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Dielectric spectroscopy – an analytical tool for monitoring the deterioration due to high energy radiation in ethylene propylene diene terpolymer (EPDM) vulcanizates

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This paper demonstrates the use of a dielectric spectroscopy technique for monitoring the high energy radiation ageing and stabilization of ethylene propylene diene terpolymer vulcanizates. The measurement of dielectric constants and dielectric losses in the frequency domain help to quantify the physico-chemical changes in the bulk due to high energy irradiation. It is found that the relaxation time calculated using an empirical approach is exponentially related to the total exposed dose. A quantitative comparison of different antirads with a control vulcanizate has been demonstrated by using parameters defined as relative efficiency indices (*REI*) and relative stability indices (*RSI*). Three types of *REI* parameters are defined and computed from dielectric measurements after irradiation over a period of time at a fixed frequency. These *REI* values are a good estimate of antirad efficiency for energy scavenging and transient charge scavenging. Two types of *RSI* parameters are defined and computed from the frequency scans of dielectric properties for a material exposed to various doses of γ irradiation. These *RSI* values provide a good estimate of the rate and extent of changes in the physico-chemical structure due to irradiation. A third type of *RSI*, computed from equilibrium swelling measurements, closely matches that obtained from dielectric data. It is concluded that the deterioration is predominantly created by a cross-linking reaction even after the addition of antirads. It is observed that polymeric antirads provide the highest efficiency stability.

1. Introduction

Dielectric polymers that have excellent flexibility and mechanical properties, are an ideal choice for insulation purposes [1]. The dielectric properties of most of these polymers are well understood and have been discussed in the literature as components in devices [2]. However, only limited use of dielectric properties such as the dielectric constant (ε') and dielectric loss (ε'') has been made in structure–property–relationship studies with the exception of glass transition temperature determination using temperature scans [3–6].

In this paper we discuss the use of ε' and ε'' frequency scans to quantitatively monitor the physico-chemical changes associated with the high energy radiation ageing of polymers.

The effect of high energy radiation, namely, γ radiation, on polymers in the presence of an oxidative environment is shown schematically in Fig. 1. The formation of short lived, transient charge species, namely, thermal electrons, protons, radicals, ions and ion-radicals due to radiolysis reactions has been extensively reported in the literature [7–10]. The monitoring of the formation and decay of such highly mobile charged species is possible by dielectric measurements since the presence of such charged species results in an increase in the ε' and ε'' values. These charged species, being small in size and highly reactive, undergo a process of diffusion and are ultimately destroyed either by recombination or by quenching by additives and absorbed oxygen. The rate of decrease in the concentration of these reactive species can therefore be monitored by performing dielectric measurements with respect to time at a constant frequency.

The absorbed oxygen on reacting with these species transforms into highly reactive singlet oxygen. The singlet oxygen then starts a cascade process of autooxidation reactions leading to chain scission and polar group insertion in the polymer chain via a free radical chain reaction mechanism. This results in an increase in the polarity and correspondingly an increase in the ε' and ε'' values. Hence the rate and extent of polymer deterioration can be indirectly derived by monitoring the rate and extent of increase in these dielectric parameters.

The increase in cross links in the polymer bulk results in a decrease in the molecular chain length between the two cross links. This leads to an increase in the segmental relaxation time which is reflected in

