plasticizing diluent liquid rubber pools discussed in the present study. This process must be associated with the tearing of the craze structure and its ultimate tearing toughness (not to be confused with the fracture toughness K_{IC} of energy release rate G_{IC} associated with the propagation of a macrocrack through the blend where vast amounts of additional energy can be dissipated in a macroscopic plastic zone made up of crazes or even distortional plastic flow). In the initially uncracked polymer, fracture is then triggered by adventitious inclusions, such as poorly adhered (ungrafted) heterogeneity particles, large liquid rubber pools, and the like. Such inclusions or imperfections prescribe, in connection with the tearing toughness of a craze, a characteristic fracture stress σ_{fa} where the local thermally assisted craze tearing process can occur athermally. Under external stresses $\sigma < \sigma_{fa}$, the same tearing process of a craze can still occur but requires time for its development. During such time, additional craze growth can occur elsewhere providing increasing overall craze strain and global tensile toughness. Thus, the lower the craze flow stress $\sigma = \sigma_c$, the more craze strain can be accumulated prior to initiation and development of a terminal fracture process, and the larger the tensile toughness of the polymer. Herein, we will not develop a specific craze tearing model, but merely demonstrate that the entire toughening process explored by us can find a unified explanation based entirely on a thermally assisted stress-dependent fracture process. In this, we follow a well known formalism of Larson and Miller,[20] developed decades ago for the time-dependent fracture of creeping metal alloys.

Figure 11   Effect of test temperature on the stress-strain behavior of films with 3% PB-3K, but with different molecular microstructures: (a) 16% 1,4 content; (b) 74% 1,4 content; and (c) 85% 1,4 content. These tests are labeled A, B, and C in the text.

Consider fracture in our blends as a thermally assisted stress-dependent process, characterizable by a stress-dependent activation free energy $\Delta G^*(\sigma)$, giving the rate of local fracture as a reciprocal time to fracture t_f, as

$$\frac{1}{t_f} = \nu \exp\left(-\frac{\Delta G^*(\sigma)}{kT}\right), \tag{1}$$

where ν is a fundamental frequency factor close to the atomic (Debye) frequency ν_D (ref. 20).

Whether this involves chain scission, chain slippage, or anything else is of no interest herein. Clearly, the stress of interest will be the local accentuated stress at the fracture site associated with a geometrical intensification mechanism, and that such intensification would be a distributed process involving the form of the craze structure and the heterogeneities. This too will be less important herein, because we will assume that such intensifications be substantially the same in the unmodified homopolymer as in the diluent modified blends (i.e., associated with the craze matter that is assumed to retain its character). Then, the overall strain to fracture, ϵ_f, in the sample, governed by the sum total of crazes that produce the craze plasticity, is related to this time to fracture through the imposed strain rate $\dot{\epsilon}$ by:

$$t_f = \frac{\epsilon_f}{\dot{\epsilon}}. \tag{2}$$

Then,

$$\ln \nu t_f = \ln \nu(\epsilon_f/\dot{\epsilon}) = \frac{\Delta G^*(\sigma)}{kT}, \tag{3}$$

or,

$$\frac{\Delta G^*(\sigma)}{k} = T \ln \nu t_f = T \ln (\nu(\epsilon_f/\dot{\epsilon})). \tag{4}$$

We separate the activation free energy $\Delta G^*(\sigma)$ into a scale factor ΔG_o and a purely stress-dependent function $g(\sigma/\sigma_o)$, where we normal-

Figure 12   Summary of the results of the tensile experiments of Figure 11 represented as the effect of test temperature on the tensile toughness for the three separate blends all of 3% PB-3K, but with different molecular microstructure of diluents.

