Electrical Conductance of Irradiated NBR/LDPE Conductive Blend during Swelling in Benzene

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ABSTRACT: The effect of γ-irradiation on both the electrical conductance, Y, and diffusion coefficient, D, of acrylonitrile butadiene rubber mixed with different concentrations (1, 3, and 5 phr) of low-density polyethylene (LDPE) that was swollen in benzene, have been studied. The diffusion coefficient decreases with increasing the γ-irradiation dose for loaded samples with 1 and 3 phr of LDPE content, while samples with 5 phr of LDPE show a significant increase of diffusion coefficient with the increase of the radiation dose. The electrical conductance was found to be highly affected by the γ-irradiation dose. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1639–1645, 1997

Key words: NBR/LDPE; benzene; swelling

INTRODUCTION

The interaction of polymeric materials with different solvents is a problem from both the academic and technological points of view.[1–7] Nitrile butadiene rubber (NBR) is one of the most widely used oil-resistant rubbers in the automotive industry,[8] prompting us to investigate its solubility properties.

Polyacrylonitrile is a polar polymer, which contains the permanent CN dipolar group. This polarity can be diluted by incorporating the nonpolar butadiene to form a copolymer of polyacrylonitrile butadiene.

Nonpolar polymeric hydrocarbons (polybutadiene) can be expected to dissolve well in saturated low molecular hydrocarbons and in their mixture (benzene). Conversely, polymers containing polar groups (polyacrylonitrile) do not dissolve in nonpolar liquids. Links between polar groups of neighboring chains are stronger and do not break easily; thus, strong intermolecular interaction between separate groups results in the formation of local crosslink points or nodes in the polymer.[9]

Irradiation of different types of rubber was studied by Tarssova et al.[10] The effect of the polymer composition on radiation-induced crosslinking was studied by several other researchers.[11–13] It is well known that the electrical conduction in polymers can be considerably enhanced by irradiation.[14]

Crosslinking and degradation are nonequilibrium radiation–chemical processes that change the structure and, hence, the physical properties of the polymer. As a rule, crosslinking and degradation occur simultaneously upon irradiation.[15] However, the ratio of their rates depends on the chemical structure of the polymer, its physical state, and the irradiation conditions.

The present investigations clarify the effect of γ-radiation on the electrical conductance and diffusion of benzene into NBR mixed with different concentrations (1, 3, and 5 phr) of low-density polyethylene (LDPE).

EXPERIMENTAL

Sample Preparation

Acrylonitrile–butadiene rubber containing approximately 75% butadiene and 25% acrylonitrile,

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Table I Composition of NBR Samples with Different LDPE Contents

Ingredients (phr)[a]	Samples		
	MH1	MH2	MH3
NBR	100	100	100
LDPE	1	3	5
Stearic acid	2	2	2
Zinc oxide	5	5	5
HAF black	40	40	40
Processing oil	10	10	10
MBTS[b]	2	2	2
PBN[c]	1	1	1
Sulphur	2	2	2

[a] Part per hundred parts of rubber by weight.
[b] Dibenthiazyl disulphide.
[c] Phenyl-B-naphthylami.

filled with different concentrations of LDPE and loaded with 40 HAF carbon black (the percolation concentration,[16]) were used in this study. The rubber and other conventional additives were mixed according to the recipe illustrated in Table I. The test samples were prepared on a two-roll mill 170 mm diameter, with work distance 300 mm, and at speed of slow roll of 18 rpm and gear ratio 1.4. The rubber composites were left for 24 h before being vulcanized at 143 $\mp$ 2°C under a pressure of about 40 kg/cm^2 for 30 min.[16,17]

All materials used in this work were supplied by the Transport and Engineering Company TRENCO, Alexandria, Egypt.

Irradiation Procedure and Electrical Measurements

A ^{60}Co gamma source model GB 150 type B manufactured by the Atomic Energy of Canada Ltd, was used for irradiation of the samples at a dose rate of 74.45 Gr/h and at a constant temperature of 35°C. After irradiation, samples were kept in a discattor under a constant humidity of 55%. Test sample had the form of disc of area 1.33 cm^2 and thickness about 0.3 cm. The electrical conductance cell electrodes were about 1 cm^2 of cross-sectional area to minimize the edge error. A regulated electrical oven was used to maintain a constant ambient temperature. The circuit used for electrical conductance measurements was interfaced with a computer device and a Kiethly digital electrometer.

