TOUGH HETEROGENEOUS POLYMERS

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ABSTRACT

The usual brittle behavior in tension of glassy homopolymers such as polystyrene can be rectified by incorporating into them heterogeneities that effectively catalyse dilatational plasticity by promoting profuse crazing without the need for any significant distortional plastic flow. This procedure which had been practiced industrially on a large scale for several decades to produce high impact polystyrene has been founded on empiricism. It is now possible to construct model heterogeneous polymers having composite particles with prescribed morphologies by using blends and emulsions of block copolymers. In this way the thermal and elastic properties of composite particles in glassy polymers can be deterministically manipulated to govern their dilatational plastic deformation resistance and their strain to fracture to maximize toughness. Here we discuss the overall principles for toughening of glassy polymers by controlled crazing, and discuss three case studies for special heterogeneous polymers to demonstrate these principles.

INTRODUCTION

Under suitable conditions that suppress fracture, glassy polymers can undergo large plastic deformation below the glass transition temperatures, limited only by the terminal network stretches of the polymer that are established by the density of molecular entanglements. This plastic behavior in which the applied stresses must overcome both a temperature, strain rate and pressure dependent scalar resistance of molecular segment rotations and a tensor resistance arising from an affine molecular orientation of entropic origin, is now quite well understood both from the molecular point of view as well as the phenomenological and operational points of view. [1-3]. In many cases this

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distortional deformation is prone to localize into narrow shear bands [4,5], most likely as a result of a flow dilatation process that has been extensibely investigated in metallic glasses [6-9], the deformation of which have much in common with polymeric glasses [10]. We will not pursue here this distortional plasticity of glassy polymers.

Under normal conditions, when the applied stress has a significant component of negative pressure ,most glassy polymers exhibit crazing. Many detailed experimental studies have established that crazes in glassy polymers are filled with traction transmitting highly drawn polymer tufts on a submicroscopic scale, and they are special cavitational localization zones where the distortional plasticity referred to above occurs on the very small scale of the individual tufts that bridge the faces of the craze [11-14]. The extension of the craze in its plane where additional polymer tufts are produced by the convolution of the air-polymer interface at the craze tip [15,16], and the thickening of the craze by the drawing of additional polymer tufts out of the half spaces of the craze flanks involve locally very large strain plastic flow. This plastic flow, however, occurs only along the thin layer of the craze border, where it is maintained by the overall "transformation" stresses of the craze lentil. The stresses away from the craze lentil remain well below general yield. This micro-mechanical point of view has proved to be essential for the understanding of the mechanisms and kinetics of the initiation, growth, and final fracture of crazes [11-16]. We will, however, also find it useful to take a more macroscopic point of view considering crazes as dilatational transformations, occurring in a substantially elastic background, and the collective action of crazes as dilatational (transformation) plasticity [17]. While, in principle, considerable dilatational plastic strains could be produced in a glassy polymer by crazing at stresses below those for general yield of the background, in practice, this rarely occurs in single phase (homo-) polymers. This is because imperfections develop in the tufty craze matter of one or more crazes which grow under stress to produce a crack which then propogates to final fracture. Hence, crazes act as fracture nuclei in glassy homo-polymers, and must be viewed as precursors to cracks.

Thus, crazing in glassy polymers plays a dual role. In homo-polymers, crazes mostly initiate and grow out of surface imperfections which also act as the terminal failure sites inside the specific crazes. This leads to fracture well before a significant fraction of the volume has been converted into craze matter, and the overall behavior is brittle. When the polymer incorporates a certain volume fraction of compliant heterogeneities craze initiation can be more effectively dispersed throughout the volume resulting in substantial dilatational plasticity and tough behavior. Although many details of the requirements that lead to tough behavior of glassy polymers through incorporation of compliant heterogeneities have been mapped out over the past few decades of industrial experience with high impact polystyrene (HIPS), definitive understanding of these requirements has not yet been achieved. This has been because few of the many important factors such as the morphology and size of particles, their adhesion to the matrix, etc. can not be independently controlled in industrial practice. Many of these factors can, however, be effectively controlled by the use of block copolymers of polystyrene (PS) and a rubber such as polybutadiene (PB). When anionically polymerized, these block copolymers consist of long chain molecules of two or more blocks of PB and PS molecules of relatively closely controlled lengths or block molecular weights. Such so-called block copolymers undergo phase separation and in the solid state reach very regular morphologies of spheres, rods, or lamellae of PB of constant diameter or thickness, dispersed quasi-randomly in a majority phase of PS. Through controlling the lengths of the individual block components of these block copolymers the morphology and its scale can be accurately controlled. With additional blending of homopolymers of PS and PB with different molecular weights the morphology can be modulated further and particles of a given morphology, dispersed in a majority phase of a glassy polymer, can be constructed with reasonable control for their sizes. [12,19-22]. Here we will summarize such a study that offers deterministic control of toughness in a glassy polymer such as PS.

TOUGHNESS THROUGH CRAZING

Sources of Toughness

We will concentrate our attention only on crazing and the dilatational plasticity that results from it. We begin by reviewing briefly the sources of toughness of glassy polymers. For this purpose we view a craze as a lenticular region with its plane perpendicular to the direction z of the major principal tensile stress. A craze can be considered as a very eccentric oblate spheroid with a radius a in its principal plane and a half thickness b parallel to the z axis. Furthermore, since the main microstructural feature of a craze consists of extended fibrils with a relatively constant extension ratio λ_n, one can view the crazing process as an extensional transformation in the z direction inside the craze, converting a much thinner oblate spheroid of half thickness b/λ_n into the current half thickness b, without any significant change of dimension inside the plane of the craze. This produces a dilatation of $\Theta_{cr} = \lambda_n - 1$ of the craze interior, in comparison with the initial solid polymer. Much evidence points into the direction that mature crazes that grow at constant velocity under a constant applied stress attain a terminal thickness $2b_f$ upon which they grow only laterally in the principal plane. When such a constant growth rate condition is reached, the volume of a craze can be idealized simply as $2\pi a^2 b_f$ in its expanded form and $2\pi a^2 b_f/\lambda_n$ in its unexpanded, "primordial" form.

Consider now a polymer sample of current volume V responding by craze yielding to an imposed current elongational strain rate $\dot{\varepsilon}_z$, developing a tensile (dilatational) flow resistance Y_{cr} until a final fracture strain ε_f is achieved as shown in Fig. 1. The specific toughness W or the total deformational energy absorbed per unit volume for this polymer is the area under the stress strain curve, or

$$W = Y_{cr}\, \varepsilon_f \,. \tag{1}$$

The strain to fracture, however, is the product of the imposed strain rate and the time to fracture t_f, i.e.,

$$\varepsilon_f = \dot{\varepsilon}_z\, t_f . \tag{2}$$

If the strain derived is entirely due to craze matter production, as assumed here, there will be no significant change in the cross-sectional area A of the part during such (dilatational) flow. Then the imposed tensile strain rate $\dot{\varepsilon}_z$ must be equal to the macro dilatation rate Θ of the polymer as might be measured by means of a dilatometer with a working fluid that is prevented from penetrating into the craze cavities. Thus, the polymer responds to the imposed tensile strain rate by undergoing an equal rate of dilatation by crazing. On the other hand, for the steady state crazing conditions described above it is possible to write readily

$$\frac{d\Theta}{dt} = (2\Theta_{cr}\, b_f)\left(\frac{2\pi a n}{V}\right)\frac{da}{dt} \quad , \tag{3}$$

where $2b_f$ is the craze thickness, Θ_{cr} is the average dilatation inside a craze as defined above, n the total number of crazes of average radius a in the current volume of the sample V ($= V_o + 2n\,\pi a^2 b_f$), where V_o is the initial volume of the sample. In Eqn. (3) the terms in the first brackets that we will abbreviate with C represent the properties of mature crazes. The second set of terms in brackets which we will abbreviate with ρ is the total active craze front length per unit volume. The last term in Eqn. (3) is the craze front velocity v. Re-assembling these groups of terms gives for the tensile strain rate

$$\dot{\varepsilon} = C\,\rho\,v \quad . \tag{4}$$

In the term C that represents the craze properties, the craze dilatation depends on the extension ratio λ_n of the fibrils which will be governed by the steady state craze traction σ_c ($= Y(\lambda_n)/\lambda_n$) transmitted across the craze where $Y(\lambda_n)$ is the true uniaxial tensile plastic resistance of the solid polymer that depends on λ_n by virtue of orientation hardening. Although $Y(\lambda_n)$ cannot usually be measured directly in macro experiments due to intervening fracture initiated by crazing, it can be readily determined from first principles as the sum of a dissipative (von Mises) plastic resistance and an entropic resistence as discussed in the introduction. In most instances, the extension ratio that has been measured in tufts of dry crazes of PS is of the order of $\lambda_n \simeq 4$[23]. Thus, on this basis, we pick the craze dilatation to be $\Theta_{cr} = 3$. The terminal thickness $2b_f$ of a mature craze, where aging most probably terminates the drawing process, varies considerably. While the crazes in homopolymers tend to be thicker, in the range of 0.5 μm, those in high impact polymers with compliant heterogeneities tend to be thinner, in the range of 0.1 μm. Although complete understanding on how or why craze thickening levels off at these dimensions is lacking, on the above basis, we evaluate the value C to be about 6×10^{-7} m in polymers with heterogeneities, and about 3×10^{-6} m in homopolymers such as polystyrene (PS).