Figure 13 Unified representation of the temperature dependence of the tensile toughness of the blends with diluents of different molecular microstructure in tests at a strain rate of 2.6×10^{-4} s^{-1}. T_m is test temperature, T_{gPB} is the T_g of the diluent mixture, and T_{gPS} is the T_g of homo-PS.

ized the stress with σ_o that will be most likely the stress level that drives the process athermally, i.e.,

$$\Delta G^*(\sigma) = \Delta G_o\, g(\sigma/\sigma_o). \tag{5}$$

This results naturally in a functional dependence of $g(\sigma/\sigma_o)$ on a universal time to fracture/temperature parameter Θ, i.e.,

$$g(\sigma/\sigma_o) = \Theta/T_o, \tag{6}$$

where

$$\Theta \equiv T \ln \nu t_f = T \ln (\nu(\epsilon_f/\dot{\epsilon})), \tag{7}$$

and

$$T_o \equiv \frac{\Delta G_o}{k}, \tag{8}$$

or alternatively,

$$\frac{\sigma}{\sigma_o} = g^{-1}(\Theta/T_o), \tag{9}$$

where $g^{-1}(\Theta/T_o)$ symbolically represents the inverse of the function g.

Table VII presents the basic information derived from the stress-strain experiments A, B, and C of the three blends of 3% PB-3K with different 1,4 content in the diluent, increasing from 16% to 85% and shown in Fig. 11(a–c), all at a constant strain rate of 2.6×10^{-4} s^{-1}. In the table, columns 1–3 give the craze flow stress at different test temperatures, resulting in fracture strains ϵ_f (given in column 3). This same information is presented in Figure 16 and shows the monotonic decrease of the flow stress with increasing test temperature and the corresponding monotonic increase in the strain to fracture. Columns 4 and 5 in Table VII give the calculated times to fracture t_f based on eq. (2), and the calculated universal time to fracture/temperature parameter, Θ, determined from eq. (7). For the latter determination, the frequency factor ν was chosen to be 10^{13} s^{-1} (examination of the correlations given herein will demonstrate that a somewhat different magnitude for ν would have left the overall conclusions the same, but would have produced an overall slight shift).

Table VIII presents the basic information derived from the corresponding stress-strain exper-

Figure 14 Effect of strain rate on the stress-strain behavior of two blends with: 3% PB-3K and different diluent molecular microstructure—(a) 16% 1,4 content; and (b) 85% 1,4 content. These tests are labeled D and E in the text.

iments D and E, performed at room temperature but at different strain rates, for the two bounding blends with PB diluents having 1,4 content in the levels of 16% and 85%, respectively, and given in Fig. 14(a,b). Figure 17 shows this strain rate dependence of the flow stresses and strains to fracture of these two blends at room temperature. Columns 1–5 of Table VIII present the same corresponding information for these experiments as was given in Table VII for the stress-strain experiments at different temperatures.

Figure 18 presents the dependences of the craze flow stresses (fracture stresses) on the corresponding universal parameters Θ for all five sets of experiments A–E. In the semilogarithmic plot, the dependences of the three sets of experiments A–C at the same strain rate, but at different temperatures for the three blends of Fig. 11(a–c), form three nearly parallel but displaced curves which, to a first approximation, are straight lines. The corresponding dependences for the additional two sets of experiments D and E at room temperature but at different strain rates also give nearly straight lines, but having different slopes, with the slopes decreasing with increasing viscosity of the diluent.

As noted above, the "universal" dependences of the fracture stresses (craze flow stress) on the temperature-modified time parameter Θ are in

Figure 15 Change in tensile toughness with strain rate in the blends with 3% PB-3K with diluents of three different molecular microstructures tested at room temperature.

Table VII   Mechanical Characteristics of PS/PB-3K Blends with 3% Liquid Rubber Pools, Prepared by the Precipitation-Molding Process, Tested at a Strain Rate of $\dot{\epsilon} = 2.6 \times 10^{-4}$ s^{-1} at Different Temperatures

