

Tensile Failure of γ -Ray Irradiated Blends of High-Density Polyethylene and Natural Rubber

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Synopsis

The effect of ^{60}Co γ -radiation on the tensile properties of thermoplastic elastomer blends of natural rubber (NR) and high-density polyethylene (HDPE) has been investigated. The samples were irradiated to absorbed doses ranging from 0.1 to 100 Mrad in air at room temperature (25°C) at a dose rate of 0.21 Mrad/hr. The effect of blend ratio and addition of carbon black (N 330) dicumyl peroxide (DCP) on the radiation resistance of the blends has also been studied. High energy radiation at a high dose rate was found to cause extensive crosslinking in the bulk, which in effect, caused a minima in the ultimate tensile strength in the range of 10–25 Mrad and a continuous decline in the elongation at break in all the blends. Chain scission, on the other hand, was restricted to the surface under the above-mentioned experimental conditions. This contention was substantiated by the results of irradiation of the samples in a nitrogen environment. Scanning electron microscopy (SEM) studies on the tensile fracture surface morphology of the blends have also been undertaken in order to gain insight to the mechanism of failure.

INTRODUCTION

Radiation effects on polymers have been investigated by many authors^{1,2} over the last few decades. In recent years, the problem of radiation degradation of polymeric materials has become of great concern as such materials are finding extensive usage in radiation environments. High-energy radiations cause both crosslinking and degradation reactions in polymeric materials. These reactions significantly change, among other things, the mechanical properties of plastics. In a series of papers Seguchi et al.^{3–6} have reported their results on ^{60}Co γ -ray irradiation of polyethylene and ethylene propene copolymer and other polymeric materials. They have carried out detailed investigations on the effect of radiation-induced oxidative degradation on mechanical properties, crosslinking and chain scission, and swelling and gel fraction of the polymers. They have also studied the effect of dose rate on the chemical and mechanical properties of the polymers. Pandur⁷ has investigated the effect of high-energy radiations including ^{60}Co γ -ray on the physical and mechanical properties of nylon 6. Takeda⁸ has described the effects of irradiation and aging temperature on the tensile properties of HDPE.

The implications of dose rate effects have also been highlighted by Clough and Gillen⁹ in their material aging studies. They have followed material degradation of some commercial cable elastomeric insulations and jackets

using ultimate tensile properties, infrared spectroscopy, and swelling measurements. Spenadel¹⁰ has studied the radiation crosslinking of polymer blends of ethylene propene copolymer and polyethylene. Ivchenko et al.¹¹ have studied the radiation modification of blends of PE with certain elastomers such as chlorosulfonated polyethylene, butyl rubber, cross-linked polyethylene, and polyisobutylene. They have reported the changes in tensile properties with irradiation doses.

In this paper we have reported our results of irradiation of NR-HDPE (natural rubber-high-density polyethylene) blends with a relatively high dose rate in air at room temperature (25°C), so that the oxidation induced by radiation might be limited to the surface of the samples.³ The samples were also irradiated in a nitrogen environment to ensure that under the given conditions (high dose rate; room temperature), oxidation was indeed limited to the surface. We have measured the tensile properties and examined the fracture surface morphologies with the help of scanning electron microscopy (SEM) to gain an insight to the changes occurring in the samples as a consequence of exposure to high energy radiation.

EXPERIMENTAL

Formulations of the mixes used are given in Table I. Blends of NR and HDPE were prepared in a Brabender Plasticorder model PLE 330, using a cam-type mixer with a rotor speed of 60 rpm while the mixer chamber temperature was set at 150°C. HDPE was melted in the mixer for 2 min and then NR as such or in master batch was added and the mix was allowed to blend for 4 min. At the end of 6 min, curative (DCP) in the form of master batch was added and the mixing continued for 2 more min. The mix was then taken out and sheeted through a laboratory mill at 1.25 mm nip setting. The sheeted material was cut into small pieces and remixed in the plasticorder at 150°C for 1 min and then finally sheeted out in the mill. This second step was found necessary to get a uniform dispersion of the ingredients. The sheeted-out stock was compression moulded in an electrically heated hydraulic press at 150°C for 3 min. The mould used was provided

TABLE I
Formulations of the Mixes

	A	A _c	B	C	C _c	C _b	C _{bc}
NR ^a	30	30	50	70	70	70	70
HDPE ^b	70	70	50	30	30	30	30
HAF ^c	—	—	—	—	—	40	40
DCP ^d	—	1.0	—	—	1.0	—	1.0

^a Crumb rubber, ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala.

^b Hostalen GA 7260, obtained from Polyolefins Industries Ltd., Bombay.

^c High abrasion furnace black (N 330) obtained from Phillips Carbon Black Limited, Durgapur, West Bengal. HAF black loading was based on the rubber phase only.

^d Di-cumyl peroxide (40%), supplied by Bengal Waterproof Ltd., Panihati, West Bengal. DCP loading was based on the rubber phase only.

with bolts and nuts so that the material inside could be held under pressure even after taking the mould out of the press. At the end of the moulding time, the sample, still under compression, was immediately cooled by plunging the mould in cold water. Aluminum foils were used between the mould surfaces to reduce shrink marks on the sheets.

Tensile testing of the samples before and after irradiation was done at 25°C as per ASTM D 412-80 test method using the Instron Universal Testing Machine (model 1195). Dumbbell specimens (2 ± 0.2 mm thick) were irradiated by ^{60}Co γ -ray at a dose rate of 0.21 Mrad/hr and 0.147 Mrad/hr at room temperature (25°C) in air and in nitrogen in γ -chamber-900 at the Bhabha Atomic Research Centre (BARC), Bombay, India.

