A New Mechanism of Toughening Glassy Polymers. 2. Theoretical Approach

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ABSTRACT: A theoretical model is presented for the toughening of brittle glassy polymers by the controlled solvent crazing action of precipitated low molecular weight rubber diluents existing in the form of randomly dispersed small spherical pools. In this mechanism the central process is the increased sorption of the diluent under the deformation-induced negative pressure existing in a boundary layer on the craze periphery where the sorbed diluent produces substantial plasticization that significantly lowers the craze flow stress to prevent premature craze fracture. The resulting expressions for the reduction of the craze flow stress with increasing volume fraction of diluent are in excellent agreement with experimental measurements.

I. Introduction

The well-known problem of brittleness of flexible-chain glassy polymers in tension has in the past been dealt with in a number of ways, which have included uniaxial and biaxial orientation;[1] blending a component of an inflexible-chain polymer with greater craze resistance into a more brittle polymer;[2] and introducing compliant composite particles into the brittle polymer to enhance craze plasticity.[3] While all of these approaches are effective to some degree, they have drawbacks, in the limited shapes of the products to which they can be applied, in requiring substantial volume fractions of craze-resistant polymer or in compromising stiffness and optical properties, not to mention increasing the cost of the product. Recent studies of blending brittle homopolystyrene with very small concentrations of low molecular weight elastomeric components[4–6] have pointed to another very effective and hitherto unappreciated possibility of toughening a brittle polymer by controlled solvent crazing. In such studies Gebizlioglu et al.[4–6] have succeeded in substantially lowering the craze yield strength of high molecular weight PS by incorporation of a few percent of low molecular weight PB, which precipitates out in the form of tiny pools of diameters less than 0.2 μm. There is now overwhelming evidence that the liquid PB in these pools acts as a plasticizing agent under the prevailing negative pressures of the craze tip and craze borders to result in a greatly increased propensity for crazing at low stresses to avoid early craze fracture from extrinsic flaws.[7] The experimental evidence for this phenomenon has been presented in detail in an accompanying paper.[6] Here we provide the theoretical details of the mechanism of this novel process of toughening.

II. Theoretical Model

II.1. Toughening by Controlled Solvent Crazing. It is now well established that crazes in glassy polymers grow by an interface convolution process both ahead[8,9] and in thickness[10] and that the rate of growth is governed, under the prevailing stresses, by the strain rate dependent plastic resistance of the polymer.[8] A reduction of this plastic resistance by plasticization results in an increased velocity of craze growth.

Consider a volume fraction f of pools of a phase-separated plasticizing liquid phase in a brittle glassy polymer, in the form of randomly dispersed spherical "particles" of diameter a. Assume furthermore that a is sufficiently small so that when incorporated into a craze as a drained cavity, it constitutes a subcritical size flaw in the spongy craze matter. We now postulate that when a craze goes through a randomly distributed field of spherical pools of potential plasticizing agent, it will intersect these pools as a sampling plane, and the contents of the pools will drain onto the already produced surfaces of craze matter and solid polymer. This occurs preferentially along the tip of the craze where the advancing craze front samples the field of particles. If the plasticizing liquid is a low molecular weight PB with low viscosity and good wetting characteristics, it should effectively coat the multiple-convoluted concave surfaces of the craze matter and solid polymer at the craze tip. We assume that this occurs at a rate much faster than the rate of production of a new craze surface in a reference polymer under dry conditions (see Appendix I). Since the PB as a possible diluent of the PS is already in equilibrium with the latter as a separate phase, it should also be in equilibrium with the free surfaces of the craze that it coats, if these surfaces were stress free. (The PB wetting the concave surfaces of the craze must actually be under a mild capillary negative pressure, which, however, should be much less than the initial negative pressure due to thermal expansion misfit in the PB existing in the spherical cavities[11] prior to its drainage onto the craze surfaces.) Both at the tip as well as at the borders of a craze where the craze tufts are drawn out of the solid polymer, however, substantial levels of negative pressures exist in a narrow fringing layer. Under these conditions the equilibrium solubility of the PB in the stressed border regions of the craze must increase

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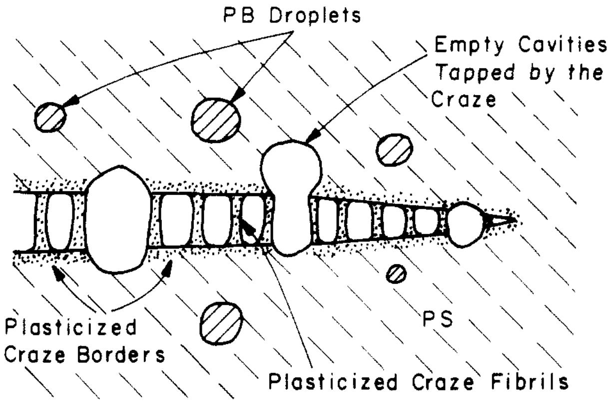

Figure 1. Schematic rendering of a craze moving through a field of encapsulated PB pools draining their contents onto the craze surfaces when tapped by the advancing craze.

by orders of magnitude, resulting also in some accompanying increase in diffusivity and reductions in viscosity and plastic resistance, provided that the negative pressure could be sustained by an external agency.

Thus, the PB drained from the pools onto the surfaces of the craze that taps into the PB pools should be very rapidly sorbed into a boundary layer of the craze borders, until the supply of free PB diluent on the surfaces is depleted or until the deformation-induced negative pressure is totally relaxed. Most likely, these processes, which involve case II diffusion in a spatially varying stress field, are exceedingly complex. At the end, however, when the available surface coverage of the PB diluent is entirely sorbed into the surface layer of the craze borders, a boundary layer of strongly plasticized polymer is created that can be stretched out easily and converted into craze matter as depicted in Figure 1. Once conversion of the plasticized layer into craze matter is complete, the craze thickening should markedly slow down. This should result in rapidly growing thin crazes.

