

Ageing Studies of Ethylene Propylene Diene Monomer Rubber/Styrene Butadiene Rubber Blends: Effects of Heat, Ozone, Gamma Radiation, and Water

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ABSTRACT: The ageing behavior due to the effects of heat, ozone, γ -radiation, and water on ethylene propylene diene monomer rubber/styrene butadiene rubber (EPDM/SBR) blends was studied. The tensile strength, crack initiation, ozone ageing, gamma radiation, and water resistance of the blends were measured and used to determine the extent of ageing. Tensile strength of blends of different compositions increased after thermal ageing for 96 h at 100°C probably due to the continued cross-linking. It has been observed that an increase in EPDM in the blends improves the ozone resistance of the blends. Crack initia-

tion was noted only in blends with lesser amount of EPDM and the cracks in such blends were found deeper, wider and continuous. With 15 kGy irradiation dose, the tensile strength of the blends found to be decreased while it increased with 80 kGy dosage of γ -radiation. The elongation at break showed a decreasing trend with increased dosage of γ -radiation. It has also been observed that the EPDM rich blends showed negligible water uptake. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2923–2929, 2008

Key words: EPDM; polymer blends; ageing

INTRODUCTION

The demand for high temperature, ozone, and weather resistant rubbery materials has increased during the last decade.^{1–3} Rubber blends are becoming preferred materials to meet these requirements.^{4,5} Earlier studies on accelerated ageing of rubber vulcanizates show that the properties such as elongation at break, tensile strength, and modulus undergo changes due to deterioration.⁶ It is well known that for many unsaturated rubbers, the hydrogen atom of α -methylene carbon is abstracted in the presence of oxygen and an oxidative reaction chain is initiated which propagates auto-catalytically and ends in chain scission. Besides scission of the main chain and of the cross-links, depending upon polymers, ageing causes the formation of more cross-links of the same type as those already present or of a different type, which may be inactive to further scission. Introduction of antioxidants and antiozonants helps to reduce the property loss of rubber vulcanizates due to ageing though these chemicals have many

limitations in performance. With the introduction of weather resistant rubbers such as EPDM, hypalon, and polysulfide, the efforts to modify the ageing characteristics of highly unsaturated rubbers gained a new momentum, through blending techniques.⁷

The effects of degrading agents on each type of polymer will be different and they depend mainly on the chemical structure of the polymer and the type of crosslinking system used. For SBR, the resistance to thermal, gamma, and ozone ageing is poor due to the presence of double bonds in the main chain. In EPDM as the reactive carbon-carbon double bond is located on a side chain, the polymer backbone structure is completely saturated and not subject to molecular breakdown via ozone attack or oxidation. Therefore, the behavior of blends of these elastomers against the action of various degrading agents is worth examining.

Excellent reports on the ageing characteristics of rubbery systems exist.^{8–10} For example, Bhowmick and White¹¹ investigated the thermal, UV-, and sunlight ageing of thermoplastic elastomeric NR/PE blends. They found that thermal ageing of the blends caused the tensile properties to deteriorate, especially at longer times, or higher temperatures of ageing after an increase of properties in the initial stage. Deuri et al.¹² investigated the ageing behavior of

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TABLE I
Compounding Recipe (phr)

Ingredients	E ₀ S	E ₁₀ S	E ₂₀ S	E ₃₀ S	E ₄₀ S	E ₅₀ S	E ₆₀ S	E ₇₀ S	E ₈₀ S	E ₉₀ S	E ₁₀₀ S
Polymer/blend	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Stearic acid	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
MBTS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
TMTD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sulfur	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50

IIR/EPDM blends and found that the ageing resistance increased with increase in EPDM content. Koshy et al.¹³ studied the ageing of different rubber-rubber blends. Sulekha et al.¹⁴ reported that the use of oligomer bound antioxidants was an effective means of protecting nonresistant rubbers against surface cracking. Vinod et al.¹⁵ investigated the effects of heat, ozone, and high energy radiation on the degradation behavior of aluminum powder filled NR composites. They found that resistance to degradation was improved, when NR was reinforced with aluminum powder. Many other interesting reports have also been appeared on the ageing characteristics of polymeric systems.¹⁶⁻²⁶