SEM observations of the tensile failure surfaces were made using a Philips 500 model scanning electron microscope. The fracture surfaces of the irradiated samples were carefully cut out from failed test pieces without touching the surfaces and then sputter coated with gold within 24 hr of testing.¹² In order to avoid contamination, the specimens were stored in a desiccator before and after gold coating till the SEM observations were made. The tilt was kept at 0° and the orientation of the photographs was kept the same in all cases. Figure 1 shows details of a tensile test specimen and the SEM scan area.

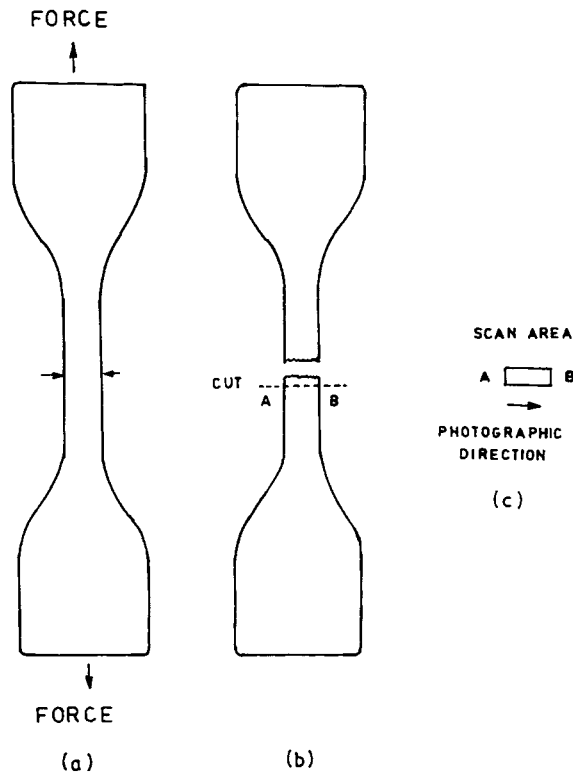


Fig. 1. Shape of tensile test specimen, tensile fracture surface, and SEM scan area.

RESULTS AND DISCUSSION

The variation of tensile strength of HDPE and NR-HDPE blends with absorbed dose is shown in Figure 2, where it is seen that the blends of NR-HDPE show a typically different trend as compared to HDPE. Unlike HDPE, which exhibits a continuous decrease in the tensile strength, the blends show a minima in the tensile strength at an absorbed dose of ~ 10 – 25 Mrad. The behavior of HDPE on exposure to high-intensity γ -radiation for prolonged periods at a high dose rate is expected,^{13,14} as a result of radiation degradation, hydrogen gas is evolved and C—C bonds are formed transforming the polymer from a thermoplastic to a thermoset material. The extensive crosslinking is accompanied by surface oxidation of the sample when the radiation exposure is carried out in air. Radiation has two major effects on the mechanical properties, it produces permanent crosslinks between carbon atoms, and it reduces crystallinity. These two effects operate in opposite directions, the former increasing the stiffness, the latter reducing it. High radiation doses have a considerable effect on the degree of crystallinity and after a certain dose, the crystallinity disappears completely, leaving a very flexible polymer with good elastic recovery. Apart from a yellow-brown coloration which may be due to conjugated unsaturation, the polymer is then almost transparent and its mechanical behavior is that of an over-vulcanized rubber. As the radiation dose is further increased, irradiated

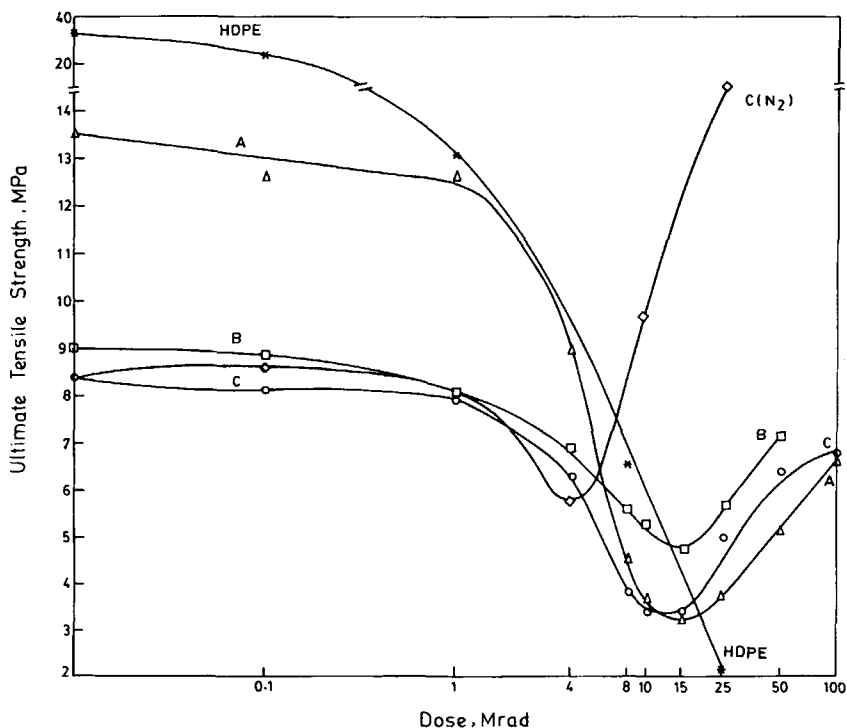


Fig. 2. Plot of ultimate tensile strength versus absorbed dose for HDPE and NR-HDPE blends.

polythene becomes stiffer and more brittle; the degree of crosslinking being increased with no compensating reduction in the degree of crystallinity, which has almost vanished. Thus after radiation at a high dose rate, around 15 Mrad, the tensile strength of HDPE is practically negligible.