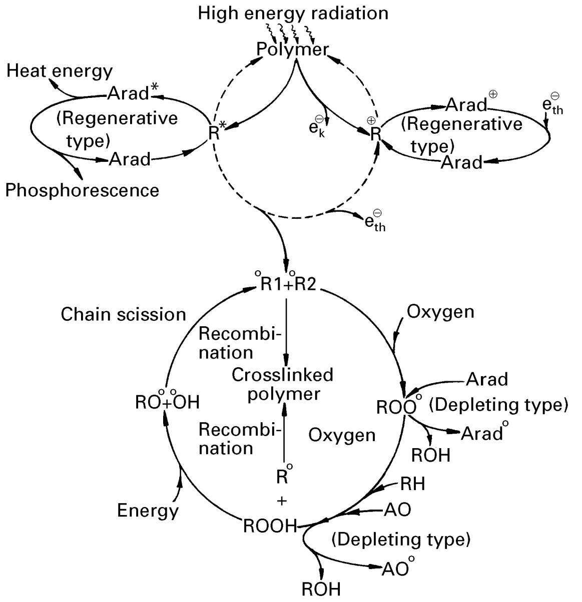

Figure 1 Schematic representation of the effect of radiation on polymers.

a shift of the corresponding ε″ peak maximum frequency (and inflection point on the ε′ curve) towards a lower value. In the case of a chain scission process being predominant in the polymer the shift is towards higher frequencies. Thus one can monitor the rate and extent of deterioration with identification of the predominant mechanism from the dielectric scans in the frequency region.

The presence of antirads in the bulk results in a retardation in the rate of formation of the transient charged species initially by energy scavenging and ion/radical scavenging actions. Further more, these antirads also prevent the oxygen reacting with the charged species by selectively undergoing reaction with these species to neutralize them. Thus one can compare the type, rate and extent of deterioration for each antirad by monitoring the dielectric properties.

In the present studies, experiments were designed to obtain following parameters.

(1) The extent of transient charge species formation and their decay rate by monitoring ε′ and ε″ at a constant frequency of 10 KHz over a period of time after exposing the specimen to γ radiation of 20 MRads.

(2) The change in dielectric constant and relaxation time parameter for different doses of γ radiation using a frequency scan.

(3) The change in cross link density due to γ irradiation by using equilibrium swelling measurements.

These experiments provide the necessary data to quantify the extent and rate of deterioration in vulcanizates with respect to the total exposed dose of γ radiation. The interpretation of dielectric data is consistent with the equilibrium swelling measurements and mechanical properties.

2. Experimental procedure

2.1. Specimen preparation

Five antirads were used for the study, namely, acenaphthene (Ac), pyrene (Py), brominated acenaphthene (BrAc) and poly acenaphthene sulphide (PAcSu), poly pyrene sulphide (PPySu). The first three are polynuclear aromatics and other two are polymeric polynuclear aromatics with bridging sulphur bonds. The antirads, BrAc, PAcSu and PPySu were synthesized in the laboratory using the previously reported procedures [11].

The compounding of the elastomers was carried out with various ingredients on an open roller mill using the recipe and conditions listed in Table I. Three test slabs (dimensions 15 × 15 × 0.2 cm) were compression moulded at 155 °C and 7 tons pressure for the optimum cure time determined from rheometry measurements (Table II) for each recipe. Discs of 6.5 cm diameter for dielectric spectroscopy, dumb-bell specimens for tensile measurements and strips for equilibrium swelling measurements were cut from these test slabs.

2.2. Ageing conditions

Ageing of the disc shaped specimens were performed using a radial $C^{60}\gamma$ radiation source at a 0.48 MRad h^{-1} dose rate. The disc specimens were suspended vertically with a distance between them of

TABLE I Recipe and compounding conditions for EPDM vulcanizates

Recipe

Material	Quantity (gm)
EPDM (Royalene 550)	100
ARD resin Poly(2,2,4-trimethyl 1,2-dihydroquinoline)	4
Paraffin wax	4
China clay	30
Aluminium silicate	40
Carbon black SRF	5
Sulphur	2
TMTD (Trimethyl thiuram disulfide)	1
Stearic acid	1
Zinc oxide	2
Antirad	4

* The following antirads were used:

Label	Antirad name
Control	––––
Ac	Acenaphthene
BrAc[a]	Brominated acenaphthene
Py	Pyrene
PAcSu[b]	Poly acenaphthene sulphide
PPySu[b]	Poly pyrene sulphide

Compounding conditions

Mixing temperature 120 °C,
Roller speeds 15 rpm front roller, 18 rpm back roller, with steam circulation.
Total mixing time 20 minutes

[a] BrAc is the fully brominated product of Ac obtained by reacting it with excess bromine using anhydrous ferric chloride as a catalyst.