SBR is an elastomer extensively used for a wide variety of products, viz., tyres and related products, belts, hoses, foot wears, foamed products, mechanical goods, etc. SBR, in general, has high resilience, better flex life, lower heat build up, and better abrasion resistance. However, with unsaturation sites, it is prone to attack by ozone or oxygen. EPDM is a rubber having excellent temperature and ozone resistance. Furthermore, depending upon the molecular weight, molecular weight distribution, percentage of ethylene content, and percentage of diene, EPDM gives better tensile/tear strength, hot green strength, higher cure rate, flow at high temperature, and higher modulus.

The objective of this investigation is to examine the ageing characteristics of sulphur cured EPDM/SBR blends and its components with special reference to the effects of heat, ozone, radiation, and water.

EXPERIMENTAL

Materials

EPDM-502 used for this study was supplied by Herdillia Unimers, Mumbai, India while the SBR-1502 was supplied by India Rubber Chemicals, Kottayam. The rubber chemicals such as sulfur (S), zinc oxide, stearic acid, mercaptobenzothiazyl disulphide (MBTS), and tetramethyl thiuram disulphide (TMTD) used were of commercial grade.

Blend preparation

The blends of EPDM and SBR, with different cross-linking systems and fillers, were prepared on a two roll

mixing mill (diameter 150 mm; speed of the slow roll 24 rev/min; gear ratio 1 : 16). The mastication of each polymer, and the subsequent blending and compounding were done between the hot rolls of the mill at 80°C. The basic recipes used for compounding are given in Table I. The compounds have been designated as E₀S, E₁₀S, E₂₀S, E₃₀S, E₄₀S, E₅₀S, E₆₀S, E₇₀S, E₈₀S, E₉₀S, and E₁₀₀S where E stands for EPDM rubber and the subscripts indicate the weight percentage of EPDM in the blends. The vulcanizing system sulfur is designated as S.

Rheometric parameters such as optimum cure (t₉₀), maximum and minimum torques (MH and ML) and scorch time (TS₂) of the blends were obtained by using a Scarabaeus GmbH Rheometer (Germany) and this had been reported in our earlier work.²⁷ The vulcanization of the blends was carried out on a hydraulic press (platen size 8' × 8') under a pressure of 1500 psi at a temperature of 160°C.

Ageing studies

The thermal ageing was studied using dumbbell-shape specimen by ageing the specimen for 96 h at 100°C in a multi-cell ageing oven (Prolific Engineers, India). The tensile strength of the dumbbell specimens before and after ageing was compared. Ozone ageing studies under static conditions were conducted (ASTM D 518 Method B) on rectangle shape specimens by exposing the test specimens to an ozone concentration of 50 parts per hundred million (pphm) in a Mast Model 700-1 Ozone Test Chamber at 40°C. The ozone ageing resistance of different blends and blend components was compared. The influence of γ -radiation of different dose rates was studied using dumbbell-shape specimen by ageing the specimens in a gamma chamber. The tensile strength and elongation at break of the specimens before and after radiation was compared. The distilled water ageing of the blends was investigated (ASTM D471-66) by using sulfur-cured specimens prepared from tensile pad. The water uptake of various specimens was studied.

