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EFFECTS OF GAMMA-RADIATION ON NATURAL RUBBER VULCANIZATES UNDER TENSION

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Abstract—The effect of γ-radiation on natural rubber vulcanizates under mechanical strain has been investigated with reference to the effect of antidegradants, fillers and vulanization system. Samples were irradiated in the dose range of 5–15 Mrad in air at room temperature (25°C) at a rate of 0.3 Mrad/h. Sol content and volume fraction of vulcanizates were also determined to gain insight into the network structure of the irradiated vulcanizates. Natural rubber vulcanizates undergo molecular scission which in effect cause a decrease in tensile strength. Generally the 300% modulus increases, the increment being more prominent at lower radiation dose. The fall in tensile strength is also high at higher doses of radiation. Carbon black and antidegradants protect rubber from γ-radiation.

INTRODUCTION

Application of rubber components in radiation therapy, nuclear plants, medical equipments etc. has been increasing and many of these components are used under mechanical strain. Although much work has been done on the effect of radiation on rubber[1–4] the influence of γ-radiation on rubber vulcanizates under mechanical strain has not been well studied. Neither has much work been done on the effect of fillers and additives like antidegradants, under the above conditions. Therefore an attempt has been made to study the influence of γ-radiation on NR vulcanizates under different levels of tensile strain.

EXPERIMENTAL

The composition of the mixes are given in Table 1 and their physical properties in Table 2. The mixes were prepared in a laboratory model two roll mixing mill and were vulcanized into thin sheets using a hydraulic press having steam heated platens maintained at a temperature of 150°C. Modulus, tensile strength and elongation of these vulcanizates were determined as per ASTM D 412-75 method A. Tear resistance of these vulcanizates was determined as per ASTM D 623-73.

Tensile dumbbells prepared from the vulcanizates were kept under tensile strain in a specially designed stretching device as shown in Fig. 7. The specimens were then exposed to γ-radiation in air in a γ-chamber (model N 900 supplied by the Bhabha Atomic Research Centre, Bombay) having a Co^{60} source. Irradiation doses of 5, 10 and 15 Mrad were given to the vulcanizates. The rate of irradiation was 0.3 Mrad/h. To give a radiation dose of 5 Mrad the samples were exposed for a period of 16 h. Correspondingly longer periods were given for higher doses. Samples were exposed under different levels of tensile strain ranging from 0 to 240%. After the required dose of irradiation the specimens were removed from the

Table 1. Composition of the mixes

	1	2	3	4	5	6	7	8
Natural rubber[a]	100	100	100	100	100	100	100	100
Zinc oxide	—	5	5	5	5	5	5	5
Stearic acid	—	2	2	2	2	2	2	2
HAF black	—	—	—	50	50	50	—	—
China clay	—	—	—	—	—	—	70	—
Graphite	—	—	—	—	—	—	—	50
Process oil	—	—	—	5	5	5	5	5
PBNA[b]	—	—	1	—	1	—	—	—
4010[c]	—	—	—	—	—	5	—	—
CBS[d]	—	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	—	2.5	2.5	2.5	2.5	2.5	2.5	2.5
DCP[e]	5	—	—	—	—	—	—	—

[a]Grade ISNR-5. [b]Phenyl-β-naphthylamine, commercial grade. [c]N-cyclohexyl N′-phenyl-p-phenylenediamine (Antioxidant 4010, Bayer (India) Ltd. [d]N-cyclohexyl benzothiazyl sulphenamide (Vulcacit CZ) Bayer (India) Ltd. [e]Dicumyl peroxide, 40% active, commerical grade.

Table 2. Properties of the mixes

Mix no.	1	2	3	4	5	6	7	8
Optimum cure time at 150°C, min	55.0	13.5	12.8	11.0	10.5	9.0	19.0	13.5
Cure rate index	1.9	14.8	15.4	12.9	12.9	16.1	8.3	14.8
300% Modulus (MPa)	2.3	1.6	1.6	11.8	10.8	12.0	4.0	4.1
Tensile strength (MPa)	10.6	23.8	24.0	25.3	26.0	22.0	14.4	18.9
Elongation at break (%)	705	1041	1045	555	589	503	693	711