According to Campbell¹⁵ and others¹⁶ both HDPE and NR have approximately the same radiation resistance. The tensile strength of a blend of NR-HDPE, therefore depends on the degree of orientation of the two phases¹⁷ (or on that of the dominant phase). If the degree of orientation of the molecular chains of the two polymers is hindered by factors such as crosslinks, the tensile strength decreases. When the blends are exposed to γ -radiation at a high dose rate, the blend undergoes crosslinking predominantly and as the absorbed dose increases, the extent of crosslinking increases so that the sample becomes progressively brittle. According to Schnabel¹⁸ and others,^{3,9,19} the influence of dose rate becomes pronounced at high dose rates; if the dose rate is rather high, after a certain irradiation time, the oxygen concentration in the interior of the specimen is depleted. Therefore, the outer layer can predominantly undergo main chain scission, while deeper layers become insoluble because of crosslinking. Thus, as the absorbed dose increases, the orientation of the blends gets restricted severely and the tensile strength shows a progressive decline. After a certain degree of crosslinking, the sample (which has become brittle) undergoes brittle distortion,²⁰ and this phenomenon is reflected in the increase in tensile strength after an absorbed dose of ~ 15 Mrad, as shown in Figure 2. A similar phenomenon was observed by Chang and Brittain²¹ during their study of the effect of crosslinking on epoxy resin systems where they concluded that as the crosslinking increased both initiation and arrest fracture toughness of the resin system decreased when the extent of curing was 87%. Beyond 87%, a stable-rough crack propagation set in, and the initiation fracture toughness appeared to increase. This behavior is characteristic for all the NR/HDPE blends studied viz. C(70:30), B(50:50), and A(30:70). In fact, in an inert atmosphere (of nitrogen) also the high rubber blend C(70:30) exhibits a similar trend (Fig. 2). In a nitrogen environment at a dose rate of 0.21 Mrad/hr, the sample undergoes crosslinking in the bulk while chain scission is minimal. The tensile strength, therefore, increases very slightly due to the onset of crosslinking at small absorbed doses but starts decreasing as the extent of crosslinking in the bulk increases at higher absorbed doses. The sample becomes extensively crosslinked and the tensile strength suddenly starts increasing. In nitrogen this phenomenon is observed at a much lower absorbed dose (4 Mrad) than in the case of samples irradiated in air, which undergo the same change at about 10–25 Mrad (Fig. 2). Figure 3 shows the stress-strain curves of the high rubber blend C(70 NR/30 PE) at different absorbed doses. There is an increase in the ultimate elongation between 0 and 1 Mrad absorbed doses. After this there is a continuous decline in the ultimate elongation with increasing absorbed doses. But the stress exhibits a different trend. There is a minima in the stress values between 8 and 15 Mrad, following which the sample starts losing its rubbery characteristics and becomes increasingly brittle as a consequence of the increase in the extent of crosslinking. The brittleness of the sample is implied in the high distortive stress

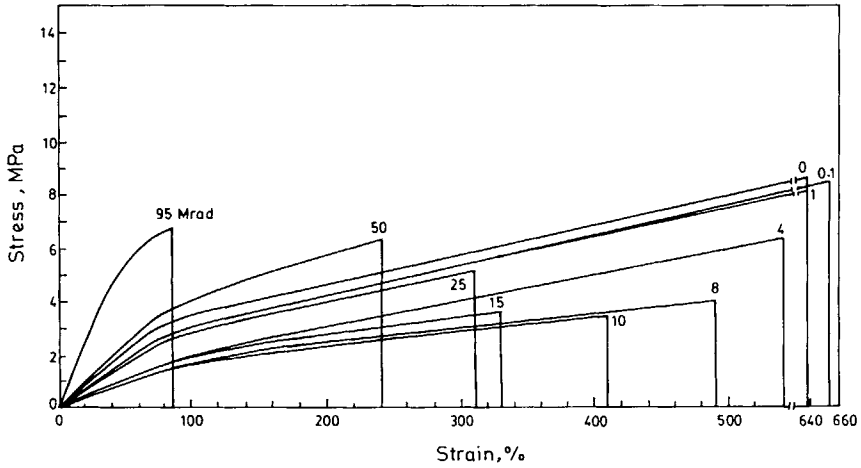


Fig. 3. Plot of stress versus strain at different absorbed doses for mix C (70 NR/30 HDPE).

registered against a low ultimate elongation evident at high absorbed doses, as shown in Figure 3.

The effect of additives on the radiation resistance of the high rubber blend, C is shown in Figure 4. The small number of crosslinks that have been incorporated through DCP in the blend during the mixing stage have a

