Results included in this chapter have been accepted for publication in Polymer Degradation and Stability.
Use of polymeric materials under the influence of degrading agents such as ozonised air, gamma radiation and thermal ageing has increased rapidly during the last few years. Hence it is very important to study the effects of such degrading agents on the performance of elastomers at different conditions. For NR, the resistance to ageing and ozone is poor due to the presence of double bond in the main chain. EVA possesses excellent ageing resistance due to its saturated backbone structure. Hence the behaviour of blends of these elastomers against the action of the various degrading agents is worth examining. The effect of degrading agents on each type of polymer will be different and depends mainly on the chemical structure of the polymer and the type of crosslink system used. Several studies have been reported on the thermo-oxidative ageing of rubbers\textsuperscript{122} and on protection of polymers against the action of ozone\textsuperscript{123}. The effects of radiation on polymeric materials and their blends have also been reported by several research groups\textsuperscript{124}.

This chapter discusses the result of the studies on the retention of tensile strength, modulus 300%, and elongation at break, after exposing test sample of NR-EVA blends to different degrading agents such as ozone, heat and gamma radiation. The effects of blend ratio and type of crosslink system in retaining the tensile properties of the blends under the influence of the above degrading agents have been examined. The details of the experimental procedures adopted for the studies on degradation and morphology are given in Chapter II.
VII.1 EFFECT OF THERMAL AGEING

It is well known that during thermal ageing, main chain scission, additional crosslink formation and crosslink breakage can take place. There is also the possibility that the existing crosslinks break and a more stable type of crosslink which is immune to further scission can be formed. The relative ratio and magnitude of such reactions that are taking 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 given in Figures VII.1 to VII.3. From Figures VII.1 and VII.3, it is seen that the percentage retention of modulus increased with period of ageing which indicated that further crosslinking of the blends which contained sulphur and mixed cure systems had taken place. It is interesting to note that the sulphur system showed maximum retention for the blends C to D and the mixed cure system showed maximum retention for blends E to G. In the case of sulphur cure, EVA cannot be vulcanised by sulphur and the sulphur which is dispersed in the EVA phase, 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 50:50 NR:EVA blend (No. F1) is due to the degradation of the uncrosslinked EVA which also forms a
continuous phase at this blend ratio. In the case of mixed cure system there was continuous increase in percentage retention of modulus for the blends which contained a higher proportion of NR and this trend was reversed in the case of blends which contained a higher proportion of EVA. This is because NR can be crosslinked both by sulphur and peroxide whereas EVA gets crosslinked by DCP only and the rate of crosslinking in the latter case is very slow. In the case of peroxide system there was decrease in percentage retention of modulus with period of ageing for the blends in which the proportion of NR was high. However, this trend was reversed in the case of blends H₂ to J₂. This indicated that for the blends which contained higher proportions of NR, main chain scission predominated over the crosslinking of the NR phase as the time of ageing is increased. Since EVA has a saturated backbone structure, main chain scission was less and crosslinking reaction predominated as evidenced by gradual increase in retention of modulus as the proportion of EVA is increased.

The percentage retention of tensile strength of the NR-EVA blends decreased with time of ageing for the sulphur (Figure VII.4), peroxide (Figure VII.5) and mixed (Figure VII.6) systems of cure, when the proportion of NR in the blend was high. However, at higher proportions of EVA in the blend, the mixed and peroxide systems of cure did not show much further drop in tensile strength after seven days ageing period. In the case of blends which contained
the peroxide cure system, the retention of tensile strength increased with increase in EVA content. This increase was more evident for blends E2 to G2 in which the EVA also formed a continuous phase. In the case of mixed cure system, minimum retention of tensile strength was observed for the blends F3 and G3. This difference between the peroxide and mixed cure systems can be due to the higher extent of crosslinking of the blends F3 and G3 compared to F2 and G2, respectively, due to the continued crosslinking reaction which takes place during ageing. It is possible that the NR phase in blends F3 and G3 gets highly crosslinked 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 crosslinking 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% was also high for the blends E3 to G3 compared to E2 to G2 justifies the above inference.

