The Effects of γ Irradiation on Toughening Mechanisms in Rubber-Modified Polymers

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SYNOPSIS

High-impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) have been subject to γ irradiation in doses up to 20 and 12.5 Mrad, respectively. During tensile testing, both longitudinal extension and lateral contraction were simultaneously measured, allowing determination of volume strain, and from this to identify the relative contributions of crazing and shear yielding to the tensile deformation process. Both materials show a dose-related increase in the strain at which crazing commences, though the relative change with dose in HIPS is much greater than in ABS. However, the contribution of crazing to total deformation remains high in HIPS when compared with ABS. Shear yielding is an important deformation process in ABS and the results indicate that this is relatively unaffected by irradiation, whereas the ability to craze is severely limited. The reduced ability to craze observed in both materials is considered to be the result of crosslinking in the rubbery phase. The notched impact strength of ABS is particularly sensitive to irradiation and again reflects the reduced ability to craze observed in the tensile testing. ABS fracture surfaces examined by scanning electron microscopy display reduced ductility in the irradiated material. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Rubber toughening is one of the most successful methods of modifying the properties of brittle polymers. A minor portion of rubber, typically between 5 and 20%, is incorporated as a disperse phase in a rigid matrix to give a material with a significantly higher fracture resistance than the parent polymer. Toughening mechanisms include crazing and shear yielding, both of which involve localized deformation of the brittle matrix associated with stress concentrations initiated by the rubber inclusions.

The irradiation of polymers is important in a number of commercial applications including medical implant devices and packaging materials. In previous work[1] on the fracture behavior of γ-irradiated polystyrene and rubber-toughened polystyrene, it was shown that impact strength reduction was much greater in the toughened polymer. The observed differences were explained in terms of the radiochemical responses of the polystyrene matrix and rubbery polybutadiene inclusions. Crosslinking in the rubbery phase was thought to occur on irradiation while the polystyrene matrix was relatively unaffected. It was suggested that energy dissipation by fibrillation became more difficult with consequent reduction in impact strength.

This work represents a further investigation of the effect of γ radiation on rubber-toughened polymers. For the two materials studied, HIPS and ABS, the differences in tensile behavior are recognized[2-5] as arising from differences in the contributions of crazing and shear yielding to the overall deformation. In HIPS crazing dominates and there is little evidence of shear yielding. In ABS, on the other hand, crazing and shear yielding proceed simultaneously so that the specimen exhibits both stress whitening and necking.[3,4] Radiation-induced crosslinking may be expected to have differing effects on these toughening mechanisms.

Determination of volume changes during tensile loading by simultaneous measurement of the linear dimensions of the specimen allows rubber toughening mechanisms to be quantified. It has proved useful[2,6-8] in enabling craze initiation and growth to

Journal of Applied Polymer Science, Vol. 48, 181–186 (1993)

CCC 0021-8995/93/010181-06

be monitored during tensile creep testing. This method distinguishes between shear yielding, which takes place essentially at constant volume, and dilatorial processes which are associated principally with craze formation and growth. In response to the principal hydrostatic tensile stress the material undergoes localized plastic deformation with formation of crazes consisting of fibrils extending in the tensile direction and voids. The craze-opening direction is aligned with the principal tensile stress.

Thus crazes consist of approximately 50% of voids by volume and do not contribute to transverse strain, but contribute significantly to longitudinal strain after the initial elastic response. It is recognized that cavitation within the rubber particles and rubber/matrix debonding may occur and contribute to volume strain, however it is considered that this contribution would be small compared with overall volume strain. Assuming constant bulk modulus during the course of the test and neglecting non-craze cavitation, the ratio of volume strain ($\Delta V/V$) to longitudinal strain provides a convenient form for expressing the contribution of crazing to the total elongation. Nevertheless because of these dilational processes the specific contribution from crazing may be less than indicated by the data. The possible responses to this experimental procedure and their interpretation are shown schematically in Figure 1.

With polystyrene changes in mechanical properties are not observed until much larger dose levels than used in this study[9,10] and as it forms the bulk of the matrix in both systems, relative changes in the volume strain to longitudinal strain relationship can be directly assigned to craze and shear yielding processes. Using this approach with two different rubber-toughened styrene-based polymers may be useful in further elucidating the effects of γ irradiation on two phase systems. To allow direct comparison with the previous work on HIPS both notched and unnotched impact strengths have also been measured for ABS. Dynamic mechanical techniques have also been applied to the materials to identify the glass transition temperature of the rubbery phase. This will allow assessment of the possible role of shifts in this transition on the toughening mechanism.