RESULTS AND DISCUSSION

Thermal ageing

The mechanical properties of the blends before and after thermal ageing were compared. Figure 1 shows

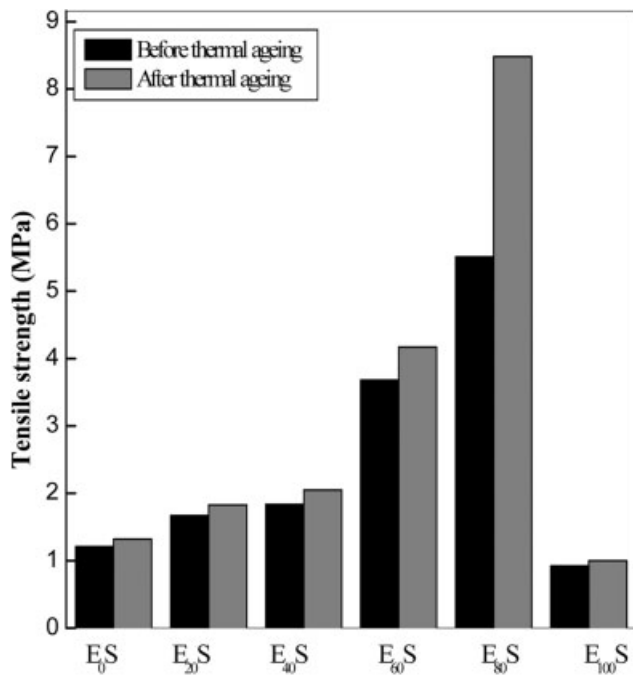


Figure 1 Thermal ageing at 100°C—comparison of tensile strength before and after ageing.

a comparison between the tensile strength of the blends before and after aging at 100°C for 96 h. It is clear from the graph that the tensile strength values were increased with increased weight percentage of EPDM in the blend. Figure 2 shows the percentage increase in tensile strength of EPDM/SBR vulcanizate after ageing at 100°C for 96 h. The increase in tensile strength of the blends might be due to the

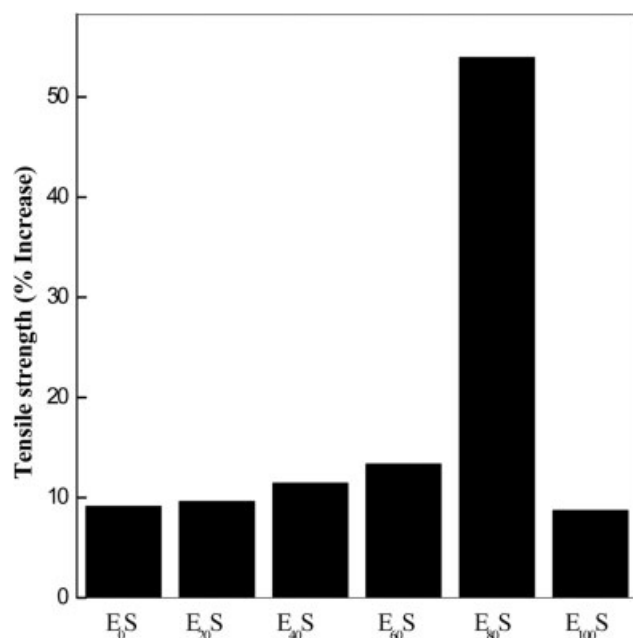


Figure 2 Thermal ageing at 100°C: % Increase in tensile strength.

TABLE II
Crosslink Density of Unaged and Aged EPDM/SBR Blends

Sample	Crosslink density $\times 10^4$ (gmol/cc)	
	Before thermal ageing	After thermal ageing
E ₀ S	0.22	0.48
E ₂₀ S	2.83	4.04
E ₄₀ S	2.87	3.36
E ₆₀ S	2.91	3.33
E ₈₀ S	2.92	3.18
E ₁₀₀ S	—	0.15

continued cross-linking of the blend components by thermal ageing. The effects of temperature and environmental conditions on the performance of polymers, including the degradation mechanisms are available in the literature.^{28–34} Generally, the retention of properties depends upon the degradation behavior of the component elastomers. Amorphous polymers degrade faster than crystalline polymers by heat. Table II shows that the crosslink density of the blends before and after thermal ageing increased with increased EPDM composition, which ultimately enhanced the TS. The semicrystallinity of EPDM rubber further contributed to an increase in TS values. Rubber vulcanizates are cured only at t_{90} . The remaining 10% is kept as an allowance during service. Thermal ageing completes this 10% curing as clear from the crosslink density values, which subsequently enhance the TS.

