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EFFECT OF  $^{60}\text{Co}$  GAMMA DOSES ON THE ELECTRICAL PROPERTIES OF 40 phr LAMP CARBON BLACK-LOADED UNVULCANIZED STYRENE-BUTADIENE RUBBER FOR THE APPLICATION IN RADIATION DOSIMETRY

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ABSTRACT

The effects of  $^{60}\text{Co}$  gamma radiation (in the range from 0.07 - 90 kGy), on the electrical conductivity,  $\sigma$ , and the relative dielectric constant,  $\epsilon'$ , of 40 phr LAMP carbon black-loaded unvulcanized styrene-butadiene rubber (SBR-1502), have been studied. The effect of shelf and thermal-oxidation ageing on both  $\sigma$  and  $\epsilon'$  for irradiated and unirradiated samples have also been investigated.

The results showed a characteristic increase in  $\sigma$  which reaches maximum value at about  $10^4$  Gy and then it decays to a minimum value at  $3 \times 10^4$  Gy while the dielectric constant,  $\epsilon'$ , exhibits a peak at a dose of about  $3 \times 10^4$  Gy.

No measurable fading effects have been noticed in the induced radiation changes over a period of 6 days at room temperature.

Calibration of the gamma irradiation dose as assessed from either the conductivity,  $\sigma$ , or the dielectric constant,  $\epsilon'$ , has led to two proposed empirical formulae.

INTRODUCTION

The effect of radiation on rubber materials is of particular interest from both the technological as well as the theoretical points of view (1-3). This effect may lead to two main changes, namely chemical and physical. Their degrees depend mainly on the total quantity of irradiation energy received by the material regardless of whether it is conveyed by incident photons or particles (4). The two main processes which are taking place as a result of irradiation of polymeric materials are cross-linking and/or degradation. One of the most important chemical and physical changes of rubbers upon irradiation is the vulcanization process.

In the present work the effect of  $^{60}\text{Co}$ -gamma radiation on the electrical conductivity,  $\sigma$ , and dielectric constant,  $\epsilon'$ , of 40 phr (part per hundred parts of rubber by weight) LAMP carbon

black-loaded unvulcanized styrene-butadiene rubber blend has been studied. In addition, the effect of storage (either shelf or thermal-oxidation ageing) on both  $\sigma$  and  $\epsilon'$  has also been investigated. This work is a continuation of a previously studied and reported one (5)

EXPERIMENTAL

The rubber used in this work is styrene-butadiene rubber (SBR-1502), non-staining, with (2,6-di-tert-butyle-4-methylphenol)-(Inol) as stabilizer. The ingredients added to one hundred gramme of rubber were: stearic acid (2g); LAMP black (40g); processing oil (10g); Dibenzthiazyle disulphide (MBTS) (2g); phenyl- $\beta$ -naphthylamine (PBN) (1g); zinc oxide (5g) and sulphur (2g). The mixture was prepared using a two-roll mill 170 mm diameter, working distance 300 mm, speed of slow roll 24 rev./min and gear ratio 1.4. The measurements of  $\sigma$  and  $\epsilon'$  and the irradiation procedure have been previously reported (5). The dose of irradiation has been calibrated, using a standard ionization chamber, and found to be 74.45 Gy/hr at the sample location. The thermal-oxidation ageing was done by using an automatically regulated electrical oven which was kept at 70 °C. The shelf ageing and all measurements were carried out at 35 °C.

RESULTS AND DISCUSSION

Effect of irradiation on  $\sigma$  and  $\epsilon'$ :

Figure (1) shows the variation in the electrical conductivity,  $\sigma$ , of 40 phr LAMP/SBR unvulcanized rubber sample with gamma ray dose, D. The marked increase in  $\sigma$  (about 120%) upon irradiation (up to 5 kGy) could be attributed to the increase in the degree of crystallinity. This is a result of the sub-vulcanization process which may have happened upon irradiation (6). Further increase in the dose results in a gradual decrease in  $\sigma$

with a minimum value at about 30 kGy. This may be due to two processes which are initiated upon irradiation of polymeric materials namely cross-linking and degradation. The significant portion of the above relation and which can be practically utilized in radiation dosimetry is that increase in the dose range (0.07 - 5 kGy). This part is conveniently expressed by the empirical formula:

$$D = 2.78 \exp(4 \times 10^9 \sigma) \quad 1$$

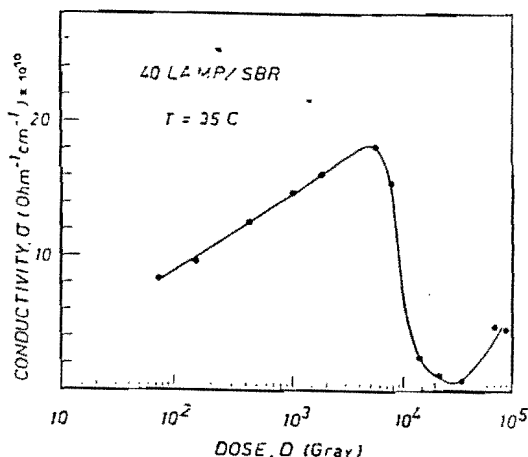


Fig. (1) Variation of the electrical conductivity,  $\sigma$ , of 40 phr LAMP/SBR unvulcanized rubber sample with gamma dose,  $D$ , at 35 °C.