Swelling Measurements

Rubber blends were weighed and inserted into a test tube containing benzene at 30°C. The rubber blends were removed from the solvent and blotted with filter paper to remove excess solvent from the surface of the sample. The rubber blends were then weighed to an accuracy of 0.1 mg at a given time and at a fixed temperature (30°C). The

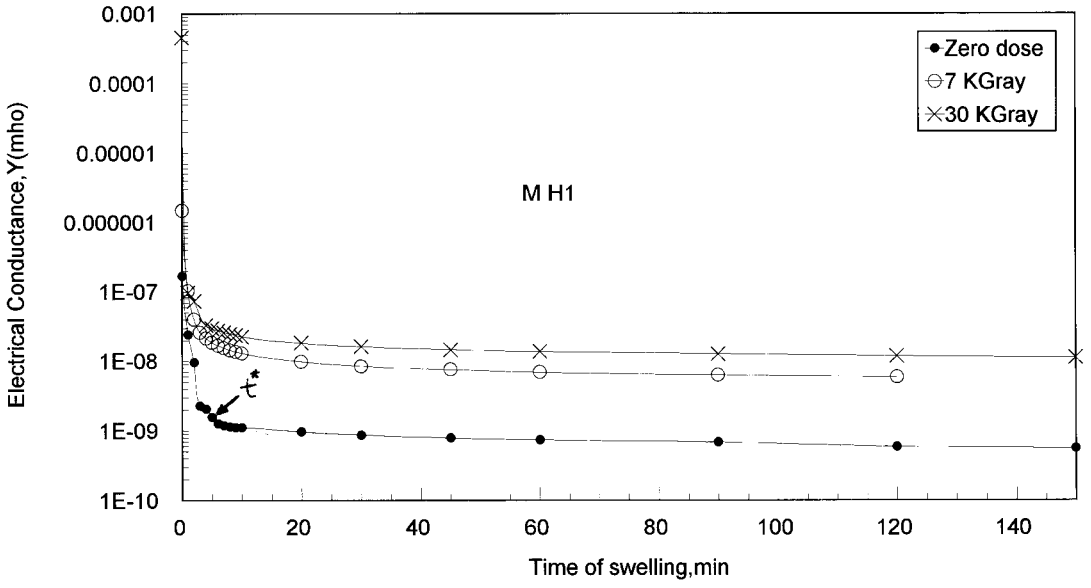

Figure 1 Time dependence of the electrical conductance of NBR mixed with 1 phr of LDPE (MH1) at different doses during swelling.