[b] PAcSu and PPySu are the melt reaction products of Ac and Py with sulphur respectively, in an inert atmosphere.

The characteristics of these materials are described in earlier publications.

TABLE II Rheometry data, moulding conditions and properties of EPDM vulcanizates

Recipe name	Minimum torque (dN m)	Maximum torque (dN m)	Induction time (min)	Scorch time (min)	Optimum cure time (min)
Control	10	69	2.0	4.0	22.5
Ac	10	67	1.9	4.3	22.5
BrAc	9	66	1.8	4.5	23.0
Py	8	68	2.0	4.5	23.0
PAcSu	10	67	1.8	4.2	22.5
PPySu	9	68	1.8	4.2	22.5

Moulding conditions

Mould dimensions: 15 × 15 × 0.2 cm.
Temperature: 155 °C
Pressure 7 tons
Time Optimum cure time

Properties

Recipe name	Tensile strength (MPa)	Elongation at break (%)	Hardness shore A units	Equilibrium[a] solvent volume fraction
Control	16.5	525	58	0.46
Ac	16.5	520	57	0.44
BrAc	16.0	515	56	0.44
Py	16.9	520	58	0.45
PAcSu	17.0	515	57	0.46
PPySu	17.4	515	58	0.45

[a] Equilibrium solvent volume fraction is for toluene as the solvent, measured after 75 h of immersion period. The volume fraction is calculated using Equations 1–3.

not less than 0.5 cm. The temperature of the specimen during the exposure was always kept below 30 °C by circulating air through the chamber. The relative humidity level was maintained at 55%.

2.3. Precautionary measures taken

The following precautionary measures were adopted in order to minimize the errors and ensure the reliability and reproducibility of the data.

(1) At least two disc specimens, five dumb-bells and two strips were cut from each test slab and marked as a single set of specimens.

(2) At least three sets of such specimens were used for each composition and their mean values are reported.

(3) Ageings for each set were performed separately and compared for each composition to determine the error in the analysis. Experiments were repeated if the deviation was found to exceed 2%.

(4) Each specimen was subjected to identical ageing conditions and preconditioning wherever required to ensure the reliability and reproducibility of the data.

2.4. Dielectric spectroscopy

The dielectric measurements were performed using an HP 4192A impedance analyser and a locally fabricated parallel plate capacitor type specimen holder. For the first set of experiments, the measurements were made at a fixed frequency of 10 KHz at a regular interval of time after exposing the specimen to 20 MRads of radiation. In the second set of experiments, all the measurements were taken between 0.1–3 MHz frequency of a 0.1 V a.c. electric field, after conditioning the exposed specimen at room temperature and 55% relative humidity for 24 h. The capacitance (*C*) and loss factor (tan δ) values were collected by PC-AT 286, a personal computer, equipped with an IEEE 488 data acquisition bus. Each recorded measurement was an average of at least 8 sample readings collected at 0.5 s intervals for each of the one hundred test frequencies. The *C* and tan δ values were then converted to ε' and ε'' values using the standard equations.

2.5. Equilibrium swelling measurements

Specimens of 0.5 × 0.5 cm surface area were cut from the strip specimens that had been kept with the disc specimens for ageing. Three pieces of each recipe were kept in glass bottles with 25 ml of freshly distilled toluene for a period of 75 h. Since there was no observable change in the solvent uptake after 72 h, the swelling was assumed to have reached its equilibrium state. The percentage increase in mass was obtained by weighing the swelled specimens immediately after removal from the solvent. The surfaces of the specimen were carefully wiped using filter paper before weighing. The volume fraction of solvent in the swollen mass was then calculated using the following equations:

$$\nu_s = \frac{V_s}{V_s + V_{r+f}} \tag{1}$$

$$V_s = \frac{M_s - M_c}{d_s} \tag{2}$$

$$V_c = V_{r+f} = \frac{M_c}{d_c} \tag{3}$$

where

V_s = volume of solvent absorbed at the equilibrium swelling,
M_s = mass of solvent absorbed at the equilibrium swelling
M_c = mass of the vulcanizate,
$V_c = V_{r+f}$ = volume of vulcanizate, i.e., the volume of elastomer plus filler,
d_c = density of vulcanizate,
d_s = density of solvent and
ν_s = volume fraction of solvent absorbed at the equilibrium swelling.

2.6. Mechanical properties

Dumb-bell shaped specimens were used for the determination of mechanical properties. The tensile strength, elongation at break and hardness were measured using appropriate ASTM methods.

3. Results and discussion

3.1. Effect of antirad addition to the vulcanizates

It is observed that the dielectric scan of all the vulcanizates, irrespective of type and nature of antirads, is similar. Moreover, the difference between corresponding ε' and ε'' values on addition of different antirads is very small and can be explained in terms of polarity differences between the different antirad molecules. It is also observed that there is no relaxation process occurring in the frequency scan, irrespective of the type and nature of the antirad used. These points clearly show that: (a) there are no physico-chemical changes in the vulcanizate bulk due to the addition of the antirads and (b) there are no relaxation processes due to antirad molecules in the frequency region of the scan.

The rheometric data (Table II) also support these inferences since there are only minor differences in the cure characteristics for different vulcanizates. The maximum torque remains almost constant indicating that all the vulcanizates have a similar cross link density. This fact is further corroborated by the data from equilibrium swelling measurements presented in Table II. The differences in tensile strength, elongation at break and hardness are only marginal indicating that all the vulcanizates have a similar physico-chemical structure.

3.2. Effect of high energy irradiation on the vulcanizates

3.2.1. Dielectric response to the formation and decay of the transient charged species

It is clear from Fig. 2(a and b) that for all the specimens their ε' and ε'' values decrease with time after removal from the radiation chamber. This expected behaviour is due to the transient charged species namely, thermal electrons, ions, radicals and ion radicals, formed *en masse* during the irradiation process, that diffuse within the bulk and are destroyed either by recombination or capture by the polymer chain/antirads/diffused oxygen.

It is also observed that the zero time values (ε'_0 and ε''_0) as well as the steady final values (ε'_f and ε''_f) are lower for the specimens containing antirads. This clearly indicates that the concentration of the charged species generated in the vulcanizate is lower when antirads are present during the irradiation and also after removal from the radiation chamber. The quantitative comparison is given in Table III in the form of various relative efficiency indices (*REI*). These *REI* values are determined using following equation.

$$(REI^0) = (Property)_{\mathrm{Control}}/(Property)_{\mathrm{Antirad}} \tag{4}$$