We will demonstrate in section II.2 that the very complex processes of sorption of the PB into the stressed surface layer should be completed at a rate much faster than the rate of deformation of the affected layer into stretched craze matter and that, therefore, the rate of craze growth is primarily governed by the rate of plastic deformation of the equilibrium sorbed layer.

We emphasize here that while the ease of craze growth through this mechanism is an important necessary condition for achieving toughness, it is also necessary to prevent premature fracture of the craze matter, starting from either entrapped inorganic particles or uncharacteristically large liquid rubber pools.

II.2. Mechanism of the Craze Flow Stress. When a craze plane extends across a field of randomly distributed spherical pools of PB diluent of average diameter a and volume fraction f in a background homopolymer matrix of high molecular weight PS, a thickness h of PB becomes available to coat the surfaces of the craze, where (see Appendix II)

$$h = \frac{16}{3\pi^2}af \tag{1}$$

While the PB is contained inside the spherical cavities of diameter a, it is under a substantial negative pressure resulting from the thermal expansion misfit between the PB and PS that results from their rather different coefficients of expansion, and the temperature difference (~75 °C) between T_g of PS and room temperature. This negative pressure is typically of the order σ = 34 MPa for

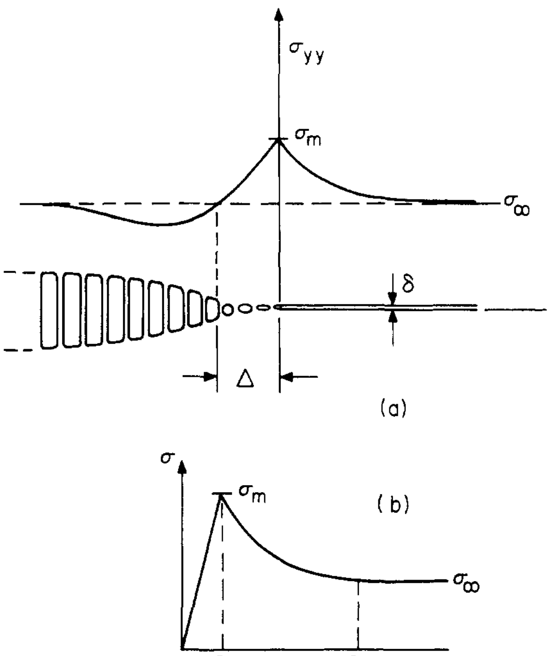

Figure 2. (a) Schematic rendering of tractions developed across a growing craze and (b) the associated developing craze microstructure within a process zone Δ under decreasing traction. Note the zone of traction depression behind the process zone Δ, which is thought to develop the necessary craze driving force.

a field of widely separated spherical particles.[11] The surrounding PS matrix is subjected to a slight complementary image pressure of $(f/(1-f))\sigma$. A small volume fraction ν_c of PB remains in solution in the matrix under these conditions. For a PB diluent of a molecular weight of 2.76 kg/mol the volume fraction (since the densities of PB and PS are closely similar, in this paper, we will not distinguish between weight and volume fraction) that remains in solution is typically of the order of (4.5–5.0) × 10^{-3}.[6]

When a craze traverses through the PS, it creates at its tip a cavitational process zone of extent Δ within which the interface convolution process produces craze matter starting with fully dense polymer at the furthest extremity of the zone where the traction reaches a maximum level of σ_m and ending up with an increment of just fully developed tufty craze matter under decreasing traction across the zone Δ as shown schematically in Figure 2. While the details of the process of craze tuft production in the zone Δ are too complex to fully describe, the net traction distribution across it has been measured by Lauterwasser and Kramer.[13] It can be argued by the similarity of this process to the one of heterophase cavitation that at the tip of the zone Δ the growing craze will concentrate a negative pressure σ given by[12] (see Appendix III)

$$\sigma = \frac{1}{3}\left[2(1+\nu_p)\frac{K_{IC}}{\sqrt{\pi\Delta}} + \sigma_\infty\right] \tag{2}$$

where K_{IC} is the critical local stress intensity that is associated with the processes in the zone Δ that move it forward in a self-similar manner, and ν_p is Poisson's ratio of the glassy polymer. The K_{IC} is balanced by a craze tip driving force, $K_{I\text{-tip}}$, that results from a characteristic traction dip at the front of the craze body, depicted in Figure 2a. Presently there is inadequate understanding of the complex three-dimensional processes of deformation in the process zone Δ to determine the extent and magnitude of the characteristic traction dip that furnishes the driving force $K_{I\text{-tip}}$. Fortunately, this deficiency is not critical since $K_{\text{I-tip}}$ ($=K_{\text{IC}}$) should develop at the far end of the process zone Δ a net traction $\sigma_m - \sigma_\infty$ given by

$$\sigma_m - \sigma_\infty = K_{\text{I-tip}}/\sqrt{\pi\Delta} \qquad (3)$$

We have from eqs 2 and 3 for the negative pressure σ at the tip of the process zone Δ where the craze matter production begins

$$\sigma = \frac{1}{3}[2(1 + \nu_p)(\sigma_m - \sigma_\infty) + \sigma_\infty] \qquad (4)$$

Lauterwasser and Kramer's[13] measurements for crazes have indicated that the traction maximum, σ_m, exceeds the far-field stress, σ_∞, usually by a small factor, α_s, and that the far-field stress, σ_∞, also acts across the main craze body (Figure 2), giving a negative pressure concentration, σ/σ_∞, at the traction peak of

$$\sigma/\sigma_\infty = (1/3)[2(1 + \nu_p)(\alpha_s - 1) + 1] \qquad (5)$$

where $\alpha_s = 0(1.15 - 1.20)$ is typical.[13] This gives

$$\sigma = 0.5\sigma_\infty \qquad (6)$$

Recognizing that the far-field crazing stress σ_∞ is typically about 35 MPa at room temperature in glassy homo-PS, having a tensile yield strength, Y, of the order of 85–90 MPa, we note that the level of negative pressure at the border of the process zone Δ is substantial.