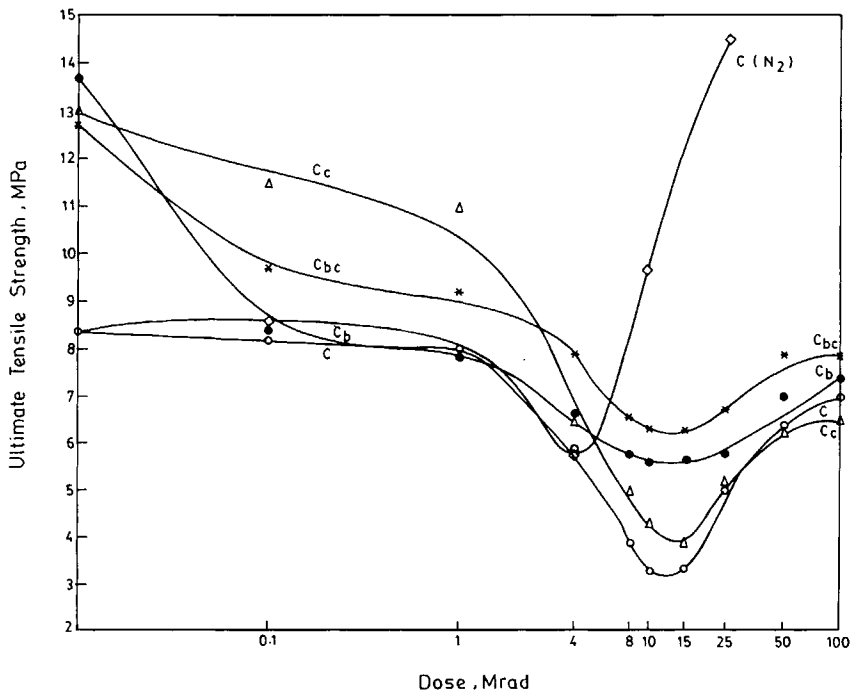


Fig. 4. Plot of ultimate tensile strength versus absorbed dose for the high rubber blends.

negligible effect on the radiation resistance of the blend. It appears that the effect of the presence of these crosslinks, minimal in number, is largely overshadowed by the extensive crosslinking occurring as a result of exposure to γ -radiation at a high dose rate. Campbell¹⁵ states that the use of certain fillers such as carbon black, especially in rubber, adds considerably to the radiation resistance; the mechanism involves absorption of some of the electrons or ions produced by radiation, surface catalysis of recombination processes, and retention of modulus in reinforced plastics. However, the effect of addition of 40 phr reinforcing carbon black is to improve the radiation resistance of the high rubber blend, C, only marginally. Both carbon black-filled high rubber blends C_b and C_{bc} show a very slight improvement compared to C. Here again, the presence of crosslinks, as in C_{bc} , has no tangible effect on the behavior of the blend when exposed to radiation.

Figure 5 shows the change in the energy at rupture values with absorbed dose for the high rubber blends C, C_b , C_c , and C_{bc} . All the blends show the same pattern with little variation. Up to 1 Mrad, at a dose rate of 0.21 Mrad/hr, the energy at rupture values remains constant, a minima is observed in all cases in the range of 4–15 Mrad as in the tensile strength values. The energy values increase subsequently in the range of 15–25 Mrad and then decrease as the absorbed dose increases further. The minimum in the energy values coincides with the phenomena of brittle distortion.²⁰

Figure 6 shows the variation of elongation at break with the absorbed dose when the radiation dose rate is 0.21 Mrad/hr. The ultimate elongation

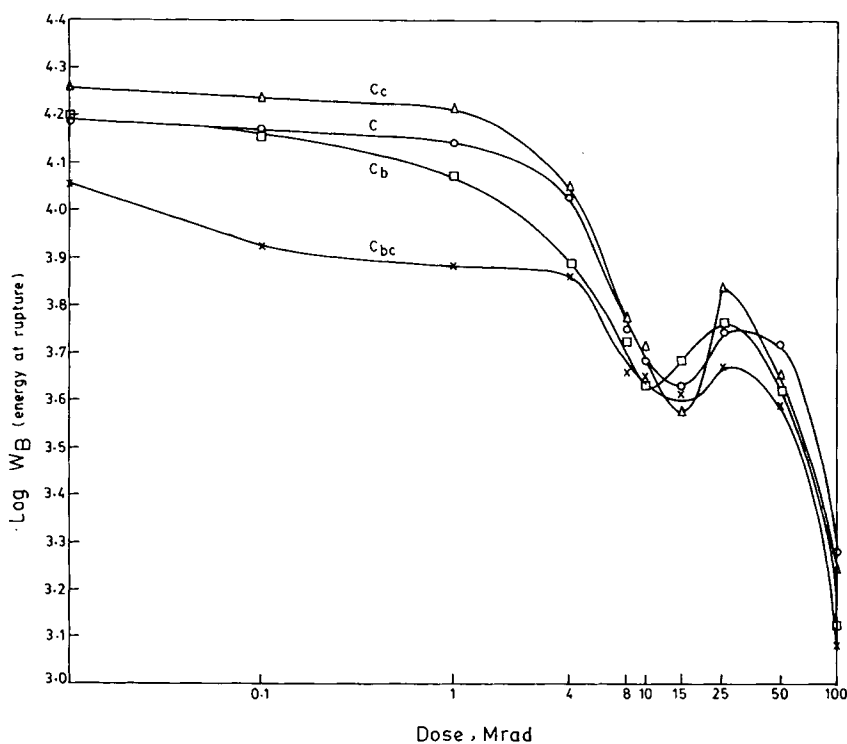


Fig. 5. Plot of $\log W_B$ (energy at rupture) versus absorbed dose for the high rubber blends.

