# **Kinetics of Crazing in Polybutadiene/Polystyrene Blends**

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#### **SYNOPSIS**

The crazing behavior of blends of polystyrene (PS) and a low molecular weight polybutadiene (PB) was examined as part of a continuing study of toughening mechanisms in thermoplastic polymers. These PS/PB blends attain high levels of toughness from the stress-activated plasticizing action of the polybutadiene (PB), a mechanism that is active only in the region of a growing craze. The plasticization is therefore localized and leads to enhanced toughness without loss in stiffness. The net result of this plasticization is a reduction in craze flow stress accompanied by an increase in craze velocity, which, in turn, allows the specimen to reach substantial strains-to-fracture in uniaxial deformation under an imposed strain rate. The ability of the PB to plasticize a growing craze is expected to be a function of the mobility of the PB. To investigate the role of diluent mobility, tensile tests and craze velocity measurements were conducted at  $-20^{\circ}$ C and compared with previously published results collected at 23°C. Although the blends displayed high levels of toughness at 23°C. the blends tested at  $-20^{\circ}$ C showed brittle behavior. Craze velocities measured at  $-20^{\circ}$ C were 2 orders of magnitude lower than the results at  $23^{\circ}$ C. Addition of 3 wt % PB at  $-20^{\circ}$ C led to craze velocities only as large as those found in pure PS at 23°C. Comparison of the craze velocities with an asymptotic theoretical model describing the dependence of the craze velocity on the PB content showed good agreement with the results at -20 °C and only fair agreement with the room-temperature results. © 1994 John Wiley & Sons, Inc.

# **INTRODUCTION**

It has now been established that the incorporation of a few weight percent of a low molecular weight polymeric diluent, forming a separate phase, in glassy polymers has a profound effect on the mechanical properties of the blends.<sup>1-5</sup> When the diluent phase separates in the form of submicron size, randomly dispersed pools, it can serve as a localized plasticizer in the region of negative pressure associated with a growing craze. This plasticization allows the craze to propagate at a faster rate under a lower imposed stress than in an unplasticized specimen.<sup>6</sup> Previous work<sup>4</sup> has demonstrated that the incorporation of 5 wt % of a low molecular weight diluent resulted in craze velocities that were 3 orders

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Journal of Applied Polymer Science, Vol. 53, 1251–1259 (1994) © 1994 John Wiley & Sons, Inc. CCC 0021-8995/94/091251-09 of magnitude faster than those found in pure polystyrene at 23°C under the same applied stress. This increase in craze velocity results in low-rate tensile toughness levels that approach those found in commercial grades of high-impact polystyrene (HIPS).

The mobility of the diluent is expected to play a strong role in its efficacy as a localized plasticizer. The diluent must be able to spread on the surface of a growing craze and diffuse into the craze matter at a rate that is competitive with the local drawing rate of craze tufts at the imposed strain rate. Qin et al.<sup>5</sup> demonstrated that the tensile toughness of polybutadiene/polystyrene (PB/PS) blends scales inversely with the viscosity of the PB.

To examine further the role that diluent mobility plays on the observed mechanical behavior of PB/ PS blends, we performed craze velocity measurements at subambient temperatures. These results and their implications in the phenomenon of localized plasticization are presented and discussed in this communication.

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## **EXPERIMENTAL**

Blends of PB/PS were prepared by a precipitation technique previously described.<sup>3–5</sup> PS of molecular weight 350,000 g/mol and a polydispersity of 2.3 was obtained from Polysar, Springfield, MA. The PB was purchased from Scientific Polymer Products and had a molecular weight of 2600 g/mol and a vinyl content of 29%.

Samples were milled into dogbone tensile specimens and tested in uniaxial tension in an Instron 4201 load frame at a strain rate of  $2.6 \times 10^{-4}$  s<sup>-1</sup>. An Instron environmental chamber was used for tensile tests conducted at  $-20^{\circ}$ C. Craze velocity measurements were made with an apparatus described in detail elsewhere.<sup>3,4</sup> Cold nitrogen gas was introduced into a cooling manifold to allow measurements to be made at  $-20^{\circ}$ C. Temperature control was achieved with a resistive heating coil placed inside the manifold.