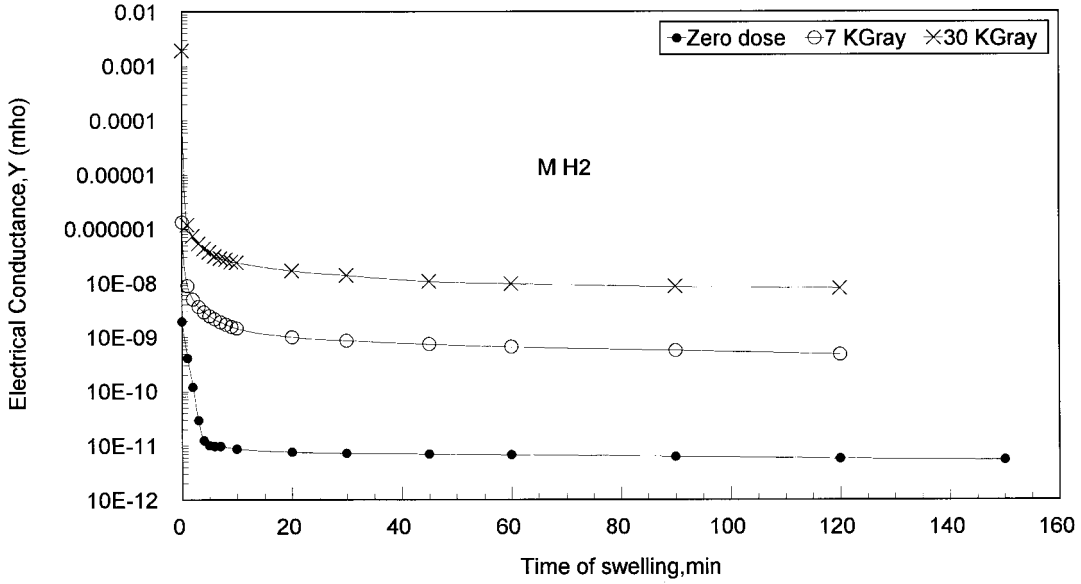

Figure 2 Time dependence of the electrical conductance of NBR mixed with 3 phr of LDPE (MH2) at different doses during swelling.

weight change was calculated by using the gravimetric method[18] and given by

$$M_t = \{(W - W_d)/W_d\}\ 100 \qquad (1)$$

where, M_t is the percent mass of solvent absorbed at time t, W_d is the dry weight, and W is the weight of swolled sample.

RESULTS AND DISCUSSION

Electrical Conductance of Irradiated NBR/LDPE Conductive Blend

The initial effects of radiation are to produce excitation and ionization, but subsequent effects depend on the chemical structure of the polymer.

Figures 1–3 illustrate the dependence of elec-

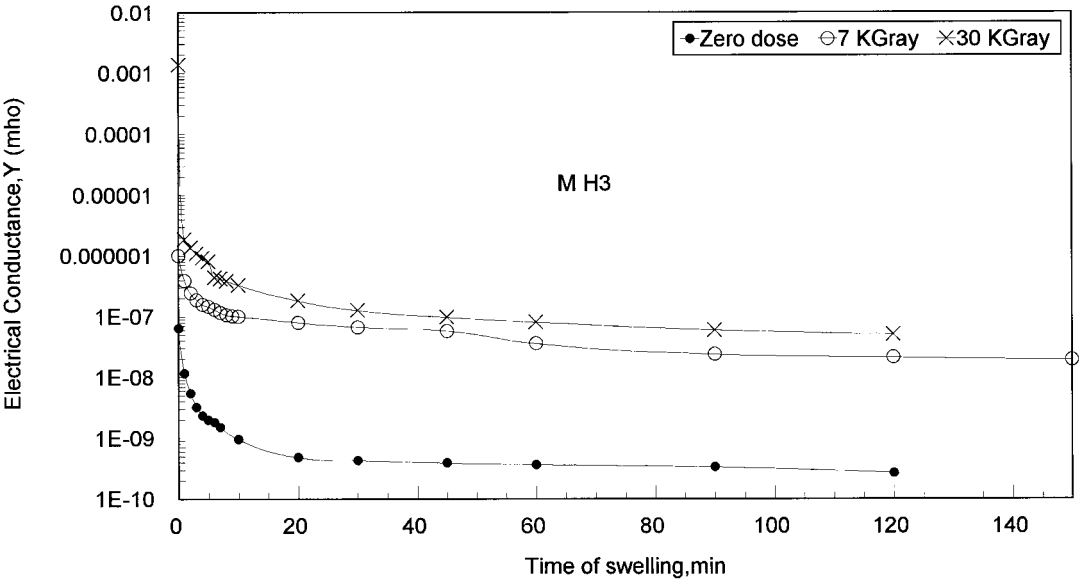

Figure 3 Time dependence of the electrical conductance of NBR mixed with 5 phr of LDPE (MH3) at different doses during swelling.

Table II Variation of Characteristic Constant, t^*, for Irradiated NBR/LDPE

	t^*, min		
Radiation Dose, KG Sample	Zero	7	30
MH1	6	4	2
MH2	6	5	4
MH3	12	6	3.5

trical conductance Y, of conductive NBR mixed with different concentration (1, 3, and 5 phr) of LDPE, respectively, on the time of swelling in benzene. In general, the conductance of these samples is hardly affected by both radiation dose and solvent (benzene) content.