In Eqn. (4) ρ represents the total length of craze front per unit volume where new craze matter is being generated in planar form and added to the already existing craze matter. It results from a kinetic balance between initiation and inactivation of craze front length and, as such, is expected to be influenced strongly by both the density of source sites on free surfaces and internal interfaces, where stress concentration exists, and by the processes affecting termination of craze growth such as blunting, mutual arrest, traverse through the entire cross-section, etc. Both initiation and inactivation depend strongly on the local stress and temperature.

The craze front velocity v is known to be governed by one of two distinct mechanisms of craze matter production. As Argon and Salama [16] have discussed in detail, under the usual levels of service stresses or stresses under which most experiments are carried out, craze matter in a homopolymer is produced by the convolution of the free surface of the solid polymer at the craze tip. This occurs in the flow or deformation of all inelastic media when a concave, meniscus-like surface of the medium is being advanced locally by a suction gradient. This is the preferred mechanism of craze advance in homopolymers. In block copolymers with uniform distributions of compliant phases of a very small size and spacing, craze advance can also occur by cavitation inside such phases to produce craze matter as has been discussed by Argon et al [24]. Both of these mechanisms of craze advance lead to very similar dependences of the craze front velocity on applied stress and temperature that is of the basic form

$$v = D_i \left\{ \exp - \frac{\Delta G(\sigma_\infty/\hat{Y})}{kT} \right\} \quad , \tag{5}$$

where D_i (i = 1,2) are pre-exponential factors for the two craze extension mechanisms, dependent on some physical constants and dimensions of the microstructure, σ_∞ is the applied tensile stress or the local maximum principal tensile stress and $\hat{Y}$ ($= 0.133\mu/(1-\nu)$ where μ is the shear modulus and ν is the Poisson's ratio) is a modulus parameter that has the meaning of the ultimate athermal plastic resistance of the polymer.

Finally, when fracture occurs, it initiates and propogates through a craze. Such initiation occurs from defects in the craze matter in the form of dust particles, surface defects, or ultimately large natural irregularities occurring in the craze matter [25,26]. As Eqn. (2) indicates, the first formed craze is subjected to the full craze traction σ_c, that for much of the craze body is equal to the applied stress σ_∞, for the entire duration t_f of straining. As in all time dependent fracture processes known in solids, we expect the time to fracture of a stressed portion of craze matter to be inversely and nonlinearly dependent on the stress carried by the craze that might be typically of the form

$$t_f = t_f\,(\sigma_\infty, T, \xi_e, \xi_i) = A(T, \xi_e, \xi_i)/\sigma_\infty^{\,f} \tag{6}$$

where ξ_e, ξ_i stand symbolically for the description of extrinsic and instrinsic defects in the craze matter from which terminal fracture initiates, and where f is a phenomenological stress exponent. In dilatational plasticity by crazing, $\sigma_\infty = Y_{cr}$, the craze yield stress. We expect that when craze sources are plentiful, resulting in a high active craze front length ρ, the craze velocity that needs to be maintained to match the imposed strain rate can be proportionally lower resulting in a lower craze yield stress and an increased craze fracture time t_f. There is very little information available currently on the important dependence of the craze fracture time t_f on the applied stress σ_∞ implied by Eqn. (6).

Assembling all detailed ingredients for the toughness W of the polymer resulting from crazing, we obtain

$$W = Y_{cr}\,\xi_f = C\,A\,\rho(Y_{cr})v(Y_{cr},\,T)/Y_{cr}^{\;f-1}. \qquad (7)$$

In Eqn. (7) the factors C and A are dependent on craze microstructure and will not vary significantly. The stress and temperature dependence of the craze velocity will be quite sensitive to the microstructural detail of phase distribution in block copolymers. The applied stress $\sigma_\infty = Y_{cr}$ producing craze yielding affects strongly both ρ and v. This makes $\rho(Y_{cr})$ one of the most important factors accessible to the materials scientist in governing toughness through microstructure control, as has been recognized intuitively by most investigators. The desirable response of a polymer is a high toughness, independent of the rate of deformation $\dot{\varepsilon}$ which normally can vary from 10^{-4} $\sec^{-1}$ of a slow tension experiment to 5×10^2 $\sec^{-1}$, typical in impact. Since the dependence of all other terms in Eqn. (7) on stress are either known or determinable, it should in principle be possible to design a set of heterogeneities that can maintain a certain density of craze front with the desired stress dependence, i.e.

$$\rho(\sigma_\infty) = \frac{W\,\sigma_\infty^{\;f-1}}{A\,C\,D_i}\,\exp\left(\frac{\Delta G(\sigma_\infty/\hat{Y})}{kT}\right) \qquad (8)$$

for the level value of the toughness W, with the meaning of the various terms as defined above.

The present discussion indicates that there is a balance that needs to be attained between the various factors that influence the toughness. Although the total active craze front length per unit volume is the most important parameter available to the investigator, the actual kinetics of the growth response of a craze and the integrity of craze matter under stress must also be controlled to attain high toughness. As with metals it is difficult to achieve both a high craze yield stress and a large strain to fracture simultaneously under any given condition of straining. On the other hand, achieving higher toughness with larger strain rates in a given microstructure should be possible if the stress dependence of ρ and **v** are stronger than that of t_f.

Below we review briefly the state of understanding of processes governing the initiation of craze fronts, their velocity of advance, and the time dependent fracture of craze matter under stress.

The Active Craze Front Density ρ

As in other branches of materials science where stress assisted nucleation of new phases, cavities, or initiation of microcracks are of concern, the initiation of crazes in stressed glassy polymer is also subject to considerable complexities that have still not been completely resolved. The early phenomenology of craze initiation has been reviewed by Kambour [11]. The earliest statement of an acceptable criterion for craze initiation is due to Sternstein and Ongchin [27], who parameterized their observations on craze initiation under bi-axial stress. Their description, however, could not be generalized unambiguously to be applicable in a three-dimensional state of stress. Such a generalization was proposed by Argon and Hannoosh [28] on the basis of detailed experiments on craze initiation under biaxial states of stress, where the craze initiation time t on surfaces with controlled topography subjected to combinations of a deviatoric shear stress s, and a negative pressure σ, was found to obey the relation:

$$\frac{AQ}{(s/Y)} - \frac{3}{2}\left(\frac{\sigma}{Y}\right) = Q\,\ell n(t/\tau), \quad \left(\frac{\sigma}{Y} > 0\right) \qquad (9)$$

In this equation Y is the tensile plastic resistance, A ($= \Delta G_o/kT$) is a temperature dependent constant with a magnitude of 9.54 in PS at room temperature, Q (= 0.0133), the measure of interaction of the deviatoric shear stress and the negative pressure [29], and τ is a characteristic time constant, dependent primarily on temperature, and possibly on some supra-molecular microstructural detail, has the dimensions of 6.0×10^{-8} sec at room temperature in PS. The deviatoric shear stress s ($= \sigma_e/\sqrt{3}$, where σ_e is the well known von Mises equivalent stress), and the negative pressure σ are the local values concentrated by surface irregularities or by diffences between the elastic and thermoelastic properties of the particulate phases and the matrix. The form of Eqn. (9) has a mechanistic basis and represents the trend of the measurements of Argon and Hannoosh [28] quite well in the range where a non-zero negative pressure is present. The correctness of this form was recently verified by Kawagoe and Kitagawa [30] who have demonstrated that it also applies to crazing in the presence of solvents. Equation (9) represents a mode of craze initiation which requires a key step of plastic deformation governed by the deviatoric stress to initiate a precursor density of submicroscopic cavities that subsequently expand under negative pressure. This is the preferred mode of craze initiation in glassy homopolymers containing no heterogeneities.