While the above-mentioned negative pressure concentration at the border of the process zone where the advancing craze taps into the pools of PB diluent is of importance, there are also concentrations of negative pressure all along the craze border where in a homopolymer additional growth of craze tufts occurs by drawing of solid polymer out of the craze wall. A full satisfactory solution of the distribution of stresses in the active drawing region of the root of the craze tuft is presently unavailable for a rate-dependent plastic response characteristic of a glassy polymer. However, a very satisfactory solution of the tuft drawing problem modeling the glassy polymer as an elastic, rate-independent plastic solid, undergoing three-dimensional orientation hardening according to a three-chain rubber network model has been obtained by Bagepalli[14] (see Appendix IV). The principal results of his finite-element solution for the distribution of negative pressure σ in the drawing region of the tuft and the principal stresses σ_r, σ_θ, and σ_z together with σ across the fully drawn stem of the tuft are given in Figures 3 and 4, respectively, in units of the tensile yield strength, Y. These figures show that the inhomogeneous drawing process results in even more substantial levels of negative pressure spread along the reentrant concave border zone between adjoining tufts and particularly high levels on the fully drawn surfaces of the craze tuft stem than what occurs at the craze tip zone.

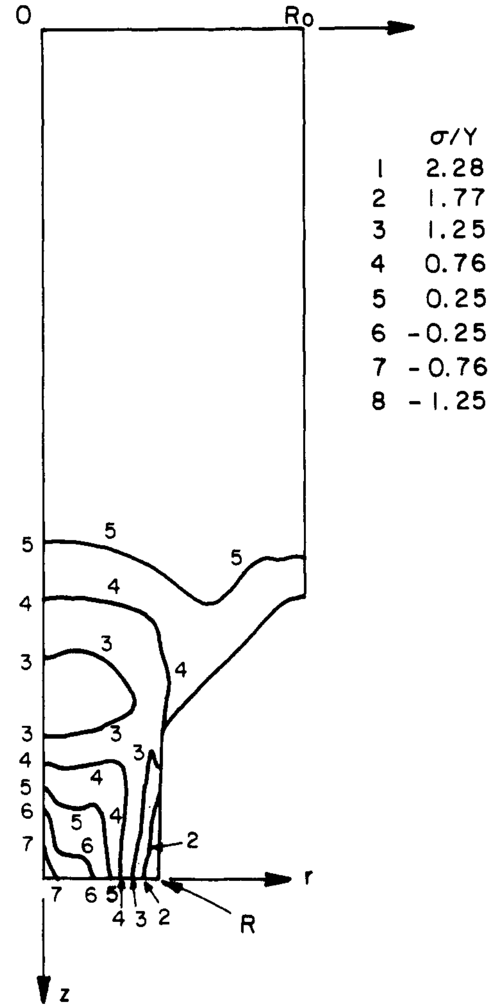

Figure 3. Distribution of negative pressure (and pressure in the root and stem regions of a typical craze tuft being drawn out of a half-space (after Bagepalli,[14] courtesy of MIT).

The presence of a negative pressure acting on a glassy polymer such as PS has important effects on the solubility of a diluent in the stressed glassy polymer. Thus, if the volume fraction of a diluent in solution in the glassy polymer is ν_0 in a standard reference state at vanishing negative pressure and absolute temperature T, then the solubility, ν, of the diluent under a negative pressure σ is given by[7,15]

$$\nu/\nu_0 = \exp(\sigma M/\rho RT) \qquad (7)$$

where M is the molecular weight of the diluent (PB in this case), ρ is its density, and R and T have their usual meaning. Thus, as a growing craze approaches a material element containing pools of PB diluent and is subjected to negative pressure, the PB will have a tendency to go back into solution. The rate of sorption of the PB diluent into the PS depends on the rate of diffusion of the former into the latter. This diffusion, which is accompanied by swelling that radically alters the initial negative pressure which is responsible for the increased solubility, is a complex case II diffusion process.[15] The interaction of the diluent PB with the plastically deforming PS subjected to negative pressure is made even more complex when the craze taps into the pools of PB and drains their contents onto the stressed surfaces of the craze in the process zone. In view of this complexity we will deal with this problem only approximately. We start out by noting that the required distance of penetration of the diluent is only of the order of the craze tuft diameter, d, over which an enhanced negative pressure exists. Thus, a proper estimate of the sorption time, t_s, of the diluent into the craze surfaces under the local negative pressure should be roughly

$$t_s = d^2/D \qquad (8)$$

where D is the diffusion constant of the PB in the region of enhanced negative pressure.

The crucial information on the diffusion constant, D, for PB (trans- or cis-1,4) into PS is not known. We can, however, obtain some estimates of D from several considerations that will furnish bounds to the required information. As a lower bound for D we might assume the PB-3K to be similar to a PS of comparable molecular weight at some effective temperature T_{eff} above T_g, where T_{eff} can be estimated from observations of the onset of