Figure 3 illustrates the percentage increase in modulus (100%) of the EPDM/SBR blends after thermal ageing at 100°C for 96 h. The graphs show that

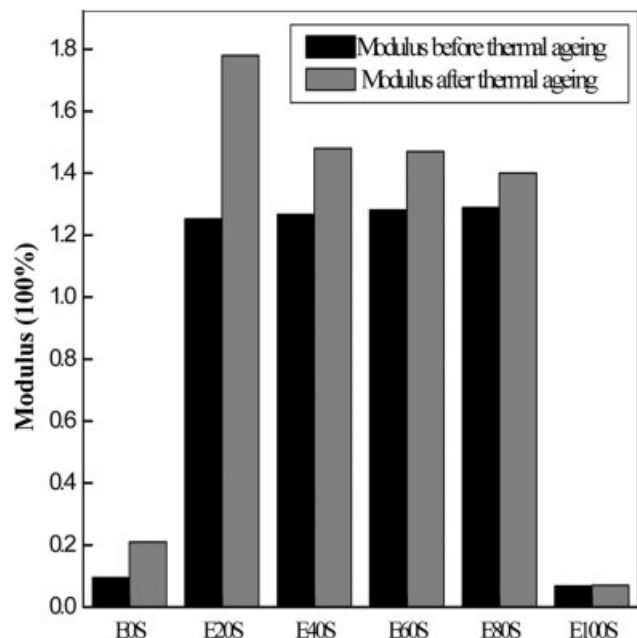


Figure 3 Comparison of modulus at 100%—before and after thermal ageing of EPDM/SBR blends at 100°C.

the modulus of all the blend compositions increases after thermal ageing. The variations in the elongation at break values of the blends after thermal ageing are presented in Figure 4. It was found that the elongation at break of the vulcanizate decreases due to thermal ageing. Thermal ageing leads to the formation of additional cross-links in the blends. It is clear from Table II that the crosslink densities increase after ageing. In general, the elongation at break of a vulcanizate with higher crosslink density is shorter than that of a vulcanizate with a lower density.³⁵

Figure 5 reveals that the hardness of all the EPDM/SBR blends increases after thermal ageing. This increase is also associated with the increase in crosslink density.

Ozone ageing

The optical photographs of the surfaces of the ozone aged samples presented in Figure 6 shows that no cracks were developed on the EPDM rich blends. However, cracks were seen initiated on the surfaces of SBR rich blends, E₀S, E₁₀S, E₂₀S, and E₃₀S at lesser exposure of time. In blend E₃₀S, shallow type cracks were appeared after 17 h of ageing. Moderate cracks were developed in blend E₂₀S after 7 h of ozone ageing. Deep cracks were noted in E₀S after 4 h of ageing while cracks were noted in E₁₀S only after 6 h of ageing. However blend compositions, E₄₀S, E₅₀S, E₆₀S, E₇₀S, E₈₀S, E₉₀S, and E₁₀₀S were not affected by ozone ageing even for 120 h. Obviously, the crack growth in SBR due to ozone attack is effectively controlled and prevented by the highly ozone resistant EPDM in these blends.