The increase in  $\sigma$  is accompanied by an increase in  $\epsilon'$  (about 55%), Fig. (2), (within the above mentioned). The first part of the curve can also be used to measure the radiation dose,  $D$ , since it obeys the following empirical formula:

$$D = 0.028 \exp(0.163 \epsilon') \quad 2$$

(0.07 <  $D$  < 5 kGy)

#### Effect of Storage:

For the present investigation a comparative study has been made on the effects of ageing (shelf or thermal-oxidation) of  $\sigma$  and  $\epsilon'$  for both unirradiated and irradiated unvulcanized-rubber samples. Ageing is believed to be significant on vulcanized rubber blends (7). Therefore, the effects of ageing time and temperature on the electrical conductivity and dielectric constant for unvulcanized 40 phr LAMP/SBR composites after irradiation were studied

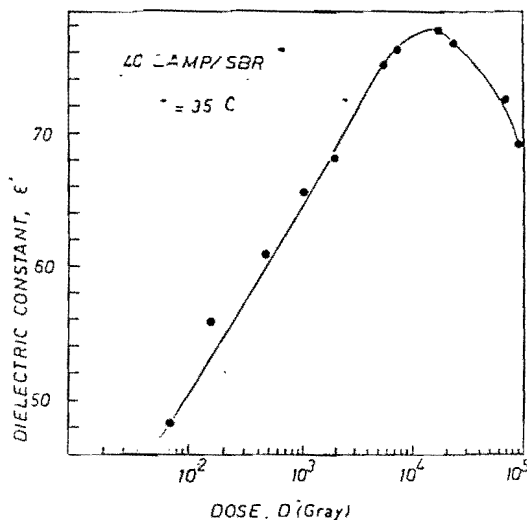


Fig. (2) Variation of dielectric constant,  $\epsilon'$ , of 40 phr LAMP/SBR unvulcanized sample with radiation dose,  $D$ , at 35 °C.

by using six samples such that:

- A shelf-aged sample without irradiation,
- An irradiated sample with 38 kGy then left for shelf-ageing,
- A thermally-aged sample at 70 °C without irradiation,
- An irradiated sample with 38 kGy then thermally aged,
- A shelf-aged sample for 140 hrs, irradiated with 38 kGy and then it was left for ageing, and
- A thermally-aged sample at 70 °C for 140 hrs, irradiated with 38 kGy then it was thermally aged at 70 °C.

Figure (3) illustrates the variation in  $\sigma$  as a function of ageing time ( $t$  in hours) for the above samples. It is noticed that  $\sigma$ , in general, increases with ageing time. This increase may be attributed essentially to the re-arrangement of carbon black particles through the rubber matrix after being displayed by the rays. Moreover, irradiating rubber sulphur mixtures makes sulphur react chemically, even at room temperature, forming cross-links with the rubber chains which leads to the increase in  $\sigma$  (8).

It can be presumed that the effect of the storage time and temperature on the rubber samples, is that a continuous thermal degradation of the macromolecules would lead to a decrease of  $\sigma$ . The orientation of the carbon black aggregates, due to thermal energy, agitation makes

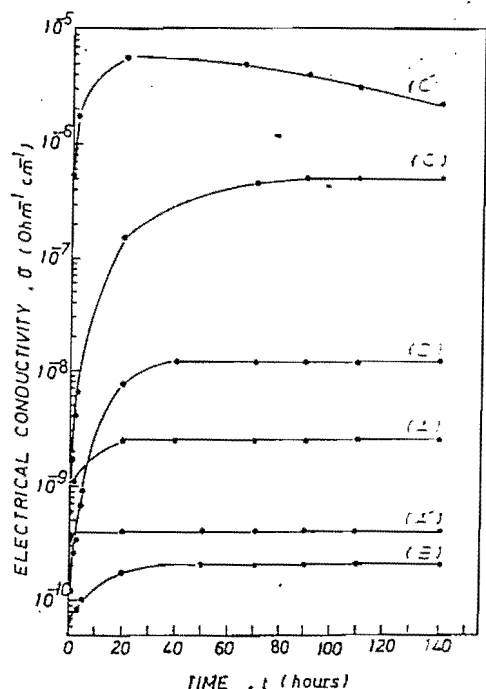


Fig. (3) Variation of  $\sigma$  with storage time,  $t$  (hours) for samples a, b, c, d, e and f at 35 °C.

