EFFECT OF GAMMA RADIATION ON THE ELECTRICAL PROPERTIES OF CARBON BLACK-LOADED UNVULCANIZED STYRENE–BUTADIENE RUBBER FOR APPLICATION TO RADIATION DOSIMETRY

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الخلاصة :

تم دراسة تأثير الجرعات المختلفة من أشعة جاما ^{60}Co على الخواص الكهربية (المقاومة النوعية ، ثابت العزل والفقد العزلي) لبعض مخاليط مطاط الالستيرين بيوتاديين (1502 SBR) المحمل بأنواع مختلفة من أسود الكربون (HAF, FEF, SRF & GPF) .

أوضحت النتائج زيادة ملحوظة في قيم المقاومة النوعية وثابت العزل وكذا الفقد العزلي عند تعرض العينات لجرعات في المدى 37–10^4 Gray . وبإستخدام علاقة رياضية وضعية أمكن بسهولة تحديد قيمة الجرعة عن طريقة قياس المقاومة النوعية للمطاط سالف الذكر.

ABSTRACT

The effect of different doses of ^{60}Co-gamma rays on the electrical properties (resistivity (ρ) and dielectric constant (ϵ') and loss (ϵ'')) of different types of carbon black (HAF, FEF, GPE, SRF and EPC)–loaded unvulcanized styrene–butadiene rubber has been studied. The results showed that remarkable changes in the electrical properties of some rubber blends have been induced due to irradiation with gamma doses in the range 0.037–90 kGy. Two empirical formulae have been given to calculate for the absorbed gamma dose from measurements of the induced changes in the electrical properties of the rubber blends.

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INTRODUCTION

There is increasing interest in radiation research and measurement technology involving high-intensity sources of ionizing radiation, such as massive ^{60}Co-gamma ray sources. Moreover, special attention has been given to the uses of gamma radiation in the range 10–10^3 Gray for insect control, seed and vegetable sprouting inhibition, vegetable and fruit shelf life extension, radiotherapy, etc. Therefore, there is a need for a dosimeter that can measure simply, directly, and reproducibly doses in this range.

In the present work, the effect of different doses of ^{60}Co-gamma rays on the electrical properties (electrical resistivity (ρ), dielectric constant (ϵ') and loss (ϵ'')) of different types of carbon black-loaded unvulcanized styrene–butadiene rubber have been studied.

METHOD

The rubber used in this work is styrene–butadiene rubber (SBR-1502), non-staining, with (2,6-di-*tert*-butyl-4-methylphenol) – (Inol) as stabilizer. Different types of carbon black were used, namely: High Abrasion Furnace black (HAF), Fast Extrusion Furnace black (FEF), General Purpose Furnace black (GPF), Semi-Reinforcing Furnace black (SRF), and Easy Processing Channel black (EPC). The critical concentration from each type of carbon black [1] was introduced in SBR according to the formulations illustrated in Table 1. This critical concentration was chosen, owing to the great sensitivity of the electrical resistivity of the rubber blend to energy transfer [2].

The preparation of the rubber blends [3] and the measuring techniques for electrical resistivity [4] have been previously described. The rubber samples were shaped at 35°C into the form of squares 2.3×2.3 cm and about 0.4 cm thick under pressure of 40 kg cm^{-2}. Good contact was attained by covering both sides of the sample with air-drying silver paste type FSPI manufactured by Johnson and Matthey, UK. The dielectric constant and dielectric loss where measured using a Tesla precision capacitance bridge type BM 400G, working at a fixed frequency of 800 Hz. The dielectric loss was calculated from the relation, $\epsilon'' = \epsilon' \tan \delta$.

A 7.4 TBq–^{60}Co gamma source manufactured by Atomic Energy of Canada Ltd., presented at the National Institute of Standards, Dokki, Egypt, was used for irradiation of the samples. At the irradiation positions, the dose rate had been calibrated using a standard ionization chamber and found to be 74.45 Gy h^{-1}. All measurements were carried out at 35°C.