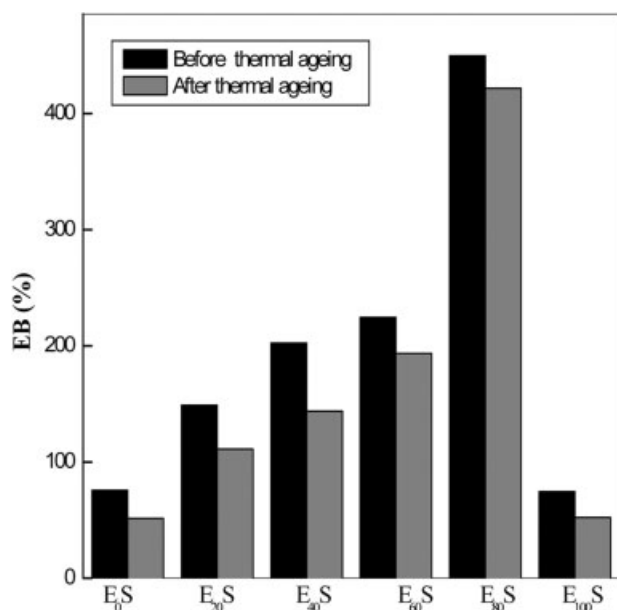


Figure 4 Comparison of EB (%)—before and after thermal ageing at 100°C.

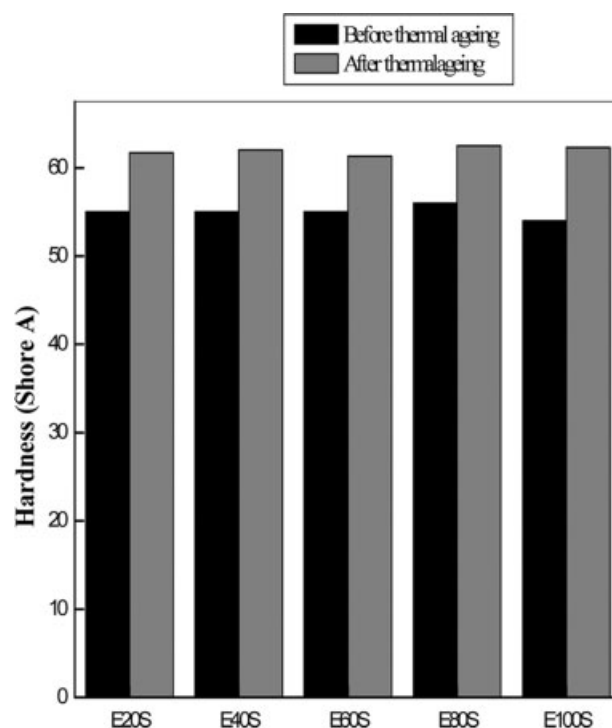


Figure 5 Comparison of hardness (shore A)—before and after thermal ageing at 100°C.

Figure 7 shows the trends in ozone crack initiation and crack resistivity of EPDM/SBR blends with respect to time. It is clear that the increased weight % of EPDM in the blends reduced the crack initiation time considerably and no cracks were found developed in other blends beyond E₃₀S.

Gamma [γ]-ray irradiation

The γ -ray radiation interacts with polymers in two ways; chain scission, which results in reduced tensile strength and elongation, and cross linking, which increases tensile strength but reduces elongation. Generally, polymers containing aromatic ring structures are resistant to radiation effects.³⁶ The radiation resistance in aliphatic polymers depends upon their levels of unsaturation and substitution.^{37,38}

Figure 8 shows that the γ -ray irradiation at 15- kGy doses lowered the tensile strength of EPDM rich blends compared with the unirradiated blends (control samples). This indicates that lower dose rate of irradiation performed under oxygen leads to a rapid decrease of the gel content due to chain scission and decrease in cross-linking. Meanwhile the increase in TS of SBR rich blends at lower level irradiation might be due to the presence of aromatic rings in the polymer, which are relatively degradation resistant. However, higher dosage of radiations enhances additional cross-linking, which increases tensile strength but reduces elongation.³⁹ The elonga-