In heterogeneous polymers containing either single phase or multiphase particles, the craze initiation condition is expected to be applicable to the glassy polymer outside the particles - provided that the stress is concentrated there over a large enough volume element to initiate the set of representative precursor processes [31]. The exact minimum size of the critical volume element is not clear, but experiments on the craze initiating efficiency of particles suggest that it is of the order of 50-100nm.

In block copolymers where large differences exist between the shear moduli of the rubbery phases and the glassy matrix, significant concentrations of negative pressure can develop inside the compliant phases upon application of a stress and also as a result of differential thermal expansion between the rubbery phase and the surrounding glassy polymer. This produces craze nuclei by internal cavitation of the rubbery phase [24]. The cavitational negative pressure of PB domains has now been well established in experiments on the thermal stress induced shift of T_g[32].

Argon et al [12] have considered in some detail the kinetic balance of crazes between initiation of craze fronts at sites of stress concentration and their inactivation by mutual arrest, and the like, to develop expressions for the active craze front density per unit volume ρ for a number of special situations. In all these considerations, which to some extent are model sensitive, ρ has been found to be inversely proportional to the time for initiation of crazes.

Growth of Crazes by Interface Convolution

Noting that the kinetics of craze growth in homopolymers is quite different from what might be expected from a mechanism of repeated cavity nucleation at the craze tip, and that craze matter is made up of topologically interconnected air passages, Argon and Salama [16] proposed that crazes grow by the repeated convolution of the craze tip interface as depicted in Fig. 2. This process which is ubiquitous as a meniscus instability in the flow of fluids, of both simple and complex rheology, furnishes a quantitatively accurate framework to explain the kinetics of craze growth in homopolymers. The key to the development is a perturbation analysis by Argon and Salama [15] that has lead to the computation of the principal wave length λ of the instability that is advancing with a velocity u_x. The analysis gives this principal wave length to be $\lambda = \beta \chi/\sigma_e$ where χ is the surface energy of the polymer, σ_e the equivalent tensile plastic resistance, and β a numerical constant of the order of 10^2 [12]. For PS at room temperature where $\chi = 5 \times 10^{-2}$ J/m^2 and $\sigma_e = 100$ MPa, λ is found to be 53 nm, which is very close to what is measured by transmission electron microscopy and low angle X-ray scattering. The analysis which considers further the instability in the tip region of a craze in which the kinetics of advance of the craze is governed by the kinetics of distortional plastic deformation of the homopolymer along the craze border results in a craze velocity given by

$$v = D_1 \exp \left\{ - \frac{B}{kT} \left(1 - \left(\frac{\sigma_\infty \lambda_n'}{\hat{Y}} \right)^{(5/6)} \right) \right\} . \tag{10}$$

In Eqn. (10) λ_n' is the extension ratio λ_n of the craze tuft multiplied by the ratio of the initial plastic resistance Y_o to the plastic resistance at the extension ratio λ_n, B is a scale factor for the activation free energy for plastic flow with a form prescribed in more detail elsewhere [1], $\hat{Y}$ the same athermal plastic resistance encountered in Eqn (5) and D_1 is a pre-exponential constant proportional to the ratio of the product of the surface energy and the molecular segment frequency to the initial tensile plastic resistance.

Growth of Crazes by Repeated Cavitation of Block Copolymer Domains

Detailed studies of crazing in pure block copolymers [24,21,22] have established that craze growth in such polymers with regular spherical, rod-like, or lamellar PB domains occurs by repeated cavitation of these rubbery domains at the tip of the craze followed by plastic drawing of the topologically continuous surrounding PS to form craze tufts. The cavitation of the PB domains at the leading end of the craze tip process zone occurs when the cavitational negative pressure is reached inside the domains under the combined action of the substantial negative pressures resulting from the differential thermal contraction between the domains and the surrounding PS matrix and the additional negative pressures set up by the applied stresses concentrated by the craze lentil in this location [12]. Argon et al [12, 24] have shown that the model of Andersson and Bergkvist [33] for crack propagation by a degrading material is ideally suited for transposition into a model to explain the growth of crazes in quasi-homogeneous block copolymers. In the context of craze growth by cavitation of an included phase, the Andersson and Bergkvist model transforms into the geometry presented in Fig. 3a and 3b [12]. The material plane of thickness δ ahead of the plane of the craze must be brought up to a normal traction level σ_m, purely elastically, whereupon, as depicted in Fig. 3b, the cavitation strength of the rubbery phase is reached. As soon as cavitation occurs in the rubbery phase of a volume fraction c, its load carrying capacity is lost resulting in the elevation of the effective stress in the surrounding glassy polymer to the level of plastic flow. This initiates the "degradation" of the solid by the plastic expansion of the now porous carcass of glassy polymer to form the craze tufts under a dropping traction down to σ_∞ as the uniaxial extension of the cavitated layer is increased from the small strain ε_m to the fully established craze strain of $(\lambda_n - 1)$. The resulting traction across the plane of the craze is sketched out in Fig. 3a showing the "mapping" of the dropping traction profile of Fig. 3b into the craze tip process zone of extent Δ in an inverted manner. The actual traction distribution is sensitive to the specific shape of the dropping portion of the traction-displacement law and is not known. On the basis of detailed analysis of the craze lentil misfit stresses [23,12] we expect that the traction will dip below σ_∞ in the front portion of the craze body just beyond Δ, and should again rise to the level of σ_∞ in the majority of the craze body. The dipped portion of the traction at the front part of the craze body results in a craze tip driving force K_I that must be balanced by the craze tip process zone resistance K_{Ic}. While the latter can be calculated with some precision from the process history of the production of mature craze matter inside Δ, the former is not known because of the undetermined nature of the traction distribution. As discussed earlier by Argon et al [24], the velocity of crazes in this modification of Andersson and Bergkvist's degrading material model is

$$\frac{da}{dt} = \frac{\Delta}{\varepsilon_{cr}} \dot{\varepsilon}_e (\sigma_e) \tag{11}$$

$$\Delta = \frac{K_{Ic}^2}{\pi(\sigma_m - \sigma_\infty)^2} \quad ; \quad K_{Ic}^2 = \frac{E_c^2 \varepsilon_m^2 \delta (1 + \frac{1}{\theta})}{(1 - \nu_c^2)} \tag{12,13}$$

where E_c and ν_c are the average Young's modulus and Poisson's ratio of the composite polymer; ε_m the elastic strain at which cavitation in the rubbery domain begins; and θ the ratio of the descending slope to the ascending slope of the material degradation law sketched out in Fig. 3b. Modeling the descending portion of the degradation law as the initial drawing traction of a bar of yielding polymer undergoing negligible strain hardening, we estimate $\theta = \varepsilon_m$, and evaluate K_{Ic}^2 to be

$$K_{Ic}^2 = \frac{\sigma_m E_c \delta}{(1 - \nu_c^2)}$$

The initial thickness δ of the cavitating layer that appears arbitrary is actually fixed by the size of the rubbery domains as transmission electron microscopy shows. Combining equations (11), (12) and (13), and using the same reasoning to establish the equivalent plastic resistance of the deforming polymer that was introduced in connection with the mechanism of craze growth by the interface convolution gives the craze velocity to be

$$\frac{da}{dt} = D_2 \exp\left[- \frac{B}{kT} \left(1 - \left\{\frac{\sigma_\infty \lambda_n}{(1 - c)\hat{Y}_c}\right\}^{(5/6)}\right)\right] \tag{14}$$

$$D_2 = \frac{\delta \dot{\varepsilon}_0}{(1 - \nu_c^2)(\lambda_n - 1)\ \pi(\sigma_m/E_c)(1 - \sigma_\infty/\sigma_m)^2} \tag{15}$$

where λ_n' has the same meaning as that in Eqn. (10). The additional term (1 - c) in the denominator reflects that only that volume fraction is made up of the drawing glassy polymer, while $\hat{Y}_c$ now represents the athermal plastic resistance of the composite calculated from the composite elastic constants