It is noticed that there is a characteristic time of swelling, t^*, after which a slight decrease in Y with time appear. It was obvious that the characteristic time, t^*, decreased with the radiation dose for all samples, as shown in Table II. This may be attributed to the growing probability of the formation of the crosslinked polymer, which probably resists the breakdown effects during the swelling process; also, the degree of crosslinking is essentially proportional to the dose.

In addition, it is suggested here that the swelling process affects the electrical conductance of the blend in two steps. The first one is the diffusion of the solvent molecules into the rubber matrix, and this swelling of the rubber matrix–low-density polyethylene does not dissolve in this solvent at room temperature[19]—It causes a breakdown in the carbon black structure, which leads to a sharp decrease in Y below t^*. Secondly, the formation of an insulating cluster of the solvent around the carbon black particles and/or aggregates results in a slight change in the electrical conductance above, t^*.[20]

A preliminary experiment has been done using the swelling test as criterion to confirm the above results.

Swelling

According to Jost,[21] the rate of solvent absorption by a polymer is a function of the quantity already absorbed, until this reaches about 60% of the equilibrium value M_m in the solvent, the following relation is valid:

$$M_t = M_m\{(4/\mathrm{h})\,(Dt/\pi)^{1/2}\} \qquad (2)$$

where h is the sample's thickness, and D the diffusion coefficient. From eqs. (1) and (2), the diffusivity, D, is given by Fick's equation:

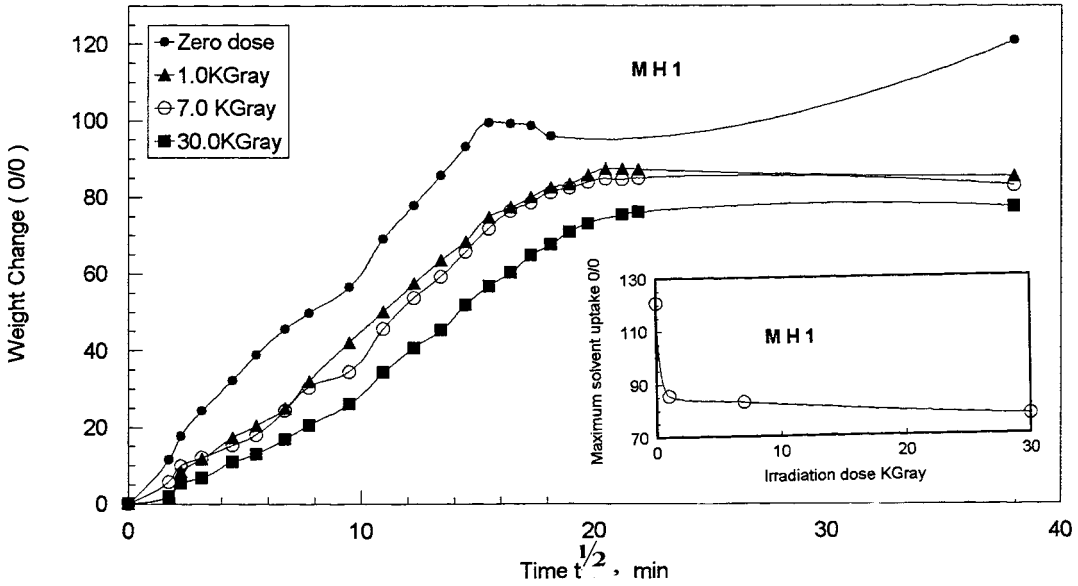

Figure 4 Solvent uptake percent versus square root of time for NBR mixed with 1 phr of LDPE (MH1) at different doses. (a) Inset: Variation of maximum solvent uptake percent with γ-irradiation dose.