Table 1. Composition of SBR Samples Containing Different Types and Concentrations of Carbon Black

Ingredient, phr*	40 EPC	50 HAF	60 FEF	70 SRF	80 GPF
SBR (1502)	100	100	100	100	100
Stearic acid	2	2	2	2	2
Carbon black	40	50	60	70	80
Processing oil	10	10	10	10	10
MBTS**	2	2	2	2	2
PBN‡	1	1	1	1	1
Zinc oxide	5	5	5	5	5
Sulfur	2	2	2	2	2

*Parts per hundred parts of rubber by weight.
**Dibenthiazyl disulfide.
‡Phenyl-β-naphthylamine.

RESULTS AND DISCUSSION

Bulk d.c. Electric Resistivity

Figure 1 shows the relation between the bulk d.c. electrical resistivity (ρ) measured at 35°C and the irradiation dose (D in Gray) for three types of carbon black (60 FEF, 70 SRF, and 80 GPF) loaded unvulcanized SBR samples. It is clear from the figure that anomalous behavior appeared through the slight increase in ρ followed by a sharp decrease to a minimum value at 65kGy for 60 FEF/SBR and 80 GPF/SBR, and at 25 kGy for SRF/SBR. The variation of ρ as a function of D in the dose range 2 kGy–60 kGy was found to be conveniently expressed by the

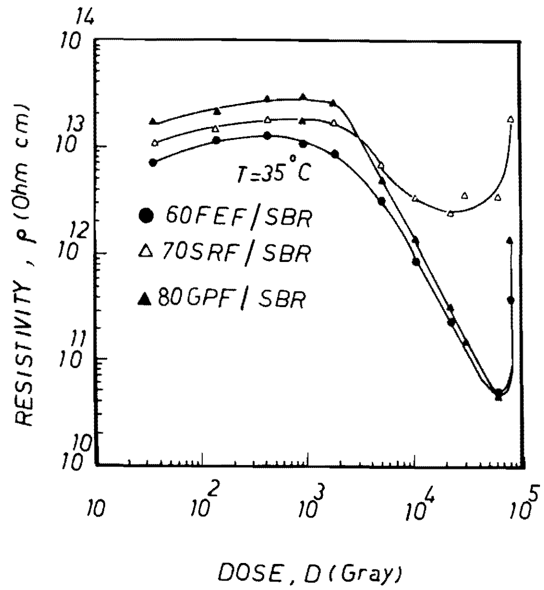

Figure 1. Bulk Resistivity as a Function of Irradiation Dose for ●, 80 GPE/SBR; ○, 60 FEF/SBR and △, 70 SRF/SBR at 35°C

empirical formula:

$$D = A\rho^{-B} \tag{1}$$

where A and B are fitting parameters whose values are given in Table 2 for the compositions used.

Table 2. The Values of the Fitting Parameters A and B

Sample	A	B
60 FEF/SBR	9.1×10^{10}	0.58
70 SRF/SBR	3.5×10^{15}	0.92
80 GPF/SBR	1.8×10^{10}	0.51

It may be presumed that the action of gamma rays on rubber results in excitation of its molecules and creation of free, energetic electrons and ions. These active species will migrate in the rubber network, causing further collisions with the surrounding molecules along their paths. The energy transferred to these molecules through collision reactions may cause an increase in the temperature along the electron track, which will lead to a decrease in the electrical resistivity (ρ). Moreover, electronic and ionic collisions with rubber molecules may cause chemical bond rupture, which will lead to creation of free radicals that may recombine again at random with other molecules. These new molecular configurations may cause the increase in ρ at higher doses. Moreover, this increase in ρ at doses higher than 60 kGy may be attributed to the important role of both sulfur and carbon black. Sulfur reacts chemically (by increasing the radiation dose) with rubber and may be attached to the polymer chains as polysulfide links [5, 6]. This occurs by opening the double bond of the rubber chain and the initiated sulfur is introduced between two chains to form a link or polysulfide link. Moreover, the formed crosslinks compact the carbon black particles between the rubber chains. Furthermore, the broadening in the minimum value of 70 SRF/SBR sample may be attributed to the smaller surface area (large particle size) of SRF black particles ($\simeq$70 nm), i.e., gamma ray can easily break adhesive forces between the particles of SRF type which are weaker in comparison with the other two types.