The maximum level of traction σ_m ahead of the cavitational process zone Δ is established when at that point the PB domains reach the critical negative pressure to cavitate them under the action of the various components of the craze tip stresses and the quite substantial thermal stresses present at the test temperature. Thus, if the critical level of craze tip stress intensity to propagate it with the required velocity is K_{Ic}, the following local stresses must be present at the point of peak traction,

$$\sigma_{rr} = \frac{K_{Ic}}{\sqrt{\pi\Delta}} \quad ; \quad \Delta = \frac{K_{Ic}}{\sqrt{\pi\Delta}} + \sigma_\infty \tag{16,17}$$

$$\sigma_{zz} = \nu_c(\sigma_{rr} + (\sigma_{\theta\theta} - \sigma_\infty)) = 2\,\nu_c \frac{K_{Ic}}{\sqrt{\pi\Delta}} \tag{18}$$

where σ_∞ is the distant tensile stress and Δ is the cavitational process zone size given by Eqns. (12) and (13). Since at the point of propagation of the craze front $\sigma_{\theta\theta} = \sigma_m$, (or from Eqn. (12)), we have

$$\frac{K_{Ic}}{\sqrt{\pi\Delta}} = (\sigma_m - \sigma_\infty). \tag{19}$$

Each of the three tensile components of the principal stresses at the craze tip separately induce a contribution to the negative pressure inside the domain. These are all linearly additive. Thus, if we term any one of the principal components as σ_i, the induced negative pressure σ_{ST} can be obtained readily from the analysis of Goodier [34]

$$\frac{\sigma_{ST}}{\sigma_i} = \frac{1}{3}\left[1 + \frac{2(1 - 4\nu_c + \nu_c^2)\left(\frac{K_{PB}}{K_c} - 1\right)}{(1 + \nu_c)\left\{2(1 - 2\nu_c) + (1 + \nu_c)\frac{K_{PB}}{K_c}\right\}}\right] \tag{20}$$

where K_{PB} and K_c are the bulk moduli of the PB and the overall composite, and ν_c is the Poisson's ratio of the composite. These quantities themselves are readily calculable from composite theory [35] and explicit forms for them can be found elsewhere [12].

The negative pressure σ_{TH} induced in the PB spheres due to the mismatch of thermal expansion betweeen them and the composite surroundings is

$$\sigma_{TH} = \frac{2(\gamma_c - \gamma_{PB})K_{PB}\,\Delta T}{2 + \frac{K_{PB}}{K_c}\left(\frac{1 + \nu_c}{1 - 2\nu_c}\right)} \tag{21}$$

where γ_c and γ_{PB} are the volumetric coefficients of expansion of the composite and the PB respectively, and the temperature difference is to be reckoned from the temperature where the two phases coexist without stress. This is taken as the T_g for PS, i.e. 368° K. Once again the volumetric coefficient of expansion of the composite can be obtained by resorting to composite theory [12].

The peak traction σ_m is obtained from the condition that the PB domains will cavitate under the action of the negative pressures induced by the three principal stresses σ_{rr}, $\sigma_{\theta\theta}$, σ_{zz}, and from the thermal mismatch σ_{TH}, by reaching the cavitational strength of PB that has been estimated to be 60 MPa at room temperature by Argon et al [12]. Thus,

$$\sigma_{PBcav} = \sigma_{TH} + [\sigma_\infty + 2(1 + \nu_c)(\sigma_m - \sigma_\infty)](\sigma_{ST}/\sigma_i) \tag{22}$$

Where σ_{TH} and σ_{ST}/σ_i are given by Eqns. (21) and (20) respectively.

Fracture of Craze Matter under Stress

A number of investigators [36-38] have studied the mechanisms of breakdown of craze matter under stress in homopolymers. The causes of such breakdown or macro cavity initiation by multiple adjacent fracture of craze matter tufts has been found to result primarily from particulate impurities trapped in the polymer during manufacturing [36,37]. In the still thickening portion of a craze, when such an entrapped particle reaches the craze borders and its interfaces are subjected to complex states of stress with large negative pressure components in the tuft drawing region, it can be torn away from its surroundings. If the size of the particle is much larger than the mean craze tuft spacing of about 50 nm, it can act as a stress enhancing imperfection on the surrounding fibrils that can enlarge the initial cavity around the particle by preferentially fracturing the neighboring fibrils. Although this is probably the most important of the causes of craze matter fracture, it has been observed also that interaction of crazes with oblique surface scratches [38] can initiate fractures in craze matter. In addition, in many dynamic experiments under high strain rate fracture conditions [39] or when high amplitude stress waves are made to traverse through crazed polymer [40], fractures are found to initiate from the craze matter borders quite often in the absence of apparent imperfections. This suggests that the craze border is weaker [38] than either the drawn tufts of the solid polymer - being a region of partially drawn polymer with high strain gradients and large spatial variations of internal stress. Currently, there is insufficient quantitative information on the time dependent fracture of craze matter or craze interface under stress that is required for the overall understanding of the toughening process.

Stress-Strain Curves and Craze Velocities

Crazing in all pure block copolymers of PS and PB, regardless of whether the morphology consists of spherical, rod-like or lamellar rubbery (PB) domains in a majority phase of PS, involves the systematic planar cavitation of the PB phase forms. Of all of these the crazing process in the morphology of PB spheres in a PS matrix is the most regular and the most amenable to analysis. Therefore, we will limit our discussion here to a selection of di-block copolymers with spherical domains which have been investigated in greater detail by Schwier et al [22]. Table I gives the molecular, morphological, and processing details of the three sets of anionically polymerized di-block copolymers. They range in volume fraction from 0.06 to 0.18 in PB. In addition to their stress strain behavior at several different strain rates at both 20° C and -20° C extensive measurements were also made on the rates of craze growth under a number of constant stress levels. Three stress strain curves for these different volume fractions are given in Figures 5a-c (the curves for blends G and L are very similar to those of blends E and M). The stress dependence of the measured rates of craze growth that correspond to these three different morphologies (i.e., B, E, M) are shown in Figures 6a-c. From these figures and associated additional observations we reach certain general conclusions. The plasticity reported is entirely due to crazing, which is apparent from the linearly strain dependent increase of the whitened fraction of the sample, and a total absence of lateral contraction associated with the axial extension. The crazes initiate predominantly from the edges of the specimens where imperfections due to cutting abound. The initiation of craze yielding obeys a different relation with a less steep stress dependence than that for maintaining craze flow which has a larger stress dependence. This is clear from yield phenomena that appear on the stress strain curves at high strain rates but not at low strain rates. The craze flow stress decreases and the strain to fracture increases with increasing volume fraction of PB. What is more interesting, however, is a very sharp decrease in the time to fracture with increasing stress in any given morphology. This information which can be obtained from the strains to fracture and the strain rate during the test as a cross plot against the craze flow stress is shown in Figure 7 where a first order correction has been made on the stress for the actual volume fraction of PS in the craze matter which alone supports the flow stress. The lines in Figure 7 follow the order of decreasing particle size which suggests that craze matter produced from block copolymer with larger particle size and, therefore, having larger diameter tufts tends to be weaker, perhaps due to more severe imperfections that it contains.

Kinetics of Craze Growth

Two limiting growth modes of crazes are of interest for comparison with the experimental results; growth by interface convolution according to Eqn. (10), and growth by micro-domain cavitation according to Eqn. (14). For this evaluation the following choices of parameters were made: in Eqn. (10), $B = 26$ Kcal/mole, $\lambda_n' = 1.85$, $D_1 = 2 \times 10^7$m/sec [16]; in Eqn. (14), B and λ_n' have the same values, $\lambda_n = 5$, $\dot{\varepsilon}_0 = 10^{13}$ sec^{-1}, the cavitation strength of PB has been taken to be 60 MPa, and all other composite moduli are obtained according to the well established relations for composites [12, 35], from the appropriate information for the specific morphologies given in Table I. The calculated stress dependent velocities for the two different limiting growth modes are plotted on Figures 6a-c as the sloping dashed line for the interface convolution model and the solid line for the micro-domain cavitation model. With this clarification we note that for blend B, with a relatively large volume fraction of PB micro-domains, the crazes grow by the repeated cavitation model as is also quite clear from the electron microscopy results as shown in Figure 4. For blend E where the volume fraction of micro-domain is only 0.11 the craze growth begins to fall somewhat under the predicted rate for micro-domain cavitation. When the volume fraction of PB is only 0.06 the craze growth rate falls all the way to the level predicted by the interface convolution model, where it will remain in homo-polystyrene, as was shown earlier by Argon and Salama [16]. Although this smooth transition between the two modes of craze growth with changing volume fraction of microdomains is pleasing, the factors that govern this transition are not yet clear.