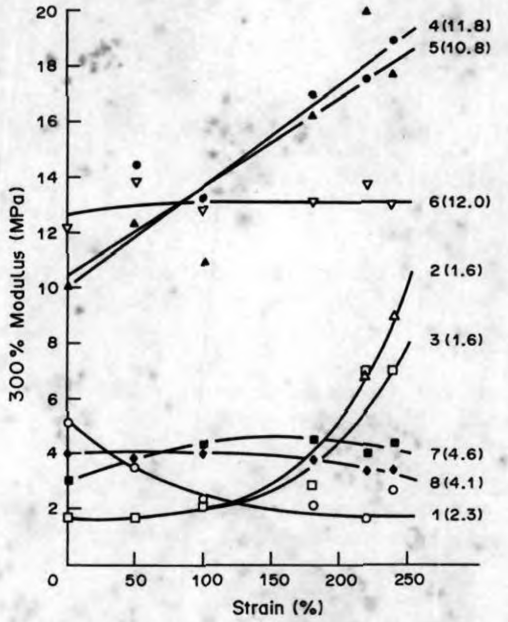

Fig. 1. Changes in tensile modulus of vulcanizates with respect to strain—radiation dose 5 Mrad. The figures in the parentheses indicate the original value of tensile modulus of vulcanizates.

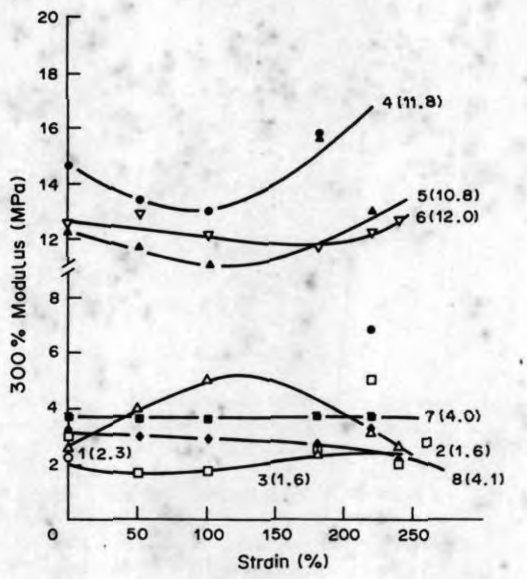

Fig. 3. Changes in tensile modulus of vulcanizates with respect to strain—radiation dose 15 Mrad. The figures in the parentheses indicate the original value of tensile modulus of vulcanizates.

stretching device and conditioned for 24 h, in the laboratory atmosphere and then tensile strength measured using a Zwick 1474 Universal Testing Machine.

Volume fraction of rubber in the benzene swollen vulcanizates, V_r, which is a measure of the crosslink density of the sample, was calculated from equilibrium swelling data using the method reported by Ellis and Welding.[(5)] Sol content was estimated by the method described by Bristow[6] according to which samples were extracted with cold acetone in the dark for 8–10 days, the acetone being replenished four times during the period. The samples were then dried to constant weight *in vacuo* at room temperature and from this, weighed portions were extracted with cold benzene in the dark for 8–10 days, the benzene being replenished four times during this period. After benzene extraction the samples were dried to constant weight *in vacuo*. The sol content was then calculated from the weight loss during benzene extraction.

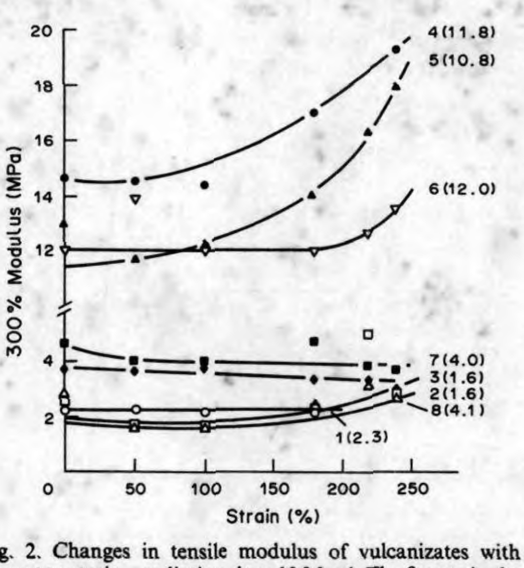

Fig. 2. Changes in tensile modulus of vulcanizates with respect to strain—radiation dose 10 Mrad. The figures in the parentheses indicate the original value of tensile modulus of vulcanizates.

