A model for Izod strength in impact-modified polystyrene

T. A. Grocela and E. B. Nauman*
Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA
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The strength of impact-modified polystyrene is related to the volume of craze matter generated in fracture. In the Izod test, crazes tend to initiate and propagate between interacting neighbours. The efficiency of craze termination is also critical to toughness, and depends upon the particle morphology. Using computer simulations of crazes propagating through an array of model particles, it has been possible to quantitatively model the crazing process and predict strength. The model is applicable to materials having a wide range of particle sizes, rubber phase volumes, and either solid or occluded particles. Predictions are in good agreement with data obtained for experimental blends as well as commercial HIPS.

(Keywords: polystyrene; fracture; craze)

INTRODUCTION

In rubber-modified polystyrene the energy of fracture is primarily dissipated in the formation of multiple crazes. Hence, strength is directly related to the volume of craze matter generated in fracture. In an Izod test, in particular, the energy dissipated by propagating crazes is far greater than that used to initiate a crack. Thus, to model impact strength in these materials it is necessary to create a quantitative model for crazing.

The rubber particles in rubber-modified polystyrene act as stress concentrators, which initiate crazes at the equator of the particle, which is normal to the applied stress[1]. Matsuo *et al.*[1] report that stress field interactions between coplanar particles are important in the initiation process. The interaction conditions are given by Oxborough and Bowden[2], who found that stress decreases rapidly with distance and approaches that of the matrix at approximately one particle diameter. A previous study[3] found the average distance to the nearest in-plane neighbour to be significant to toughness. This separation distance equals one particle diameter for monodispersed particles with a volume fraction of 7%.

EXPERIMENTAL STUDIES

As described previously[4], samples of rubber-modified polystyrene were produced by the method of compositional quenching. Materials used for the matrix phase and dispersed phase were chosen to resemble those in commercial HIPS. Unlike HIPS, the particles produced by this method were solid rubber. The nearly spherical particles were predominantly in the size range of 0.3–0.8 μm. The size distribution was narrow, and no particles larger than 1.2 μm were observed.

The addition of a high molecular weight block copolymer ensured good adhesion between particles and the matrix. Samples were prepared with rubber volumes up to 23%. Toughness was measured by a notched Izod impact test carried out according to ASTM standard D-256. Samples of a typical commercial HIPS made by the Dow Chemical Company were also measured for strength, and used for comparison. The HIPS contained approximately 22% rubber phase volume in the form of occluded particles which averaged 4 μm in size.

CRAZING MODEL

Craze initiation and propagation

Craze initiation is favoured between closely neighbouring particles. However, previous studies[1,2] have assumed that neighbouring particles are exactly coplanar, which is not typically true. Even when the particles are offset, the stress fields of the particles interact, affecting the initiation and propagation of crazes. To a reasonable approximation, the stress intensity decreases parabolically with distance from the particle surface:

$$\sigma=(s-\sqrt{\sigma_s}-1)^2+1 \qquad (1)$$

where σ is the stress intensity relative to the applied stress, σ_s is the stress intensity factor at the particle surface, and s is the distance from the surface normalized by the particle diameter. For separation distances greater than one diameter the stress is equal to the applied stress. Assuming that the stress fields are additive[1], the stress intensity at the equator of the particles can be calculated for any separation distance. Likewise, the stress intensity for off-equator positions can be found using the same parabolic form. Surface stress intensity factors are given by Furno[5] as a function of position from the equator, and are listed in *Table 1*. Using these, the stress field

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*To whom correspondence should be addressed

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Table 1 Stress intensity factors

Position	Stress intensity factor
0°	2.0
5°	1.63
10°	1.58
20°	1.45
30°	1.25
40°	1.0