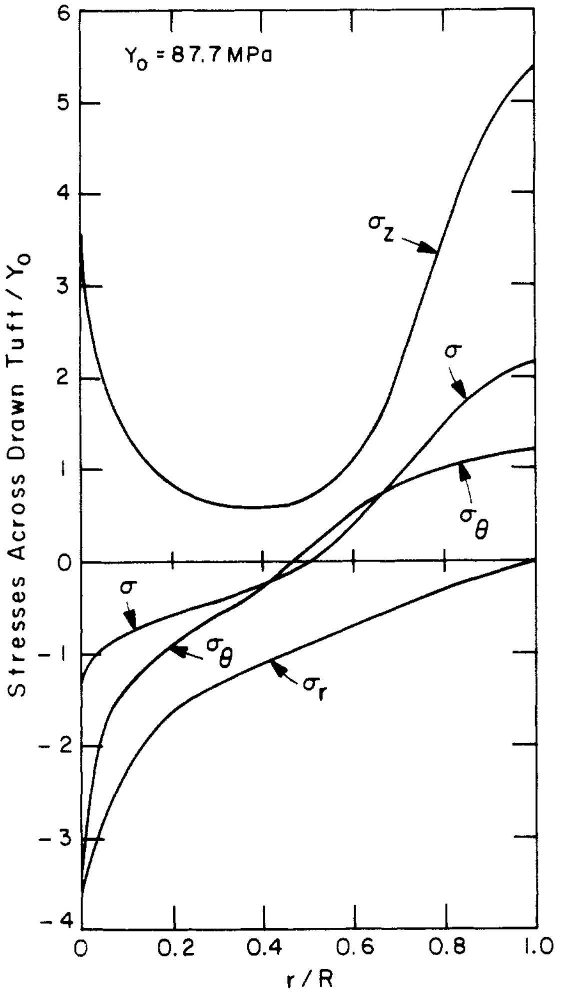

Figure 4. Distribution of individual stress components acting in a plane across the fully developed stem of a drawing craze tuft (after Bagepalli,[14] courtesy of MIT).

disentanglement during crazing, to be ~120 °C.[16] From the experiments of Green[17] it is known that the diffusion constant, D, for PS of a molecular weight M_w = 2.5 kg/mol in high molecular weight PS is between 10^{-13} and 10^{-12} cm^2/s at 120 °C. We consider this value as a lower bound to D. We can obtain another estimate from considerations of diffusion of PB molecules of molecular weight 2.5 kg/mol in PB, which for these low molecular weights should be by Rouse diffusion, for which the diffusion constant is

$$D = \frac{M_0 kT}{\zeta_0 M} \tag{9}$$

Here M_0 and M are the molecular weights of a monomer and the polymer, respectively, kT have their usual meaning, and ζ_0 is the monomeric friction coefficient for polybutadiene, 1.8×10^{-7} dyn·s/cm at T = 298 K. We estimate the value of this diffusion constant, which we take to be an upper bound, to be $D = 4.4 \times 10^{-9}$ cm^2/s. With these two bounds we estimate the mean sorption time t_s of PB-2.76K into a depth $d \approx 2.75 \times 10^{-8}$ m to be between 1.7 ms and 7.5 s at room temperature (see Appendix I). Clearly, this range of uncertainty is too vast to reach clear quantitative conclusions. Since the PB of predominantly the 1,4 form is a very flexible molecule with a smaller cross-sectional area than PS of comparable molecular weight, we expect that the effective sorption time should be at least as short as the lower bound estimate given above which considers no effect of negative pressure. Clearly, in the presence of a substantial negative pressure, as we discuss below, the sorption time could be several orders of magnitude less than the lower bound estimate. Therefore, we will assume that the sorption time can be considered to be nearly instantaneous on the time scale of craze advance over craze tuft dimensions. In any event this is what the experiments imply.

If the PB coating of thickness h is sorbed into the stressed craze surfaces to a depth of αd (see Figure 3), a volume fraction ν of PB diluent becomes established in a time t_s in this boundary layer of thickness αd, which is simply

$$\nu = \frac{h}{h + \alpha d} \approx \frac{h}{\alpha d} \quad \text{for } h/\alpha d \ll 1 \tag{10}$$

where the coefficient α is not readily determinable by modeling in view of the very complex and interactive actions of combined sorption and plastic drawing. It will be used as an adjustable constant in comparing model predictions with experiments. Making use of the fundamental result of the interface convolution mechanism of craze matter production, which states that the product of the craze traction, σ_∞, and the craze tuft diameter, d, is a constant, i.e.

$$\sigma_\infty d = C \tag{11}$$

and using eq 1, we have

$$\nu = \frac{16}{3\pi^2} \frac{af\sigma_\infty}{\alpha C} \tag{12}$$

On the other hand, the effect of sorbed diluent on the viscosity, η, and the terminal plastic resistance, $\hat{Y}$, of a glassy polymer is expected to be[15,19]

$$\eta = \eta_0' \exp(-\beta_1 \nu) \tag{13}$$

$$\hat{Y} = \hat{Y}_0 \exp(-\beta_2 \nu) \tag{14}$$

where the coefficients β_1 and β_2 in the exponents are best determined experimentally, and η_0' and $\hat{Y}_0$ are, respectively, the standard state, zero pressure, steady-state viscosities, and terminal plastic resistances of the pure polymer at the temperature of interest. The standard steady-state viscosity, η_0', can be obtained from an appropriate WLF or Arrhenius shift. This viscosity, however, is not of interest here. Of more interest in craze growth is the terminal plastic resistance, $\hat{Y}_0$, which is defined as[8]

$$\hat{Y}_0 = 0.133\mu/(1 - \nu_p) \tag{15}$$

where μ is the shear modulus and ν_p is Poisson's ratio. From the crazing theory of Argon and Salama[8] the velocity of crazes growing through the sorbed layers can now be stated directly as[12]

$$v = D_1 \exp\left[-\frac{B}{kT}\left(1 - \left(\frac{\sigma_\infty \lambda'}{\hat{Y}}\right)^{5/6}\right)\right] \tag{16}$$

where

$$\lambda' = \frac{\lambda_n}{(1 + Y_h(\lambda_n)/Y_0)} \tag{17}$$

and Y_0 is the initial tensile yield strength of the unoriented glassy polymer, and $Y_h(\lambda_n)$, the orientation hardening component of the plastic resistance at the terminal craze extension ratio, λ_n. In eq 16 above B is a characteristic activation energy for a unit conformational transition event in a plastically relaxing cluster. The magnitudes of B have been measured for a series of glassy polymers by Argon and Bessonov,[20] and their adaptation to the crazing problem has been discussed by Argon and Salama.[8] Finally, D_1 is a preexponential factor dependent on surface free energy and applied stress, which, however, will be normalized out and is of no concern.