CRAZING IN HOMO-POLYSTYRENE WITH COMPOSITE BLOCK COPOLYMER PARTICLES

Heterogeneous Polymers with Block Copolymer Particles

As mentioned above, a desirable way of achieving significant amounts of dilatational plasticity in commerical polymers is by dispersing the crazing process uniformly over the entire stressed volume of the polymer. This is achieved industrially with high impact polystyrene (HIPS) and acrylo nitrite-butadiene-styrene (ABS) where the crazes are initiated from composite particles embedded in a matrix of high molecular weight polystyrene. The morphology of the typical HIPS or ABS particles consist of PS occlusions surrounded by a small volume fraction of a topologically continuous phase of PB. When care is taken to graft the PS and PB phases at their interfaces and to the surrounding matrix, these composite particles become effective craze initiators by virtue of the stress concentration that they produce. Although the mechanism of crazing in these industrial materials has been investigated for many years and authoritative treatises [31] exist on the subject, definitive understanding of the action of the composite particles to promote dilatational plasticity is still quite incomplete for reasons that were detailed in the introduction. Better understanding of the mechanisms that govern dilatational plasticity and optimize toughness of heterogeneous polymers is achievable through the investigation of model polymers in which composite particles with controlled morphology are made up of block copolymers. Such investigations have been carried out by us [12, 19,20] and by Kawai and coworkers [41]. We summarize here our investigations.

Heterogeneous Polymers with Pure and Modified K-Resin Particles

Argon et al [12] and Gebizlioglu et al [19,20] have used a commercial block co-polymer blend marketed by the Phillips Petroleum Co. under the trade name of KRO-1 as the basic ingredient to construct composite particles for dispersal in high molecular weight PS to form model heterogeneous polymers. When KRO-1 Resin is dispersed in high molecular weight PS by solvent casting techniques, micron size composite particles having the typical KRO-1 Resin morphology are obtained, as shown in Figure 8. When additional polybutadiene with appropriately low molecular weight of $\bar{M}_w$ = 3 Kg/mole (PB3K) is blended into the previous blend, the PB3K goes into solution in the PB blocks of the KRO-1 Resin. This results in a morphological transformation to form particles with concentric spherical shells of alternating layers of PS and modified PB, as shown in Figure 9. These particles with transformed morphology have significantly increased compliance and thermal expansion misfit against the background of high molecular weight PS. Both of these effects help enhance the craze initiation efficiency of the particles under a tensile stress. The optimum effects are reached when the maximum amount of PB3K can be solubilized into the concentric spherical shell morphology. This is achieved with a PB3K/KRO-1 blend ratio of 0.5. The stress strain curves of the high molecular weight PS without any K-Resin and with a volume fraction of 0.21 of unmodified KRO-1 particles are shown in Figure 10. Clearly, the effect of the relatively large volume fraction of the unmodified KRO-1 particles in the homo-polystyrene is minimal. In comparison, the stress strain curves of the same PS but with the above mentioned PB3K/KRO-1 blend of concentric spherical shell particles with the same volume fraction of 0.21 are shown in Figure 11. The difference in behavior between Figs. 10 and 11 is dramatic. Thus, while the craze flow stress of the PS with the spherical shell particles has dropped from 30 MPa to about 10 Mpa, the plastic strain to fracture has increased from about 0.045 to over 0.8. The differences in the craze initiation efficiency between the unmodified and modified KRO-1 particle morphologies are demonstrated directly in the electron micrographs of Figures 12a and b of craze distribution in the polymer at the time of fracture.

Crazing Stresses in Heterogeneous Polymers with K-Resin Particles

The craze initiation in a number of such heterogeneous polymers with real as well as idealized composite particles of the types discussed above has been modelled by Boyce et al [42]. The criterion for craze initiation that was used was the one of Argon and Hannoosh [28] given in Eqn. (9) above. The deviatoric stresses and negative pressures around the particles were obtained using both analytical and finite element methods. Here we will be interested only in the specific results for the "homogenized" KRO-1 particle shown in Figure 8 and the spherical shell particle containing additional low molecular weight, PB3K, polybutadiene at a blend ratio of PB3K/KRO-1 of 0.5 shown in Figure 11.

In the analysis of the KRO-1 particle, first the modulus and the average thermal expansion coefficient of the particle are obtained from the moduli and coefficients of thermal expansion of PB and PS by considering that the PS in this morphology is topologically continuous, permitting the use of Chow's method [35,43]. The details on how the elastic and thermal expansion responses of the particles are obtained are given elsewhere [12,20]. The results indicate that the quasi-isotropic KRO-1 particle with a volume fraction of 0.23 PB has shear and bulk moduli that are 0.69 and 0.861 that of the corresponding moduli of PS, and that the average thermal expansion coefficient is 3 x 10^{-4} K^{-1} or 1.5 times that of PS. To calculate the stress concentrations due to these particles under the combined action of the thermal expansion misfit and the applied stress, the interactions of the surrounding particles must also be considered. For the spherically symmetrical thermal expansion misfit problem this is straightforwardly done by reinterpreting these interactions as a finite sphere problem with a centrally placed misfitting sphere. **Boyce** et al [42] have found that for a volume fraction of C_p = 0.21 of particles the three principal stresses around the particle due to differential thermal expansion are σ_{rr} = 6.41 MPa. $\sigma_{\theta\theta} = \sigma_{\phi\phi}$ = -5.64 MPa respectively. The application of a distant tensile stress σ_∞ produces additional principal stresses $\sigma_{rr} = 0.10\ \sigma_\infty$, $\sigma_{\theta\theta} = 1.314\ \sigma_\infty$, $\sigma_{\phi\phi} = 0.02\ \sigma_\infty$ for the same volume fraction of particles where the interaction between particles is obtained from an earlier study of Broutman and Panizza [44]. With this information, the critical stress σ_∞ to initiate crazing from the KRO-1 particles can be obtained by evaluation of Eqn. (9) for the typical values of $Q\ \ell n(t/\tau) = 0.282$ and $AQ = 0.127$ to obtain σ_∞ = 36.9 MPa. This is considerably higher than the measured value of the flow stress of c.a. 30 MPa shown in Figure 10. We save comment on this lack of agreement to the general discussion below.

Crazing Stresses in Heterogeneous Polymers with Spherical Shell Particles

Since the concentric spherical shell particles are radially symmetric but highly anisotropic, special finite element procedures are necessary to evaluate the stresses around them due to the combined action of the thermal expansion misfit and the effect of the applied distant tensile stress. In the modeling of this specific geometry, for the blend ratio of PB3K/KRO-1 of 0.5, Boyce et al [42] have found for an overall particle volume fraction of 0.21 that was experimentally investigated, differential thermal expansion induced stresses of σ_{rr} = 11.41 MPa, $\sigma_{\theta\theta} = \sigma_{\psi\phi}$ = -10.24 MPa respectively in the PS matrix immediately outside the particles. The application of a distant tensile stress σ_∞ produces additional local principal stresses which, including the consideration of particle interactions, are $\sigma_{rr} = 0.26\ \sigma_\infty$, $\sigma_{\theta\theta} = 1.994\ \sigma_\infty$, $\sigma_{\phi\phi} = 0.092\ \sigma_\infty$ for the same particle volume fraction of 0.21. Substitution of these values into the craze initiation condition of Argon and Hannoosh (Eqn.(9)) for the same typical values of the coefficients quoted above gives a craze initiation stress of σ_∞ = 18.3 MPa. This is much higher than the experimentally observed value of c.a. 10 MPa shown in Figure 11. Once again we defer the discussion of this lack of agreement to the following section.