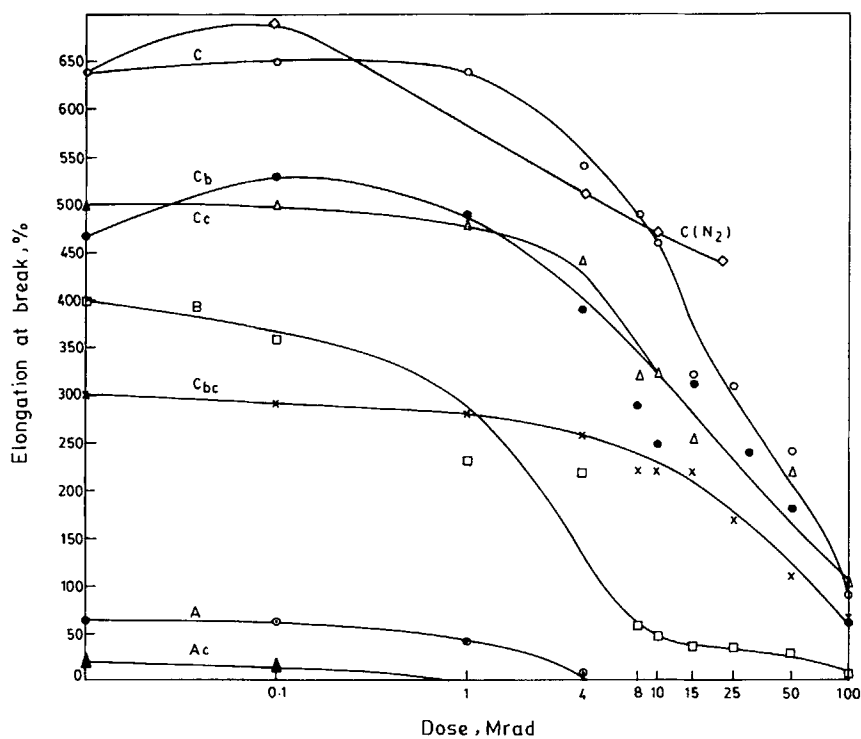


Fig. 6. Plot of elongation at break versus absorbed dose for all the blends.

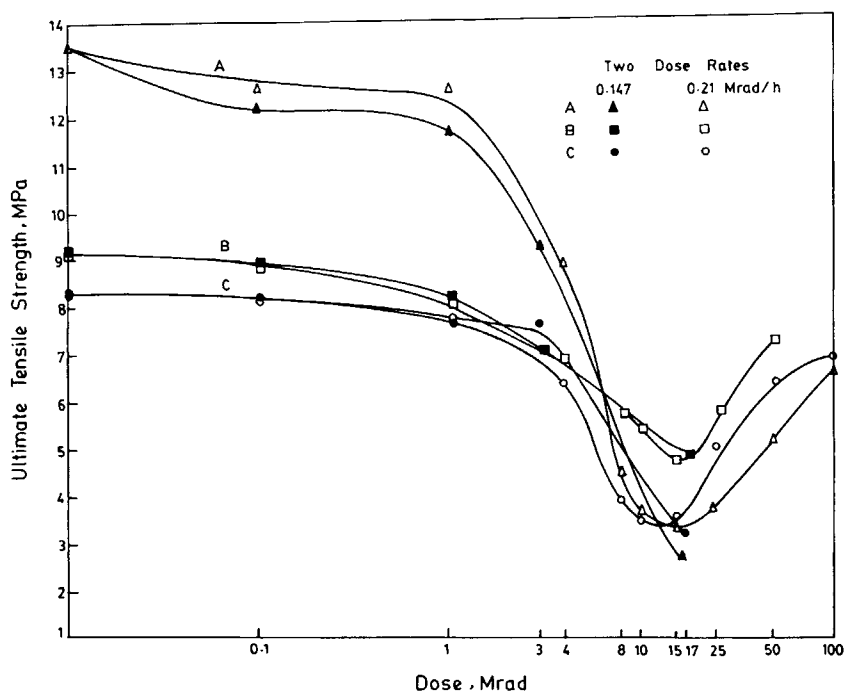


Fig. 7. Plot of ultimate tensile strength versus absorbed dose at two dose rates viz., 0.147 Mrad/hr and 0.21 Mrad/hr.

is found to decrease progressively as the absorbed dose increases in all the blends. This trend is expected since the material becomes increasingly brittle as a consequence of the increase in the number of crosslinks in the bulk of the sample as the absorbed dose increases. The high rubber blends have higher ultimate elongations compared to the high plastic blends. At low absorbed doses (i.e., about 1 Mrad), the ultimate elongation of the blends remains essentially constant. A slight increase, in certain cases, in the ultimate elongation in the range of 0.1 Mrad is also observed. This increase may be attributed to the commencement of crosslinking in the bulk of the sample as a result of the radiation and is observable only in the uncrosslinked high rubber blends C and C_b. The ultimate elongation shows a similar pattern when the sample (mix C) is irradiated in a nitrogen environment. The initial increase in the elongation at break is followed by a gradual decrease as the extent of crosslinking increases (Fig. 6).

Figure 7 shows a comparison of two different dose rates viz., 0.147 Mrad/hr and 0.21 Mrad/hr. These two high dose rates have almost the same effect on the tensile strength of the blends A, B, and C. Up to 1 Mrad there is little change in the tensile strength in both cases and then the tensile strength starts decreasing gradually at first, and then at a faster rate reaching a minimum in the range of 10–25 Mrad. The high plastic blend shows the highest fall in the strength while B shows maximum retention of strength under both dose rates.