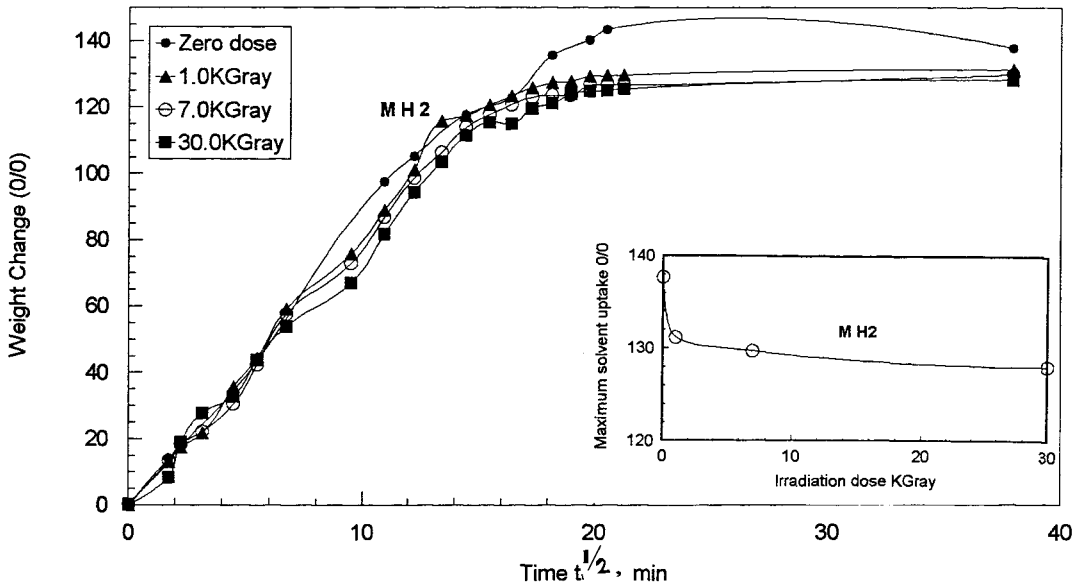

Figure 5 Solvent uptake percent vs. square root of time for NBR mixed with 3 phr of LDPE (MH2) at different doses. (a) Inset: Variation of maximum solvent uptake percent with γ-irradiation dose.

$$D = \pi/t(hM_t/4\ M_m)^2$$

$$D = \pi(h\vartheta/4M_m)^2 \qquad (3)$$

where, ϑ, is the initial slop of the plot of M_t vs. $t^{1/2}$.

The percentage increase in weight due to swelling—in benzene—for all irradiated samples is plotted against the square root of time, in $\text{min}^{1/2}$. The curves are shown in Figures 4–6. The dependence of maximum weight changes with γ-irradiation dose for all samples are plotted in the inset of figures.

The general feature of the figures show that, γ-dose has a slight effect on the percent weight change of all samples. The early linearity is due to the low equilibrium volume swelling values for those samples and solvent, while the nearly hori-

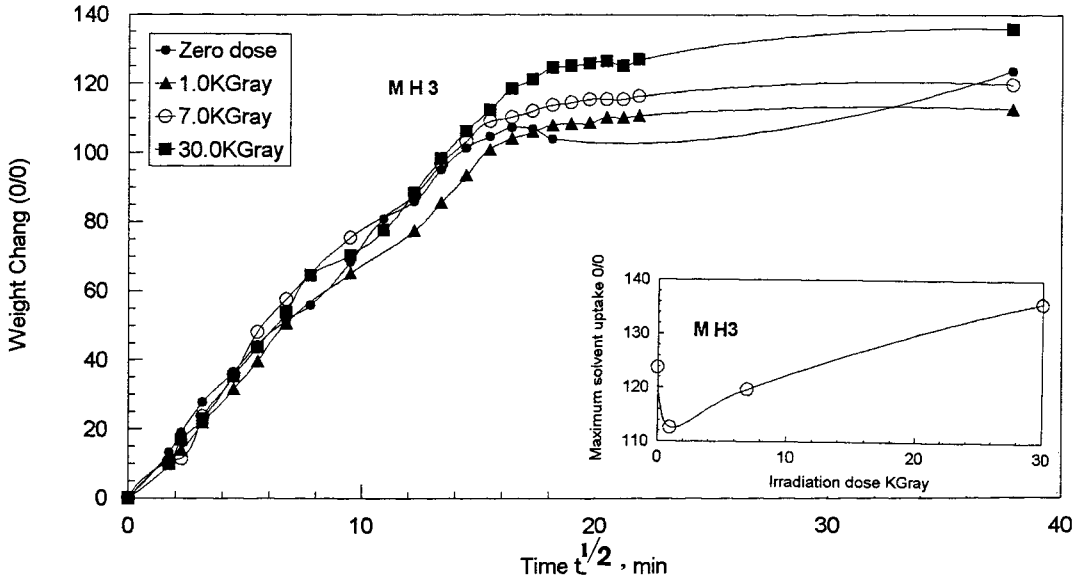

Figure 6 Solvent uptake percent vs. square root of time for NBR mixed with 5 phr of LDPE (MH3) at different doses. (a) Inset: Variation of maximum solvent uptake percent with γ-irradiation dose.