σ (MPa)	T(K)	ϵ_f	t_f (s)	Θ(K)	σ/σ_o	Θ/T_o
A. Experiments with Diluent Compositions of 16% PB-3K, 1,4 Isomer, and 84% PB-3K 1,2 Isomer Content [Fig. 11(a)] ($\sigma_o = 737$ MPa, $T_o = 2200$K, $\nu = 10^{13}$ s^{-1})						
27.5	283	7.87×10^{-3}	30.3	9,437	3.73×10^{-2}	4.29
19.5	296	0.061	234.6	10,476	2.65×10^{-2}	4.76
12.3	313	0.138	531	11,333	1.67×10^{-2}	5.15
8.0	333	0.350	1346	12,367	1.09×10^{-2}	5.62
3.5	353	0.484	1862	13,224	0.475×10^{-2}	6.01
B. Experiments with Diluent Compositions of 74% PB-3K, 1,4, Isomer, and 26% PB-3K, 1,2 Isomer Content [Fig. 11(b)] ($\sigma_o = 985$ MPa, $T_o = 2200$K, $\nu = 10^{13}$ s^{-1})						
28.5	273	0.070	269	9,699	2.89×10^{-2}	4.41
20.5	296	0.178	685	10,793	2.08×10^{-2}	4.91
13.0	313	0.284	1092	11,560	1.32×10^{-2}	5.22
10.0	333	0.350	1346	12,370	1.02×10^{-2}	5.62
7.08	353	0.287	1100	13,000	0.719×10^{-2}	5.91
C. Experiments with Diluent Compositions of 85% PB-3K, 1,4 Isomer, and 15% PB-3K, 1,2 Isomer Content [Fig. 11(c)] ($\sigma_o = 593$, $T_o - 2200$K, $\nu = 10^{13}$ s^{-1})						
39.0	233	0			6.58×10^{-2}	
33.0	253	0.02	77	8,672	5.57×10^{-2}	3.94
18.0	273	0.17	654	9,942	3.04×10^{-2}	4.52
10.0	296	0.49	1,885	11,093	1.69×10^{-2}	5.04
8.5	313	0.72	2,770	11,800	1.43×10^{-2}	5.39
6.0	333	0.79	3,380	12,673	1.01×10^{-2}	5.76
2.5	353	0.80	3,077	13,401	0.42×10^{-2}	6.09

the form of straight lines, suggesting a general dimensionless representation as:

$$\ln\frac{\sigma}{\sigma_o} + \frac{\Theta}{T_o} = 1 \qquad (10)$$

where σ_o and T_o are the two normalization parameters referred to herein. These parameters can be determined readily from the curves by noting that,

$$T_o = -\frac{d\Theta}{d \ln \sigma} \qquad (11)$$

and that σ_o can be established by any fit that adjusts the ordinate on the ln σ axis of these lines. The normalization parameters found by this procedure are summarized in Table IX. The dimensionless stress, σ/σ_o, and dimensionless temperature, Θ/T_o, values calculated for the various

Figure 16   Trends in the dependence of strain-to-fracture and flow stress on temperature at constant strain rate, demonstrated in experiments A, B, and C shown in Fig. 11(a–c).

Table VIII   Mechanical Characteristics of PS/PB-3K Blends with 3% Liquid Rubber Pools, Prepared by Precipitation Molding Process Tested at $T = 295$K at Different Strain Rates

σ (MPa)	$\dot{\epsilon}$ (s^{-1})	ϵ_f	t_f (s)	Θ (K)	σ/σ_o	Θ/T_o
D. Experiments with Diluent Composition of 16% PB, 1,4, Isomer, and 84% PB-3K 1,2 Isomer Content [Fig. 14(a)] ($\sigma_o = 51.9$ MPa, $T_o = 5820$K, $\nu = 10^{13}$ s^{-1}						
31.94	1.3×10^{-2}	0.007	0.54	8,650	0.616	1.48
30.20	2.6×10^{-3}	0.014	5.38	9,325	0.582	1.60
25.51	1.3×10^{-3}	0.045	34.6	9,878	0.492	1.69
22.65	2.6×10^{-4}	0.115	442.3	10,628	0.437	1.83
E. Experiments with Diluent Compositions of 85% PB-3K, 1,4 Isomer, and 15% PB-3K 1,2 Isomer Content [Fig. 14(b)] ($\sigma_o = 210$ MPa, $T_o = 2720$K, $\nu = 10^{13}$ s^{-1})						
26.10	1.3×10^{-1}	0.029	0.22	8,390	0.124	3.08
18.00	1.3×10^{-2}	0.149	11.46	9,550	0.086	3.51
12.80	1.3×10^{-3}	0.223	171.50	10,300	0.061	3.79
9.64	2.5×10^{-4}	0.501	1,927	11,100	0.046	4.08

stress-strain experiments A–E, are given in columns 6 and 7 of Tables VII and VIII.