SEM STUDIES

The SEM photomicrograph (Fig. 8) of the tensile fracture surface of the high rubber blend, C, shows a rough surface with few tear lines. The main fracture front can be seen at one end of the surface. After irradiation up to 1 Mrad at a dose rate of 0.21 Mrad/hr, the fracture surface (Fig. 9) retains the same quality of roughness and similar features, indicating that the effect of radiation is almost negligible. Figure 9 shows an outwardly propagating radiating fracture path, the point of initiation of the fracture lies at the

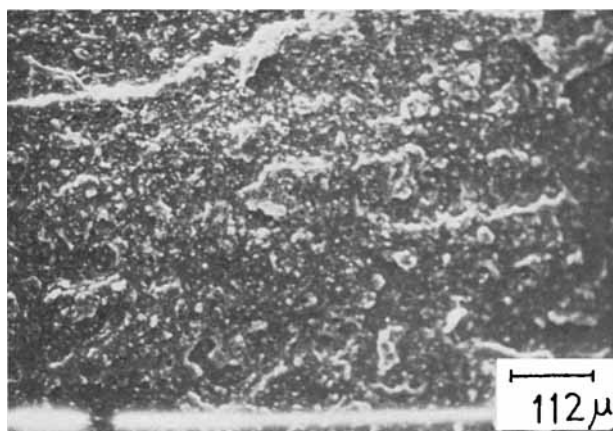


Fig. 8. SEM tensile fractograph of mix C, unirradiated: rough surface with few tear lines.

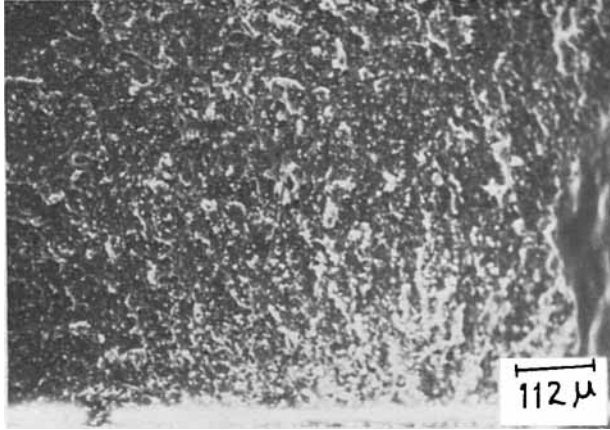


Fig. 9. SEM tensile fractograph of mix C, irradiated up to 1 Mrad: features show similar degree of roughness as the unirradiated sample.

right-hand corner. In contrast, the fractograph (Fig. 10), of the same blend, after an absorbed dose of 25 Mrad, shows a number of tear lines curving inward from the surface and joining the straight horizontal fracture path extending from one end of the surface to the other. The surface still retains some of the rough texture. After irradiation up to 100 Mrad, the fracture surface morphology (Fig. 11), indicates further degradation which is evident from the large number of smooth tear lines curving inwardly on the fracture surface. These inward curving lines suggest that their origin lies on the surface of the sample, implying thereby extensive degradation in the form of chain scissions on the surface. Figure 12, the SEM fractograph of C_c after irradiation up to 100 Mrad, shows features which are similar to a great degree to those of the irradiated (up to 100 Mrad) blend C, as shown in Figure 11. There is essentially no difference between the two; this obser-

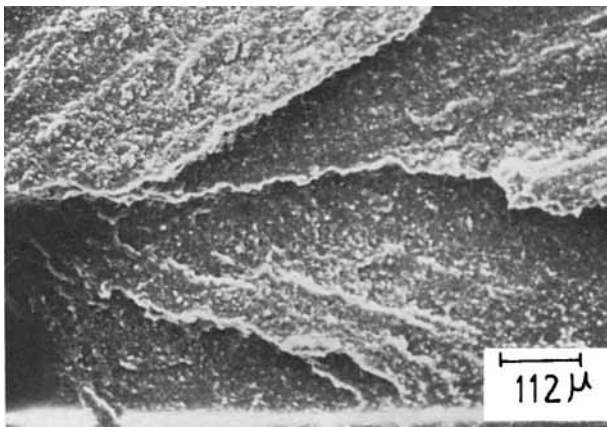


Fig. 10. SEM tensile fractograph of mix C, irradiated up to 25 Mrad: large number of tear lines branching from the main horizontal fracture path.

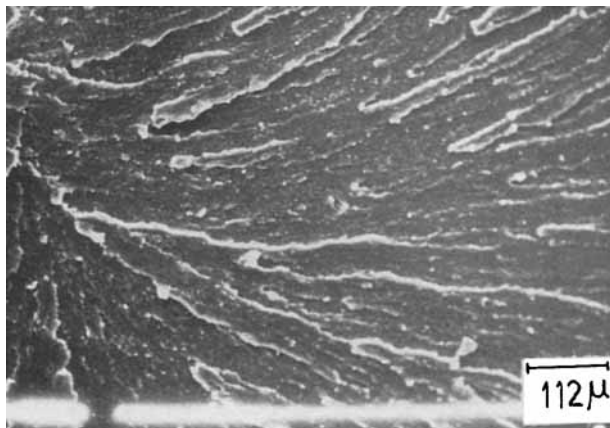


Fig. 11. SEM tensile fractograph of mix C, irradiated up to 100 Mrad: large number of smooth tear lines curving inwardly from the outer surface.

vation is in conformity with the experimental observation (Fig. 5). Figure 13, the SEM photomicrograph of the tensile fracture surface of mix C irradiated up to an absorbed dose of 4 Mrad in a nitrogen atmosphere, shows features similar to those of the unirradiated sample (Fig. 8). Figure 14, the SEM fractograph of mix C irradiated up to 25 Mrad in nitrogen, shows a rough surface with few short and curved tear lines characteristic of low reinforced natural rubber vulcanizates.²² In contrast to the SEM fractograph of the sample irradiated in oxygen (Fig. 10), the fractograph of the sample irradiated in nitrogen (Fig. 14) shows no tear lines originating from the surface. This implies that surface degradation (due to chain scission) is negligible when the sample is irradiated in a nitrogen environment. On the other hand, the rapid increase in the tensile strength (Fig. 4) and the slow

