Fracture of Irradiated Polystyrene

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Synopsis

Samples of polystyrene and high impact polystyrene of the butadiene copolymer type, have been subjected to irradiation in air to give received doses of up to 50 Mrad. Tensile and impact properties of the materials were measured using standard techniques. Whilst polystyrene showed little change in mechanical properties with received dose, the two phase high impact material showed significant effects with elongation at break and impact strength being reduced by an order of magnitude over the dose range examined. This behavior is thought to be associated with radiation induced crosslinking in the polybutadiene phase reducing the ability of the rubber to dissipate fracture energy. Micrographs of the tensile fracture surfaces of irradiated high impact polystyrene show evidence consistent with this mechanism.

INTRODUCTION

It is well established that the tensile properties of polymers are sensitive to γ radiation induced structural change, but less information is available regarding changes in impact strength on irradiation. It must be presumed that the changes in molecular architecture consequent on irradiation will influence impact resistance, and while radio-chemical mechanisms in thermoplastics are well defined, the technological consequences of the structural rearrangements have been the subject of fewer investigations.

Two phase systems, such as semi-crystalline polymers, in which the phases are chemically similar but differ physically, have been the subject of much investigation. In polyolefins the predominant structural change occurs in the amorphous region or on the surface of the crystals.[1-3] The onset of crosslinking reduces the ability to plastically deform, hence these materials, in which the amorphous phase is above T_g at room temperature, show progressive reduction in elongation at break with increasing radiation dose. In general the gross effect of irradiation on the mechanical behavior of glassy polymers is much smaller. The materials studied in this work are polystyrene and high impact polystyrene, the latter being a two phase system in which both components are amorphous but chemically and physically different.

Polystyrene shows a high degree of resistance to irradiation, a phenomenon generally ascribed to the protective influence of the benzene ring,[4] whereas butadiene polymers can be expected to show much higher radiation susceptibility. High impact polystyrene, of the butadiene copolymer type, in addition to radiation-induced change in each of the individual phases, offers the opportunity of interfacial modification. Polystyrene may undergo both crosslinking and scission reactions on irradiation, whilst polybutadiene, which predominantly crosslinks, offers the additional reaction of cyclization.[5]

The purpose of this study was to quantify the effects of radiation dose on the tensile and impact properties of polystyrene and high-impact polystyrene. Dose levels of up to 50 Mrad were used to allow identification of the level at which mechanical changes became technologically significant. A further aspect of the work was a comparison of the response of the high impact material relative to the homopolymer.

EXPERIMENTAL

Tensile and impact strength specimens after BS2782 were prepared by injection molding from polystyrene (BASF Polystyrol 158K) and high impact polystyrene (BASF Polystyrol 472C). The latter material has a styrene to butadiene ratio of 94 : 6. Irradiation was carried out in air, using a cobalt 60 source, at a dose rate of 0.156 Mrad h^{-1} to give received doses of 2.5, 5.0, 10, 20, and 50 Mrad. Tensile tests were carried out at a strain rate of 1 min^{-1}. Impact strength was measured using an Izod pendulum type instrument according to BS 2782 method 306A. Both notched and unnotched specimens were tested and fracture surfaces were examined by scanning electron microscopy. In all mechanical measurements at least five specimens were tested.