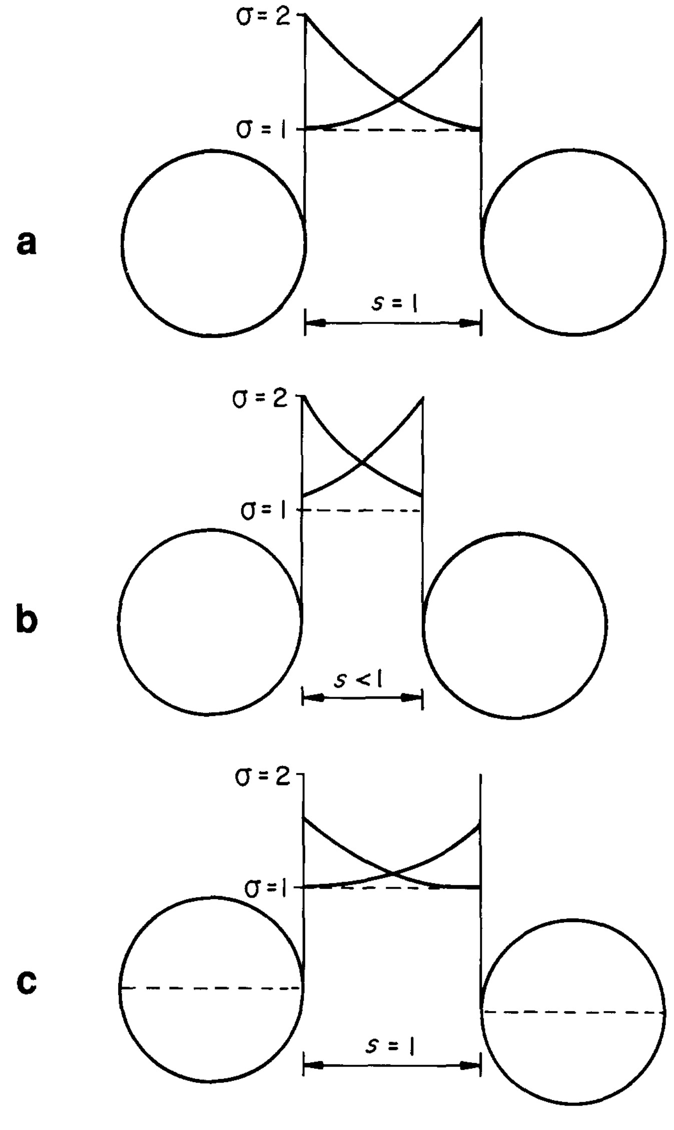

Figure 1 Stress field interaction of two particles which have: (a) $s = 1$, (b) $s < 1$ and (c) equators offset

interaction between two equal-sized particles can be estimated for any separation distance (see *Figure 1*).

Calculation shows that particles offset by 5° must be within $s = 0.185$ of one another to provide an off-equatorial stress concentration which exceeds the equatorial value of $\sigma = 2$. Clearly, for the stress concentration at non-equatorial positions to exceed those at the equator, the particles must be very close. For volume fractions less than 25%, the average nearest neighbour is not close enough to initiate crazes at even a 5° offset. Calculation shows $s = 0$ at about 16°. Thus, crazes cannot initiate on the particle surface at an angle greater than 16°, regardless of the proximity of neighbours, because initiation at the equator is always favoured.

It is often noted[1,2] that crazes propagate perpendicular to the applied stress. The behaviour results from the structure of the crazes themselves, which consist of fibrils that are drawn parallel to the applied stress. Examination of crazes by Argon[6] shows that they always grow perpendicular to the maximum principal tensile stress, even when under multi-axial stress. Thus, it is expected that the primary direction of propagation of a craze initiating at the equator of a particle is in the plane of the equator.

This is confirmed using data from Furno[7]. *Figure 2* shows the distribution of Von Mises' Equivalent Stress in the matrix around two offset rubber particles which are one diameter apart. Note that the stress contours about the equator, though somewhat circular in shape, are quite flattened. Because the contours are flattened, the line of maximum stress for a craze initiating at the surface is on the equatorial plane unless the neighbouring particle is very close indeed. The particles must be much closer than one diameter for one particle to drastically affect the stress at the surface of its neighbour. The present model assumes that all crazes propagate in the equatorial plane. This should be an excellent approximation for rubber volumes less than 25%.