## **RESULTS AND DISCUSSION**

## Tensile Studies: -20°C

The stress-strain response of the PB/PS blends at  $-20^{\circ}$ C and a strain rate of  $2.6 \times 10^{-4}$  s<sup>-1</sup> is shown in Figure 1. The waviness of the stress-strain plots are of instrumentation origin and should be ignored. The mechanical response of these blends varies dramatically from those found at room temperature; the former blends show only slight amounts of di-

latational plasticity. However, from these results, it was possible to determine the craze flow stress, the strain-to-fracture, and the tensile toughness for the various samples. These results are plotted in Figures 2-4 in comparison with data obtained at  $23^{\circ}$ C.<sup>4</sup> Whereas the craze flow stress data collected at  $23^{\circ}$ C demonstrated a steady decrease with PB content, the data collected at  $-20^{\circ}$ C showed little or no change with PB modification.

The high craze flow stress at  $-20^{\circ}$ C affects the mechanical properties in a very direct way. Adventitious inorganic heterogeneities, dormant at the relatively lower stresses at 23°C, now have sufficient stress concentrated at their periphery to initiate cracks in crazes as soon as the latter begin to grow. This crack initiation results in premature fracture, which is evident in the uniformly low strains-to-fracture at  $-20^{\circ}$ C shown in Figure 3. As a result, there was no change in tensile toughness with PB content (Fig. 4), unlike the room-temperature results that showed a maximum toughness at 4% PB.

#### Spreading Rate Measurements

The results from the stress-strain experiments suggest that lowering the temperature decreased the mobility of the diluent sufficiently to prevent plasticization in the blends. In an effort to verify this conjecture, spreading rate studies of the liquid diluent PB were conducted at room temperature and at  $-20^{\circ}$ C. A drop of PB was placed on a film of PS that had been molded between two glass plates to provide a reproducibly smooth surface. The rate of



**Figure 1** Mechanical behavior of PB (2600 g/mol)/PS blend as a function of weight percent PB tested in uniaxial tension at subambient conditions. Samples were prepared by precipitation blending.  $T: -20^{\circ}$ C; strain rate:  $2.6 \times 10^{-4}$  s<sup>-1</sup>.



**Figure 2** Effect of PB content on the craze flow stress of PB/PS blends at  $(\Box) -20^{\circ}$ C and  $(\blacktriangle) +23^{\circ}$ C. Strain rate:  $2.6 \times 10^{-4}$  s<sup>-1</sup>.

propagation of the front of the drop was measured with a light microscope.

Two qualitative observations were made: First, the PB drop spread quickly under the influence of its own weight initially, then leveled off to a constant spreading rate. Second, the liquid drop occasionally did not spread uniformly, but rather found a preferential path to follow. This was probably due to some surface chain orientation, possible trace amounts of surface contaminants, or the presence of surface flaws.



**Figure 3** Effect of PB content on the strain-to-fracture of PB/PS blends at  $(\Box)$  -20°C and  $(\blacktriangle)$  +23°C. Strain rate:  $2.6 \times 10^{-4} \text{ s}^{-1}$ .



**Figure 4** Effect of PB content on the tensile toughness of PB/PS blends at  $(\Box) = 20^{\circ}$ C and  $(\blacktriangle) + 23^{\circ}$ C. Strain rate:  $2.6 \times 10^{-4}$  s<sup>-1</sup>.

A simple cooling apparatus was constructed for the low-temperature measurements. A nozzle was attached to a clear plastic box, which was then connected to a liquid nitrogen cylinder equipped with a needle valve. The box was wrapped in heating tape, which was powered by a temperature controller. A thermocouple was placed inside the box to monitor the temperature. The PS film and a small trough of PB were placed in the box and were subsequently cooled down to  $-20 \pm 3^{\circ}$ C. A glass micropipette was inserted into a small hole in the top of the box, dipped in the PB trough, then touched against the PS film to place a drop on the surface. The subsequent drop advance was then measured.