TABLE I
Effect of Dose on Tensile Properties and Molecular Weight Distribution

Dose received (Mrad)	0	2.5	5.0	10	20	50
Polystyrene:						
Elastic modulus (GPa)	1.1	1.2	1.2	1.1	1.1	1.1
Standard deviation	0.03	0.02	0.04	0.02	0.01	0.02
Tensile strength (MPa)	47.8	49.3	49.6	49.4	48.9	48.6
Standard deviation	0.8	1.0	1.7	0.4	0.7	1.1
Elong. at break (%)	6.1	5.7	5.6	6.2	6.2	5.0
Standard deviation	1.0	0.6	0.5	1.1	0.9	0.4
$Mn \times 10^4$	10.7	8.5	9.3	9.2	8.1	6.9
$Mw \times 10^4$	29.6	27.1	29.5	31.5	30.5	26.5
High Impact Polystyrene:						
Elastic modulus (GPa)	0.59	0.62	0.59	0.60	0.61	0.67
Standard deviation	0.02	0.01	0.02	0.02	0.01	0.01
Yield strength (MPa)	19.0	20.2	20.3	20.9	22.5	22.7
Standard deviation	0.4	0.4	1.0	0.5	0.4	1.3
Tensile strength (MPa)	16.3	17.9	18.2	18.3	18.9	22.7
Standard deviation	0.7	0.4	0.6	0.6	0.5	1.3
Elong. at break (%)	66.9	64.5	65.7	64.5	23.5	3.4
Standard deviation	7.1	7.7	6.8	13.0	7.4	0.2
$Mn \times 10^4$	6.8	6.5	6.8	6.4	6.4	6.6
$Mw \times 10^4$	26.2	20.5	21.1	21.2	24.5	30.6

Molecular weight distribution was assessed by gel permeation chromatography using toluene as solvent. Materials were also examined spectroscopically as 1.0% solutions in THF over the range 280 nm to 340 nm. Infrared spectra were recorded for polymer films cast from THF solution.

RESULTS

Table I details the measured tensile properties and molecular weight averages as a function of received dose. Izod impact results are given in Table II.

Figure 1 shows the impact fracture surface of unirradiated polystyrene and Figure 2 shows that of a specimen which has received a 50 Mrad dose. Figures 3 and 4 show electron micrographs of impact fracture surfaces of unirradiated, and 50 Mrad specimens of high impact polystyrene. Figures 5 and 6 show the fracture surfaces of the same materials broken in tension.

DISCUSSION

With a two-phase system such as high impact polystyrene, differences in equilibrium air concentration in the phases and in diffusion rates through them will exist. This may influence overall radiation-induced changes and results reported must be viewed in the light of sample geometry chosen.

The changes in the measured mechanical properties for polystyrene are small and are in general agreement with the relative insensitivity of this material to irradiation. Comparison of the impact fracture surfaces, shown in Figures 1 and 2, confirms that there is no change in the mechanism of fracture. Both surfaces suggest rapid brittle fracture and the similarity of features is consistent with the small change in measured impact strengths.

Molecular weight distribution changes in polystyrenes are a function of irradiation conditions, and are particularly dependent on the relationship between the rate at which air can diffuse into the specimen and the rate of radical

TABLE II
Izod Impact Test Results

| Dose received (Mrad)	0	2.5	5.0	10	20	50
Polystyrene:						
Un-notched (J)	1.19	1.12	1.02	1.11	1.17	1.02
Standard deviation	0.08	0.06	0.09	0.07	0.09	0.05
Notched (J)	0.15	0.11	0.09	0.10	0.10	0.10
Standard deviation	0.02	0.01	0.02	0.01	0.01	0.02
High Impact Polystyrene:						
Un-notched (J)	8.48	7.07	5.10	5.25	5.10	0.85
Standard deviation	3.61	3.91	1.90	2.84	0.78	0.13
Notched (J)	0.70	0.62	0.59	0.56	0.48	0.29
Standard deviation	0.02	0.01	0.02	0.02	0.02	0.01
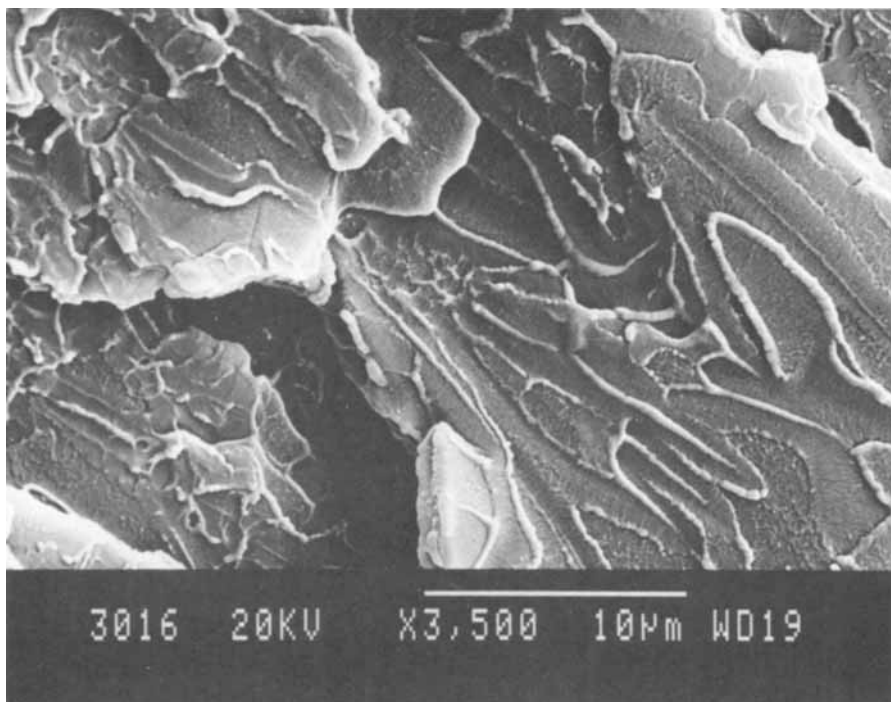
Fig. 1.   Fracture surface of unirradiated polystyrene, ×3500, notched impact specimen.