RESULTS AND DISCUSSION

The properties of the mixes are given in Table 2. As expected the peroxide vulcanizates are poor in

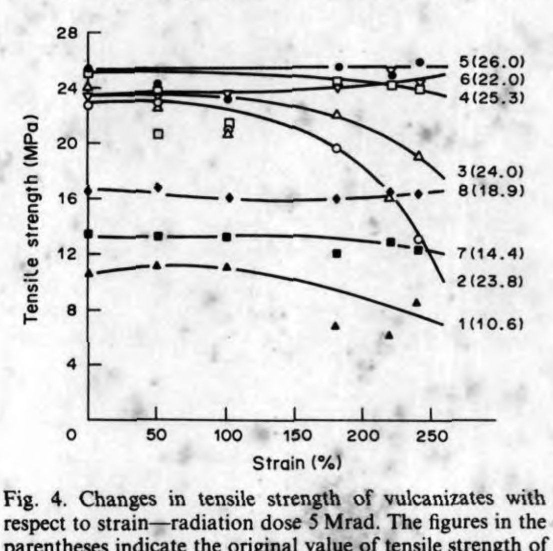

Fig. 4. Changes in tensile strength of vulcanizates with respect to strain—radiation dose 5 Mrad. The figures in the parentheses indicate the original value of tensile strength of vulcanizates.

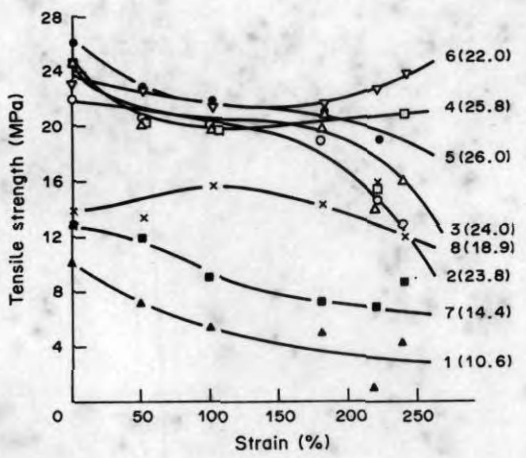

Fig. 5. Changes in tensile strength of vulcanizates with respect to strain—radiation dose 10 Mrad. The figures in the parentheses indicate the original value of tensile strength of vulcanizates.

stength compared to the sulphur cured ones. Addition of carbon black does not improve tensile stength, but there is an appreciable enhancement in modulus. But both china clay and graphite enhances modulus slightly, but reduces tensile strength. China clay is also found to influence the cure rate.

The effect of irradiation under tension on the tensile modulus of the vulcanizates is shown in Figs 1–3. In the case of the peroxide vulcanizate, the original modulus is 2.3 MPa, which increases to 5 after irradiation of 5 Mrad under zero strain and drops progressively as the strain in the specimen is raised. However, beyond 100% tensile strain the effect is rather slow possibly because the maximum damage has already taken place. When the radiation dose is raised to 10 Mrad modulus is found to remain rather constant irrespective of the tensile strain during irradiation. When the irradiation dose has

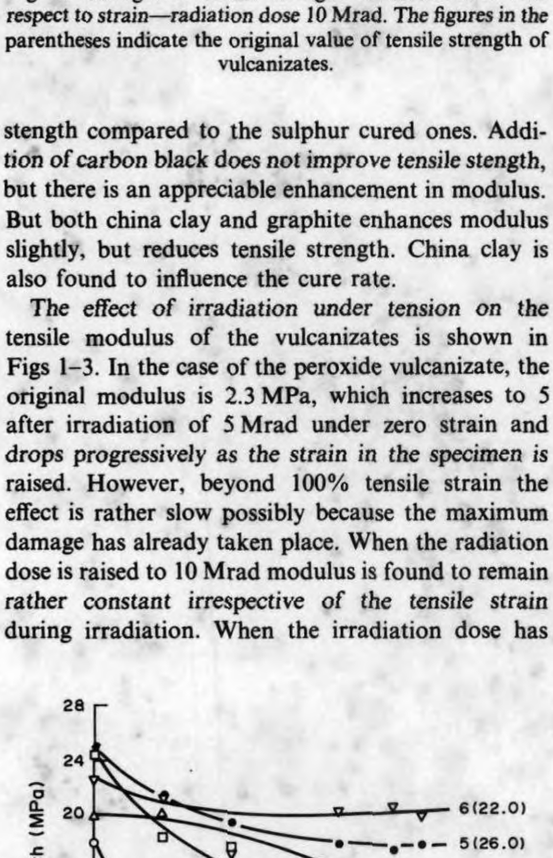

Fig. 6. Changes in tensile strength of vulcanizates with respect to strain—radiation dose 15 Mrad. The figures in the parentheses indicate the original value of tensile strength of vulcanizates.

been raised to 15 Mrad, the sample undergoes extensive degradation and the 300% modulus could not be measured.

