Polymer Degradation and Stability **36** (1992) 137–147

Studies on the effect of blend ratio and cure system on the degradation of natural rubber—ethylene-vinyl acetate rubber blends

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(Received 6 February 1991; accepted 22 February 1991)

The effects of blend ratio and type of cross-link system on thermal ageing, γ-radiation and ozone resistance of blends of natural rubber and ethylene-vinyl acetate (EVA) rubber have been evaluated. The morphology of the blends is such that the EVA forms a continuous phase when its proportion in the blend is 40% or more. The resistance of the blends to thermal ageing, γ-radiation and ozone attack is better for those which contain a higher proportion of EVA. These properties are also highly dependent on the type of cure system used.

INTRODUCTION

Blending of elastomers is carried out with specific objectives such as improvement in processing characteristics or technological properties or the imparting of resistance against the action of degrading agents on one of the components of the blend. The properties of the blends depend on several factors such as morphology, interfacial adhesion, extent of cure, solubility of compounding ingredients in each phase, etc. Studies on blends of natural rubber (NR) and ethylene propylene diene rubber (EPDM), nitrile rubber (NBR) and polyvinyl chloride (PVC), NR and NBR,[1–3] etc., have indicated that very useful properties can be achieved by the proper choice of the components and their blend ratios. Blending of EPDM or NR with isotactic polypropylene (PP) or high density polyethylene (HDPE) is reported to give elastomers having thermoplastic characteristics.[4–7] Most of the elastomers and their blends gradually loose their properties during long periods of service not only due to mechanical forces but also due to the action of heat, oxygen, ozone, light, high energy radiation, etc. The effect of these degrading agents on each type of polymer is different and depends mainly on the chemical structure of the polymer.

Several reviews have outlined the effects of thermo-oxidative ageing of rubbers[8,9] and also the degradation and protection of polymers in the presence of ozone.[10] The effects of radiation on polymeric materials and their blends have also been reported by several research groups.[11–14]

High energy radiation causes both cross-linking and degradation which considerably change the mechanical properties of polymers. Tensile strength, elongation, modulus of elasticity, hardness and softening temperatures are decreased as a result of chain scission. On the other hand, cross-linking increases these properties.[12] The cross-linking of ethylene-vinyl acetate (EVA) by high energy radiation has been reported by Sweet.[14] The radiation modification of blends of polyethylene (PE), butyl rubber, cross-linked PE and polyisobutylene has been investigated by Ivehenko *et al.*[15] The effect of γ-radiation on the mechanical properties and

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Polymer Degradation and Stability 0141-3910/92/$05.00

failure behaviour of blends of hytrel/PVC and NR/PE has been reported by De and his co-workers.[16,17] Skowronski *et al.*[18] have studied the photo-degradation of PVC/EVA and PVC/nitrile rubber blends.

In this paper, the authors present the results of their studies on the influence of thermal ageing, ozone and γ-radiation on blends of natural rubber and ethylene-vinyl acetate. The effects of blend ratio and cure systems on the resistance of the blends to these degrading agents are reported.

EXPERIMENTAL

The NR used for the study was ISNR-5 grade rubber, light colour. Ethylene-vinyl acetate rubber (EVA Exxon 218) was manufactured by Exxon Chemical Company (Houston, TX). The vinyl acetate content of the EVA was 18% by weight. Its melt flow index was 1·7 g/10 min, density 0·939 g/cm^3 and Vicat softening point 64°C. All other ingredients used were of rubber chemical grade.

Blends were prepared in a laboratory model intermix (Shaw Intermix KO) set at a temperature of 80°C and a rotor speed of 60 rpm. NR was masticated for 2·0 min and then blended with EVA for 2·5 min. The final temperature of the blend inside the intermix was in the range 110–128°C, depending upon the blend ratio. The blends contained 0, 10, 20, 30, 40, 50, 60, 70, 80 and 100% of EVA and are designated A, B, C, D, E, F, G, H, I and J, respectively. The blends were compounded in a two-roll laboratory mill according to the test recipes given in Table 1. Compounds which contained sulphur as curative are designated $A_1, B_1, C_1, \ldots$, etc., and those having dicumyl peroxide (DCP) $A_2, B_2, C_2, \ldots$, etc. Compounds which contained the mixed cure system consisting of sulphur and DCP are designated $A_3, B_3, C_3, \ldots$, etc. The dosage of sulphur and DCP in the mixed cure system is not according to the proportion of NR and EVA in the blend because their distribution in these two elastomers can be different. The compounded blends were moulded to optimum cure in a steam heated hydraulic press at 160°C to obtain the required test samples. Blends with 50% or more of EVA could not be vulcanised fully with sulphur and hence could not be evaluated for physical properties. Dumbbells conforming to ASTM D-412 were punched from the sheets along the mill grain direction and used for tensile testing.

Table 1. Formulation of the compounds

Ingredients	Sulphur system (1)	DCP system (2)	Mixed system (3)
Polymer	100·0	100·0	100·0
Zinc oxide	5·0	5·0	5·0
Stearic acid	1·5	1·5	1·5
Styrenated phenol	1·0	1·0	1·0
Dibenzothiazyl disulphide	0·8	—	0·8
DCP (40% active ingredient)	—	4·0	4·0
Sulphur	2·5	—	2·5

The effect of thermal ageing was determined by ageing the samples in a multicell ageing oven. The samples were aged at 70°C for 4, 7 and 10 days. Ozone resistance was determined according to ASTM D-1149-81. Samples were exposed to ozonised air in an ozone test chamber (MAST model 700-1) for 85 h. The concentration of ozone was maintained at 50 pphm and the inside temperature at 37·5°C. The samples were irradiated with γ-rays from a ^{60}Co source at a dose rate of 0·321 Mrad/h in a γ-chamber to doses of 10, 20, 30, 50 Mrad. The tensile testing before and after irradiation and thermal ageing was carried out according to ASTM D-412-80 test methods. SEM observation of the blends was made using a JOEL 35-C scanning electron microscope. One end of the uncured blend in a cylindrical shape was immersed in benzene for about 48 h to extract the NR phase. These samples were then dried at 40°C in an air oven without disturbing the extracted surface which was examined under the SEM for morphological study. Photographs of the extracted surface were taken at 1000× magnification in all cases.