EXPERIMENTAL

Tensile and impact specimens according to BS2782 Part 3, Method 320B were injection moulded from HIPS (BASF Polystyrol 472C) and ABS (BASF Terluran 967K). Specimens were irradiated in air using a cobalt 60 source at a dose rate of 0.156 Mrad/h to give received doses up to 12.5 Mrad for ABS and 20 Mrad for HIPS.

Tensile testing was carried out at a longitudinal strain rate of 0.08/s using an Instron 4302 universal testing machine. Instron 2620 and 2640 contact extensometers were used to measure longitudinal and transverse strain.

The experimental procedure adopted was to monitor transverse strain as a function of tensile strain during conventional tensile testing. Data analysis was similar to that developed by other workers for tensile creep experiments[8] and tensile dilatometry.[11] The dilational response has two com-

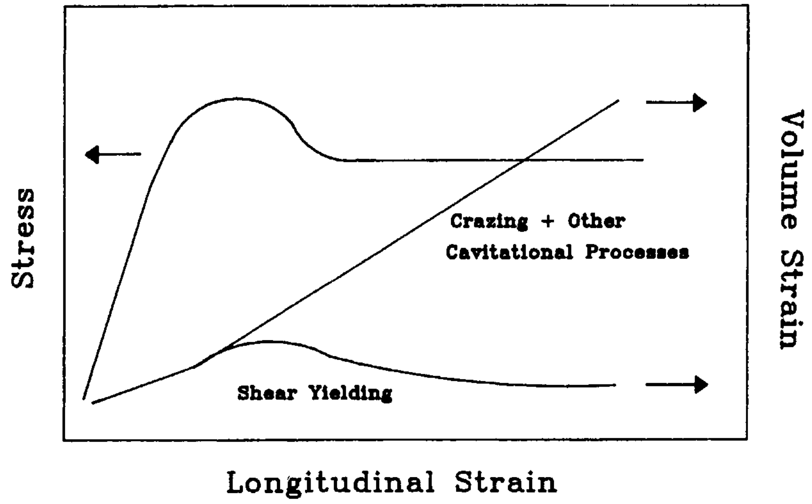

Figure 1 Possible responses from tensile dilatometry and their interpretations.

Table I Tensile Properties of Irradiated ABS

Dose (Mrad)	Modulus (GPa)	Yield Stress (MPa)	Fracture Stress (MPa)	Elongation at Break (%)
0	1.03	40.0	32.8	16.2
2.5	1.04	40.6	32.9	16.0
5.0	1.06	41.9	32.7	15.6
7.5	1.09	41.4	33.1	16.2
10.0	1.10	41.5	32.9	14.2
12.5	1.13	41.7	34.0	12.0

ponents, an elastic effect arising when Poisson's ratio is not 0.5 and the range of cavitation processes associated with crazing. In the experimental analysis allowance was made for Poisson's ratio effects by extrapolating the linear portion of the volume strain curve back to the point at which the volume strain is equal to the instantaneous volume strain. The slope of the line of $\Delta V/V$ versus longitudinal strain will be unity for the case where crazing is the sole deformation process and zero for the case of shear yielding. A line of intermediate slope indicates both processes are occurring and the slope of the line denotes their relative magnitudes. The onset of crazing will be indicated by a change of slope in the plot of volume strain against longitudinal strain.

Izod impact strengths were measured on notched and un-notched specimens according to BS2782. Fracture surfaces were examined by scanning electron microscopy.

The dynamic mechanical response of the irradiated materials was examined using a Polymer Laboratories DMTA instrument. A frequency of 1 Hz and a strain of ×4 was used over the temperature range of −100 to 20°C at a heating rate of 2.9°C/min.

RESULTS

Tables I and II detail the tensile and impact results obtained with ABS.

Table II Impact Strength of Irradiated ABS

Dose (Mrad)	Un-notched (J)	Notched (J)
0	13.06 ± 1.01	6.43 ± 0.24
2.5	12.83 ± 1.20	6.04 ± 0.36
5.0	12.89 ± 0.95	1.55 ± 0.21
7.5	12.94 ± 1.04	1.94 ± 0.23
10.0	12.32 ± 1.04	1.69 ± 0.19