In the case of the unfilled sulphur cured samples 300% modulus is found to remain constant up to a tensile strain of 100% beyond which it is found to increase rather abruptly when the irradiation dose has been limited to 5 Mrad. When the dose has been raised to 10 Mrad, the increase in modulus beyond 100% strain has been found to be only marginal as seen from Fig. 2. At 15 Mrad irradiation level the effects are much different especially in the case of Mix 2 which does not contain antioxidant. The maximum increase in modulus is observed when the tensile strain was around 150%.

Presence of carbon black in the sulphur cured samples is found to improve the radiation resistance. In the case of samples 4 and 5 at an irradiation dose of 5 Mrad modulus is found to increase almost linearly with increase in the strain level. The difference between the two samples is only marginal indicating that 1 phr of phenyl-β-naphthylamine (PBNA) does not influence the radiation resistance of black filled NR compounds. However, mix 6 which contain 5 phr N-cyclohexyl N'-phenyl p-phenylenediamine shows practically no change in modulus at 5 Mrad level. Even at 10 and 15 Mrad of irradiation dose changes in modulus are observed only when the strain in the specimens was above 180%. Influence of strain on radiation resistance is not significant in the case of china clay and graphite filled vulcanizates. In both cases modulus is found to remain rather constant irrespective of the strain in the sample.

Reduction in tensile stength is a better measure of irradiation damage in rubber vulcanizates. The effect of irradiation under different levels of tensile strain on the tensile strength of the vulcanizates at radiation doses of 5, 10 and 15 Mrad are shown in Figs 4–6 respectively. At 5 Mrad level, the tensile strength of peroxide cured vulcanizates is found unaffected up to 100% strain, beyond which it is found to drop. At 10 Mrad level and zero strain there is practically no drop in tensile strength. However, when the sample was under tensile strain, irradiation causes a significant drop in tensile strength and the drop increases with the increase in the strain. At 15 Mrad dose there is a drastic drop in tensile strength even when the sample was irradiated under zero strain. There is no significant further drop in tensile strength as the strain in the specimen was raised.

At 5 Mrad dose rate, the unfilled sulphur cured vulcanizates do not show any significant reduction in tensile strength up to about 50% strain. But beyond 50% the samples undergo degradation rapidly. However, the rate of degradation is less in the samples containing 1 phr of PBNA. The observations are the same at 10 Mrad dose. However, at 15 Mrad even at zero strain sample No. 3 containing no antioxidant shows a significant reduction in tensile strength,

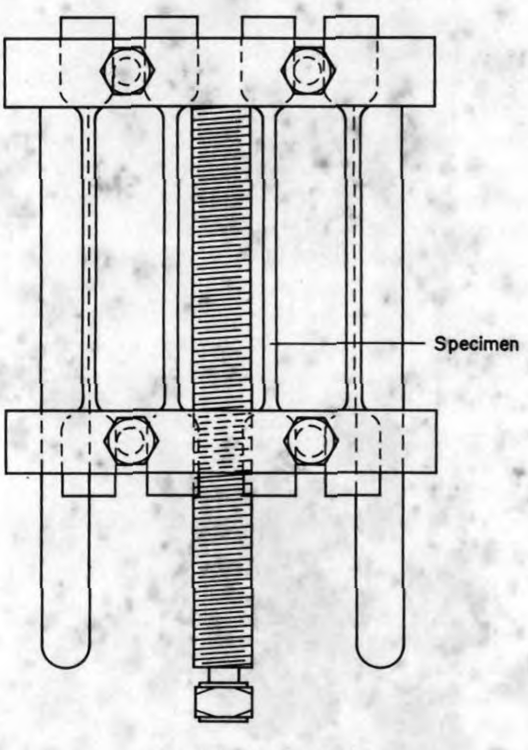

Fig. 7. Stretching device.

whereas sample No. 4 which contains 1 phr of PBNA does not show any reduction in tensile stength. But in both cases, when the irradiation was done under strain there is a fairly rapid degradation upto about 100% strain. Even under these conditions, it is found that antioxidant PBNA protects the rubber from radiation degradation although on a limited scale.

As observed earlier carbon black is found to protect rubber from radiation degradation but only at lower levels of radiation dose. At 5 Mrad there is no appreciable reduction in tensile strength even when samples were under 180% elongation. However, when the strain was larger, tensile strength was found to decrease. But the presence of 1 phr of PBNA is again found beneficial under these conditions as seen from Fig. 4. At 10 Mrad dose, when the specimens were irradiated under strain a limited extent of degradation is observed even in the samples containing PBNA. At 15 Mrad dose, when the specimens were under zero strain, no significant reduction in tensile strength was observed. However, when the irradiation was carried out under strain there is a fairly rapid degradation in the case of Mix 4 containing no antioxidant. But in the case of Mix 5 which contains 1 phr of PBNA the rate of degradation with respect to the degree of strain is less and at all levels of strain studied. Mix 5 was found to be significantly better than Mix 4 indicating again that antioxidant is effective in protecting rubber from irradiation damage. Mix 6 which contains 5 phr of *N* cyclohexyl-*N'* phenyl-*p*-phenylenediamine (Antioxidant 4010), is found to be resisting radiation at all levels of irradiation dose and at all levels of strain studied. In fact at 5 and 10 Mrad doses tensile strength is found to increase slightly when the sample was irradiated under tensile strain.