DISCUSSION

Craze Growth in Block Copolymers with Rubbery Spherical Micro-Domains

It is now generally accepted that the precursor processes of micro-cavity formation on a molecular scale that occur in crazable homopolymers under stress and eventually result in the nucleation of visible crazes requires quasi-homogeneous conditions over a volume element of roughly 50 - 100 nm or larger [45,12]. Thus, the sizes of the rubbery domains or their mean distances in the block copolymers with spherical micro-domains that we discussed above, and have shown in Figure 4, are too small to initiate crazes themselves. In these block copolymers, crazes must initiate from surface imperfections or from other more macro inhomogeneities. Another possibility, that of the collective action of an appropriate cluster of micro-domains as a craze nucleus, will become apparent presently, and will be discussed below.

The major observation about these block copolymers is the demonstration of a new mechanism of craze matter production by systematic cavitation of the rubbery domains in a plane followed by the plastic drawing of the now porous PS carcass. We have demonstrated that this mechanism, when properly modeled as the growth of a planar cavitational front by the degrading material model of Andersson and Bergkvist [33], can account very well for the observed kinetics of craze growth in block copolymers with a high volume fraction of spherical rubbery micro-domains. When the volume fraction of rubbery domains becomes too small, the mechanism for the growth of the craze reverts back to the now well established interface convolution process inititally proposed by Argon and Salama [16].

We note further from Figure 5 that the flow stresses for most of these polymers are well above 30 MPa and within the range of the crazing stresses reported for homo-polystyrene [28]. Thus, craze initiation from surface defects should be the prominent mode in these materials and is indeed observed [22]. The stress strain curves shown in Figure 5 are, however, quite regular and reproducible to suggest that a more intrinsic mode of initiation might also be possible in these block copolymers. Large negative pressures on the order of 30 MPa exist in the spherical micro-domains due to thermal expansion misfit, and the calculated maximum tractions σ_m (Figure 3) for the propagation of the cavitational zones are only in the range of 40 - 45 Mpa [12, 22], Hence, relatively small stress concentrations by the collective action of a tight cluster of spherical micro-domains could satisfy both the stress conditions discussed above to initiate crazes in the interior. Such internal initiation of craze nuclei by clustered cavitation of micro-domains has been observed by Argon et al [24] in profusion in block copolymers with lamellar morphology. Finally, we note that these block copolymers with spherical micro-domains have craze flow stresses that are equal to or higher than any homopolymer or any commercially available toughened heterogeneous polymer such as HIPS or ABS, but still have larger strains to fracture. Figure 7 furnishes a partial explanation. The craze matter formed in this manner is apparently much more regular than that of homo-polystyrene, and its strength, even on a properly normalized scale, shows it to be higher, the smaller the rubbery domain size. This important subject, however, requires much further study before definitive conclusions can be drawn.

Craze Initiation in Heterogeneous Polymers with Composite Particles

We have demonstrated here that block copolymers can be used to form composite particles in majority phases of homopolymers and that additional blending of appropriate homopolymers can effectively modulate the morphology of such composite particles to radically alter their performance. Such model heterogeneous polymers make it possible to investigate the mechanisms of toughness that are derived through craze plasticity. Here we have reported on only two of a larger set of such heterogeneous polymers which we have investigated and reported on in greater detail elsewhere [12, 19,20]. The investigation has clarified a number of important points related to the properties of the composite particles. First, the overall rubber content and topological distribution of this rubber is important in governing the thermal expansion misfit of the particles in relation to the surrounding matrix. The distribution of such thermal residual stresses that must be present in all such heterogeneous polymers is affected markedly by the morphology of the particle. In each case the thermal stresses contribute significantly to the deviatoric stress outside the particle that is the main instrument in the micro-porosity development preceding the nucleation of visible crazes. Second, the distribution of the rubber inside the composite particle governs its overall stiffness which affects both the deviatoric stress and the negative pressure outside the particles. The importance of this has been demonstrated with morphological transformations at roughly constant composition that have had major effects in reducing the craze stress and improving toughness.

In a quantitative assessment of the craze initiation process by the use of the generally successful criterion of Argon and Hannoosh [28], the agreement reported in the previous section must at best be termed poor. This is not likely because of any inadequacy of the craze initiation criterion that was used which has been demonstrated recently to be even successfully applicable to problems of solvent crazing. Rather, through this quantitative disagreement another very important phenomenon has emerged.

We note now that for the quasi-isotropic KRO-1 particles, the craze initiation stress was calculated to be 36.9 MPa which was considerably higher than the measured flow stress of 30 MPa shown in Figure 10. The calculated level is likely to be correct. Detailed transmission electron microscopy of the moderately crazed samples with such particles gave no evidence of craze initiation by the particles at the flow stress levels of 30 MPa. All crazes appeared to have initiated at surface defects and the effect of the composite particles is, at best, one of craze arrest. The fact that neither the flow stress nor the strain to fracture of a sample containing such particles was significantly different from homo-polystyrene, as shown in the strss strain curves of Figure 10, is consistent with this observation.

We note further, however, that the calculated level of the craze initiation stress of 28.3 MPa for the modified spherical shell particles was far in excess of the actually measured flow stresses of about 10 MPa shown in Figure 11. In this case it has been amply demonstrated (Figure 12b) that such particles indeed initiate crazes at these low stresses and with remarkable profusion. The detailed stress analysis of Boyce et al [42] for these particles, however, leaves very little room for error. Thus, it must be concluded [20] that the effectiveness of such particles is unexplanable by notions of homogeneous nucleation on which the Argon and Hannoosh [28] criterion has been based. Rather it is necessary, and most likely, that craze initiation from the border of such spherical shell particles involves processes of heterogeneous nucleation where apparently effective use is made of some catalytic interface configurations that markedly relax the craze initiation process. A formal computation demonstrates that the required effect is a major one. The constant A appearing in Eqn. (9) and having the magnitude of 9.54 at room temperature involves activation parameters that control the precursor shear processes giving rise to the micro-pore formation process. This parameter can be considered available for change to obtain a fit between theory and experiment. Such a fit to bring down σ_∞ to 10 MPa can be obtained for the quoted levels of local stress concentration only when the constant A is taken as low as 3.1. Such a vast reduction of the activation energy of an intrinsic deformation resistance in the homo-polystyrene is most unlikely - unless the latter has been radically lowered by swelling or other unaccounted means of plasticization, or if some proto-pores already exist on the interface between the particle and the matrix. The structure of block copolymer interfaces are now a current area of intense study [46], but there are no previous studies that can presently shed light on to this problem.

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TABLE I

MORPHOLOGICAL DETAILS OF PS/PB DIBLOCK COPOLYMERS WITH SPHERICAL DOMAINS

Polymer Code	c_{PB}	Casting Solvent	PB - $\overline{M}_w$ Kg/mole	PS - $\overline{M}_w$ Kg/mole	δ(*) Å	b(**) Å
B(SB9/S4)	0.18	MEK/THF	230	230	700	1090
E(SB9/S4)	0.11	MEK/THF	230	200	730	1340
B(SB7)	0.11	MEK/THF	59	560	360	660
L(SB7/S4)	0.06	TOLUENE	59	284	500	1140
M(SB7/S4)	0.06	MEK/THF	59	284	400	910

(*) δ is sphere diameter.

(**) b is center to center spacing of spherical domains.

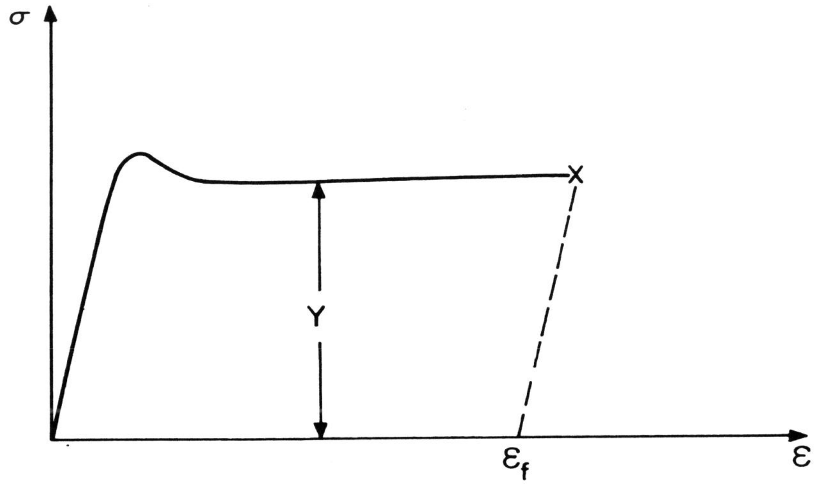

Figure 1. Typical stress-strain curve of a polymer exhibiting dilatational (craze) plasticity.