generation.[6-10] The results obtained here suggest that under the irradiation conditions and sample geometry used, chain scission processes are more important than crosslinking reactions; behavior which is consistent with that of materials irradiated in air.[6,8] However, even at the highest received dose, the absolute values of molecular weight remain sufficiently high to have minimal effect on the gross mechanical behavior.

In the case of the high-impact material the mechanical property changes on irradiation are more marked. Modulus, tensile strength, and yield strength all suggest a slight but consistent increase in stiffness and strength with dose, whilst elongation at break results indicate substantial embrittlement at the higher dose levels. Impact strength results confirm the trend observed in tensile behavior. In particular, the substantial fall in impact strength of both notched and un-notched samples, of high received dose, correlates well with the elongation at break results.

Molecular weight distribution shows a general increase in polydispersity with the greatest influence coming from an increase in the higher molecular weight chain population. This indicates that chain combination processes are more important than in the polystyrene homopolymer and must be presumed to involve the polybutadiene component. A progressive red shift of the aromatic absorption was observed in the UV-visible spectrum and is characteristic of polystyrene irradiated in air,[7,8] and has been associated with the introduction of polyene[11] or phenyl alkyl ketone[8] structures to the chain ends. Infrared spectra showed a dose-related peak at 1695 cm^{-1} which tends to support the
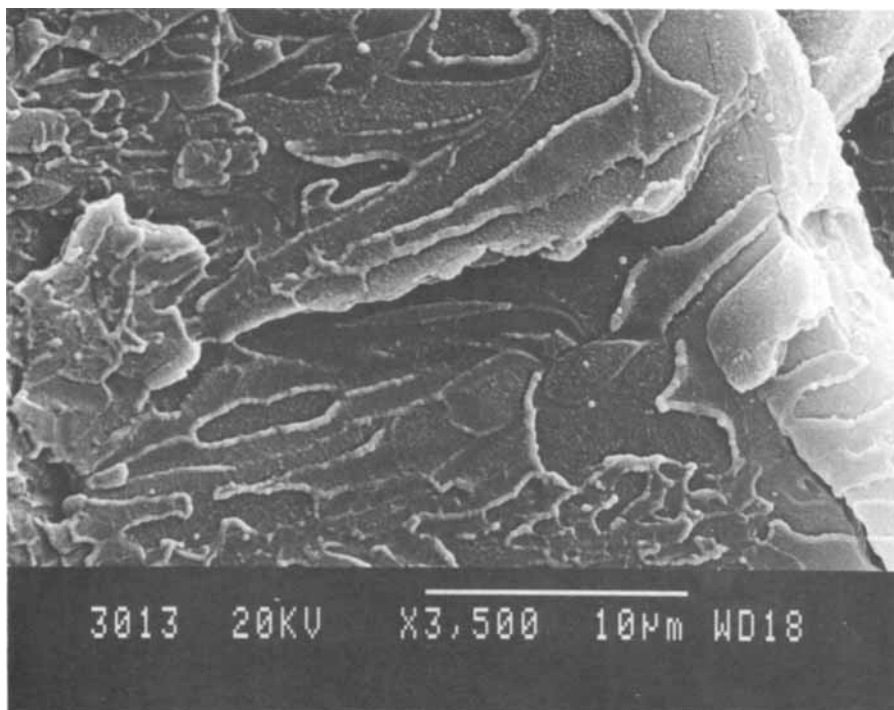
Fig. 2.   Fracture surface of polystyrene which has received 50 Mrad, ×3500, notched impact specimen.