On kinematical grounds the craze strain rate, $\dot{\epsilon}_c$, must be[12]

$$\dot{\epsilon}_c = b_c \rho_c v \qquad (18)$$

where b_c is the product of the primordial craze thickness, b_p, and the effective uniaxial transformation strain, ϵ^T $(=\lambda_n - 1)$, of a craze, and ρ_c is the total active craze front length per unit volume, giving together with eq 16

$$\dot{\epsilon}_c = b_c \rho_c D_1 \exp\left[-\frac{B}{kT}\left(1 - \left(\frac{\sigma_\infty \lambda'}{\hat{Y}}\right)^{5/6}\right)\right] \qquad (19)$$

In practice, when the craze strain rate equals the imposed machine strain rate, $\dot{\epsilon}$, the evolved far-field stress, σ_∞, becomes the craze flow stress, σ_c, which gives from eqs 12, 14, and 19

$$\sigma_c = \frac{\hat{Y}_0 A}{\lambda'} \exp(-\beta_2 \nu_c) \exp\left(-\left(\frac{16}{\pi^2}\frac{\beta_2 a \sigma_c}{3\alpha C}\right) f\right) \qquad (20)$$

where

$$A = \left[1 - \frac{kT}{B} \ln\left(\frac{b_c \rho_c D_1}{\dot{\epsilon}}\right)\right]^{6/5} \qquad (21)$$

and ν_c is the PB diluent remaining in homogeneous solution in the PS at the solubility limit. Recognizing that

$$\sigma_{0c} = \frac{A \hat{Y}_0}{\lambda'} \exp(-\beta_2 \nu_c) \qquad (22)$$

is the craze flow stress of the reference material at the solubility limit of the diluent, we write the basic equation for the normalized craze flow stress, σ_c/σ_{0c}, for the range $f \geq 0$ as

$$\frac{\sigma_c}{\sigma_{0c}} = \exp\left[-\left(\frac{16}{\pi^2}\frac{\beta_2 a \sigma_{0c}}{3\alpha C}\right) f \left(\frac{\sigma_c}{\sigma_{0c}}\right)\right] \qquad f \geq 0 \qquad (23)$$

When the PB diluent is all in homogeneous solution, i.e., $f = 0$, and $\nu < \nu_c$, the reduction of the craze flow stress with diluent concentration in solution can be described more directly by eqs 14 and 19 alone, giving

$$\sigma_c/\sigma_0 = \exp(-\beta_2 \nu) \qquad 0 \leq \nu \leq \nu_c; \quad f = 0 \qquad (24)$$

where

$$\sigma_0 = (\hat{Y}_0/\lambda')A \qquad (25)$$

is the reference craze flow stress of the pure homo-PS.

II.3. Craze Velocity. With use of the developments of section II.2 and with comparison of the predictions with experimental information on the decrease of the shear modulus with PB diluent in solution and the decrease of the craze flow stress with PB diluent, both in the range where the diluent is all in solution and the range where it has precipitated out at a volume fraction f of spherical pools of diameter a, expressions can be given for the craze velocity in terms of the two adjustable constants α and β_2.

Thus, the craze velocity when all diluent is in solution (i.e., $0 \leq \nu \leq \nu_c$) is

$$\nu = D_1 \exp\left[-\frac{B}{kT}\left(1 - \left(\frac{\sigma_\infty \lambda'}{\hat{Y}_0 \exp(-\beta_2 \nu)}\right)^{5/6}\right)\right] \qquad (26)$$

and when PB diluent has precipitated out in the form of pools of diameter a and when a volume fraction f is made up of encapsulated free diluent in addition to the concentration ν_c remaining in solution ($f \geq 0$), the craze velocity is

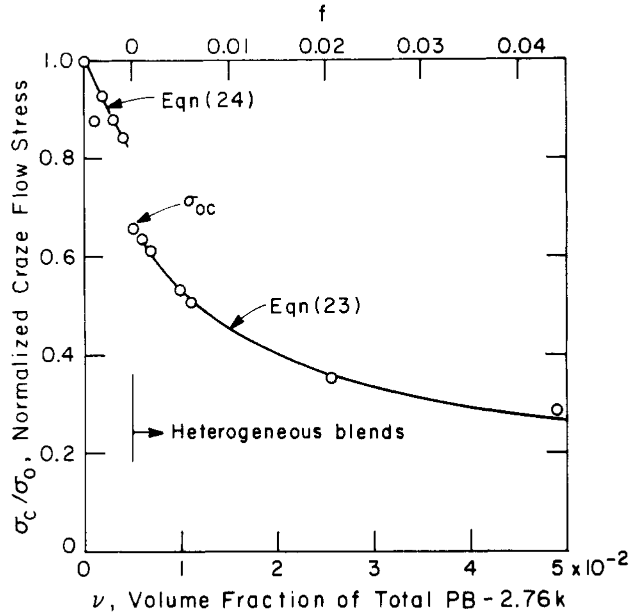

Figure 5. Calculated decreases of crazing stresses on both homogeneous and heterogeneous PB/PS blends, σ_0 is the reference craze flow stress of pure PS, while σ_{0c} is the craze flow stress of the reference material at the solubility limit of the diluent.

$$v = D_1 \exp\left[-\frac{B}{kT}\left(1 - \left(\frac{\sigma_\infty \lambda'}{\hat{Y}_0 \exp\left(-\beta_2\left(\nu_c + \frac{16}{3\pi^2}\frac{af}{\alpha d}\right)\right)}\right)^{5/6}\right)\right] \qquad (27)$$

In eq 27 d is the actual diameter of the craze matter tuft, and σ_∞ is the far-field tensile stress driving the growth of the crazes.