The "universality" of the correlation is explored in Figure 19, which demonstrates a remarkable behavior pattern, for all sets of experiments in the normalized form of representation. This, however, should not be surprising. It merely indicates

Figure 17   Trends in the dependence of strain-to-fracture and flow stress on strain rate at room temperature, demonstrated in experiments D and E shown in Fig. 14(a,b).

that the ideas that have led to the form of representation of the fracture process and its time dependence, given by eq. (9), have merit and that the connection between ln σ and Θ is a linear one. Nevertheless, the fact that all experimental results, when expressed in normalized form, give rise to a single tight behavior pattern is a strong indication that a single fracture process governs and that the approach to toughening by reduction of the flow stress is very effective. Only the two endpoints in Figure 19 are well below the common behavior pattern. These represent conditions of the highest temperature and the longest fracture times, indicating that, under these extreme conditions, the fracture process begins to become qualitatively altered, possibly due to chain slippage or other concurrent structure change processes. The more important information is associated with the normalization parameters presented in Table IX. Herein, we note that the temperature parameter T_o is the same for the three experiments, A–C, performed at different temperatures, but at the same low strain rate of 2.6×10^{-4} s^{-1}. This indicates, from eq. (8), that the scale factor ΔG_o of the rate controlling fracture process is the same and that the diluents with increasing fluidity (increasing PB-1,4 content) decrease the reference plastic resistance represented by σ_o. This effect, however, is not monotonic. The parameter σ_o for the PB diluent with 74% 1,4 content in experiment B indicates less plasticization than either of the extreme blends. Nevertheless, as Figure 12 shows, the temperature-dependent toughness of these

Figure 18 Dependence of fracture stress on the "combined" time-to-fracture/temperature parameter, Θ, for experiments A–E, at a constant strain rate but different temperatures and constant temperature but different strain rates.

blends is intermediate between the two other blends with both more and with less viscous diluents. The source of this irregularity is unclear.

We note from Table IX that, in experiment E at room temperature at different strain rates with the PB-3K diluent with 85% 1,4 content, the temperature normalization parameter T_o is somewhat larger than those in the constant strain rate experiments A–C, but only marginally so. Moreover, the points of these experiments fall with the same family of points of the constant strain rate experiments A–C and overlap with them as Figure 19 shows. The stress normalization parameter σ_o, however, now is considerably lower at 210 MPa, indicating a lower intercept and a less rate-dependent behavior. Nevertheless, the association of these high strain rate experiments of blends with low viscosity diluents with those at the lowest strain rate experiments indicates that the mechanism of fracture must remain qualitatively the same (i.e., still substantially influenced by the beneficial plasticization effect of the diluent). Figure 15, however, shows that, as the strain rate increases, in the range of the tests, the tensile toughness of this blend decreases monotonically. In a separate communication presenting a model of the interaction of extending crazes with diluent pools, we demonstrate that this decline is only partly a result of monotonically decreasing coverage of the craze front and craze

Table IX   Normalization Constants in Stress-Strain Experiments for Unified Representation of Stress Dependence of Times-to-Fracture (All Diluents Are 3K Molecular Weight at 3% in the Blend)