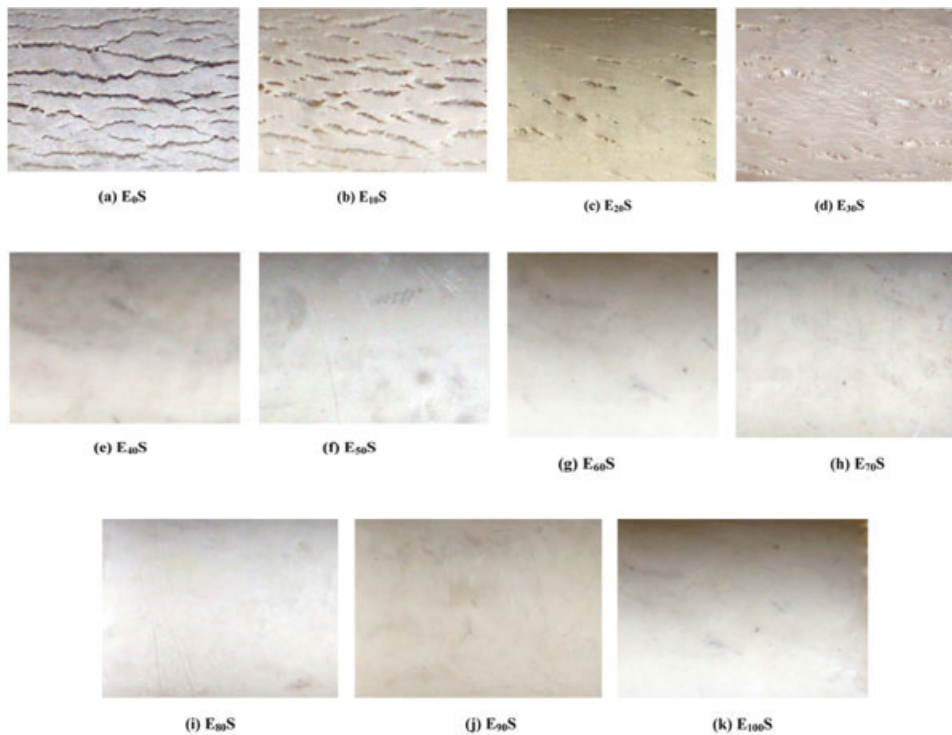


Figure 6 Optical photomicrographs of ozone exposed (120 h) sulfur cured EPDM/SBR blends (a–k). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion at break was found to be lowered by chain scission due to the radiation effect, as shown in Figure 9. Figures 10 and 11 illustrate the comparison of tensile strength and elongation at break respectively of the blend, with a control sample, containing 80 wt % of EPDM at 80 kGy irradiation. It is clear from Figure 10 that tensile strength was increased at 80-kGy dosages compared with the EPDM/SBR blend at 15 kGy dose and also to the unirradiated control sample.

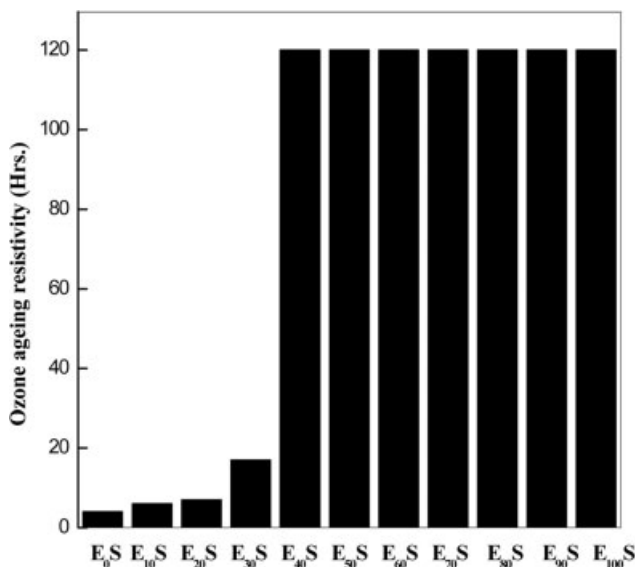


Figure 7 Ozone ageing resistivity of EPDM/SBR blends.