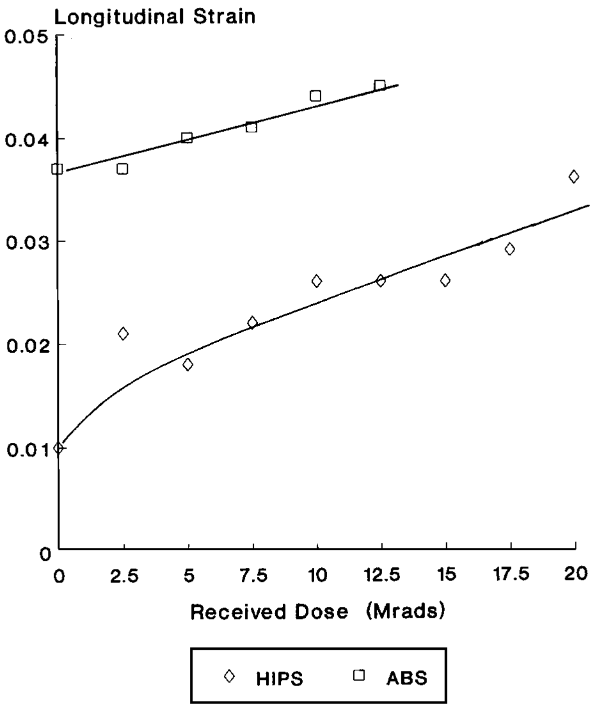

Figure 2 Effect of irradiation dose on strain at which crazing is initiated.

Figure 2 shows the effect of dose on the longitudinal strain at which crazing is initiated for both HIPS and ABS. Figure 3 shows the normalized in-

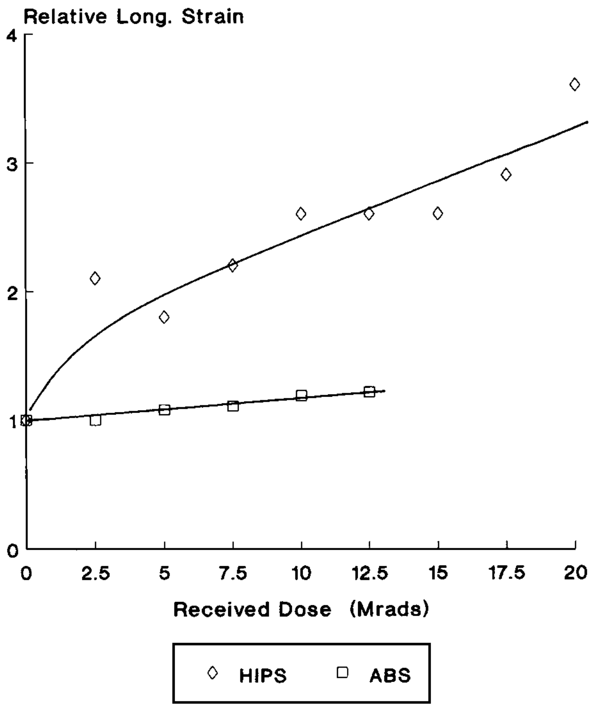

Figure 3 Effect of irradiation dose on the normalized increase in strain to craze.

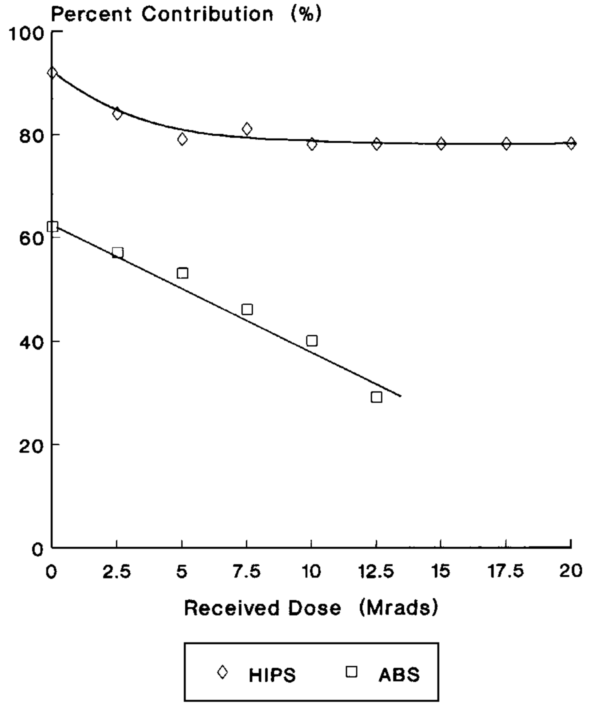

Figure 4 Effect of irradiation dose on the contribution of crazing to total deformation.

crease in strain to craze. The contribution of crazing to the total deformation for the same materials is displayed in Figure 4. Impact fracture surfaces for ABS are shown in Figures 5 and 6. Table III lists the glass transition temperatures of the rubber phase of the irradiated polymers.