Figure 2 shows the dependence of ρ on D for 40 EPC/SBR and 50 HAF/SBR samples. It is clear that, approximately no change occurs in the value of ρ for 40

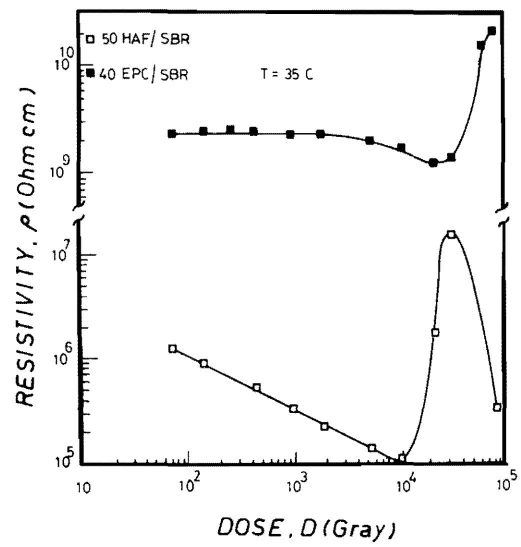

Figure 2. Bulk Resistivity as a Function of Irradiation Dose for: □, 50 HAF/SBR and ■, 40 EPC/SBR at 35°C

EPC/SBR sample upon irradiation for doses up to 12 kGy. This may be due to the type of carbon black which has high tendency to form stable structures [6]. Further irradiation causes degradation processes in the host material followed by breakdown in the carbon black aggregates which may lead to the increase of ρ.

The linear portion in the curve in Figure 2 for 50 HAF/SBR sample was found to fit formula (1) with $A = 4 \times 10^{13}$ and $B = 1.93$. It may be presumed that, the action of gamma rays on unvulcanized rubber composites results in scissions in rubber chains, breakdown in the carbon black aggregate structure, formation of conjugated structure and bonds, and the presence of several functional groups on the surface of carbon black, such as hydroxyl, carbonate, and stable free radical groupings [7, 8], which may act as centers of linkages between carbon black and rubbers, leading to a decrease in the carbon–carbon interspacing distances. However, the radiation effects phenomena on unvulcanized rubber are very complicated since the share of each radiation-induced process varied with the irradiation dose, type, and concentration of carbon black.

Dielectric Constant (ϵ') and Dielectric Loss (ϵ'')

Figure 3 shows the variation of ϵ' for different types of carbon black-loaded SBR unvulcanized composites as a function of irradiation dose. It is clear that, the behavior of the three samples, namely 60 FEF/SBR, 70 SRF/SBR and 80 GPF/SBR is approximately the same. This may be attributed to the role of carbon black in the three types of rubber which is of the same origin (Furnace black) and has nearly similar physical properties (large particle size and low tendency to form aggregations). On the other hand, the sample which contains channel black (40 EPC/SBR) showed gradual increase in ϵ' upon irradiation in the dose range 0.037–11 kGy. This variation was found to be conveniently expressed by the formula:

$$D = a \exp(b\epsilon') \tag{2}$$

where $a = 1.77 \times 10^{-20}$ and $b = 2.06$.