The results for the room-temperature measurements are shown in Figure 5. The large discrepancy in the y-intercept in these plots resulted from differences in drop size; a larger drop spread quickly over a larger distance under the influence of its own weight, after which the spreading became independent of drop size. The spreading rate was determined from a fit to the data in this latter region. An average spreading rate of  $9.7 \times 10^{-8}$  m/s was measured at room temperature. The results for the low-temperature studies, an example of which is shown in Figure 6, were almost an order of magnitude slower, having a spreading rate of  $1.1 \times 10^{-8}$  m/s. It should be noted that these spreading rates probably represent a lower bound on the actual spreading rate in a craze. In crazes, the presence of free radicals due to chain fracture<sup>7</sup> will increase the surface energy of the matrix polymer and will, hence, result in faster spreading.



**Figure 5** Spreading rate data for PB on PS at 23°C for three drop sizes. The value of the *y*-intercept is a function of the initial drop size. Subsequent steady-state growth is independent of drop size.

Although the rate of spreading will be a strong function of temperature, it is also a function of the relative surface energies of the diluent and the glassy polymer. Blends of the same low molecular weight PB used in this study and poly(methyl methacrylate) (PMMA) yielded a similar morphology of submicron pools of diluent surrounded by the glassy polymer, but displayed little increase in toughness at room temperature.<sup>3</sup> Spreading rate studies on these blends indicated that spreading ceased after the initial rapid gravitational spreading.<sup>3</sup> This ob-

0.3 -20°C 0.25 Distance, mm 0.2 0.15 0.1 0.05 0 50 100 150 200 250 0 Time, min

Figure 6 Spreading rate data for PB on PS at  $-20^{\circ}$ C.

servation would suggest that the drop formed a finite contact angle, although it was not readily measurable. This result is not surprising, as PMMA has lower surface energy than that of PS  $(35 \text{ vs. } 40 \text{ dyne}/\text{ cm})^8$ ; thus, PB is less inclined to spread spontaneously on the PMMA surface. These results point out the necessity of choosing diluent-matrix combinations that not only form the desired morphology, but that also possess the surface energies necessary for rapid wetting and subsequent diffusion.

These results point to the strong dependence that the mechanical properties have on the rate of diluent spreading. As will be shown in the next section, a reduction in spreading rate will lead directly to decreased craze velocities.

### **Craze Velocity Measurements**

To complement the tensile studies, craze velocity measurements were made on these blends at  $-20^{\circ}$ C. Samples of blends containing 0-5 wt % PB were examined in the same fashion as previously described.<sup>4</sup> Craze lengths were measured photographically as a function of time, and examples of the data are plotted in Figures 7 and 8. In Figure 7, a 1% PB/PS blend was crazed at  $-20^{\circ}\text{C}$  at three different stresses (28, 34, and 44 MPa). The slope of the craze length-time plot (equal to the craze velocity) increased with increasing stress. The effect of PB content on the craze velocity is shown in Figure 8, where the results obtained at an applied stress of 28 MPa at  $-20^{\circ}$ C are plotted. The slope of the length-time plot increased with PB content, i.e., there is a rise in the craze velocity with PB content



Figure 7 Craze growth for 1% PB/PS blends at -20°C as a function of applied uniaxial tensile stress.



Figure 8 Craze growth behavior of PB/PS blends at  $-20^{\circ}$ C and an applied stress of 28 MPa as a function of PB content.

at constant stress. Note that the data collected at 28 MPa and 1% appearing in both plots has been shifted down the y-axis in Figure 7 for better clarity.

The entire set of craze velocity results at  $-20^{\circ}$ C and the previously reported<sup>4</sup> results at  $23^{\circ}$ C are plotted in Figures 9 and 10. There is a similar trend for both sets of results, i.e., at a given stress, the velocity increases with increasing PB content. It was necessary to apply a higher range of stresses to achieve measurable craze growth in the subambient measurements than were previously needed at room temperature (20-55 MPa vs. 10-40 MPa) to over-



**Figure 9** Craze velocity dependence on applied tensile stress for PB/PS blends containing varying weight percents of polybutadiene (2600 g/mol): ( $\Box$ ) 0% PB; ( $\blacktriangle$ ) 1% PB; ( $\diamondsuit$ ) 3% PB; ( $\blacksquare$ ) 5% PB. The solid lines represent the best fit to the data. T: 23°C.