RESULTS AND DISCUSSION

Morphology of the blends

Figure 1 is the photomicrograph of the blend G (60:40, EVA:NR). The holes on the surface are formed by extraction of the NR phase. At this blend ratio NR remains as dispersed particles in the EVA matrix. The size of the dispersed particles is also small compared with their size in blends which contain a higher proportion of NR. As the proportion of NR in the blend is increased to 50% (blend F), the size of the holes increases

Fig. 1. SEM photomicrograph of blend G.

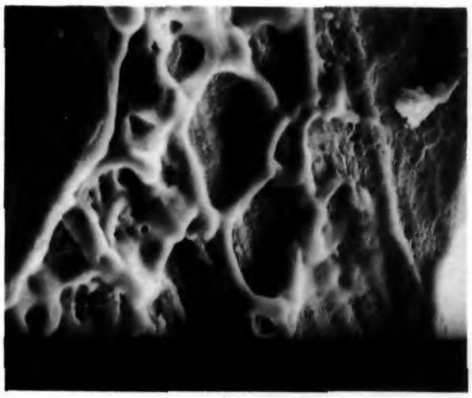

Fig. 2. SEM photomicrograph of blend F.

severalfold (Fig. 2). The boundary of EVA separating the holes has narrowed down to a thin layer. When the EVA:NR ratio is 40:60 (blend E) this narrow boundary layer is seen to be broken, since it is unable to withstand the forces due to the swelling of the NR phase (Fig. 3). It is possible that in blends E and F, both NR and EVA form continuous phases because of the higher proportion of the NR phase and lower melt viscosity of the EVA phase. The photomicrograph of the 30:70 EVA:NR blend shows particles of EVA remaining on the benzene extracted surface (Fig. 4) which indicates that EVA forms the dispersed phase at this blend ratio. Thus, the morphology of the EVA–NR blends appears to be such that the EVA forms the dispersed phase when its proportion is below 40% and NR forms the dispersed phase when its proportion is 40% or less. In the range 40:60 to 50:50 EVA:NR, both the polymers remain as continuous phases leading to a sponge-like structure for the blend.

Fig. 3. SEM photomicrograph of blend E.

Fig. 4. SEM photomicrograph of blend D.

Effect of thermal ageing

It is well known that during thermal ageing, main chain scission, more cross-link formation and cross-link breakage can take place. It is also possible that the existing cross-links break and a more stable type of cross-link, which may be immune to further scission, can be formed. The relative ratio and magnitude of such reactions which take place during ageing govern the amount of change in each property.

The percentage retention of modulus 300% after ageing the test samples of NR–EVA blends containing three different types of cure systems is shown in Figs 5–7. Figures 5 and 7 show that the percentage retention of modulus increases with ageing time which indicates that further cross-linking of the blends which contain sulphur and the mixed cure system has taken place. Whereas the sulphur system shows maximum retention for the blends C to E, the mixed cure system shows maximum retention for blends E–G. In the case of the sulphur cure, EVA cannot be vulcanised by sulphur and the sulphur which is dispersed in the EVA phase also slowly migrates to the NR phase as ageing proceeds, due to the difference in concentration of free sulphur present in each phase during that time. The decrease in retention of modulus of the

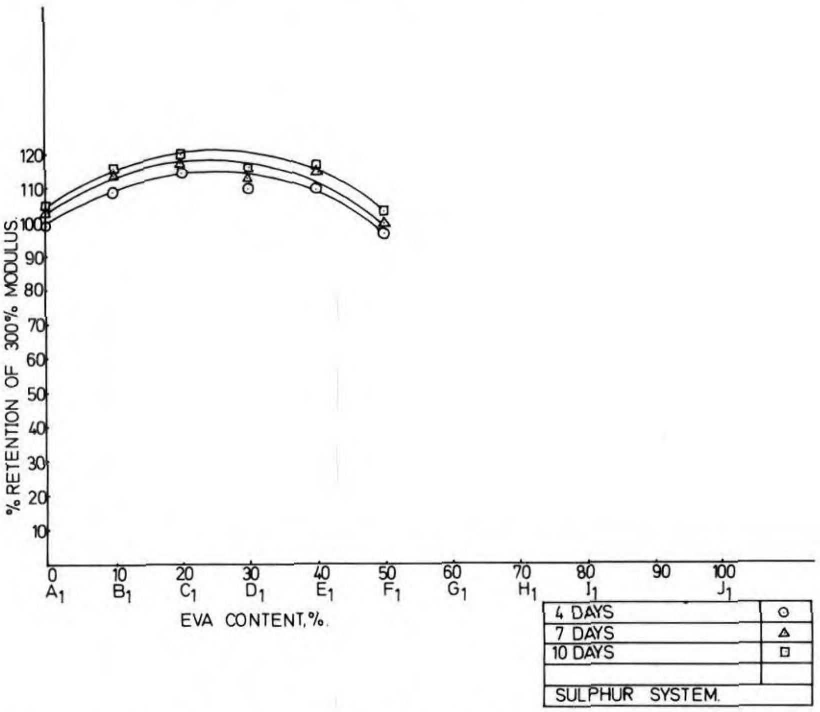

Fig. 5. Retention of 300% modulus of sulphur cured blends after thermal ageing (○, 4 days; △, 7 days; □, 10 days).