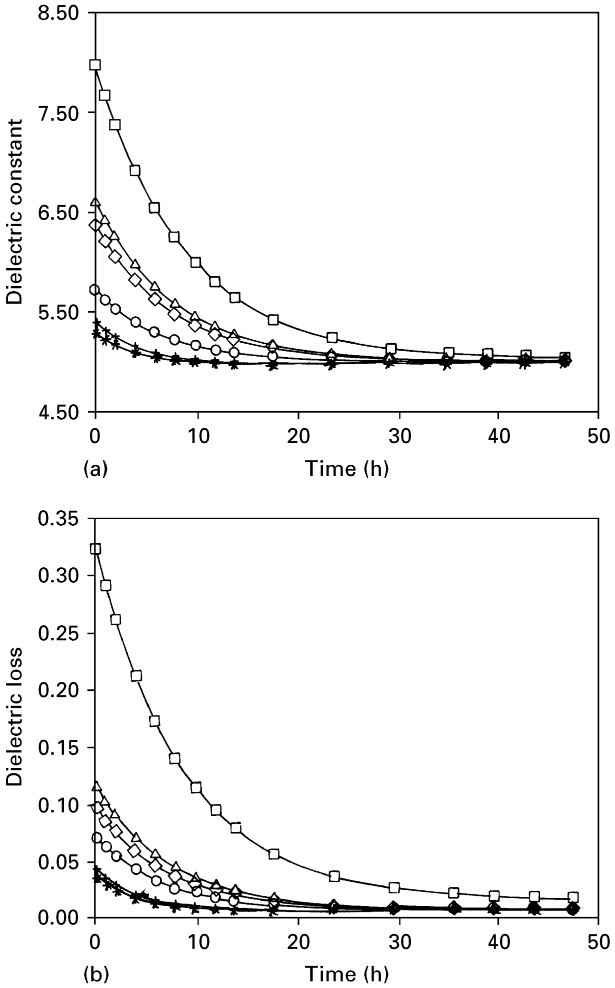

Figure 2 Variation in (a) dielectric constant and (b) dielectric loss parameter of ethylene propylene diene terpolymer (EPDM) vulcanizates at 10 KHz as a function of time after a 20 MRads γ irradiation. Key: (□) control, (△) Ac, (◇) BrAc, (○) Py, (+) PAcSu and (∗) PPySu.

TABLE III Relative efficiency indices corresponding to transient charged species formation and their decay kinetics

Recipe name	$(REI^o)_{\varepsilon'}$	$(REI^o)_{\varepsilon''}$	$(REI^f)_{\varepsilon'}$	$(REI^f)_{\varepsilon''}$	$(REI^r)_{\varepsilon'}$	$(REI^r)_{\varepsilon''}$
Control	1.000	1.000	1.000	1.000	1.000	1.000
Ac	1.213	2.807	1.003	1.895	1.145	1.173
BrAc	1.257	3.327	1.004	1.902	1.189	1.221
Py	1.407	4.519	1.005	1.906	1.313	1.326
PAcSu	1.494	7.487	1.007	2.098	1.969	2.033
PPySu	1.517	8.439	1.008	2.100	2.172	2.259