Although the stress fields of neighbouring particles cannot override the influence of the principal stress, the direction of propagation within the plane depends strongly on the interactions of other particles. The particles cause a stress concentration in the matrix up to an angle of 40° from the equator. Therefore, propagation towards the nearest in-plane neighbours is favoured provided they lie close enough for the particle stress fields to interact.

Craze termination

Initiation and propagation of crazes depend almost entirely on the stress distribution in the matrix, and are

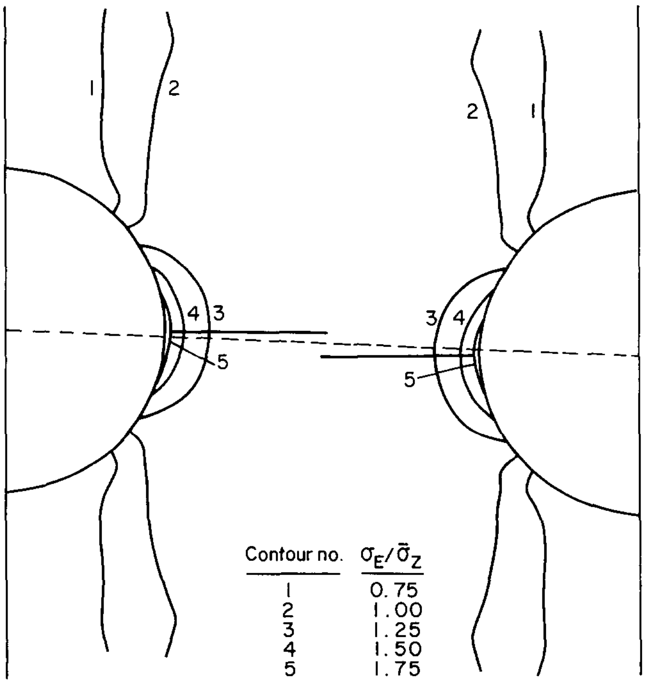

Figure 2 Von Mises' equivalent stress about two offset particles under uniaxial tension. Reproduced from Furno[5]

largely independent of particle morphology. On the other hand, termination depends critically upon particle morphology. The deformation behaviour of a HIPS particle intercepting a craze is distinctly different from that of a solid rubber particle[7]. The solid particle tends to deform as a whole. The elongation is accompanied by a lateral contraction of the particle which causes rubber fibrillation at the equator. Occlusions in a HIPS particle reinforce it, preventing large extensions of the particle as a whole. When a craze propagates into the centre of an occluded particle, fibrillation can occur between the occlusions contacted by the craze. When a craze propagates into a position near the poles, however, the strains imposed by the matrix crazes are entirely accommodated by the rubber surface layer of the particle.

The morphology of the solid rubber particles allows for extensions which are easily accommodated by the rubber when a craze contacts the particle interface. It is suggested from a previous result[3] that termination occurs if the craze intersects a neighbouring particle within a $d/2$ bandwidth. A craze contacting an occluded particle is terminated if the craze is intercepted within the occluded region of the particle. Because the rubber fibrillates at the poles, a craze contacting the outer rubbery region near the poles tends to propagate around the particle. If a craze comes only partially into contact with the poles, propagation proceeds around the particle, where there is less resistance to drawing than between the occlusions. To accurately represent a HIPS particle without losing the essence of the deformation mechanism, the occluded particles are modelled as composites having a core–shell type structure[8].

SIMULATION SCHEME

Computer simulations of crazes propagating through an array of particles were used to model crazing in materials containing either solid or occluded particles. The simulations randomly placed either core–shell or solid particles into a two-dimensional domain. The size of the domain was chosen to ensure that those crazes which were initiated could also be terminated within the domain. Periodic boundary conditions were used. All particle arrays were monodisperse so that any effects of size distribution were ignored. All lengths were scaled in terms of one particle diameter so that varying size particles could be simulated using the same program. Particles were placed at random locations until the desired particle volume fraction was reached. The simulation then selected particles at one end of the domain as sites for craze initiation. Crazes having a specified thickness of 0.5 μm were propagated in a straight line from the equators of the chosen particles.