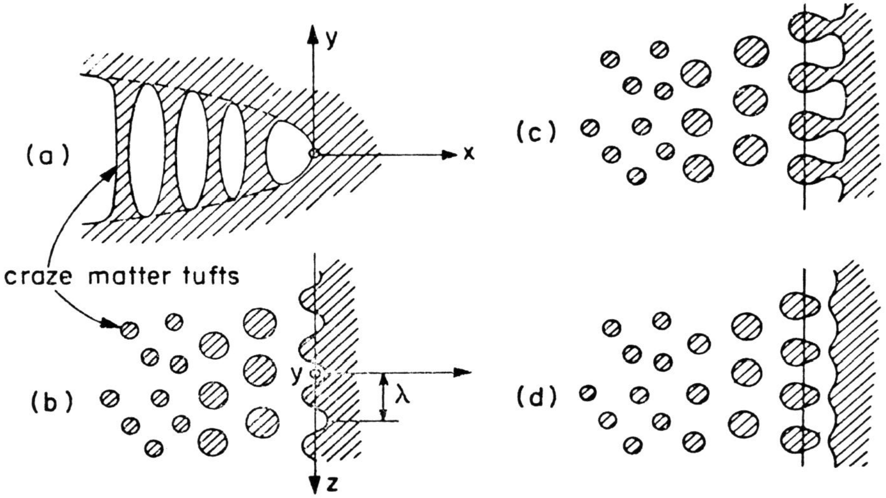

Figure 2. The interface convolution (meniscus break-up) process producing craze matter in homopolymer under stress (after Argon and Salama [16], courtesy of Taylor and Francis).

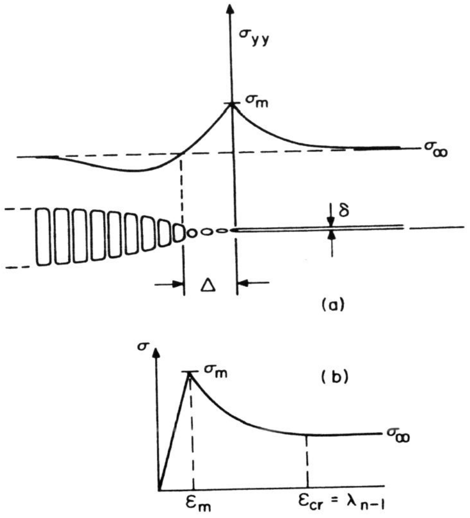

Figure 3. Sketch of a craze and its tractions for the growth process by repeated cavitation of heterophases at the craze tip. In the process zone Δ, mature craze matter tufts are established as material points enter at the right and exit at the left: a) traction distribution across craze; b) sketch of traction - displacement law for craze matter production.

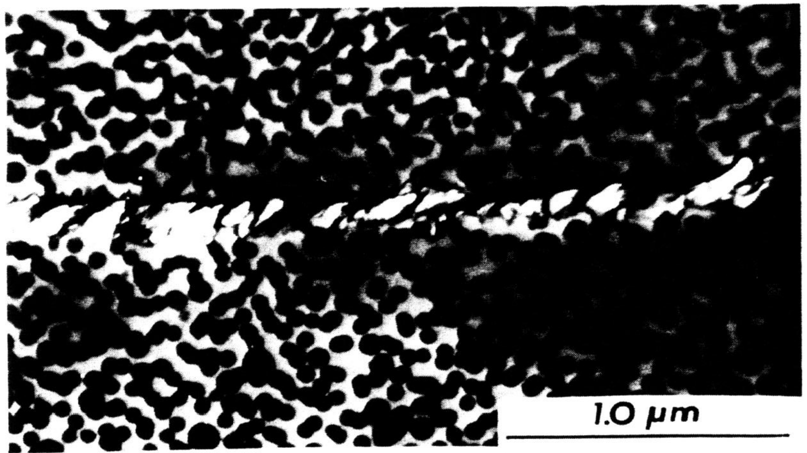

Figure 4. Micrograph of a craze in a di-block with spherical morphology. Note the very narrow nature of the craze involving only about one layer of spherical domain. (from Argon et al [12], courtesy of Springer).

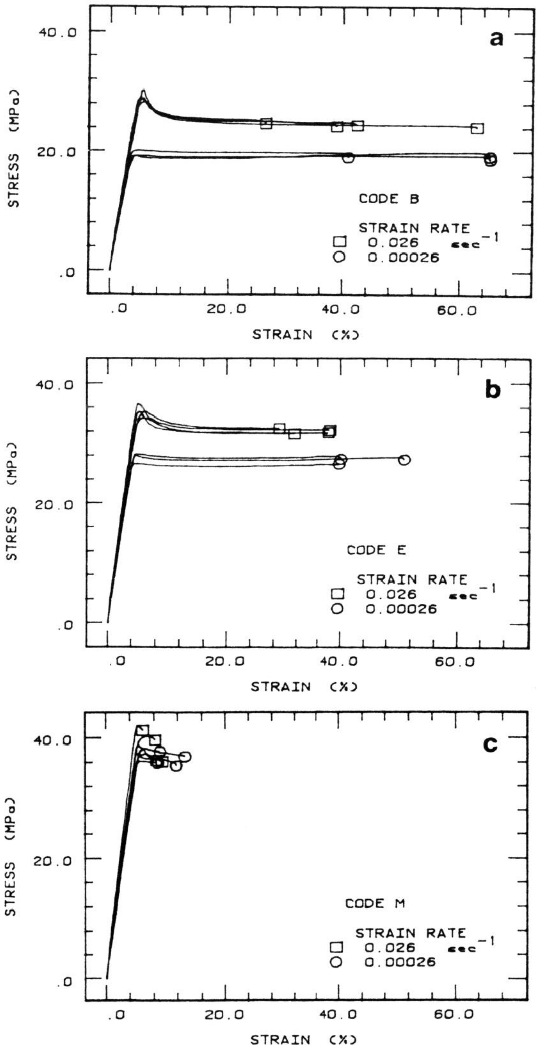

Figure 5. Stress-strain curves of three di-block blends having spherical morphology with: a) c_p = 0.18 of PB (code B); b) c_p = 0.11 of PB (code E); c) c_p = 0.06 of PB (code M).

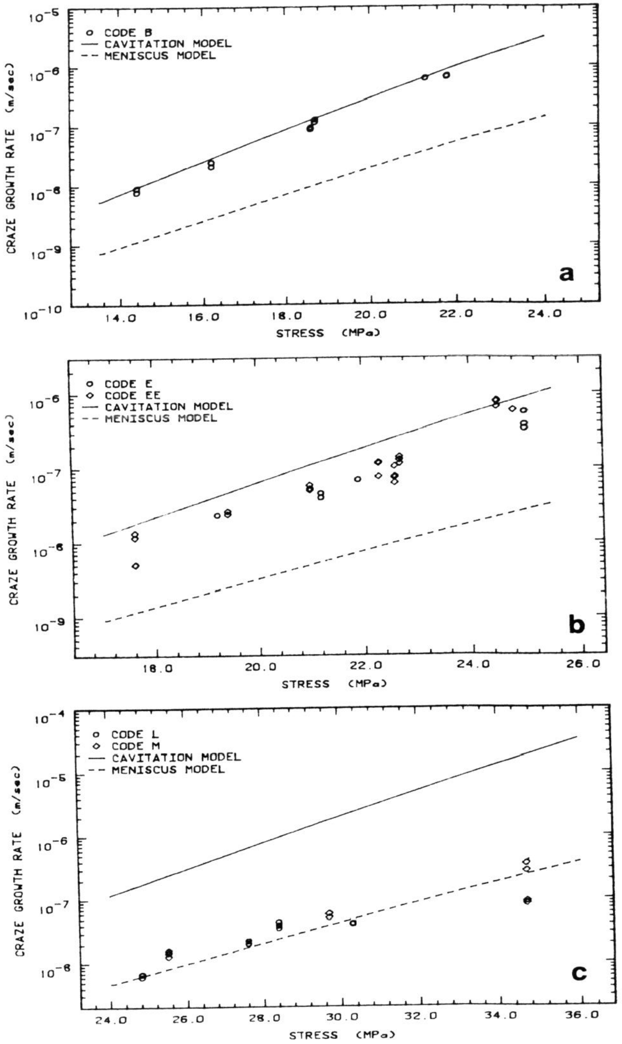

Figure 6. Stress dependence of craze velocity in the same three di-blocks with spherical morphology given in Figure 5, with a) c_p = 0.18 of PB; b) c_p = 0.11 of PB; c) c_p = 0.06 of PB.