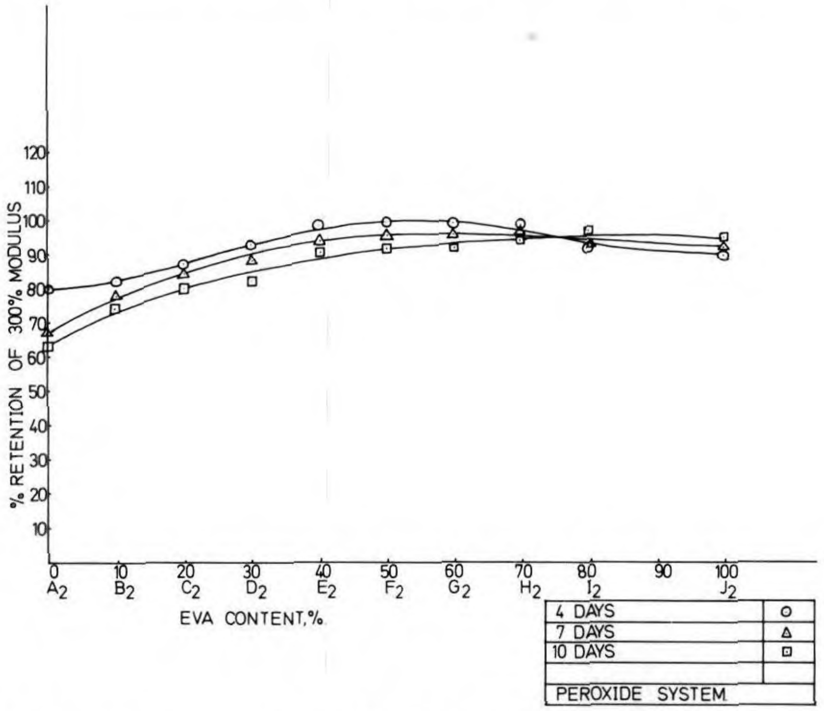

Fig. 6. Retention of 300% modulus of peroxide cured blends after thermal ageing (○, 4 days; △, 7 days; □, 10 days).

50:50 NR:EVA blend (F_1) is due to the degradation of the non-cross-linked EVA which also forms a continuous phase at this blend ratio. In the case of the mixed cure system, there is a continuous increase in percentage retention of modulus for the blends which contain a higher proportion of NR and this trend is reversed in the case of blends which contain a higher proportion of EVA. This is because NR can be cross-linked by both sulphur and peroxide whereas EVA is cross-linked by DCP only and the rate of cross-linking in the latter case is very

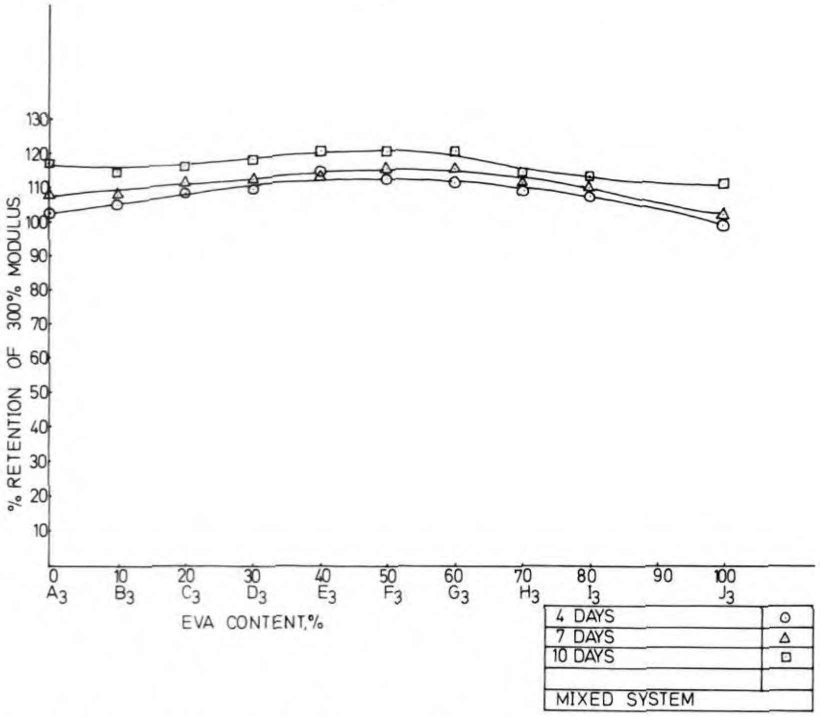

Fig. 7. Retention of 300% modulus of mixed cure blends after thermal ageing (○, 4 days; △, 7 days; □, 10 days).

low. In the case of the peroxide system, there is a decrease in percentage retention of modulus with period of ageing for blends in which the proportion of NR is high. However, this trend is reversed in the case of blends H_2–J_2. This indicates that for the blends which contain higher proportions of NR, main chain scission predominates over cross-linking of the NR phase as the time of ageing is increased. Since EVA has a saturated backbone structure, main chain scission is less and cross-linking predominates, as shown by a gradual increase in retention of modulus as the proportion of EVA is increased.

The percentage retention of tensile strength of the NR–EVA blends decreases with time of ageing for the sulphur (Fig. 8), peroxide (Fig. 9) and mixed (Fig. 10) systems of cure, when the proportion of NR in the blend is high. However, at higher proportions of EVA in the blend, the mixed and peroxide systems of cure do not show much further drop in tensile strength after seven days' ageing. In the case of blends which contain the peroxide cure system, the retention of tensile strength increases with increase in EVA content. This increase is more evident for blends E_2 to G_2 in which the EVA also forms a continuous phase. In the case of the mixed cure system, minimum retention of tensile strength was observed for blends F_3 and G_3. The difference between the peroxide and mixed cure systems can be due to the higher extent of cross-linking of blends F_3 and G_3 compared to F_2 and G_2, respectively, due to the continued cross-linking reaction which takes place during ageing. It is possible that the NR phase in blends F_3 and G_3 becomes highly cross-linked during ageing because of the presence of a higher dosage of sulphur owing to its preferential migration to the NR phase. As the extent of cross-linking increases, the NR phase becomes less deformable and acts as stress raisers in the EVA matrix, leading to lower tensile values. The observation that the retention of modulus 300% is also high for blends E_3–G_3 compared to E_2–G_2 justifies this inference.