When SBR is the continuous phase, the matrix is more γ -ray resistant and at lower dosages, the cross-linking reaction predominates over chain scission and in such blends the TS increases. However, EPDM having an aliphatic chain is weak to resist γ -ray irradiation of lower doses where chain or cross-link degradation is dominating over additional cross-link for-

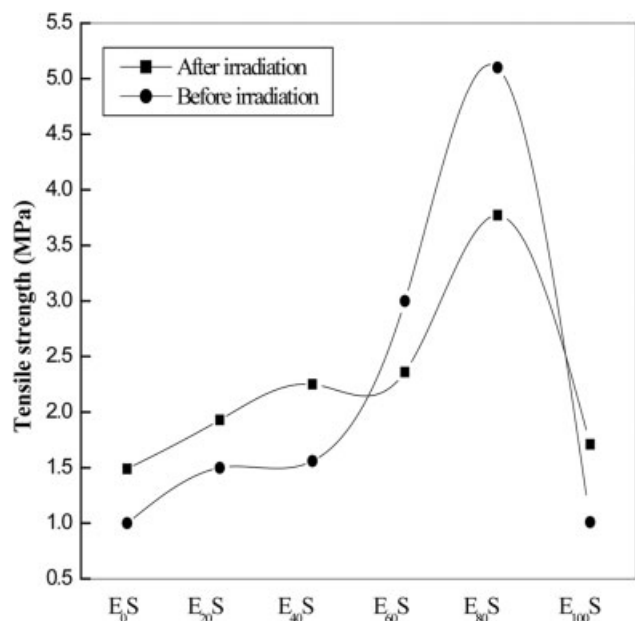


Figure 8 Effect of gamma irradiation on the tensile strength of EPDM/SBR blends at 15-Gy irradiation dose.

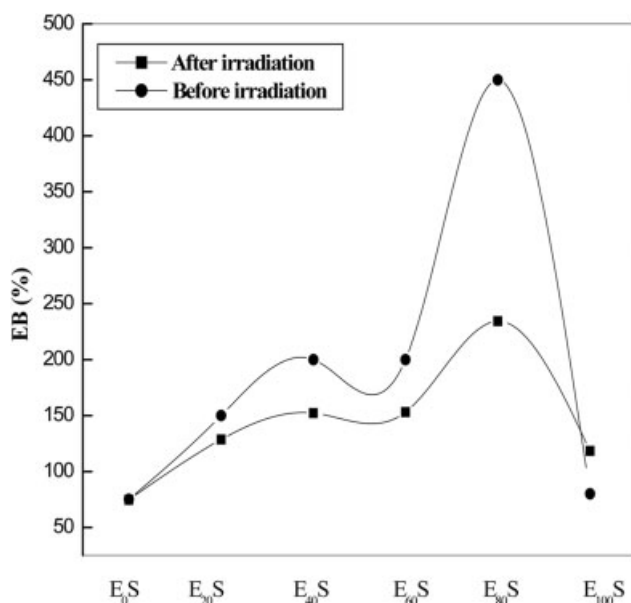


Figure 9 Effect of gamma irradiation on the EB (%) of EPDM/SBR blends at 15-kGy irradiation dose.

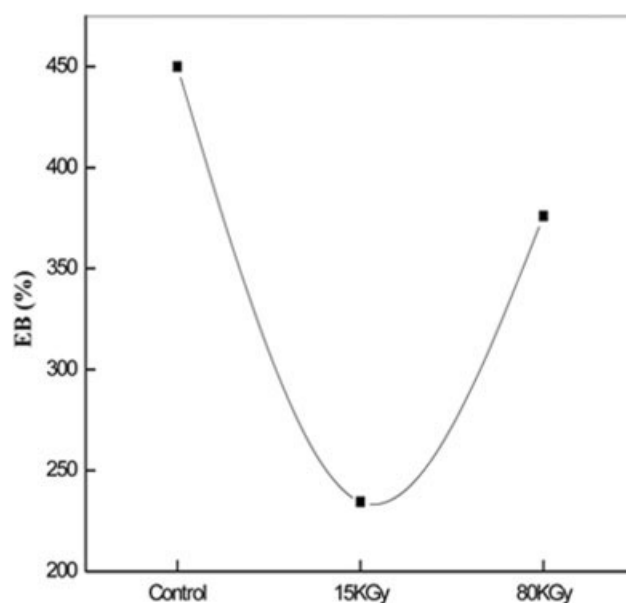


Figure 11 Effect of γ -irradiation dose on the EB of the effective blend E₈₀S—comparison with control sample.