III. Comparison with Experiments

We compare first the decrease of the craze flow stress in the region of homogeneous blends of high molecular weight polystyrene HH-101 PS ($\bar{M}_w$ = 268 kg/mol; $\bar{M}_n$ = 112 kg/mol) with PB diluent ($\bar{M}_w$ = 2.76), of total diluent volume fraction ν, less than $\nu_c = 0.005$ at the solubility limit. Here the craze yield stress of pure homo-PS was found to be $\sigma_0 = 37.5$ MPa by Gebizlioglu et al.,[6] with the decrease of the craze yield stress with increasing ν given by Figure 9 of the accompanying paper.[6] When the data point for $\nu = 0.001$, which is clearly anomalous, is ignored, the rest of the decreasing trend of σ_c can be readily fitted to eq 24 by a choice for $\beta_2 = 43.6$. With this choice the trend predicted by eq 24 is shown in Figure 5.

For the heterogeneous blends we make the assumption that the diameters of all the PB diluent pools remain constant at a value $a = 0.2$ μm. (This is not exactly so for blends with f exceeding 0.006 where larger diameter PB pools are observed.) Furthermore, we take the SAXS constant $C = 2.5 \times 10^{-7}$ MPa·m as determined by Brown et al.[7] and the reference flow stress of the heterogeneous blends at concentrations $f \rightarrow 0$ to be $\sigma_{0c} = 24.5$ MPa, and, of course, $\beta_2 = 43.6$ as determined from the homogeneous blends. We then obtain the best choice for the proportionality constant α, which gives the effective range of sorption of the free PB diluent into the craze surfaces.

The best fit of the data to eq 23, shown in Figure 5, is achieved through a choice of $\alpha = 8.74$. This indicates that the depth of penetration of the diluent is larger than expected and that on this basis it must be concluded that the craze tufts are entirely affected by the diluent. Even so, the value of α is too large for comfort. We observe, however, that α would decrease sharply if all of the diluent in the pores is not available and that part of it remains physically trapped in the pores. This is likely since completely empty pores are not observed in TEM micrographs where crazes go through PB pools. Nevertheless, the conclusion that the diluent must have affected the entire craze tuft is fully consistent with the interpretation of the SAXS measurements of Brown et al.[7] and is also discussed in the accompanying paper.[6]

With the values of α and β_2 being determined, the rate of growth of individual crazes under an applied stress σ_∞ can be determined from eqs 26 and 27 with the best choices for the other parameters being taken over from other direct craze growth measurements reported by us[8,12,21] for homopolymers and diblock copolymers. These values are $B = 25.3$ kcal/mol and $\lambda' = 1.85$ (for homo-PS). The effective craze tuft diameter, d, can be obtained from eq 11 for the experimentally determined factor C given above, and the other relevant factors can be taken as $\nu_c = 5 \times 10^{-3}$ and $\hat{Y}_0 = 0.18$ GPa, for the blends under discussion, with D_1 considered to be uncertain and adjustable. Apart from some preliminary measurements reported in ref 6, there are at present insufficient direct measurements for growth of individual crazes by this mechanism to be compared with the predictions of eqs 26 and 27. Since the blends are nearly transparent, such measurements are readily possible and are presently being carried out.

IV. Discussion

The model for craze growth by controlled solvent crazing presented here is consistent with all presently available experimental results. The plasticization that results from the increased sorption of the low molecular weight PB diluent into the craze surfaces is a highly interactive and complex process. The present development that we have provided is in the nature of a model-inspired dimensional analysis. On the basis of the excellent fit of the model to experimental results, we conclude that the process should operate in a very wide range of strain rates and provide effective toughening since the local sorption appears to be very rapid. The rate dependence of the overall deformation should then be that of plastic flow in the equilibrium sorbed state of the polymer. As we discuss in Appendix III, for the mechanism to become inoperative, the craze advance time over a distance of a tuft diameter must become shorter than the local sorption time. The typical craze velocities in diblock copolymers strained at the usual rates of 10^{-2} s^{-1} are estimated to be 10^{-6} m/s.[21] As is demonstrated in Appendix I the peak sorption limited craze velocity is estimated to be 6.5×10^{-4} m/s, giving, by direct scaling upward, a sorption limited peak strain rate of 6.5 s^{-1}. While this rate is quite attractively high it is, nevertheless, 3 orders of magnitude less than what is found in a Charpy impact experiment of an unnotched bar.

Finally, it is interesting to note that the plasticization that we are discussing here is limited by the supply of the PB in the pools. When crazes propagate through the polymer and have tapped all the PB pools, there can be no further plasticization. This should result in a finite average cutoff plastic strain, $\epsilon_{\text{cut-off}}$, which we can estimate readily. When a planer craze sweeps through the volume, it will touch and drain PB pools in a zone of approximately two pool diameters. Thus, the minimum distance between plasticized crazes can be no less than one pool diameter. If the primordial polymer slab thickness that gives rise to one craze is h_p and the uniaxial transformation strain characteristic of a craze is ϵ^T, then the limiting craze plasticity strain by the plasticization mechanism is

$$\epsilon_{\text{cut-off}} = h_p\epsilon^T/l_c = h_p\epsilon^T/a \qquad (28)$$

Taking the primordial slab thickness of a craze to be 10 nm, the transformation strain to be 4 (for PS), and the PB pool diameter to be 0.2 μm, we find that the cut-off strain is of the order of 0.2, or just about what was actually obtained in the experiments. We note further that the volume fraction of diluent PB in the form of the pools does not enter into this consideration. It affects merely the plastic resistance of the craze matter as given by eqs 20 and 23.