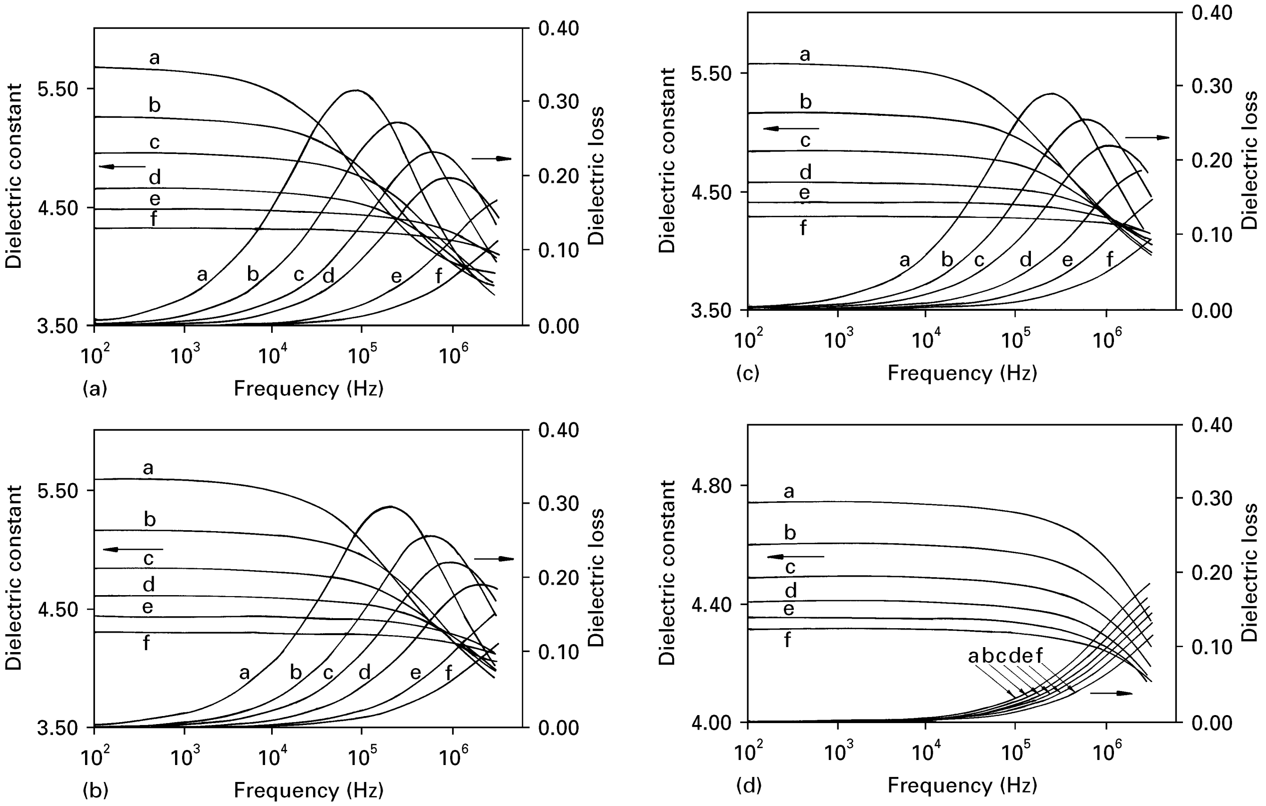

Figure 3 Frequency scan of dielectric constant and dielectric loss parameters of EPDM vulcanizates after different doses of γ irradiation (a) control (b) Acenaphthene (c) BrAc (d) PPySu. The γ doses were, (a) 200 MRads, (b) 160 MRads, (c) 120 MRads, (d) 80 MRads, (e) 40 MRads and (f) unirradiated.

where $(Property) = \varepsilon'_0$ or ε''_0

$$(REI^f) = (Property)_{\text{Control}}/(Property)_{\text{Antirad}} \quad (5)$$

where $(Property) = \varepsilon'_f$ or ε''_f

The (REI^o) are always greater than 1.00 for the vulcanizates containing antirads. This indicates a lower concentration of charged species being formed by the irradiation. These values are therefore a direct measure of the relative efficiency of antirads to function as energy and charge scavengers. A similar trend is found for the (REI^f) as that for (REI^0). These values being a direct measure of the extent of physicochemical changes due to the irradiation, they represent the relative efficiency of the antirads.

It is found that the decrease in ε' and ε'' values with respect to time (Fig. 3(a–d)) follows first order reaction kinetics for all the vulcanizates. The third type of efficiency index (REI^r) is computed from the first order rate constant for the decreasing ε' and ε'' values using the following equation:

$$(REI^r)_{\varepsilon' \text{ or } \varepsilon''} = \{(RateConstant)_{\text{control}} /(Rate\ Constant)_{\text{Antirad}}\}_{\varepsilon' \text{ or } \varepsilon''} \quad (6)$$

The values being greater than 1.00 for vulcanizates containing antirads, it is clear that antirads improve the quenching rates of the diffusing transient species and also reduce the rate of reaction with diffused oxygen as compared to the control vulcanizate.