VII.2 EFFECT OF γ-RADIATION

\(\gamma\)-radiation is a powerful means for crosslinking elastomers. But exposure to higher dosage of it, degrades the polymer. The extent of crosslinking/degradation undergone by each polymer depends on the nature of polymer and the presence of initiators/sensitisers. In the case of NR-EVA blends, it is observed that presence of EVA
increased the percentage retention of modulus 300% after γ-irradiation. This was true for all the three different cure systems examined (Figures VII.7, VII.8 and VII.9). While the NR vulcanisate (A) showed lower retention of modulus with increase in irradiation dosage, EVA vulcanizate (J) showed regular increase in retention of modulus. This observation indicated that while NR undergoes degradation, EVA gets crosslinked 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 crosslinking. The NR rich blends in general showed maximum retention of modulus after exposing them to 20-30 Mrad of radiation. This is probably because at these doses, the degradation level was much lower compared to the extent of crosslinking undergone by both NR and EVA phases. On exposure to 50 Mrad of radiation, it is noticed that the retention of modulus was always lower for the NR rich blends, while the EVA rich blends maintained a higher retention at this dosage (Figures VII.8 and VII.9). This change in pattern of radiation resistance of the blends was associated with a change in morphology of the blends. At blend ratio 60:40 EVA:NR (blend G) the NR phase remained as dispersed phase only (Figure III.1). Since the continuous matrix of EVA undergoes crosslinking reaction the modulus retention is increased with increase in exposure to γ-rays.

The retention of tensile strength after exposure of the NR-EVA blends to γ-radiation is shown in Figures VII.10, VII.11 and VII.12.
for the sulphur, peroxide and mixed cure systems, respectively. From Figures VII.10 and VII.11, it is seen that as the EVA content in the blend is increased, the retention of tensile strength is increased for the blends which contained sulphur and peroxide cure systems. But, when a mixed type of cure system was used, higher retention of tensile strength was noticed only for those blends which contained a higher proportion of EVA. In the case of all the three types of cure systems, higher doses of γ-radiation gave only lower percentage retention of tensile strength. This could be due to the degradation of the NR phase in NR rich blends and excessive crosslinking of the EVA when it formed a continuous phase.

VII.3 EFFECT OF EXPOSURE TO OZONE

Unsaturated elastomers, especially those containing activated double bonds 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 latter type of elastomers.

The photographs of the NR-EVA blends after exposure to ozonised air containing 50 ppm ozone concentration are shown in Figures VII.13 to VII.16. The samples at the top side of the photograph are those taken out after 8 hours of exposure and the bottom
ones are those exposed for 85 hours. From the photographs it is clearly evident that the ozone resistance of the blends increased as the proportion of EVA in the blend is increased. In the case of blends which contained 40 per cent or more of EVA (blends E, F, G etc), no crack was observed even after exposing the samples in ozonised air for periods beyond 85 hours. The morphology of the blends described in Chapter III indicated that at 40 per cent concentration of EVA in the blend, it also formed a continuous phase. It is possible that EVA which has a saturated backbone structure formed a protective layer during processing of the blends, due to its lower melt viscosity, resulting in complete protection against ozone attack. Blends B to D, in which the EVA remained as dispersed particles, also showed wide difference in intensity of the cracks formed. The intensity of the cracks, both after 8 hours and 85 hours of exposure, decreased for the samples from A to D. This is due to the increase in 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 crosslink system also was found to have a profound influence on the ozone resistance of the blends. This effect became highly prominent as the proportion of EVA in the blend 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 (A₂, B₂, C₂, D₂ less than A₁, B₁, C₁, D₁ and A₃, B₃, C₃, D₃, respectively). This could be due to the
presence of less flexible carbon-carbon crosslinks formed during peroxide cure, which increased the stress required to produce the critical strain encountered in the ozone attack.
Figure VII.1
Plots of retention of 300% modulus of sulphur cured blends after thermal ageing.
Figure VII.2
Plots of retention of 300% modulus of peroxide cured blends after thermal ageing.
Figure VII.3
Plots of retention of 300% modulus of mixed cureblends after thermal ageing.
Figure VII.4
Plots of retention of tensile strength of sulphur cured blends after thermal ageing.
Figure VII.5
Plots of retention of tensile strength of peroxide cured blends after thermal ageing.
Figure VII.6
Plots of retention of tensile strength of mixed cure blends after thermal ageing.
Figure VII.7
Plots of retention of 300% modulus of sulphur cured blends after γ-irradiation.
Figure VII.8
Plots of retention of 300% modulus of peroxide cured blends after γ-irradiation.
Figure VII.9
Plots of retention of 300% modulus of mixed cure blends after γ-irradiation.
Figure VII.10
Plots of retention of tensile strength of sulphur cured blends after $\gamma$-irradiation.
Figure VII.11
Plots of retention of tensile strength of peroxide cured blends after γ-irradiation.
Figure VII.12
Plots of retention of tensile strength of mixed cure blends after γ-irradiation.
Figure VII.13
Photograph of NR vulcanisates after 8 h and 85 h exposure.

Figure VII.14
Photograph of blend B (90:10 NR:EVA) after 8 h and 85 h exposure.
Figure VII.15
Photograph of blend C (80:20 NR:EVA) after 8 h and 85 h exposure.

Figure VII.16
Photograph of blend D (70:30 NR:EVA) after 8 h and 85 h exposure.