mation. However, when dosage is enhancing, the cross-link formation can get activated and a dominance of cross-linking reaction can give better results. Similar observations exist in literatures.³⁶

Water ageing

Table III illustrates the water uptake (mass %) of various EPDM/SBR blends after water immersion. The results show that the water uptake was negligible in majority of the blends due to the presence of

water resistant EPDM. For instance, in blend E₈₀S, the percentage of water uptake after 7, 14, 21, and 42 days of water ageing have been noted only as 1.63, 2.09, 2.87, and 3.19% respectively.

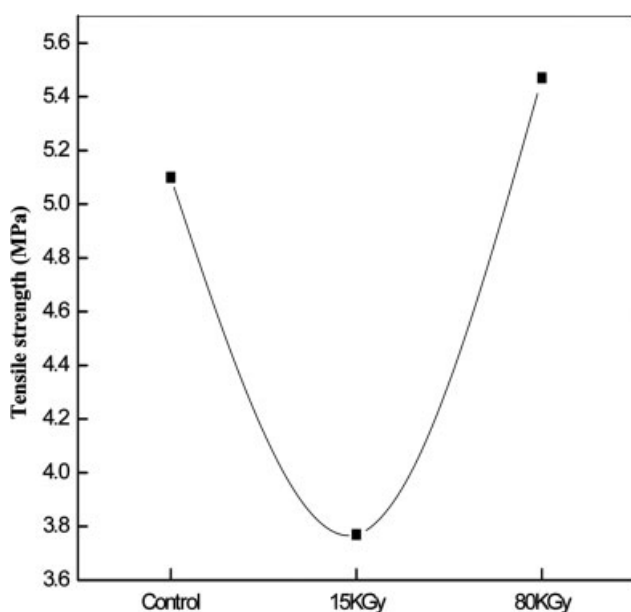


Figure 10 Effect of γ -irradiation dose on the TS of the effective blend E₈₀S—comparison with control sample.

CONCLUSION

In the present study, thermal, ozone, gamma, and water ageing characteristics of EPDM/SBR blends were investigated. A comparison of the mechanical properties of the blends before and after thermal ageing showed an increase in the tensile strength while a decrease in the elongation at break. The percentage increase in tensile strength of the blends was found to increase with increase in EPDM content. The ozone ageing studies showed that cracks were initiated only in few blends where the amount of EPDM was lesser to prevent crack growth. No ozone cracks were noticed in blends with EPDM level above 30 wt %. The γ -ray irradiation studies showed that the radiation interacts with polymers by chain

TABLE III
Distilled Water Uptake by EPDM/SBR Blend Vulcanizates

Samples	Water uptake (%)			
	After 7 days	After 14 days	After 21 days	After 42 days
E ₁₀₀ S	+0.07	+0.25	+0.331	+0.44
E ₈₀ S	+0.48	+0.70	+0.726	+1.12
E ₆₀ S	+0.48	+0.87	+0.938	+1.32
E ₄₀ S	+0.99	+1.31	+1.549	+2.23
E ₂₀ S	+1.63	+2.09	+2.499	+3.05
E ₀ S	+2.09	+2.58	+2.898	+3.26

scission and cross-linking. The chain scission resulted in reduced tensile strength and elongation and the cross-linking added an increased tensile strength and reduced elongation. Only negligible water uptake was noted in the blends, which makes the blends suitable for severe out door weathering applications.

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