DISCUSSION

Comparison of the effects of irradiation on the tensile properties of ABS with results previously obtained with HIPS[1] shows similar general behavior. Slight increases in modulus, yield stress, and fracture stress are observed. Again, elongation at break falls with increasing dose and can be seen to be the most sensitive property to radiation-induced changes. Tensile property changes at low doses, for instance the 2.5–5.0 Mrad encountered in sterilization procedures, are small and not likely to be of technological significance. Unnotched impact strength is relatively insensitive to dose but the notched impact strength is seen to fall rapidly with increasing dose. In general terms this suggests that crack initiation is relatively dose insensitive whereas crack propagation is affected by dose-related toughness decrease. For ABS reductions in notched impact strength are most marked in contrast to the behavior of HIPS,[1] where unnotched impact strength is most affected implying differences in the relative crack initiation and propagation stresses in the two materials. The

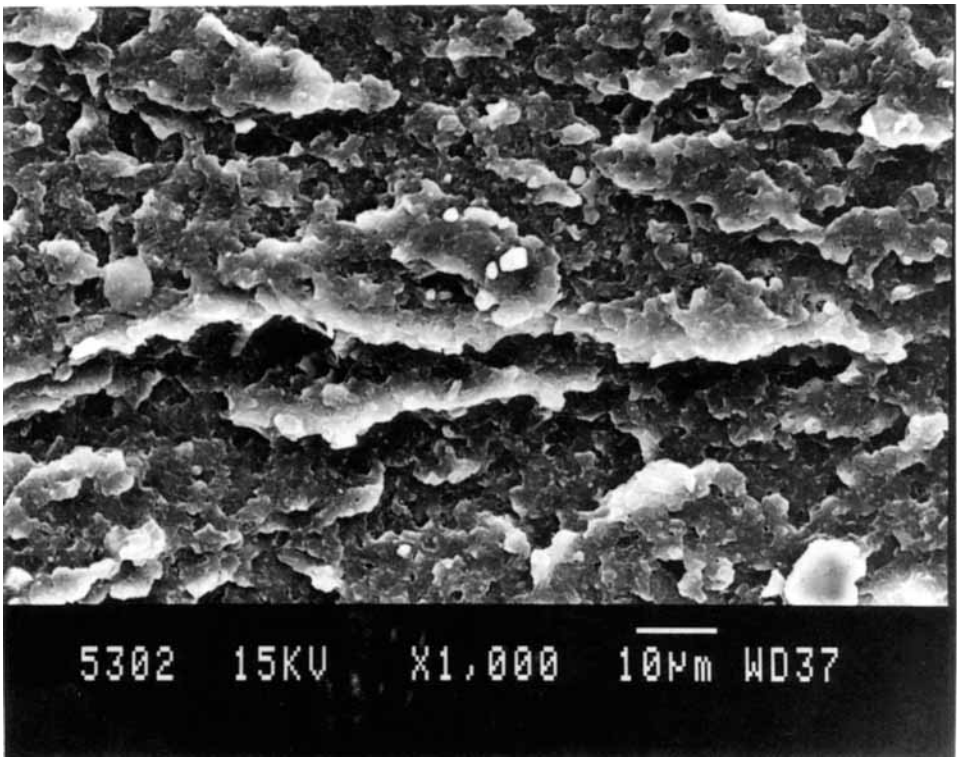

Figure 5 Un-notched impact fracture surface of unirradiated ABS.