Experiment	Diluent Composition	Strain Rate (s^{-1})	Temperature Range (K)	σ_o (MPa)	T_o (K)
A	16% (1,4)	2.6×10^{-4}	283–353	737	2,200
B	74% (1,4)	2.6×10^{-4}	273–353	985	2,200
C	85% (1,4)	2.6×10^{-4}	233–353	593	2,200
D	16% (1,4)	2.6×10^{-4}–1.3×10^{-2}	295	51.9	5,820
E	85% (1,4)	2.6×10^{-4}–1.3×10^{-1}	295	210	2,720

Figure 19 "Universal" dependence of the normalized fracture stress (craze flow stress) on the normalized combined time-to-fracture/temperature parameter for all experiments. The form of the tight behavior pattern suggests a single mechanism of fracture that is considered to be tearing of crazes.

border with the plasticizing diluents, and that more fundamental local processes at the craze borders must be involved.[19] Finally, experiment D, with the blend having the highest viscosity diluent, stands apart from the rest in Figure 19. Table IX shows that it has a T_o that is more than twice as high as that of the low viscosity diluent blend E and has a remarkably low σ_o at 51.9 MPa. This indicates an almost flat unplasticized behavior with little sensitivity to Θ (i.e., a nearly athermal response). This is clearly demonstrated in the nonnormalized representation of Figure 18. Whereas the σ_o values for blends A–C and E in these experiments merely represent a stress intercept, that of experiment D, in the high viscosity diluent blend, must come close to the true athermal limiting stress of the fracture process where diluent plasticization is substantially absent, giving the response of the unmodified homopolymer itself. It should be expected that all blends in experiments in the low Θ range (i.e., at low temperatures and short times-to-fracture limit) would revert to the behavior of the unmodified homopolymer, giving a flattened dependence in the nonnormalized representation of Figure 18, as blend D exhibits.

Tensile Toughness in Diluent Modified Blends

Since in all stress-strain behavior, developing at least a noticeable level of craze plasticity the flow stress remains substantially constant as the specimen continues to fill with increasing numbers of craze bands until fracture occurs, the tensile toughness W (as the area under the stress-strain curve) is simply:

$$W = \epsilon_f \sigma = \sigma_o \epsilon_f (\sigma / \sigma_o). \qquad (12)$$

From the linear representation of the $\ln \sigma$ and Θ connection of eq. (10), however, we have,

$$\epsilon_f = \frac{\dot{\epsilon}}{\nu} \exp\left(\frac{T_o}{T}\left(1 - \ln\left(\frac{\sigma}{\sigma_o}\right)\right)\right), \qquad (13)$$

giving for the tensile toughness,

$$\frac{W}{\sigma_o} = \left(\frac{\dot{\epsilon}}{\nu}\right)\left(\frac{\sigma}{\sigma_o}\right) \exp\left(\frac{T_o}{T}\left(1 - \ln\left(\frac{\sigma}{\sigma_o}\right)\right)\right). \qquad (14)$$

To proceed further, and give a predictive expression for the tensile toughness as a function of strain rate at any given test temperature, a specific strain rate dependence of the craze flow stress needs to be introduced. A convenient phenomenological dependence of σ and $\dot{\epsilon}$ is of a power-law form,

$$\frac{\dot{\epsilon}}{\dot{\epsilon}_o} = \left(\frac{\sigma}{\sigma_o}\right)^m, \qquad (15)$$

where σ_o can be the same normalization constant introduced in the section on "Universal Time-Temperature Characterization of Fracture of Glassy Polymers"; but, $\dot{\epsilon}_o$ now represents merely a scaling parameter of the strain rate, involving, among other things, the density of active craze fronts and craze borders in the deforming sample. The exponent m, herein also merely represents a parameter giving the nonlinear connection of the craze strain rate on the craze stress level. This, form, while convenient, has not much mechanistic merit, in that m will have to be temperature-dependent. A more mechanistically sound form of the strain rate stress connection of craze plasticity was given earlier by Argon and colleagues[7] and is developed further in a separate communication on the plasticity of diluent modified blends.[19] More specifically, the fitting parameters $\dot{\epsilon}_o$ and m for the room temperature experiments at different strain rates can be extracted from Table VIII for experiment E. They are:

Figure 20 Calculated dependence of tensile toughness on strain rate at room temperature in the E tests at room temperature.

$$\dot{\epsilon}_o = 5.91 \times 10^4 \text{ s}^{-1} \tag{16a}$$

and

$$m = 6.26. \tag{16b}$$

With eq. (15), the expression for the tensile toughness becomes,

$$\frac{W}{\sigma_o} = \left(\frac{\dot{\epsilon}_o}{\nu}\right)\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_o}\right)^{1+1/m}$$

$$\times \exp\left(\frac{T_o}{T}\left(1 - \ln\left(\frac{1}{m}\ln(\dot{\epsilon}/\dot{\epsilon}_o)\right)\right)\right). \tag{17}$$

As a check on the utility of the expression in eq. (17), we determine the dependence of the tensile toughness on strain rate of the experiments in set E for the blends with the low viscosity diluents. For this, we recall that, for this experimental set, $\sigma_o = 210$ MPa and $T_o = 2720$K. These, and the values for $\dot{\epsilon}_o$ and m determined in connection with eqs. (16a) and (16b), we calculate by eq. (17) the decrease of tensile toughness with increasing strain rate. The result is shown in Figure 20 by the broken line, together with the experimental results from Figure 15. The agreement is very good, partly because the phenomenological constitutive connection of eq. (15) was obtained from Fig. 14(b).

CONCLUSIONS

The range of toughening by prepackaged diluents was increased substantially from what had been reported by Gebizlioglu and colleagues[5] by the development of a new precipitation-molding technique that can incorporate larger volume fractions of plasticizing low molecular weight, liquid rubber (PB) diluents in pools of diameter <0.2 μm. The new technique of incorporating PB diluent was very reliable for packaging diluents up to 4% by volume without any deleterious agglomeration into larger pools. The most effective molecular weight of PB diluent that maximizes the toughening effect was found to be 3 kg mol^{-1}. Whereas diluents of smaller molecular weight tended to remain in solution in PS, those of larger molecular weight were too viscous to be effective.

At the 3% by volume of 3K diluent of PB incorporated, a further dimension of toughening was to increase the 1,4 content of the PB microstructure that leads to significant reductions in the diluent viscosity at any temperature above the T_g of the diluent. Thus, best results were obtained with PB diluents composed of 85% 1,4 content. In all blends, tensile toughness at a given strain rate increased with increasing temperature, until the effect of the reduction of the plastic resistance of the homopolymer (PS) due to the approach to its T_g became a prevalent effect.

In all blends, the tensile toughness at room temperature decreased monotonically with increasing strain rate. This was less rapid in the blends with the least viscous diluents. Even for this case, however, the toughening dropped down to the low levels of the unmodified homopolymer at strain rates of ~ 10 s^{-1}. This indicates that, whereas very effective, the diluent toughening mechanism is lost when the crazes outrun the sorption of the diluent and its associated plasticization effect. All toughening effects could be correlated by a normalized representation of the fracture stress of the blends by a universal temperature/time-to-fracture parameter that suggested strongly that the terminal mechanism of fracture is qualitatively the same in all blends, but is modulated by the specific plasticization effect of different diluents.

APPENDIX: THE PRECIPITATION-MOLDING METHOD OF BLEND PREPARATION

To exploit the diluent-induced toughening effect beyond what had been reported by Gebizlioglu and colleagues,[5] a new method was devised to obtain conditions for phase separation of the diluent rubber from the homopolymer in solvents to suppress agglomeration of liquid rubber into larger pools.

Three steps are involved in the new procedure. During the first step, a solution is prepared of the homopolymer (PS) and the low molecular weight liquid rubber (PB) in a common reagent grade solvent such as toluene, xylene, or THF. In this, typically 5 g of polymer with varying ratios of PS and PB are dissolved in 100 mL of solvent. In the preliminary experiments, different concentrations of polymer in solution were tried as discussed in the text. The solutions were kept overnight in a flask to obtain complete dissolution; occasional shaking was administered, but there was no prolonged mechanical stirring.