Effect of γ-radiation

γ-Radiation is a powerful method for cross-linking elastomers. But exposure to higher dosages degrades the polymer. The extent of cross-linking/degradation undergone by each polymer depends on the nature of the polymer and the presence of initiators/sensitisers. In the case of NR–EVA blends, it is observed that the presence of EVA increases the percentage retention of modulus 300% after γ-irradiation. This is true for all three cure systems examined (Figs 11–13). While the NR vulcanisate (A)

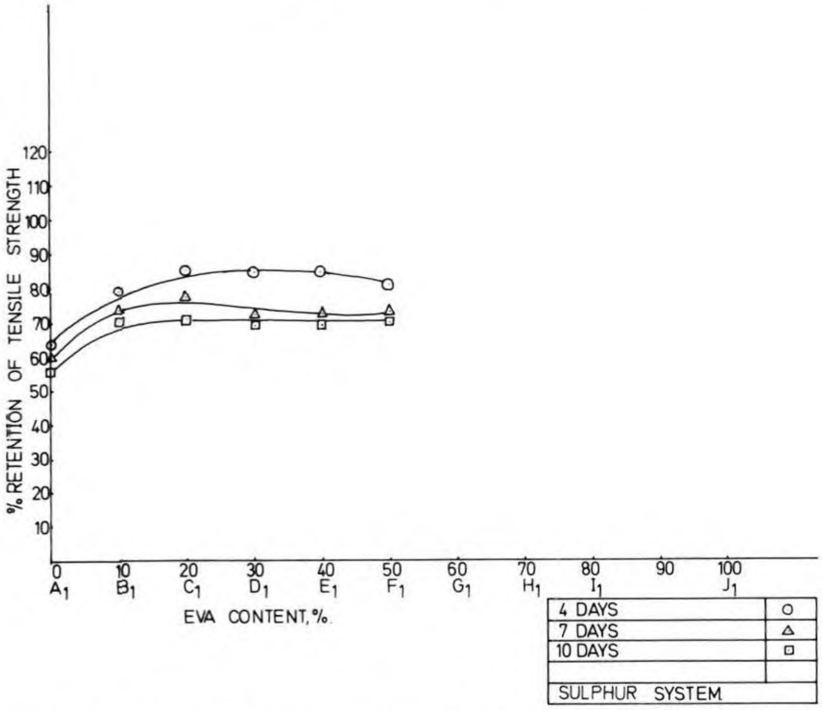

Fig. 8. Retention of tensile strength of sulphur cured blends after thermal ageing (○, 4 days; △, 7 days; □, 10 days).

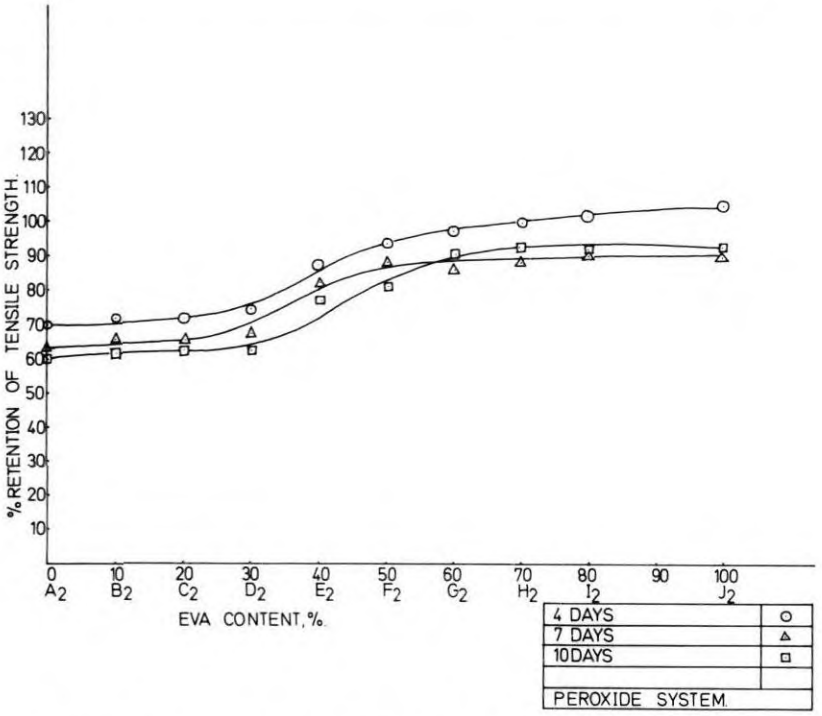

Fig. 9. Retention of tensile strength of peroxide cured blends after thermal ageing (○, 4 days; △, 7 days; □, 10 days).

showed lower retention of modulus with increase in irradiation dosage, EVA vulcanisate (J) showed a regular increase in retention of modulus. This observation indicates that while NR undergoes degradation, EVA gets cross-linked during γ-ray exposure. It has already been reported that EVA undergoes brittle type fracture during tensile failure, after exposure to γ-radiation, due to continued cross-linking.[19] The NR-rich blends in general show maximum retention of modulus after exposure to 20–30 Mrad of radiation. This is probably because, at these dosages, the degradation level is much lower compared to the extent of cross-linking