The termination site for each simulated craze was located by examining the position of any intercepting particles. In the case of the occluded particles, when the entire thickness of the craze was intercepted by the core diameter, the craze was terminated. For the solid rubber particles, termination occurred when a half thickness of the craze was intercepted by the particle. The programs calculated craze travel distances from initiation to termination. In propagating the crazes, it was assumed that a craze which contacted a particle, but was not terminated, would continue to propagate in a straight line.

MODEL OF IZOD STRENGTH

The improvement in Izod strength due to the rubber particles is proportional to the total energy dissipated by crazing minus the energy absorbed by the material when there is no toughness improvement:

$$I - I_0 \propto E - E_0 \tag{2}$$

Here, I is the Izod strength of a blend, I_0 is the strength of crystal polystyrene, E is the energy dissipated by the blend, and E_0 is the energy for the same type of blend at the highest rubber volume fraction which produces no improvement in strength. For the experimental blends, this volume fraction was 7%. The energy dissipated is directly related to the craze volume, and is calculated as:

$$E = C N_p \varepsilon \psi u \tag{3}$$

where C is a constant having units of energy dissipated per length of craze, $N_p \varepsilon$ is the number of effective particles, ψ is the number of crazes per particle, and u is the distance travelled per craze. E_0 is calculated from the same equation using values for the appropriate rubber volume.

Because the Izod test is basically two-dimensional, all energy is dissipated in the plane of the propagating crack. Hence, it is primarily the rubber particles lying within that plane which are initiating and terminating crazes. The actual number of particles in the plane of the test is unnecessary for calculation of strength. Only a relative number is needed. The ratio of total number of particles in a plane for any two blends is given by:

$$\frac{(N_p)_1}{(N_p)_2} = \frac{r_2^2}{r_1^2} \cdot \frac{\phi_1}{\phi_2} \tag{4}$$

where N_p is the total number of particles, r is the radius of the particles, and ϕ is the rubber volume fraction.

The effective number of particles is found by multiplying the total number of particles by an effectiveness, ε, given by:

$$\varepsilon = (D/u)_0 \tag{5}$$

where D is the particle diameter and the subscript indicates that it is calculated at 7% rubber volume. When a craze contacts a particle, but is not terminated, a crazing site has been used ineffectively. Effectiveness is expected to be inversely proportional to the number of particles which contact but do not terminate a craze. For a constant rubber volume, u/D indicates the number of particle diameters a craze travels, which is directly related to the number of bypassed particles. Therefore, $(D/u)_0$ measures effectiveness, and is consistent with the constraint that E must equal E_0 at 7% phase volume. Equation (5) is admittedly *ad hoc* in nature and should ultimately be replaced by a more fundamental result. It does give testable predictions which have been partially confirmed by the present study. It finesses an obvious question regarding the ultimate fate of crazes which are not terminated by a rubber particle. These crazes will spontaneously terminate if the stress in the matrix is below that necessary for craze propagation. In a dynamic test, the stress increases with time so that at least one craze will continue to grow, leading to catastrophic failure.

Craze lengths in the compositionally quenched materials and HIPS were calculated using the computer simulation described previously. By fixing the particle diameter of the compositionally quenched particles at

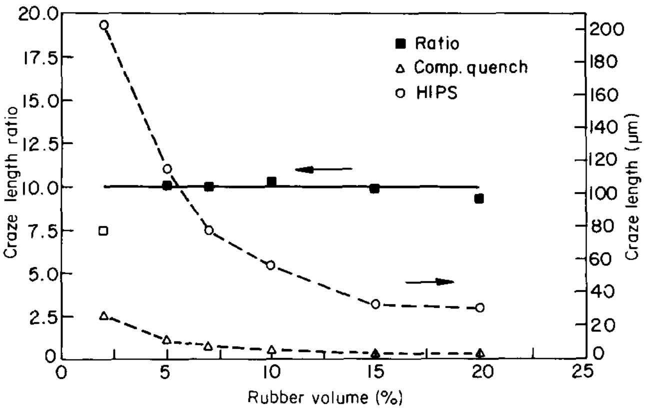

Figure 3 Craze lengths and length ratio of compositionally quenched material to HIPS