It must be emphasized, however, that the toughness of a glassy polymer depends as much on avoidance of fracture as on plasticization. In fact as is discussed in the companion paper, the effectiveness of the present mechanism is predicated upon maintaining the sizes of the PB diluent pools smaller than what would constitute a supercritical flaw in craze matter. In the preliminary experiments reported by Gebizlioglu et al.,[6] this limitation appears with a volume fraction of about 6×10^{-3} of precipitated free PB diluent when pools of diameters in the range of 1.0 μm or over are encountered. Clearly possibilities should exist in controlled precipitation to retain the pool size small enough to avoid premature fracture. This has indeed been achieved now and will be reported elsewhere.

It is interesting to note that the mechanism of local plasticization discussed here through the solvent crazing action of the low molecular weight PB also satisfactorily explains a number of earlier anomalous effects. It had been noted by Gebizlioglu et al.[4] that the remarkably low craze flow stresses in blends with concentric spherical shell (CSS) particles that were obtained by initiating a morphological transformation in KRO-1 Resin with the addition of low molecular weight PB ($M_w = 3$ kg/mol) could not be explained by improved craze-initiating potency due to the increased compliance of the CSS particles.[11] It was noted furthermore that with the expected levels of active craze front density per unit volume in these blends the low flow stress could also not be accounted for from the known kinetics of craze growth in pure homopolystyrene.[22] Other supporting experiments on these blends, which exhibited very large amounts of rubbery type strain recovery in extensively crazed samples, indicated that the craze matter at room temperature behaved as if it were close to its T_g.[23] It is now clear that the PB-3K that had associated itself with the KRO-1 Resin particles in these blends was not bound into that block copolymer and could apparently drain out onto the crazes that initiated from the compliant CSS particles, resulting in the same plasticization process discussed in this paper. That the PB-3K was not permanently linked into the KRO-1 Resin was also indicated by the reprecipitation of PB into pools inside the composite particles once the added PB-3K component exceeded a certain volume fraction.

Finally, the analysis that has led to eqs 23 and 24 had assumed that the sorption of the 1,4-PB-2.76K is nearly instantaneous on the time scale of craze advance. While this was compatible with the upper bound estimate of the diffusion constant and its further increase under a negative pressure, it would be far from being so if the lower bound estimate of the diffusion constant is considered. To reach more realistic conclusions, the case II diffusion constant of low molecular weight PB in PS needs to be determined, particularly in the presence of a negative pressure. Such measurements are now being carried out.

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Appendix I. Sorption of PB into PS

In the case II sorption problem of PB into PS of interest here, the actual penetration of the sorbed species producing swelling is preceded by a diffusion precursor. The zero-pressure diffusion constant, D, for this precursor process was given by eq 9 in the text.

Considering that the sorption of PB is driven by the increased solubility of the PB in PS in the regions of the craze microstructure where there are locally substantial levels of deformation-induced negative pressure, we conclude that such enhanced sorption should therefore be limited to a depth equal to the wavelength of the craze microstructure. Then the characteristic time t_s for sorption should be

$$t_s = d^2/D \qquad \text{(AI-1)}$$

The relevant diffusion constant D of PB-2.76K in PS at room temperature is taken to be near the Rouse diffusion constant of PB-2.76K in PB, which in turn is estimated to be $D = 4.4 \times 10^{-9}$ cm^2/s from eq 9 of the text.

Thus, for a craze microstructure formed under a stress of 20 MPa and with use of the measured SAXS products $C = \sigma_\infty d$ of 5.5×10^{-7} MPa·m, we obtain a craze tuft dimension $d = 2.75 \times 10^{-8}$ m and then finally from eq AI-1 for the characteristic sorption time $t_s = 1.7 \times 10^{-3}$ s.

While this characteristic sorption time estimated above should be considered only with caution in view of the complexity of the local process, it can serve in obtaining another estimate for the rate of deformation above which the solvent crazing response of the polymer becomes diffusion limited. Schwier et al.,[21] who have performed extensive matching measurements of craze growth and stress–strain experiments on a series of diblock copolymers, noted that typically in a diblock strained at a rate of 10^{-2} s^{-1} undergoing craze plasticity with a flow stress of about 20 MPa the corresponding craze velocity is of the order of 10^{-6} m/s. On the other hand, the limiting velocity of a plasticized craze by the sorption process discussed here should be roughly $v_l = d/t_s$ or 1.6×10^{-5} m/s. Thus, considering a direct relationship between external strain rate and craze velocity, we conclude that a diffusion limitation to the toughening effect should be encountered at a strain rate of roughly 0.16 s^{-1}. This is an attractively high rate but about 4 orders of magnitude less than what prevails in a Charpy impact experiment on an unnotched bar. Clearly the estimates made here are on very shaky information and cannot be taken for anything more serious than the crude bounding analyses given above. Information for better estimates is currently unavailable and is being actively pursued by us at the present.

Appendix II. Depth of Coverage of Craze Surfaces with Drained Polybutadiene

Consider a set of spherical pools of PB of actual diameter a, distributed randomly in the volume of the PS matrix. If a sampling plane cuts through the spheres, it reveals an area fraction, f, of PB spheres that is equal to its volume fraction in space. The average diameter, α, of the circles of intersection between the spheres and the plane is[24]

$$\alpha = (\pi/4)a \qquad \text{(AII-1)}$$

The average area, A, that can be allocated to an average circular cut of particle of diameter α on the sectioning plane is on the average

$$A = \pi\alpha^2/4f \qquad \text{(AII-2)}$$

When the content of a spherical region of volume $\pi a^3/6$ drains onto the plane of the cut and covers the area A on both sides, it will do so to a depth of h that should be

$$h = (16/3\pi^2)af \qquad \text{(AII-3)}$$

Appendix III. Concentration of Negative Pressure ahead of the Craze Tip

The concentration of stresses and particularly negative pressure ahead of a craze is complicated because of insufficient understanding of the processes of craze matter formation and drawing in a processing zone of extent Δ ahead of the craze tip. Within the zone Δ material elements arriving at the craze tip begin an extensional transformation, which when completed, transforms them into fully developed craze matter characteristic of a uniaxial transformation strain ϵ^T where the zone Δ joins into the craze body. The treatment given here, and that in the text, follows earlier statements of this process and is approximate.