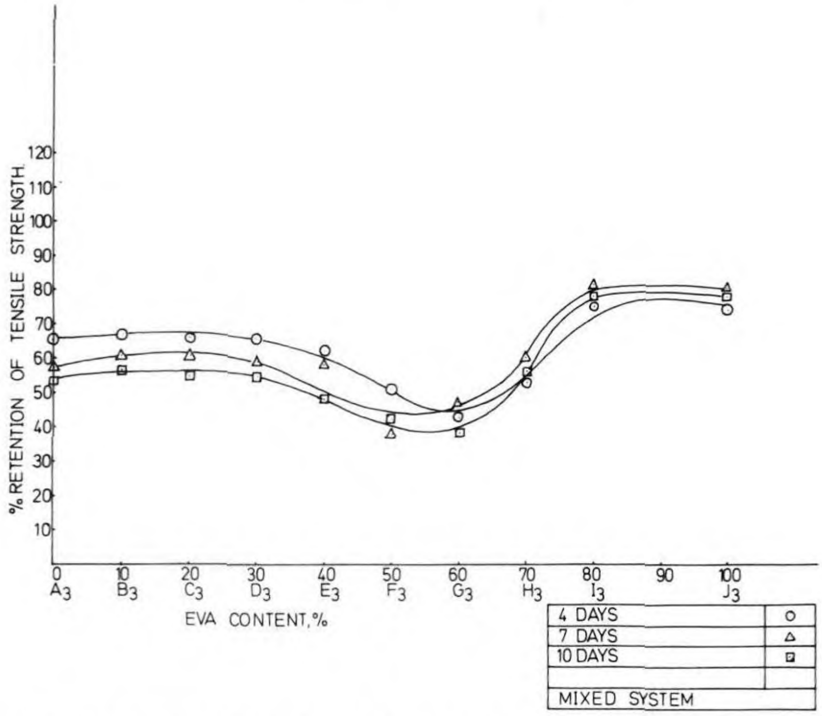

Fig. 10. Retention of tensile strength of mixed cure blends after thermal ageing (○, 4 days; △, 7 days; □, 10 days).

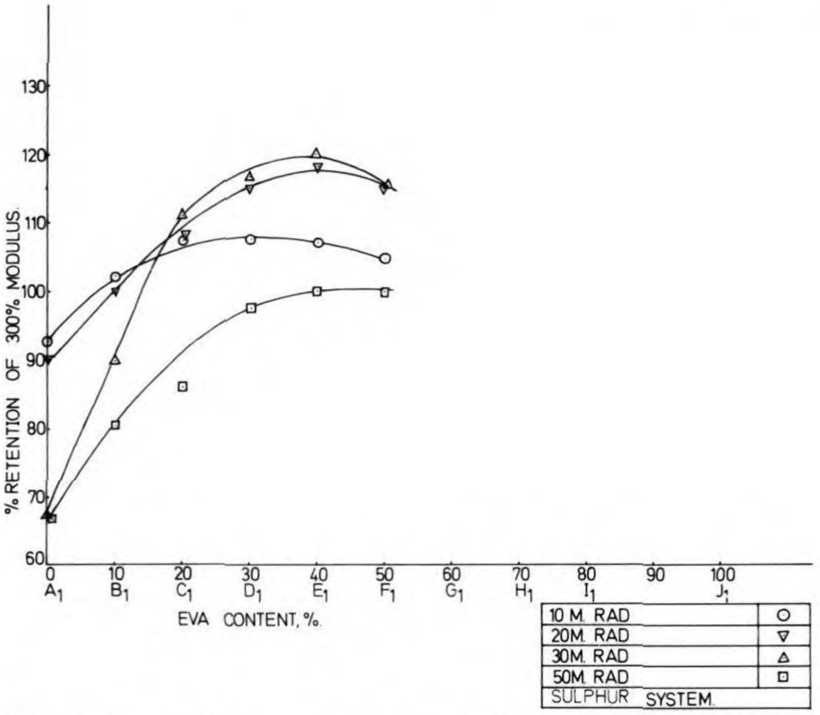

Fig. 11. Retention of 300% modulus of sulphur cured blends after γ-irradiation (○, 10 Mrad; ▽, 20 Mrad; △, 30 Mrad; □, 50 Mrad).

undergone by both NR and EVA phases. On exposure to 50 Mrad of radiation, it is seen that the retention of modulus is always lower for the NR-rich blends, while the EVA-rich blends maintain a higher retention at this dosage (Figs 12 and 13). This change in pattern of radiation resistance of the blends is associated with a change in the morphology of the blends. At blend ratio 60:40 EVA:NR (blend G) the NR phase remains as dispersed phase only (Fig. 1). Since the continuous matrix of EVA undergoes cross-linking, the modulus retention is increased with increase in exposure to γ-ray dosage.