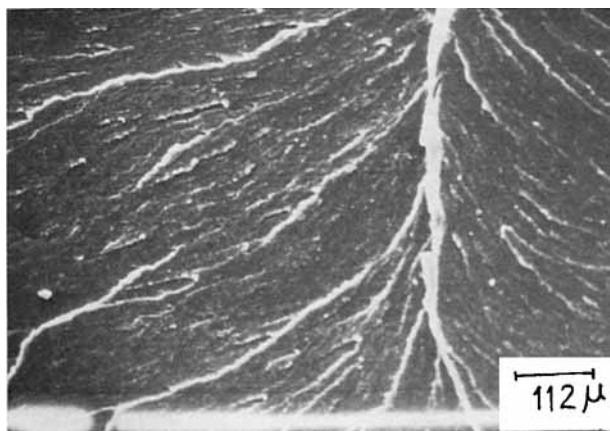


Fig. 12. SEM tensile fractograph of mix C, irradiated up to 100 Mrad: large number of tear lines.

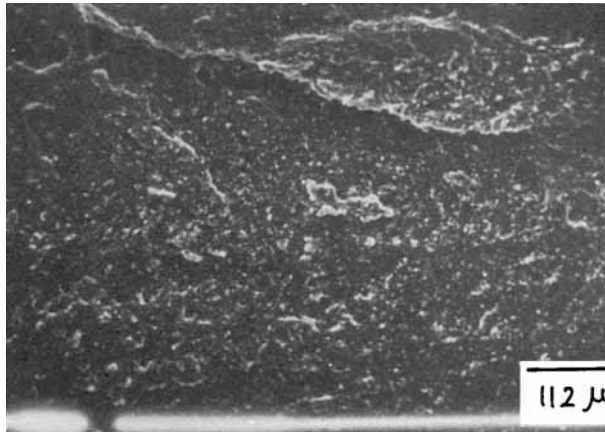


Fig. 13. SEM tensile fractograph of mix C, irradiated up to 4 Mrad in nitrogen: few tear lines on a smooth surface.

fall in the ultimate elongation (Fig. 7), with increasing absorbed dose, indicate extensive crosslinking in the bulk as a consequence of which the thermoplastic elastomer blend starts behaving like a natural rubber vulcanizate.

Before irradiation, the SEM fractographs of C_b and C_{bc} are shown in Figures 15 and 16, respectively. They show a lot of dissimilarity: C_b shows a rough surface with a parabolic tear line, while C_{bc} shows a smoother surface with a number of cracks indicating the high degree of stiffness of the sample. However, after irradiation up to 25 Mrad at a dose rate of 0.21 Mrad/h, the two blends exhibit very similar fracture surfaces as seen in Figures 17 and 18. A rough zone at one end of the surface and pits over the entire surface in both cases indicate that the effect of crosslinks incorporated during the mixing stage, as in C_{bc} , is insignificant in view of the large-scale

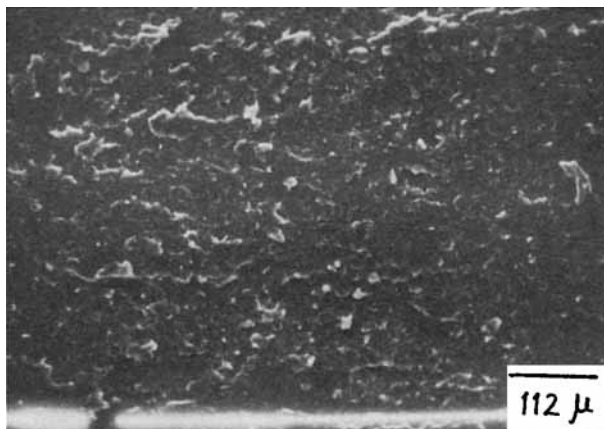


Fig. 14. SEM tensile fractograph of mix C, irradiated up to 25 Mrad in nitrogen: short rounded tear lines, rough surface.

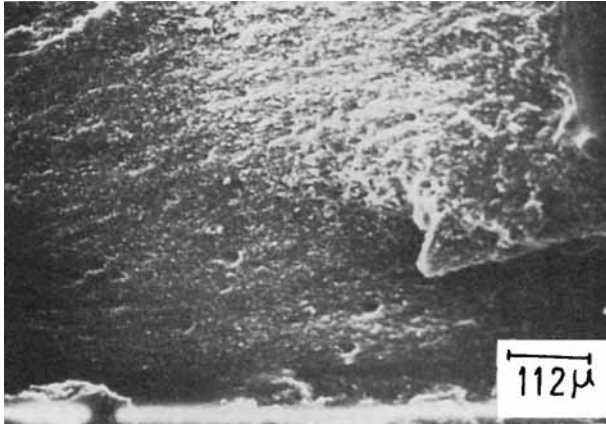


Fig. 15. SEM tensile fractograph of unirradiated mix C_b: rough surface with a parabolic tear line.

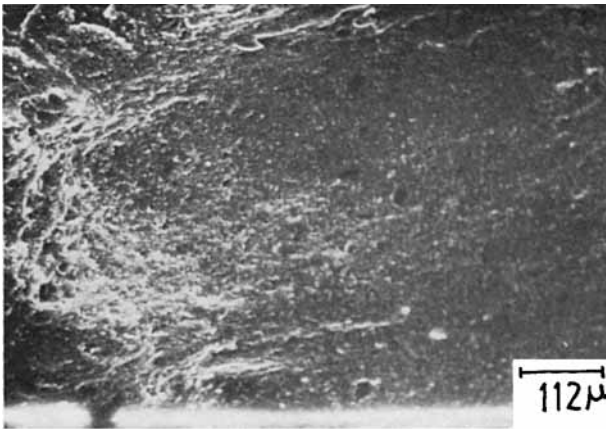


Fig. 16. SEM tensile fractograph of unirradiated mix C_b: smooth surface with cracks and pits.