In the second step, the prepared solutions were added dropwise into a large precipitation bath containing a liter of methanol, which is a poor solvent of the polymer component of the first solution. Under a relatively rapid rate of stirring of the methanol bath, the solid polymer phase separated into flat flocules of submillimeter size at times short enough to trap the liquid rubber diluent into submicron size uniformly dispersed pools. As described in the text, a variety of conditions for flocculation were tried, consisting of a wide temperature range and initial solutions with different solid polymer components in solution. The best conditions for achieving the desired fine dispersion of liquid rubber pools involved the use of very dilute initial solutions in xylene to increase the nucleation rate of flocules, and relatively high temperatures in the precipitation bath nearing the boiling point of methanol. The precipitated polymer mass was filtered out and placed in a vacuum oven to dry for $\sim$ 24 h at 60°C.

The final step in the preparation was compression molding the flocules into films. These films were produced on a laboratory press (Carver, Inc., Menomonee Falls, Wisconsin) operated at 170°C and a pressure of $\sim$ 4–5 MPa. Typical film production times were in the range of 5–10 min.

REFERENCES

1. Kambour, R. P.; Bernier, G. A. Macromolecules 1968, 1, 190.
2. Dettenmaier, M.; Leberger, D. In Advances in Polymer Science, Vol. 91/92; Kausch, H. H. Ed.; Springer: New York, 1990; p 119.
3. Kruse, R. Polymeric Polyblend Compositions Toughened by Addition of Liquid Polymers of a Conjugated Diene Monomer; U.S. Pat. 4,154,715, 1979.
4. Gebizlioglu, O. S.; Argon, A. S.; Cohen, R. E. Polymer 1985, 26, 535.
5. Gebizlioglu, O. S.; Beckham, H. W.; Argon, A. S.; Cohen, R. E.; Brown, H. R. Macromolecules 1990, 23, 3968.
6. Brown, H. R.; Argon, A. S.; Cohen, R. E.; Gebizlioglu, O. S.; Kramer, E. J. Macromolecules 1989, 22, 1002.
7. Argon, A. S.; Brown, H. R.; Cohen, R. E.; Gebizlioglu, O. S.; Kramer, E. J. Macromolecules 1990, 23, 3975.
8. Piorkowska, E.; Argon, A. S.; Cohen, R. E. Macromolecules 1990, 23, 3838.
9. Kato, K. Polym Eng Sci 1967, 7, 38.
10. Kramer, E. J. In Advances in Polymer Science, Vol. 52/53; Kausch, H. H., Ed.; Springer: New York, 1983; p 1.
11. Schwier, C. E.; Argon, A. S.; Cohen, R. E. Phil Mag 1985, 52, 581.
12. Murray, J.; Hull, D. J Polym Sci Poly Phys Ed 1970, 8, 583.
13. Doyle, M. J.; Maranci, A.; Orowan, E. Proc Roy Soc 1972, A329, 137.
14. Kambour, R. P.; Vallance, M. A.; Farraye, E. F.; Grimaldi, L. A. J Mater Sci 1986, 21, 2435.
15. Yang, A. C. M.; Kramer, E. J.; Kuo, C. C.; Phoenix, L. Macromolecules 1986, 18, 2010.
16. Brown, H. R. Macromolecules 1991, 24, 2752.
17. Spiegelberg, S. H.; Argon, A. S.; Cohen, R. E. J Appl Polym Sci 1993, 48, 85.
18. Spiegelberg, S. H.; Argon, A. S.; Cohen, R. E. J Appl Polym Sci 1994, 53, 1251.
19. Argon, A. S. J Appl Polym Sci, in press.
20. Larson, F. R.; Miller, J. Trans ASME 1952, 74, 765.
21. Brandrup, J.; Immergut, E. H. Polymer Handbook, 2nd ed.; John Wiley & Sons, Inc.: New York, 1975.
22. McClintock, F. A.; Argon, A. S. Mechanical Behavior of Materials; Addison-Wesley: Reading, MA, 1966.