latter. The similarity of the spectra to those obtained with the homopolymer suggests that chemical processes in the polystyrene component of the high-impact material have not been influenced by the butadiene phase.

Comparison of the impact fracture surfaces for un-irradiated and the 50 Mrad specimens shown in the figures, demonstrate a reduction in ductility with dose. This increased brittleness is responsible for the evident micro-cracking and surface debris in the irradiated materials. These effects account for the fall in measured impact strength.

The tensile fracture surfaces, shown in Figures 5 and 6, are taken from the initiation region of the fracture and again display evidence of reducing ductility with increasing dose. Apparent in the 50 Mrad material are a series of hemi-spherical cavities. These are not obvious in the corresponding impact specimen, and this change in behavior is thought to arise from the large difference in strain rates at fracture. The size and distribution of these cavities suggest that they are associated with the rubber domains in the material.[12] The principal toughening mechanism in high-impact polystyrenes is presumed to be craze formation and extension under stress[13-15] with the rubber regions acting as craze-initiation sites. Crack pinning by fibrillation of rubber particles in the crack path is also considered to be important in increasing the work required to fracture the specimen, as is the degree of interaction or bonding between the two phases of the system.

The tendency of a polymer to crosslink on irradiation is often described by the radiation chemical yields $G(X)$.[16] Values of $G(X)$ for polystyrene vary
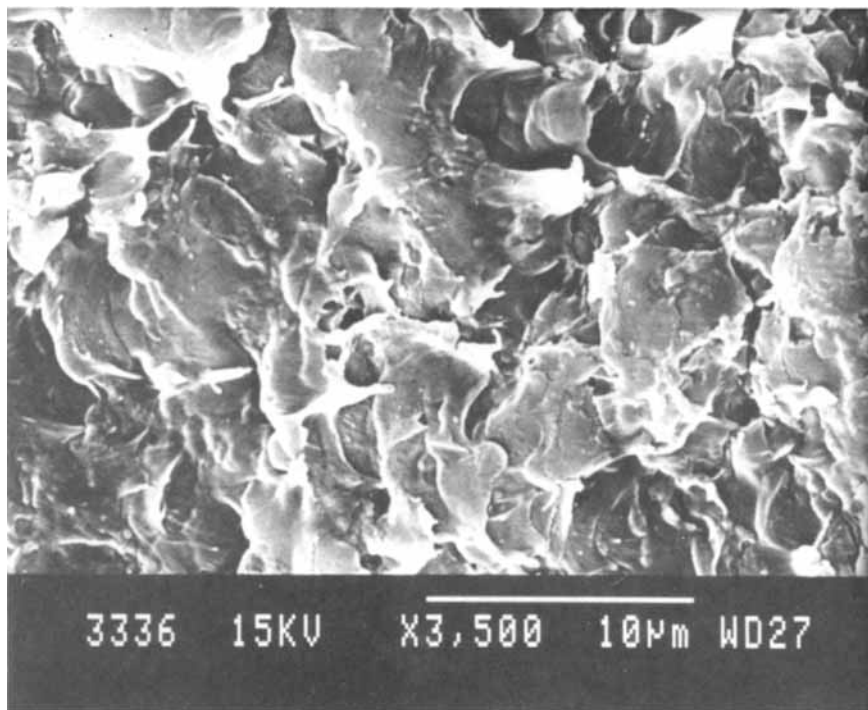
Fig. 3.   Fracture surface of unirradiated high-impact polystyrene, ×3500, notched impact specimen.