The retention of tensile strength after exposure

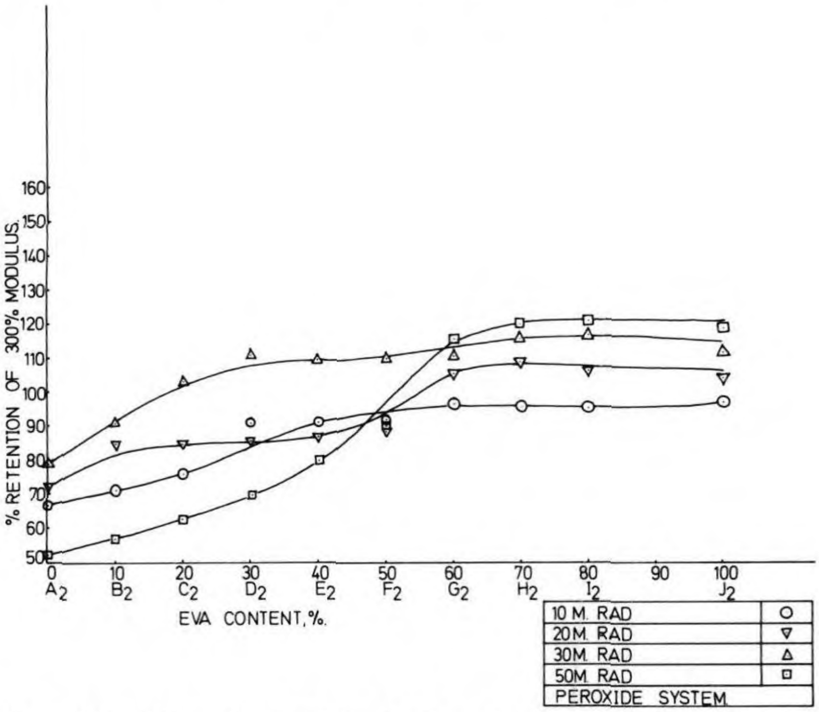

Fig. 12. Retention of 300% modulus of peroxide cured blends after γ-irradiation (○, 10 Mrad; ▽, 20 Mrad; △, 30 Mrad; □, 50 Mrad).

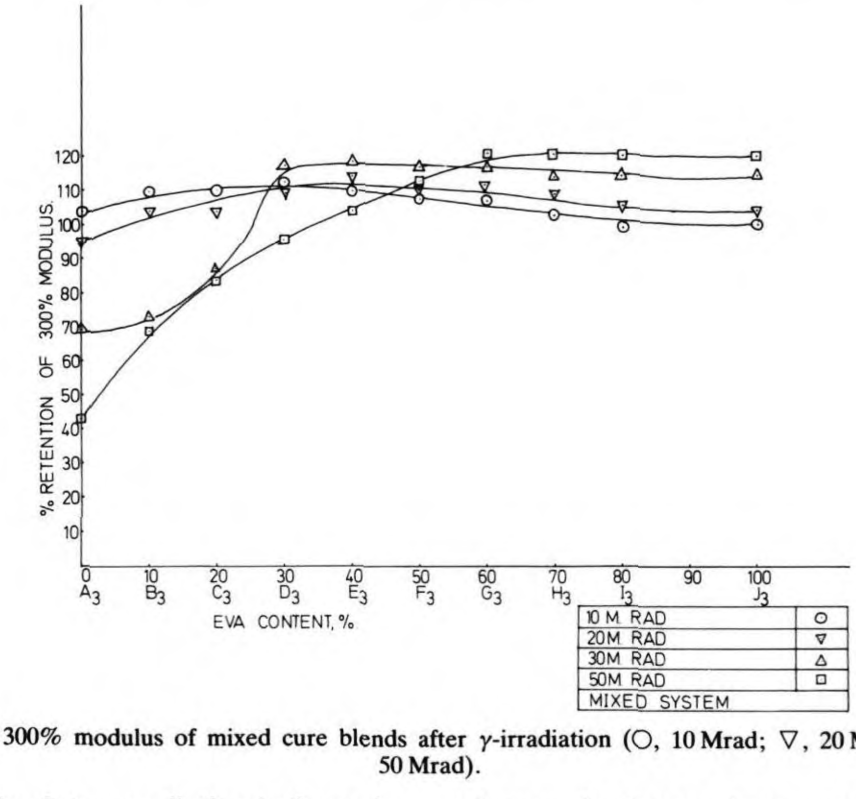

Fig. 13. Retention of 300% modulus of mixed cure blends after γ-irradiation (○, 10 Mrad; ▽, 20 Mrad; △, 30 Mrad; □, 50 Mrad).

of the NR–EVA blends to γ-radiation is shown in Figs 14, 15 and 16 respectively for the sulphur, peroxide and mixed cure systems. From Figs 14 and 15 it may be seen that as the EVA content in the blend is increased, the retention of tensile strength is increased for the blends which contain sulphur and peroxide cure systems. However, when a mixed type of cure system is used, higher retention of tensile strength is noticed only for those blends which contain a higher proportion of EVA. For all three cure systems, higher dosages of γ-radiation gave only lower percentage retention of tensile strength. This could be due to the degradation of the NR phase in

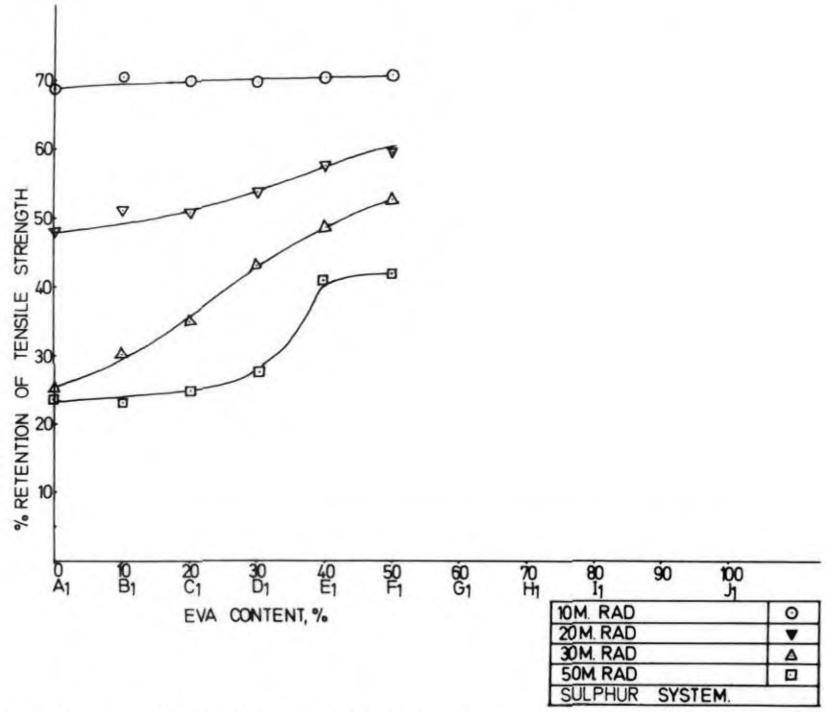

Fig. 14. Retention of tensile strength of sulphur cured blends after γ-irradiation (○, 10 Mrad; ▽, 20 Mrad; △, 30 Mrad; □, 50 Mrad).