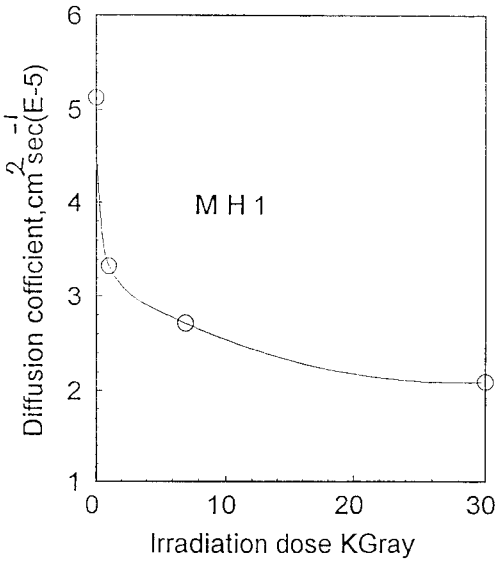

Figure 7 Dependence of diffusion coefficient on γ-dose for NBR mixed with 1 phr of LDPE (MH1).

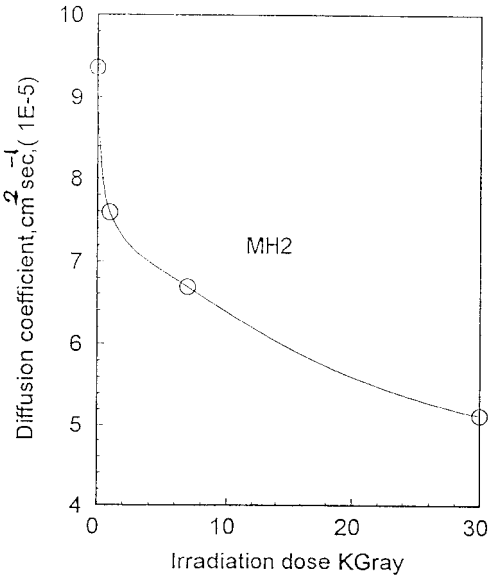

Figure 8 Dependence of diffusion coefficient on γ-dose for NBR mixed with 3 phr of LDPE (MH2).

zontal part of the curve means that the rubber blend degradation or extraction of its soluble ingredients is extremely small. It is clearly noticed that weight uptake of solvent for acrylonitrile butadiene rubber mixed with 1 or 3 phr of low-density polyethylene shows a significant decrease with the increase of radiation dose, while the samples with 5 phr of LDPE show a significant increase with an increase of radiation dose.

The slope ($\vartheta = \partial M_t/\partial t^{1/2}$) of the straight lines in the early part of the curves in the figures was calculated, and M_m was obtained from the maximum point of the curves. By using eq. (3), the diffusion coefficients, D, were calculated. Figures 7–9 represent the dependence of diffusion coefficient on the irradiation dose for all above samples. The results show the decrease of the diffusion coefficient for MH1 and MH2 samples with an increase of radiation dose; this may be explained as under the action of very low γ-doses up to 3 Mrad,[22] and by using the fact that irradiation of polyethylene in the presence of oxygen, leads to an increase of oxidative degradation of the polymer,[23] this radiation induces C—C and C—H bond scissions forming the free radicals, which react with another molecule or macroradical forming crosslink.[9,24] The anomalous behavior detected in MH3 sample—higher concentration of LDPE—may be attributed to the fact that the degradation process is faster than the crosslinking process under the effect of radiation.