considerably, depending upon experimental conditions, but are always at least an order of magnitude lower than polybutadiene. Typical values are[16]: Polystyrene—0.045 and Polybutadiene—3.8. It can therefore be presumed that substantial crosslinking has occurred in the rubber phase at the higher-dose levels. The possibility of interphase crosslinking must also be considered. With the high-impact material, the electron micrographs from all fracture surfaces indicate changes in microductility with increasing dose. The hemispherical pits evident in material which has received 50 Mrad dose are considered to be of particular significance. As the size and form of these pits is consistent with rubber particle pull out, they must be presumed to be connected with the changes in tensile behavior. In general terms, the maximum extensibility of a crosslinked elastomer will vary directly with the square root of the molecular weight between crosslinks. Thus, radiation-induced changes can be expected to influence the mechanisms of reinforcement, and will have particular effect on the ability to crack pin by fibrillation. It is probable that crosslinking in the rubber phase has proceeded to such an extent that energy dissipation by fibrillation is no longer significant.

CONCLUSIONS

The effects of γ radiation on the mechanical properties of high-impact polystyrene are much greater than those observed in the homopolymer. The changes
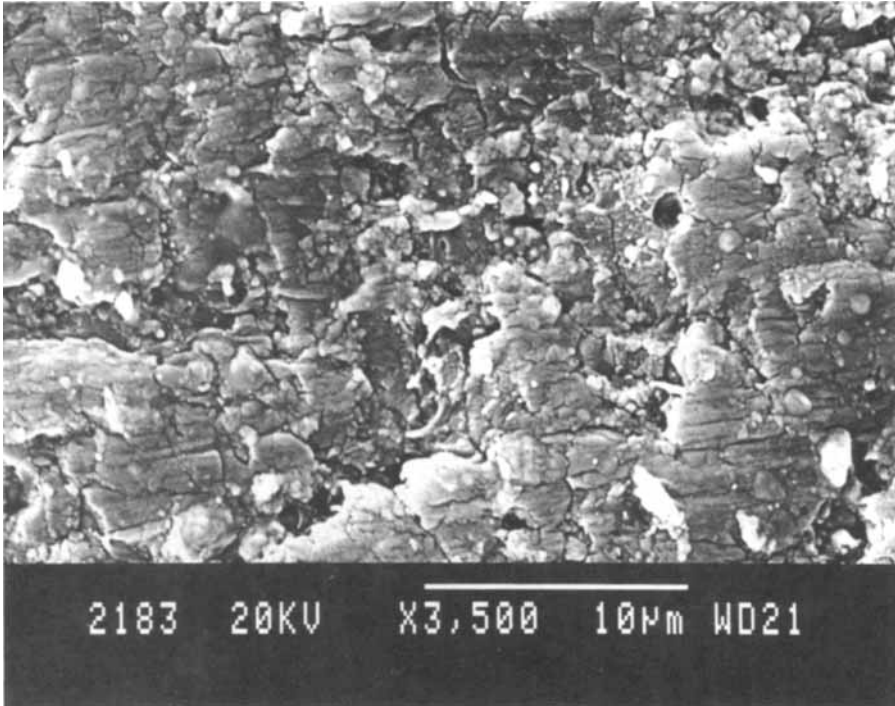
Fig. 4.   Fracture surface of high impact polystyrene which has received 50 Mrad, ×3500, notched impact specimen.