**Figure 10** Craze velocity dependence on applied tensile stress for PB/PS blends containing varying weight percents of PB (2600 g/mol): ( $\Box$ ) 0% PB; ( $\blacktriangle$ ) 1% PB; ( $\diamondsuit$ ) 3% PB; ( $\blacksquare$ ) 5% PB. The solid lines represent the best fit to the data.  $T: -20^{\circ}$ C.

come the substantial rise in plastic resistance that governs the kinetics of drawing of craze tufts at the lower temperature. Apart from a different scaling effect resulting from the plasticization, these measurements are similar to the craze growth behavior reported by Argon and Salama<sup>9</sup> in PS homopolymer at  $-20^{\circ}$ C.

The craze velocities at  $-20^{\circ}$ C were 1–2 orders of magnitude lower than the room temperature values; the data for the 3% blend at  $-20^{\circ}$ C lay directly on the best fit of the room temperature data for homo PS. In other words, 3 wt % of PB produces a plasticization effect that directly compensates for a reduction in temperature of 43°C in homo PS. Consistent with this observation is the fact that the 5% results at  $-20^{\circ}$ C fall between the room-temperature data for the 1 and 3% blends. These observations allow making some crude estimates of the amount of required PB plasticizing the crazes in the blends to achieve levels of toughness at low temperature similar to those at room temperature. The calculation is based on the presumption that all crazes growing at a given velocity are experiencing a similar local environment (a "local effective temperature" or chain mobility). To raise the local effective temperature of the plasticized crazes in the 3% blend at  $-20^{\circ}$ C sufficiently so that their craze velocities are commensurate with those of PS at room temperatures, the craze matter must contain about 27% dissolved PB.<sup>3</sup> Clearly, this is the amount of sorbed PB present locally in the craze borders after the PB

in the pools has drained out onto the craze surface and is diffused into the craze surface during the craze tuft drawing process; the bulk of the material still contains 0.4 wt % soluble PB and 2.6% insoluble PB that remains in pools not contacted by the crazes.<sup>4</sup>

Superposition of the data from the two temperature regimes leads to another interesting observation concerning the expected mechanical properties of the blends at low temperatures: The fact that the 3% (-20°C) blend data lay on the roomtemperature data for homo PS suggests that the mechanical behavior of these two systems would be similar. Likewise, the 5% ( $-20^{\circ}$ C) blend should exhibit stress-strain behavior similar to a 2% blend at room temperature. Comparison of the results in Figures 2-4 supports these statements. The 3% $(-20^{\circ}C)$  blend showed little signs of toughening through localized plasticization, evidenced by a strain-to-fracture essentially identical to that of pure PS at room temperature. The 5%  $(-20^{\circ}C)$  blend had the same value for the strain-to-fracture as that of the 2% blend at 23°C. These results point out the strong dependence of the macroscopic mechanical behavior of this system on the localized craze kinetics.

#### **Comparison with Model**

In a previous publication on craze velocities in PB/ PS blends,<sup>4</sup> the experimental craze velocities obtained at room temperature were compared with an asymptotic model that described the effect of PB content on the stress dependence of the craze velocity.<sup>‡</sup> The model is based on the well-known Taylor meniscus instability mechanism and describes the repeated breakup and formation of craze tufts at the tip of a growing craze.<sup>10,11</sup> The modification of the model to account for the plasticizing action of the low molecular weight diluent has been described in detail elsewhere.<sup>4,6</sup> The dependence of the craze velocity, v, on the volume fraction *f* of phase-separated diluent is written as<sup>4,6</sup>

$$\mathbf{v} = \frac{D}{\sigma_{\infty}\lambda'} \exp\left\{-\frac{B}{kT}\left[1\right] - \left(\frac{\sigma_{\infty}\lambda'}{\hat{Y}_{0}\exp\left(-\beta_{2}\left(\nu_{c} + \frac{16af\sigma_{\infty}}{3\pi^{2}\alpha C}\right)\right)}\right)^{5/6}\right]\right\}$$
(1)