The increase in ϵ' values may be due to the formation of dipole groups or segments which are formed through breakage of chemical bonds during irradiation. Moreover, the sulfur atoms in the unvulcanized composites may combine at random as heterocyclic groups along the main chain [9, 10]. These groups have relatively high moments per one atom of combined sulfur which increases the value of ϵ'.

The dielectric loss (ϵ'') for the samples 60 FEF/SBR, 70 SRF/SBR, and 80 GPF/SBR has been measured before and after successive exposures to ^{60}Co gamma doses in the range 0.037–90 kGy. Figure 4 illustrates the variation of ϵ'' as a function of D for the above samples. The results for ϵ'' confirm the measured resistivity data for these samples.

The ϵ'' data for the two samples 50 HAF/SBR and 40 EPC/SBR were out of range of our measuring equipment.

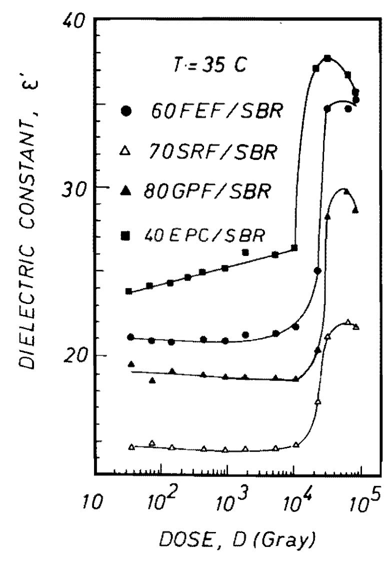

Figure 3. Variation of Dielectric Constant as a Function of Irradiation Dose for: ■, 40 EPC/SBR; ●, 60 FEF/SBR; ▲, 80 GPF/SBR and △, 70 SRF/SBR at 35°C

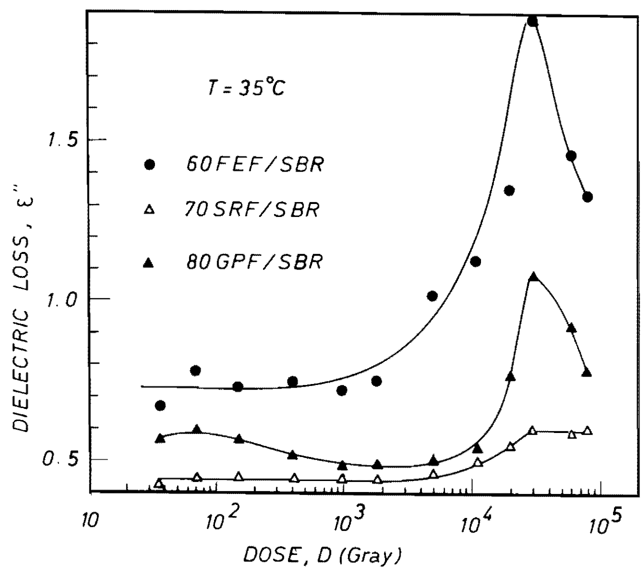

Figure 4. Variation of Dielectric Loss at 35°C as a Function of Irradiation Dose for: ●, 60 FEF/SBR; △, 70 SRF/SBR and ▲, 80 GPF/SBR

CONCLUSION

It may be concluded that the induced irradiation changes in both ρ and ϵ' are rather dependent on the type of carbon black. These remarkable changes can be used as a direct, easy, inexpensive, nontoxic, and sensitive method for evaluation of the irradiation dose. Only measurement of either ρ or ϵ' for the sample after irradiation is necessary to evaluate the dose, applying the two suggested empirical formulae.

However, some work still has to be done to render the method applicable, such as, effect of shelf and thermal oxidative ageing of the samples before and after irradiation on the detector renderet, application of the styrene–butadiene rubber filled with other types of carbon black, and study of the effect of gamma rays on vulcanized rubber. This work is already done by our laboratory and will be presented in the First Egyptian – British Seminar on Radiation Physics which will be held in Cairo, Egypt 24–27 November 1985.

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