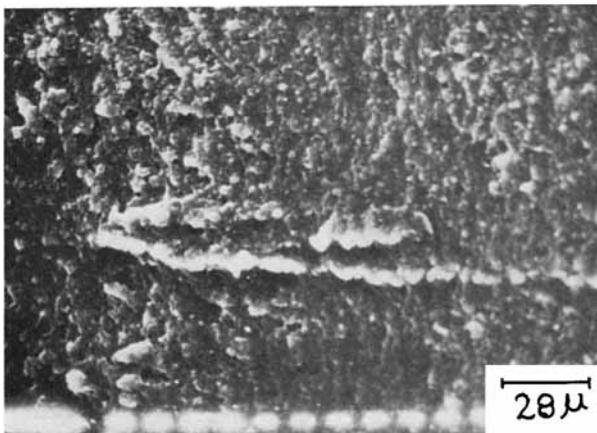


Fig. 17. SEM tensile fractograph of mix C_b: irradiated up to 25 Mrad: rough surface with pits.

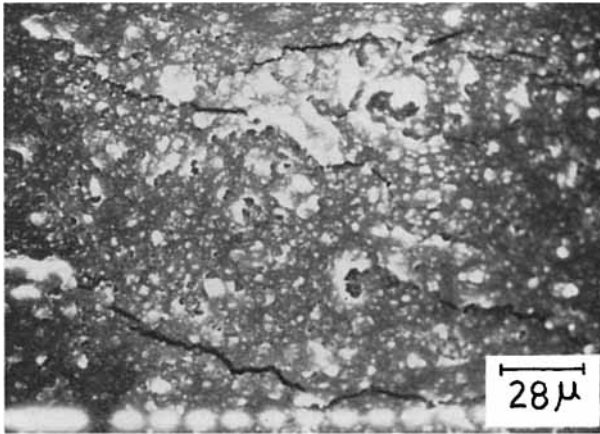


Fig. 18. SEM tensile fractograph of mix C_{bc} irradiated up to 25 Mrad: rough surface with pits.

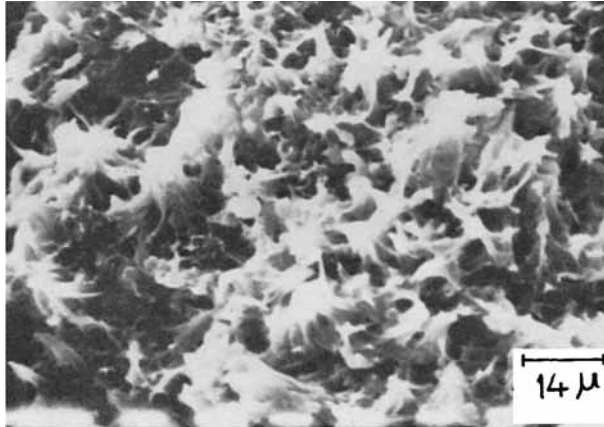


Fig. 19. SEM tensile fractograph of mix A irradiated up to 25 Mrad: fibrils and peaks.

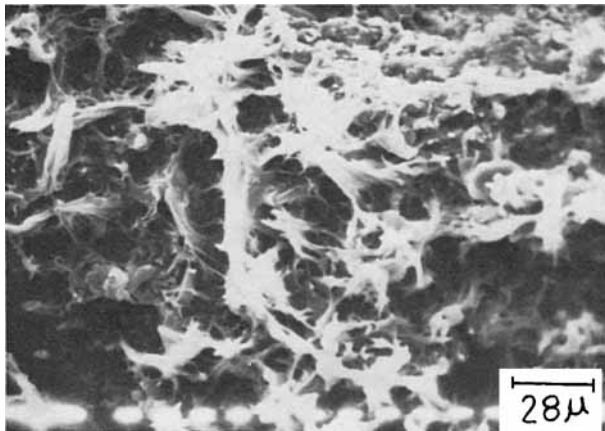


Fig. 20. SEM tensile fractograph of unirradiated mix A_c: fibrils and peaks.

cross-linking reactions occurring during the process of irradiation. Also, the absence of smooth tear lines and the presence of a rough zone in C_b and C_{bc} unlike in C imply that the former retain more strength than the latter after irradiation up to 25 Mrad. This observation is in keeping with Campbell's¹⁵ observation of improved radiation resistance in the presence of carbon black.

We have shown earlier²³ that in the case of the high plastic blend, A, the effect of introduction of crosslinks through DCP, as in A_c , is reflected in the fractograph of A_c in the form of pronounced fibrils and peak formations not evident to an equally distinct degree in the fractographs of A. Therefore, the similarity between Figure 19 of blend A after irradiation up to 25 Mrad and Figure 20 of A_c before irradiation supports the contention that at high dose rates on irradiation, the bulk undergoes crosslinking in preference to chain scission which is more or less restricted to the surface.

The authors would like to express their thanks to Dr. T. S. Murthy and Mr. A. B. Majali of the Bhabha Atomic Research Centre, Bombay for the use of their radiation facility and to Mr. B. R. Dhanawade for his assistance in a number of the aging exposures.

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Received August 17, 1985

Accepted October 30, 1985