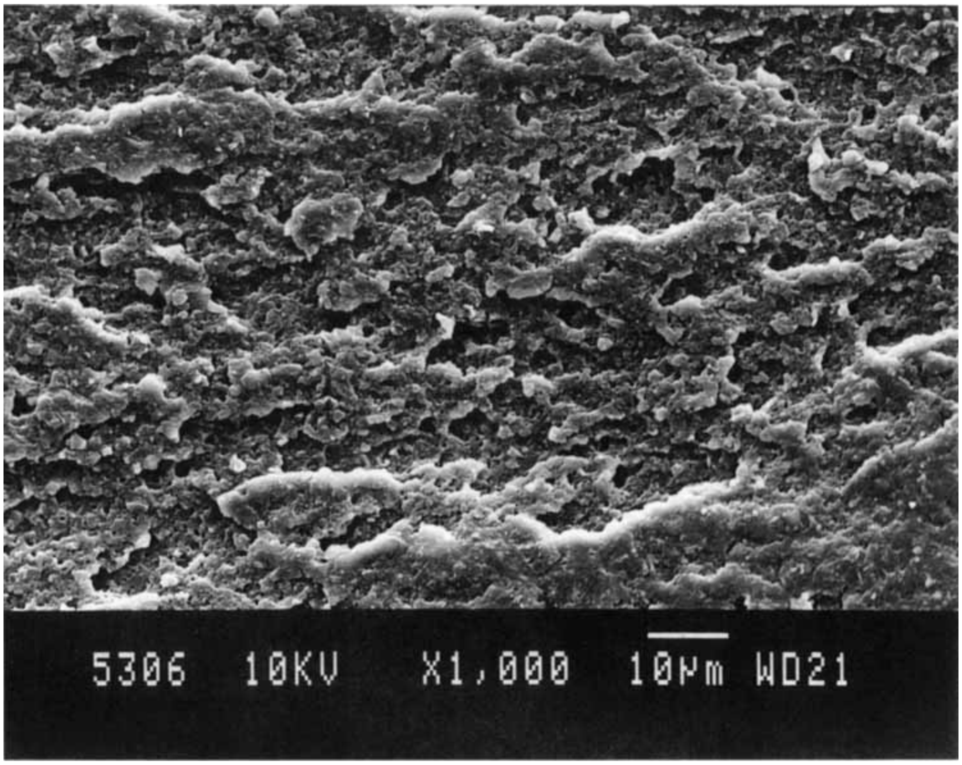

Figure 6 Un-notched impact fracture surface of 10 Mrad ABS.

fracture surfaces clearly display features which indicate a reduction in ductility following irradiation.[12] These results again emphasizes the importance of consideration of impact behavior when evaluating the effects of γ sterilization of plastics.

Both materials show a dose-related increase in the strain at which crazing is initiated; however, the relative change is appreciably greater with HIPS. The two materials also show significant differences in the importance of crazing to total deformation behavior. With HIPS, the crazing contribution has fallen and stabilized after 5 Mrad, whereas with ABS crazing shows a continuing decline in importance over the dose range examined.

Table III T_g **of Rubber Phases as a Function of Received Dose**

Dose (Mrad)	T_g ABS (°C)	T_g HIPS (°C)
0	−81.6	−77.6
2.5	−81.9	not measured
5.0	−81.1	not measured
7.5	−79.1	not measured
10.0	−79.9	−76.1
12.5	−77.2	not measured
20.0	—	−75.0

In HIPS crazing is the sole inelastic deformation mechanism and behavior is thus dependant on the ability of the included phase to initiate and control this process. Radiochemical yields[9] for scission and crosslinking for the various polymer segments found in ABS and HIPS, indicate that crosslinking will occur in the rubber phase, while the styrene-based matrix will remain relatively unaffected at the dose levels used here. Relatively few crosslinks or branches induced in the matrix material on irradiation may limit the ability of this phase to undergo localized yielding in craze initiation. However assuming that the principal effect of the irradiation is to increase the crosslink density within the rubbery domains a reduction in the relative difference between the moduli of the two phases will result. The shift of 4.4°C in the rubbery phase T_g, observed with ABS, is consistent with such a change. It is thought that the increase in modulus resulting from the increased crosslinking, which is responsible for the observed T_g shift will reduce the ability of the rubber to initiate crazing, with subsequent loss of toughness. With ABS in addition to crazing, deformation can occur by shear yielding. The lower sensitivity to dose observed here indicates that the latter process is relatively unaffected by changes in crosslink density in the rubbery phase.

There are significant differences in the rates of strain experienced by materials in uniaxial tensile testing and in impact testing. The results suggest that the two toughening mechanisms in ABS have different rates of response. At higher rates of strain, crazing and crack fibrillation are more important and these are limited in the irradiated material by increased crosslink density in the rubber phase. At the lower strain rates encountered in the tensile tests, shear yielding can play a more effective toughening role. While the higher strain rates experienced in the impact testing will have the effect of further raising the effective T_g of the rubbery material, it is unlikely that the rate of deformation in conventional Izod impact testing will bring the transition close to ambient temperature. It is therefore assumed that the butadiene phase is rubber-like under both tensile and impact testing conditions.

CONCLUSIONS

The most important changes in mechanical properties which occur when ABS is subject to γ irradiation are dose-related reductions in elongation at break and notched impact strength. The overall response is generally similar to HIPS. In both materials, the principal chemical rearrangement associated with irradiation is crosslinking in the rubbery component. This reduces the relative moduli of the two phases and limits the ability of the rubbery inclusions to act as craze initiators. In ABS the alternative toughening mechanism of shear yielding is relatively unaffected by irradiation. Also, with ABS significant reductions in notched impact strength occur at dose levels likely to be encountered in commercial sterilization procedures. A similar observation already has been made with HIPS and may have more general implications for rubber-toughened systems.

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Received July 26, 1991
Accepted July 2, 1992