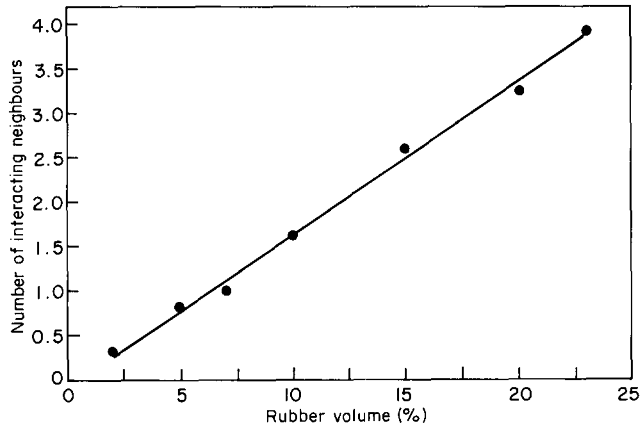

Figure 4 Number of interacting neighbours *versus* rubber volume for particles in a plane

0.5 μm, and that of the HIPS particles at 4.0 μm, craze lengths could be compared. For all rubber volumes of interest, the ratio u_H/u_{CQ} remained constant at approximately 10 (see *Figure 3*).

The number of crazes associated with a given particle depends on two factors, either of which may be limiting. The number of crazes initiated depends upon the number of neighbours interacting with a given particle. However, the number of crazes may be limited by the number that can fit around the equator of the particle. The number of interacting neighbours was calculated using a computer program similar to the one described in a previous paper by Grocela and Nauman[4]. The number of interacting particles was found to be independent of the particle diameter, and to vary linearly with rubber volume (see *Figure 4*).

In HIPS particles the equator is large enough to accommodate 25 crazes which are 0.5 μm in size. Therefore the number of crazes per particle is limited by the number of interacting particles. For a volume fraction of 23%, the average number is 3.9. In the case of the 0.5 μm solid particles, the number of crazes per particle is limited by the equatorial distance. Because the solid particles deform significantly, the lateral contraction decreases the equatorial distance. Considering this $\lambda^{-1/2}$ contraction[5,7] ($\lambda = 4.8$ for PS), the compositionally quenched particles can only accommodate two crazes.

PREDICTION OF STRENGTH

Equation (6) can be used to predict the Izod strength of the compositionally quenched material and HIPS. A single data point is required to obtain the proportionality constant. Taking the ratio of the unknown strength to the known:

$$\frac{I-I_0}{I_D-I_0}=\frac{E-E_0}{(E-E_0)_D} \qquad (6)$$

where I_D is the measured Izod strength and $(E-E_0)_D$ is the calculated energy difference corresponding to that strength. The energy contribution for both materials is calculated from equations (3)–(5) and the computed values for u and ψ. The Izod strength is then calculated as:

$$I=(I_D-I_0)\cdot\frac{(E-E_0)}{(E-E_0)_D}+I_0 \qquad (7)$$

For this work, the chosen data point was the Izod strength of the compositionally quenched material at 23% rubber volume and 0.5 μm particle size, where $I_D = 4.13$ ft-lb/in. The values for the other compositionally quenched blends as well as for HIPS were predicted by the model. From experiment, the Izod strength of HIPS was reported as 1.33 ft-lb/in., in good agreement with the predicted value of 1.25 ft-lb/in. Predictions for the compositionally quenched materials were also quite accurate. The experimental data are shown as distinct points in *Figure 5*, while the solid lines represent model predictions.

The Izod strength of other types of rubber-modified polystyrenes can be predicted using the model provided the rubber particles in the unknown materials deform in a similar manner to either HIPS or solid particles. For example, the calculated strengths of two hypothetical blends containing large-diameter solid particles are shown as dashed lines in *Figure 5*. The 4 μm solid particles are predicted to give a slightly higher impact strength than for HIPS particles because the solid particles are more efficient craze terminators. The 2 μm particles give intermediate performances compared to the 4.0 μm and 0.5 μm solid particles, as expected.