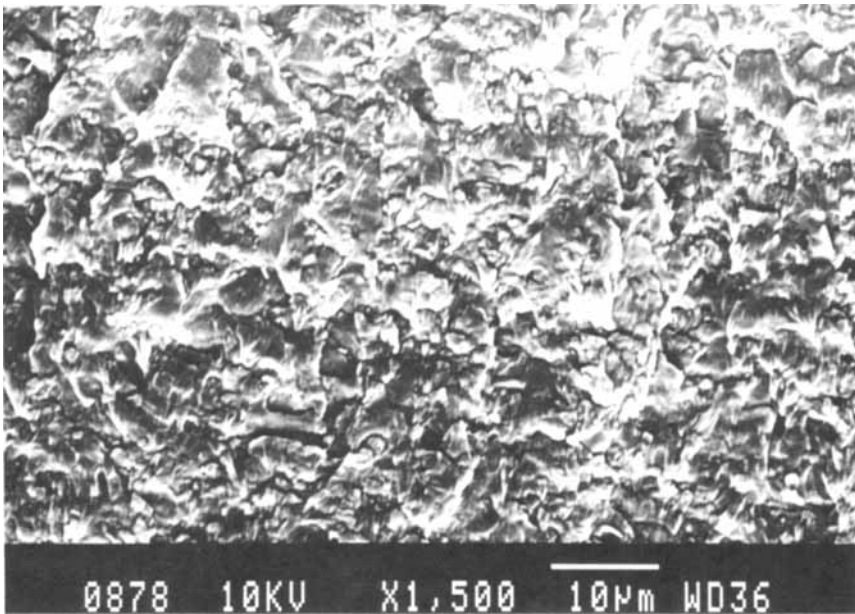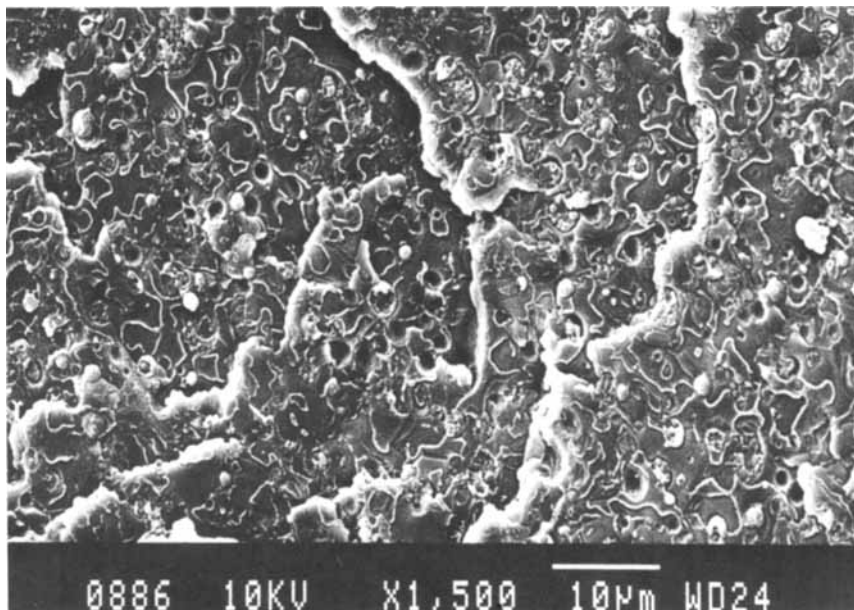Fig. 5.   Fracture surface of unirradiated high impact polystyrene broken in tension, ×1500.

Fig. 6.   Fracture surface of high-impact polystyrene which has received 50 Mrad and been broken in tension, ×1500.

recorded are functions of dose received and principally effect toughness and impact resistance. While the irradiation of the two-phase system can be explained by consideration of the changes which will occur in each phase in isolation the gross effect in any composite material is determined by the relative changes in the two phases. In particular crosslinking in the rubbery phase reduces its ability to toughen the composite leading to a change in the basic mechanism of fracture.

From a technological point of view, the response of the system to irradiation only shows marked changes in tensile properties at dose levels considerably higher than those used in standard sterilizing procedures for thermoplastics in medical and packaging applications. These changes do not become significant until dose levels exceed 10 Mrad. However impact strength shows a steady fall with received dose. This effect, which is not usually considered, may be important in specific applications.

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