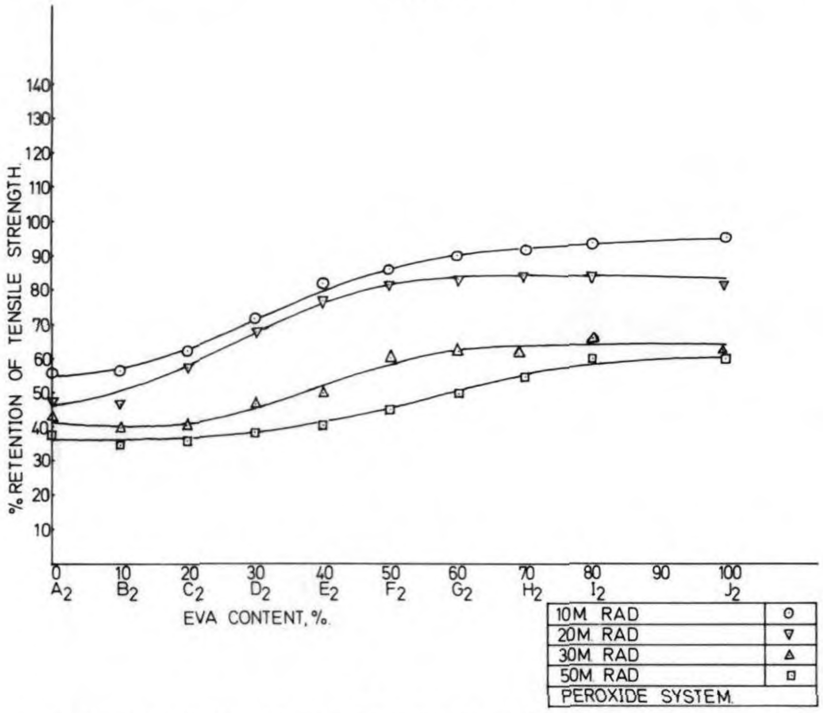

Fig. 15. Retention of tensile strength of peroxide cured blends after γ-irradiation (○, 10 Mrad; ▽, 20 Mrad; △, 30 Mrad; □, 50 Mrad).

NR-rich blends and excessive cross-linking of the EVA when it forms a continuous phase.

Effect of exposure to ozone

Unsaturated elastomers, especially those containing an activated double bond in the main chain, are severely attacked by ozone, resulting in deep cracks in a direction perpendicular to that of the applied stress. Protection against ozone attack can be achieved by blending the unsaturated elastomers with those containing a saturated main chain. The morphology of the blends plays a vital role on the extent of protection imparted by the saturated elastomers.

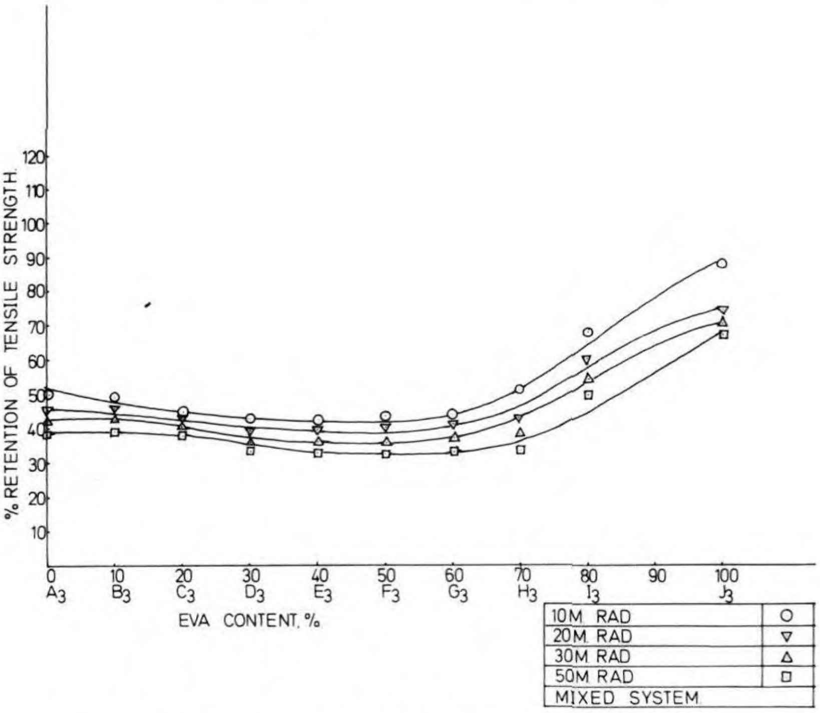

Fig. 16. Retention of tensile strength of mixed cure blends after γ-irradiation (○, 10 Mrad; ▽, 20 Mrad; △, 30 Mrad; □, 50 Mrad).

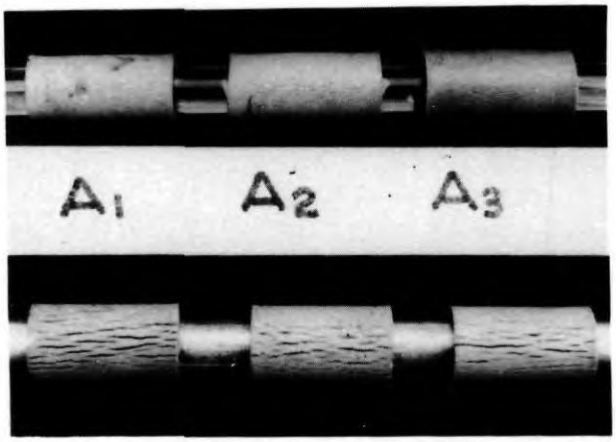

Fig. 17. Photograph of NR vulcanisates after 8 and 85 h of exposure.