For HIPS, the model can be used to predict an optimum particle size. A plot of predicted strength *versus* particle diameter is shown in *Figure 6*. Performance of the blends is poor when the particle size is close to that of the craze thickness. At a particle size of approximately 3 μm, strength reaches an optimum. Thereafter, toughness

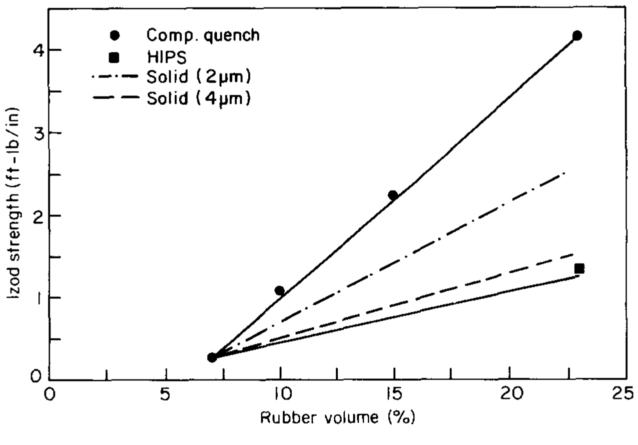

Figure 5 Izod data and predicted strengths for various polystyrene blends

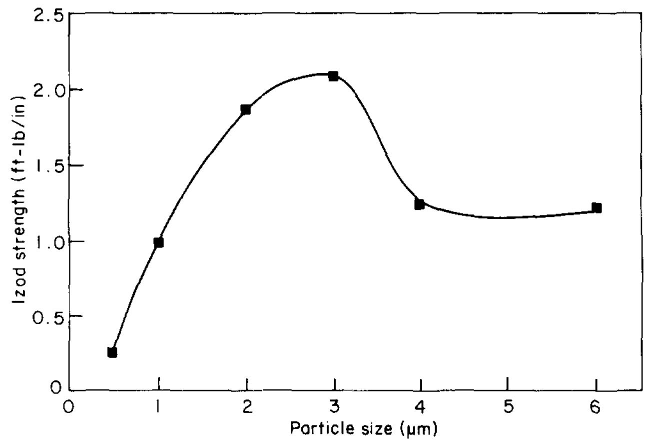

Figure 6 Predicted Izod strength of HIPS blends having various particle sizes

decreases. Consistent with experiment, the predicted optimal size for HIPS is much larger than that for the compositionally quenched materials. It is also in reasonable agreement with the 3–4 μm value which has been reported as the experimentally determined optimum for HIPS[9].

The small discrepancy may be attributed to two factors. HIPS particles are modelled as having a constant composition. Because HIPS is made by chemical reaction, the rubber layer thickness may not be proportional to the particle size, as was assumed here. The current model also fails to consider the broad particle size distribution of HIPS. If the real particles could be made monodisperse, they might indeed be more effective at the smaller particle size because the total rubber volume would be used more efficiently.

The numerical data in *Figure 6* represent a limited number of simulation runs and thus show some scatter. It is clear, however, that the model predicts an asymptote in Izod impact strength with increasing particle diameter. Note that the model contains only one absolute distance, the craze thickness. When the particle diameter becomes large relative to the craze thickness, the equator can accommodate an essentially infinite number of crazes. For large particles, the number of crazes per particle is determined only by the number of interacting particles which, in turn, depends only on the volume fraction of rubber and not on the absolute size.

CONCLUSIONS

In the high-speed Izod test, crazes in rubber-modified polystyrene tend to initiate at the equators of particles, and propagate in the plane of the equator towards interacting neighbours. Termination of crazes is dependent on the morphology of the intercepting particles. By quantitatively modelling the crazing process, the energy dissipated by the formation of multiple crazes has been calculated. The Izod impact strength of impact-modified polystyrene containing various size particles and rubber volumes can be predicted using the crazing model and limited data. The strength of experimental materials has been predicted quite accurately. The optimum particle size for commercial HIPS has also been predicted, and is in reasonable agreement with reported values. The advantage of the model over previous ones is that it is applicable to a wide range of particle sizes, and is valid for both solid rubber and occluded particles. The model gives testable predictions which have been partially verified in the present study.

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