From inspection of Figures 1–3 and 4–6, a direct correlation between the electrical conductance and the weight change percent was deduced in Figure 10(a)–(c). This figure shows that as the solvent molecules diffuse through the rubber matrix, the electrical conductance is decreased by the degradation and destruction process of the crosslinking rubber. As the γ-dose increases, the time needed for diffusion decreases for all samples.

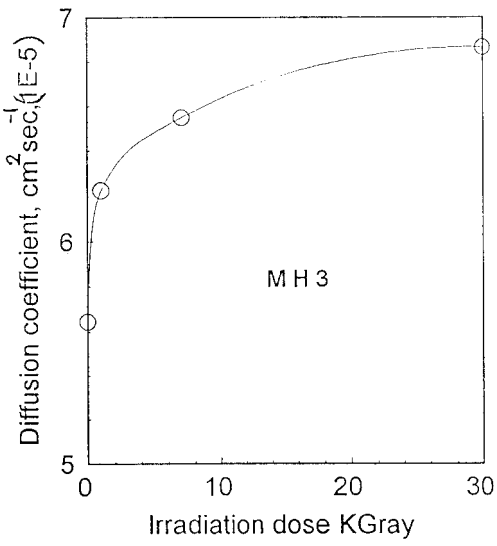

Figure 9 Dependence of diffusion coefficient on γ-dose for NBR mixed with 5 phr of LDPE (MH3).

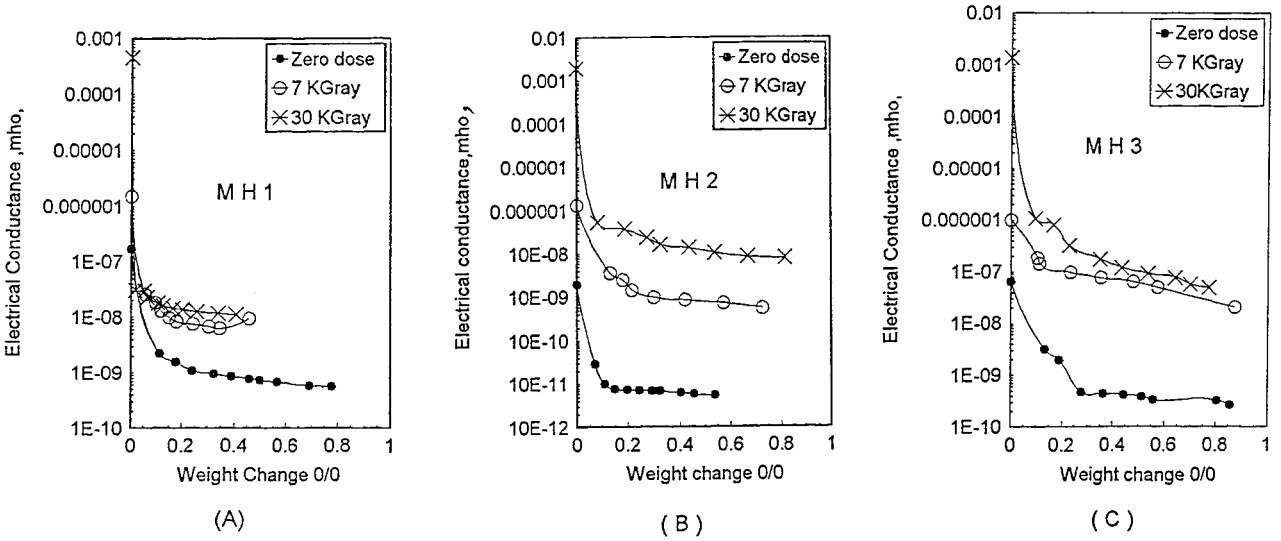

Figure 10 The electrical conductance Y, for irradiated LDPE/NBR and its dependence on solvent uptake percent. (a) Irradiated NBR mixed with 1 phr of LDPE. (b) Irradiated NBR mixed with 3 phr of LDPE. (c) Irradiated NBR mixed with 5 phr of LDPE.

CONCLUSION

The above data leads to the following conclusion: as a γ-dose increases, the electrical conductance incrases, and the swelling is rendered lower in irradiated samples—except MH3—due to the relative increase in the stable structure.

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