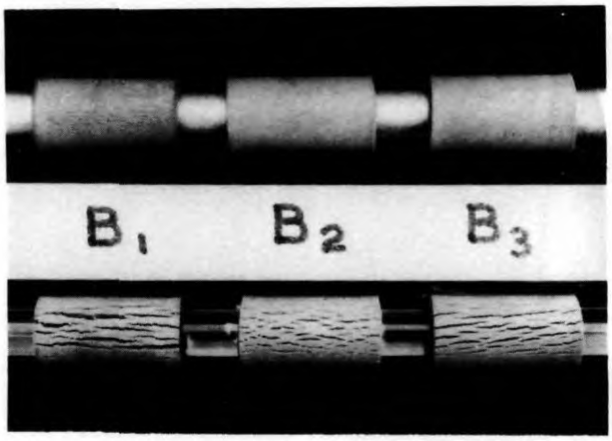

Fig. 18. Photograph of blend B (90:10 NR:EVA) after 8 and 85 h of exposure.

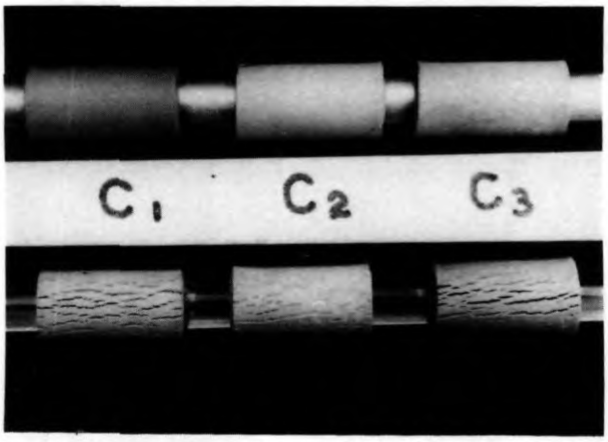

Fig. 19. Photograph of blend C (80:20 NR:EVA) after 8 and 85 h of exposure.

Photographs of the NR–EVA blends after exposure for 8 and 85 h to ozonised air containing 50 pphm ozone are shown in the top and bottom sections respectively of Figs 17–20. It is clearly evident that the ozone resistance of the blends increases as the proportion of EVA in the blend is increased. For blends which contain 40% or more of EVA (blends E, F, G, etc.), no cracks were observed even after exposing the samples in ozonised air for periods beyond 85 h. The morphology study reported in this paper indicated that at 40% concentration of EVA in the blend, it also forms a continuous phase. It is possible that EVA which has a saturated

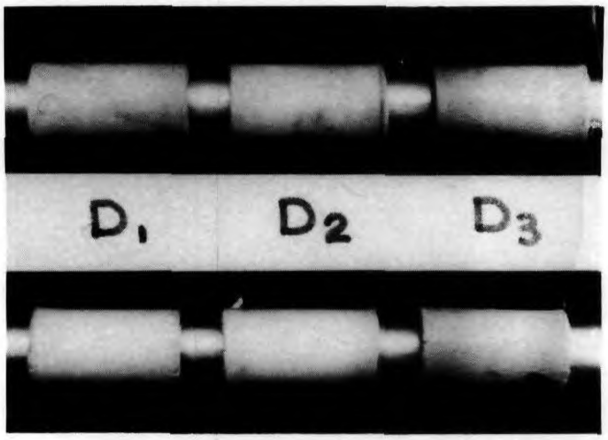

Fig. 20. Photograph of blend D (70:30 NR:EVA) after 8 and 85 h of exposure.

backbone structure forms a protective sheath during processing of the blends, due to its lower melt viscosity, resulting in complete protection against ozone attack. Blends B–D, in which the EVA remains as dispersed particles, also show a wide difference in the intensity of the cracks formed. The intensity of the cracks, after both 8 and 85 h exposure, decreases from samples A to D. This is due to the increase in the critical stress of the blends from B to D because of the presence of the dispersed particles of EVA, which has a crystalline structure. The nature of the cross-link system was also found to have a profound influence on the ozone resistance of the blends. This effect becomes highly prominent as the proportion of EVA in the blend is increased. In all the samples from A to D, the peroxide cure system gave cracks of lower intensity compared to the other two types of cure systems. This could be due to the presence of less flexible carbon–carbon cross-links formed during peroxide cure, which increases the stress required to produce the critical strain encountered in ozone attack.

CONCLUSIONS

The following conclusions may be drawn from this study:

(1) The morphology of the NR–EVA blends is such that EVA forms a continuous phase when its proportion in the blend is 40% or more.
(2) Thermal ageing and γ-radiation resistance of the NR–EVA blends are better for blends which contain a higher proportion of EVA.
(3) Among the three different cure systems studied, the mixed cure system was found to give lower retention of tensile strength after thermal ageing and γ-irradiation. However, the retention of modulus 300% is better for this system.
(4) Complete protection against ozone attack is given by EVA when its proportion in the NR–EVA blend is 40% or more.
(5) The ozone resistance of NR–EVA blends is also dependent on the type of cure system. The peroxide cure system was found to be better in this respect.

ACKNOWLEDGEMENT

The authors are grateful to Dr M. R. Sethuraj, Director, Rubber Research institute of India for granting permission to undertake this work at the Chemistry and Rubber Technology Division of the Institute.

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