where  $\lambda' = \lambda_n / [1 + Y_h(\lambda_n) / Y_0]$ ,<sup>6</sup>  $Y_h$  is the orientation hardening component of the plastic resistance at the craze extension ratio  $\lambda_n$ , and  $Y_0$  is the initial yield strength. In eq. (1), D is defined as<sup>12</sup>

$$D = \frac{9\pi^2 n \chi \dot{\epsilon}_0}{(1+2n)2^{(1-n)}}$$
(2)

where  $\chi$  is the surface energy of pure PS;  $\dot{\epsilon}_0$ , a preexponential frequency factor in the plastic strain rate expression; and n, a plastic strain rate exponent. Additional parameters in eq. (1) are the athermal plastic resistance,  $\hat{Y}_0$ , which is a unique function of the shear modulus and Poisson's ratio of the matrix material;  $v_c$ , which represents the amount of soluble diluent in the matrix; a, the diameter of the diluent pools; C, a constant based on the product of the craze tuft diameter and the applied stress;<sup>6</sup> and  $\sigma_{\infty}$ , the far field tensile stress. The two unknown parameters from the original craze model for unmodified glassy polymers, B and  $\lambda'$ , were found from comparison of the model to craze velocity data collected for pure PS.<sup>4</sup> The remaining parameters,  $\beta_2$ and  $\alpha$ , which were introduced to account for the plasticizing behavior of the PB, were determined from measurements of the craze flow stresses of the blends. The expressions used to find these latter parameters are written as<sup>6</sup>

$$\frac{\sigma_c}{\sigma_{0c}} = \exp\left[-\left(\frac{16\beta_2 a \sigma_{0c}}{3\pi^2 \alpha C}\right) f\left(\frac{\sigma_c}{\sigma_{0c}}\right)\right] \quad f \ge 0 \quad (3)$$

The previous expression is for blends that contain phase-separated diluent pools. For homogeneous blends, in which f = 0 and  $\nu < \nu_c$ , the craze flow stress has a much simpler expression:<sup>6</sup>

$$\frac{\sigma_c}{\sigma_0} = \exp(-\beta_2 \nu) \quad 0 \le \nu \le \nu_c, \quad f = 0 \quad (4)$$

In these expressions,  $\sigma_0$  is the craze flow stress of pure PS, and  $\sigma_{0c}$ , the flow stress of the blend at the solubility limit.

A previous paper<sup>4</sup> described how the two parameters,  $\beta_2$  and  $\alpha$ , were determined from comparison of eqs. (3) and (4) to the craze flow stress found at varying PB contents (Fig. 2). As can be seen in Figure 2, the craze flow stress data collected at  $-20^{\circ}$ C did not decrease with PB modification. It was therefore not possible to determine  $\beta_2$  and  $\alpha$  at  $-20^{\circ}$ C. However, we have pointed out previously<sup>4</sup> that  $\beta_2$  and  $\alpha$  will depend on the strain rate. As strain rate and temperature are related, it is reasonable to

<sup>&</sup>lt;sup>1</sup> The model assumes that the time for the diluent sorption into the craze surfaces is negligible in comparison with the time to draw the craze tufts.

use the same values of  $\beta_2$  and  $\alpha$  as were previously found, namely, 13 and 2.2. To complete the model, the two remaining parameters, B and  $\lambda'$ , were set to their measured values of 18.8 kcal/mol and 0.64, as determined from craze velocity measurements on pure PS at  $-20^{\circ}$ C. The parameters for comparison of the model to the data at  $-20^{\circ}$ C are shown in Table I.

The PB content in the model was set according to the amount of phase-separated PB and soluble PB (as the densities are close to 1, weight fraction and volume fraction are used interchangeably), then compared with the experimental craze velocities for the PB/PS blends at  $-20^{\circ}$ C as a function of applied stress. These relationships are shown in Figures 11(a-d) along with the room-temperature results. The results for the  $-20^{\circ}$ C system were in very good agreement with the experimental data; the correlation between the theoretical results and the experimental data was much better than for the case of the room-temperature measurements. For both sets of test conditions, however, the model deviated from the experimental data as PB content increased.