During irradiation of a rubber vulcanizate two types of reactions occur, crosslinking and chain scission. While the former causes an increase in modulus, the latter tends to reduce it. The data given in Table 3 show that generally crosslink density is not much affected by irradiation under strain except in peroxide vulcanizates at higher doses and at higher strains. The results also indicate that peroxide vulcanizates are more susceptible to radiation degradation than sulphur vulcanizates. The results of sol content determinations, as given in Tables 4–6, also indicate that chain scission under irradiation is also more predominant in the peroxide vulcanizates. It is also seen that as the strain in the sample is increased the degree of chain scission is increased. The sol content of sulphur cured vulcanizates, both unfilled and filled, increases as the strain in the sample is increased. It is also seen that antioxidant PBNA helps in preventing chain scission only slightly. However, the effect of

Table 3. Changes in volume fraction of rubber

Mix. no.	Dose rate (Mrad)	Strain (%) 50	100	180	220	240
1	5	0.21	0.21	0.21	0.21	0.20
2	5	0.22	0.22	0.22	0.23	0.22
3	5	0.22	0.23	0.23	0.23	0.22
1	10	0.21	0.21	0.21	0.21	0.20
2	10	0.22	0.22	0.22	0.22	0.22
3	10	0.22	0.24	0.22	0.24	0.25
1	15	0.21	0.20	0.21	0.17	0.18
2	15	0.22	0.23	0.23	0.23	0.22
3	15	0.22	0.22	0.23	0.24	0.25

Table 4. Changes in sol content of vulcanizates at radiation dose 5 Mrad

Mix no.	Strain (%) 50	100	180	220	240
1	1.0	1.5	1.8	4.1	3.0
2	0.4	0.6	1.0	1.5	1.8
3	0.5	0.5	0.7	1.0	1.8
4	1.1	1.7	2.0	2.5	1.8
5	1.9	2.0	2.3	2.5	1.8
6	0.23	0.27	0.29	0.22	0.27
7	0.66	0.76	0.90	1.53	1.54
8	0.71	0.63	0.92	0.52	0.58

Table 5. Changes in sol content of vulcanizates at radiation dose 10 Mrad

Mix no.	Strain (%) 50	100	180	220	240
1	1.0	1.5	1.8	4.5	3.7
2	0.5	0.5	0.6	1.9	1.7
3	0.5	0.5	0.5	1.9	1.8
4	1.6	1.7	2.0	2.7	1.8
5	2.0	2.0	3.0	2.5	1.8
6	0.3	0.27	0.35	0.31	0.39
7	1.10	0.96	0.95	2.64	2.00
8	0.98	0.76	1.11	0.86	1.17

Table 6. Change in sol content of vulcanizates at radiation dose 15 Mrad

Mix no.	Strain (%) 50	100	180	220	240
1	5.1	5.0	5.0	7.0	7.0
2	1.5	1.9	2.0	2.5	2.0
3	0.5	0.5	0.6	2.0	1.8
4	1.7	1.9	2.9	2.7	2.5
5	1.9	2.0	3.0	3.7	2.3
6	0.45	0.46	0.46	0.45	0.77
7	1.23	1.99	1.02	3.17	2.78
8	1.35	2.79	2.18	1.43	2.08

5 phr of anti-oxidant 4010 in preventing chain scission is very significant. It is also worth noting that china clay and graphite filled vulcanizates show fairly lower values for sol content at 5 Mrad indicating that both these fillers are contributing less towards chain scission than carbon black.

CONCLUSIONS

The following conclusions have been drawn.

(1) Exposure to radiation under tension causes decrease in tensile strength of NR vulcanizates.

(2) As the strain in the sample increases, the degradation is more rapid.

(3) The decrease in tensile strength is mainly due to molecular chain scission.

(4) Antioxidants and fillers like carbon black protect NR vulcanizates from radiation damage. Antioxidant 4010 at 5 phr is found to be a very effective protective system.

(5) For exposure to radiation, sulphur vulcanizing system is better than the peroxide system.

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