Considering a craze matter processing zone of total length R ahead of the craze as a plastic zone akin to what exists in front of a mode III crack, it is possible to write by analogy a statement for mode I loading[25] that gives the traction maximum $\sigma_{\theta\theta} = \sigma_m$ at the extremity R of this process zone beyond which purely elastic behavior should hold, as

$$\sigma_m = K_I/\sqrt{\pi R} + \sigma_\infty \qquad \text{(AIII-1)}$$

In eq AIII-1 the first term on the right-hand side gives the concentrated traction at $r = R$ and the second term gives the distant field term. When the craze begins to move ahead at $K_I = K_{IC}$, the processing zone reaches its critical length, Δ.

The principal uncertainty in the determination of the craze tip driving force K_I, which appears in eq AIII-1, is the lack of understanding of what governs the magnitude and the extent of the traction deficiency shown in Figure 2a, which as a steady-state "dart" is what drives the craze forward. While the critical value K_{IC} of this driving force is calculable from the likely set of processes that produce craze matter at the craze tip (see refs 12 and 21), the determination of the peak concentration of negative pressure ahead of the craze makes this unnecessary. Assuming that such a critical level of K_{IC} exists, we can write the three principal stress components at the extremity of the zone Δ to be

$$\sigma_{rr} = K_{IC}/\sqrt{\pi\Delta} \qquad \sigma_{\theta\theta} = K_{IC}/\sqrt{\pi\Delta} + \sigma_\infty \qquad \text{(AIII-2a,b)}$$

$$\sigma_{zz} = \nu_p(\sigma_{rr} + (\sigma_{\theta\theta} - \sigma_\infty)) = 2\nu_p K_{IC}/\sqrt{\pi\Delta} \qquad \text{(AIII-2c)}$$

The concentrated negative pressure, σ, then becomes

$$\sigma = (\sigma_{rr} + \sigma_{\theta\theta} + \sigma_{zz})/3 \qquad \text{(AIII-3)}$$

$$\sigma = (1/3)[2(1 + \nu_p)K_{IC}/\sqrt{\pi\Delta} + \sigma_\infty] \qquad \text{(AIII-3a)}$$

where ν_p is Poisson's ratio of the solid polymer. On the other hand, from eq AIII-1 for $\sigma_{\theta\theta} = \sigma_m$ where $K_I = K_{IC}$ and $R = \Delta$ we have

$$K_{IC}/\sqrt{\pi\Delta} = \sigma_m - \sigma_\infty \qquad \text{(AIII-4)}$$

giving finally

$$\sigma = (1/3)[2(1 + \nu_p)(\sigma_m - \sigma_\infty) + \sigma_\infty] \tag{AIII-5}$$

From the experimental measurements of Lauterwasser and Kramer,[13] it is known that $\sigma_m = \alpha_s \sigma_\infty$, where $\alpha_s = O(1.15-1.2)$. This gives for the negative pressure concentration for $\nu_p \simeq 0.3$ and $\alpha_s \simeq 1.2$

$$\sigma/\sigma_\infty = (1/3)[2(1 + \nu_p)(\alpha_s - 1) + 1] \simeq 0.5 \tag{AIII-6}$$

Appendix IV. Drawing of Periodically Arranged Glassy Polymer Tufts out of a Half-Space

The desirability of obtaining a solution of the craze tuft drawing problem out of a half-space has long been recognized. It is envisioned that at the craze border, as the craze widens under stress, the roots of periodically arranged craze tufts traverse uniformly at constant velocity in a self-similar geometry into the half-space and continuously convert the solid polymer into tufty craze matter. The proper modeling of this complex problem requires a constitutive relation for plastic deformation that incorporates strain rate sensitivity, pressure dependence, and perhaps even free-volume enhancing rejuvenation processes (if close to T_g), in addition to orientation hardening. While large strain solutions of material having such a constitutive response are unavailable, a very good large strain finite element solution using an elastic and rate-independent plastic constitutive relation with three-dimensional orientation hardening has been obtained by Bagepalli.[14]

The constitutive relation representing the inelastic behavior of the polymer combines elasticity, rate-independent plastic response obeying a Mises criterion, and molecular orientation hardening modeled by a three-chain entropic rubbery resistance discussed by Treloar.[26] The solution was obtained by the large-strain ABAQUS finite element code and is fully three dimensional. The starting geometry considers a round glassy polymer bar as a member of a periodic and close-packed arrangement of parallel bars, drawing out of a half-space. To simulate the attachment of the drawing bar into a half-space, half of its length is built into a cylindrical rigid cavity while the other half of a slightly reduced initial diameter is pulled downward. The drawing is continued under a monotonically decreasing overall tensile resistive force until a fully established toroidal arch develops around the bar as shown in Figure 3 and when the overall drawing force also nearly levels off. The distribution of negative pressure throughout the bar for this state of deformation is given in Figure 3. The distribution of stresses acting across the fully drawn stem of the tuft for this state is shown in Figure 4. These distributions are instructive and outline the regions that are subjected to deformation-induced negative pressure which could become subject to sorbing a diluent.

It must be noted, however, that the solution illustrated in Figures 3 and 4 does not pertain to a steady state. The motion upward of the root region of the toroidal arch requires the equivalent of a circumferential "fracture" process, which with an associated blunting is necessary to accomplish a "stationary state" of upward advance of the drawing front. In this sense the advance of the circumferential interface closely resembles the advance of a blunted crack by a ductile fracture process.[27,28] The need for such "fracture" (or chain scission) has also been recognized by Kramer and co-workers.[29]

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