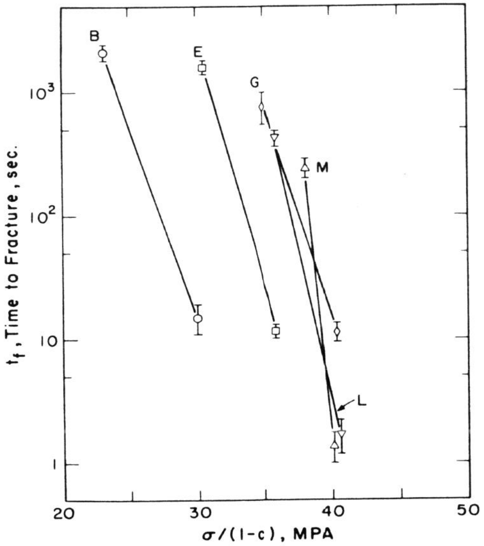

Figure 7. Stress dependence of craze matter fracture times for five different di-blocks with spherical morphology, with characteristics given in Table I.

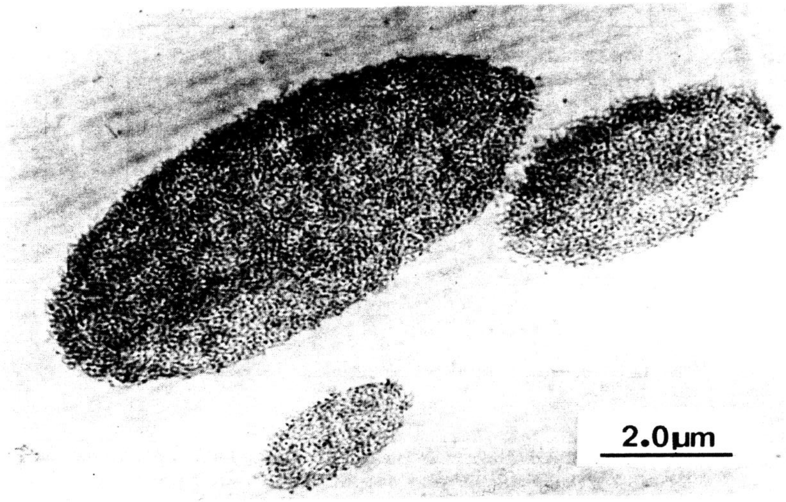

Figure 8. Particles of KRO-1 Resin dispersed in high molecular weight PS.

Figure 9. Particles with concentric spherical shells of PB and PS made by blending additional PB3K into KRO-1 particles to obtain a particle blend ratio PB3K/KRO-1 of 0.5.

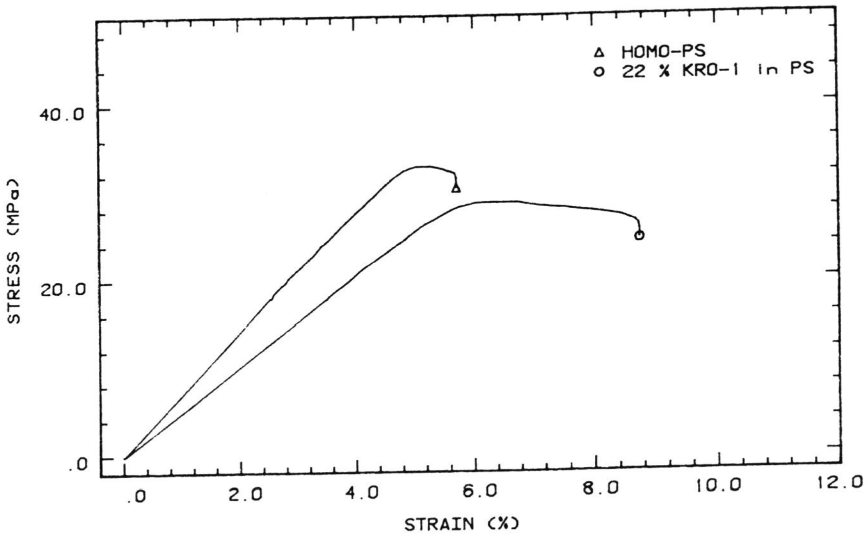

Figure 10. Stress-strain curves of homo-PS , and PS with a volume fraction of 0.22 of KRO-1 particles.

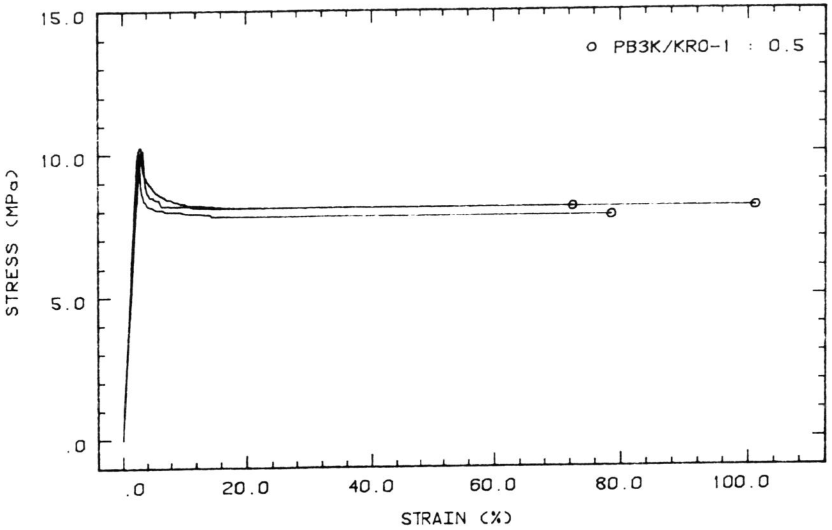

Figure 11. Stress-strain curves of heterogeneous polymer with a volume fraction of spherical shell particles having a blend ratio PB3K/KRO-1 of 0.5.

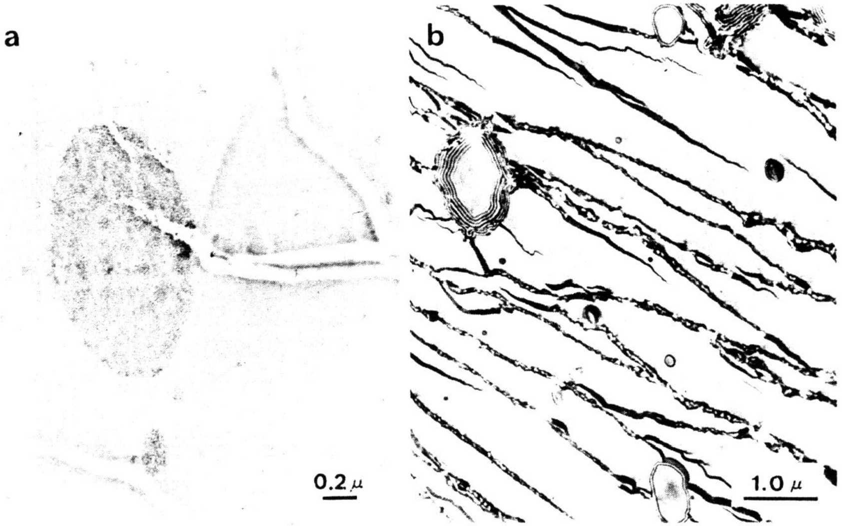

Figure 12. Crazes in two heterogeneous polymers with particle volume fractions of 0.22: a) with KRO-1 particles; b) with spherical shell particles.