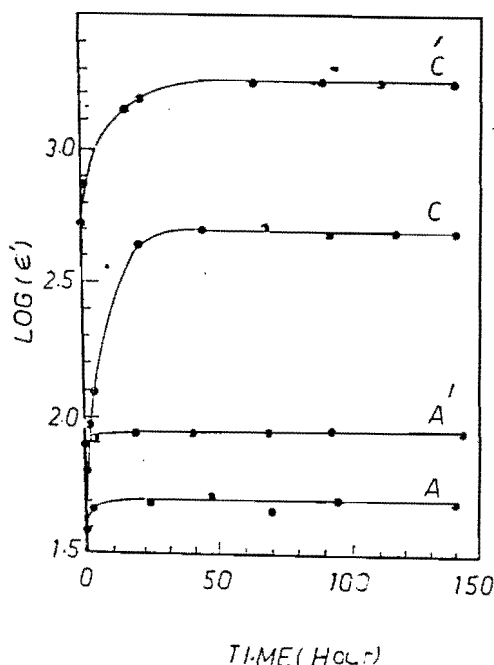


Fig. (4) Variation of  $\epsilon'$  with storage time,  $t$  (hours) for samples a, c, e and f at 35 °C.

paths of charge carriers, leading to an increase in  $\sigma$ . The later process predominates at the first storage hours together with an increasing probability of the scission mechanism. After a period of storage, equilibrium between the two processes is reached. The value of  $\sigma$  at this equilibrium state would depend on the storage temperature.

On the other hand, the effect of radiation on the samples is the creation of energetic electrons and ions which migrate through the rubber matrix causing some break age of chemical bonds and forming deficient regions. These bond scissions may cause the remarkable decrease in  $\sigma$  of the irradiated sample.

Storage of the samples at relatively elevated temperature (70 °C) results in a competition between the recombination of the radiation forming free radical mechanism, which leads to the decrease in  $\sigma$ , and the reorientation of the carbon black aggregates, due to thermal aggitation which leads to an increase in  $\sigma$ .

Figure (4) shows the variation of  $\epsilon'$  as a function of the storage time,  $t$ , for samples a, c, e and f. It is clear that,  $\epsilon'$ , for shelf and thermally aged

samples, increased upon irradiation. Moreover,  $\epsilon'$  for irradiated samples increases to a certain level when shelf or thermally stored. The increase in  $\epsilon'$  may be due to the formation of new polar groups as a result of irradiation of gamma rays. It can be presumed that irradiation leads to the replacement of hydrogen atoms in the molecules of the rubber composites with electronegative atoms such as oxygen or nitrogen. A progressive increase of  $\epsilon'$  will be followed. Furthermore, when the samples are stored at an elevated temperature (70 °C) the energy of thermal aggitation at some points of the sample becomes comparable with that energy sufficient for the rupture of some bonds.

Moreover, the presence of hydrogen atoms in the rubber molecules greatly decreases the energy of the C-C bond. Hence, high molecular hydrocarbons and some of their derivatives possess comparatively low stability and are easily degraded by heating (9). This may lead to the formation of more polar groups up to a stable state.

## CONCLUSION

It may be concluded that,  $\sigma$  and  $\epsilon'$  of 40 phr LAMP/SBR unvulcanized sample were changed upon irradiation. The radiation induced changes in both  $\sigma$  and  $\epsilon'$  depending on the irradiation dose. The remarkable increase in both  $\sigma$  and  $\epsilon'$  with radiation dose up to 5 kGy can be used as a direct, nontoxic, easy, inexpensive and sensitive method to evaluate the irradiation dose.

Utilizing the radiation induced changes in  $\sigma$  and  $\epsilon'$  for unvulcanized 40 phr LAMP/SBR rubber blend as gamma ray dosimeter, is practical since measuring  $\sigma$  or  $\epsilon'$  at room temperature, with simple equipments, is only needed to evaluate the dose D. The application of the empirical formulae 1 and 2 for the measured values of  $\sigma$  or  $\epsilon'$  can be used to calibrate the measurements in terms of the dose.

Storage of either unirradiated or irradiated rubber samples, even at room temperature, caused remarkable changes in both  $\sigma$  or  $\epsilon'$ .

No measurable fading has been noticed in the induced radiation changes when the specimens were stored at room temperature for about 6 days.

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2

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