In the previous article,<sup>4</sup> the lack of good agreement of the model with the experimental craze velocities was attributed to an underestimation of the amount of diluent that participates in the localized plasticization phenomenon in the region of a growing craze. The fact that the model compares better to the data obtained at  $-20^{\circ}$ C supports this attribution, as less PB would be able to spread and diffuse into the craze matter due to decreased mobility at these reduced temperatures. Thus, the amount of PB in the craze matter predicted by the model would be closer to the conditions at  $-20^{\circ}$ C than those found at  $23^{\circ}$ C.

Table I Parameters for Craze Velocity Model at  $-20^{\circ}C$ 

$\hat{Y}_0$	261 MPa <sup>a</sup>
а	$0.04 \ \mu m^b$
C	$2.5  imes 10^{-7} \mathrm{MPa} \cdot \mathrm{m^{c}}$
x	$5 imes 10^{-2}~{ m J/m^{2}d}$
n	0.05 <sup>d</sup>
$\epsilon_0$	$10^{13} \mathrm{s}^{-1 \mathrm{d}}$
$\beta_2$	13.5 <sup>b</sup>
α	$2.2^{\mathrm{b}}$
В	10 kcal/mol <sup>b</sup>
λ'	0.6 <sup>b</sup>

<sup>a</sup> After Schwier et al.<sup>13</sup>

<sup>b</sup> Determined experimentally.

<sup>c</sup> After Brown et al.<sup>14</sup>

<sup>d</sup> After Argon et al.<sup>12</sup>

Comparison of the craze velocity data obtained at  $-20^{\circ}$ C with the room-temperature results allowed calculation of the amount of PB dissolved in the craze matter based on the relative reduction in  $T_{e}$ . This calculation suggested that 27 wt % PB was dissolved locally at the craze borders in a 3% blend at -20°C. The model, which utilizes a stress-dependent soluble fraction of diluent, predicts a soluble PB content between 2.4 and 4.4 wt % for a stress range from 20 to 40 MPa. Although the calculation performed on the experimental results was based on a simplified analysis, the large discrepancy between the predicted soluble PB fraction and actual PB fraction is too large to be accounted for by the assumptions made in this analysis. It is evident that the parameters that describe the amount of soluble PB in eq. (1) are not an accurate representation of what actually occurs and therefore need to be reevaluated.

Further insight into the localized plasticization phenomenon was established with the spreading rate studies presented in this work. In the derivation of the asymptotic model, the transient processes of spreading and diffusion were ignored, with the assumption that these processes occurred on a time scale that is small compared with the craze propagation rate. The spreading results shown in this work demonstrated that the spreading rate is of the same order of magnitude as that of the craze velocities and must therefore be a rate-limiting step for some test conditions. To account for this process, as well as the temperature dependence of the spreading rate, the viscosity of the diluent should be incorporated into the model. Qin et al.<sup>5</sup> demonstrated that the toughness of PB/PS blends with PBs of varying viscosities could be normalized according to the difference in glass transition temperature (a measure of the viscosity of the PB) of the PB and the test temperature, which suggests a WLF-type dependence that must relate to the rate of advance of the Case II diffusion front into the craze surfaces.

## **CONCLUSIONS**

The role of temperature in the tensile toughness of polystyrene/polybutadiene blends was ascertained as part of the continuing investigation of the localized plasticization phenomenon. Blends of polystyrene containing a few weight percent of phase-separated low molecular weight polybutadiene, which showed significant levels of toughness at room temperature, lost all toughness when tested at  $-20^{\circ}$ C. Craze velocities obtained at  $-20^{\circ}$ C in these blends



were 2 orders of magnitude lower than those found at 23°C, which points to the strong dependence of the observed mechanical properties of these blends on the crazing behavior. Comparison of the model describing the stress-dependent craze velocity with the low-temperature craze velocity data further indicates the need to reevaluate the parameters that predict the amount of PB sorbed into the region of a growing craze. This research was supported by NSF/MRL through the Center for Material Science and Engineering at M.I.T. under Grant No. DMR-90-22933.

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