Based on Table III, an order of the efficiency and stabilization by antirads can be arrived as follows:

PPySu > PAcSu > Py > BrAc > Ac > Control

3.2.2. Dielectric response to γ radiation ageing

It is observed that on exposure to γ radiation, a dielectric relaxation is observed for all the vulcanizates, except for those with the antirads PAcSu and PPySu,

TABLE IV Parameters of dielectric frequency scan data fitting using the Havriliak and Negami equation

Recipe name	α	β	ε″ peak maxima frequency (KHz) 0 (MRads)	40 (MRads)	80 (MRads)	120 (MRads)	160 (MRads)	200 (MRads)
Control	0.2842	0.6371	*(10472)*	*(4365)*	933	590	234	82
Ac	0.2840	0.6372	*(10472)*	*(5755)*	2041	935	562	195
BrAc	0.2843	0.6374	*(10716)*	*(6026)*	2691	1048	575	235
Py	0.2841	0.6370	*(10532)*	*(6762)*	2951	1380	812	578
PAcSu	0.2842	0.6373	*(10706)*	*(8129)*	*(6761)*	*(6026)*	*(4467)*	*(3382)*
PPySu	0.2840	0.6371	*(10705)*	*(8165)*	*(6919)*	*(6143)*	*(5371)*	*(4579)*

Recipe name	Total exposed dose of γ radiation 0 (MRads)		40 (MRads)		80 (MRads)		120 (MRads)		160 (MRads)		200 (MRads)	
	τ $(\times 10^7)$	ε''_{max}	τ $(\times 10^7)$	ε''_{max}	τ $(\times 10^7)$	ε''_{max}	τ $(\times 10^7)$	ε''_{max}	ε $(\times 10^7)$	ε''_{max}	τ $(\times 10^7)$	ε''_{max}
Control	0.128	*(0.156)*	0.302	*(0.178)*	1.426	0.204	2.227	0.238	5.616	0.277	16.441	0.321
Ac	0.128	*(0.147)*	0.230	*(0.169)*	0.646	0.195	1.404	0.225	2.345	0.260	6.817	0.299
BrAc	0.122	*(0.138)*	0.219	*(0.160)*	0.487	0.186	1.251	0.221	2.285	0.256	5.712	0.290
Py	0.126	*(0.156)*	0.195	*(0.160)*	0.446	0.182	0.962	0.204	1.644	0.234	2.285	0.277
PAcSu	0.123	*(0.151)*	0.163	*(0.156)*	0.194	*(0.163)*	0.221	*(0.177)*	0.295	*(0.184)*	0.391	*(0.199)*
PPySu	0.123	*(0.149)*	0.163	*(0.155)*	0.194	*(0.163)*	0.220	*(0.169)*	0.247	*(0.180)*	0.290	*(0.190)*

Values in the parentheses are obtained by extrapolation using the constants α, β and the relaxation parameter using the Havriliak and Negami equation.

in the frequency scan between 1×10^{-4}–3 MHz. The peak maxima frequency values for ε″ corresponds exactly to the inflexion point in the ε′ curves for all the measurements, indicating the presence of a relaxation process. It can be further observed from Fig. 3(a–d) that only one relaxation process is occurring with a broad and asymmetric dispersion around the peak maxima which is a typical characteristic of polymeric materials.

For the quantitative analysis of these dielectric scans, the empirical equation due to Havriliak and Negami is used Equation [12, 13]. This equation is a combination of the Cole–Cole equation [14] and Cole–Davidson equation [15] and it fits the asymmetry around the peak maxima frequency and the broad dispersion range.

$$\varepsilon^* = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (i\omega\tau)^{1-\alpha})^{\beta}} \tag{7}$$

The constants α and β are obtained by iterative methods so that they satisfy a set of data for each vulcanizate. The computational output is given in Table IV. It is clear that the addition of antirads has virtually no effect on these shape parameters since they remain almost constant.

As is shown in Table IV, the ε″ peak maxima is shifted to a lower frequency as the total exposed dose is increased, i.e., the relaxation time is increased. This can be considered as proof of an increase in the cross link density in the material. Fig. 4(a and b) indicates that the relaxation time parameter (τ) obtained from the Havriliak and Negami equation and static dielectric constant, ε_s, are exponentially related to the total exposed dose. The relative stability indices (*RSI*) listed in Table V are obtained from the curves of (i) Log(τ) versus total exposed dose and (ii) Log (ε_s) versus total exposed dose, using the following equations:

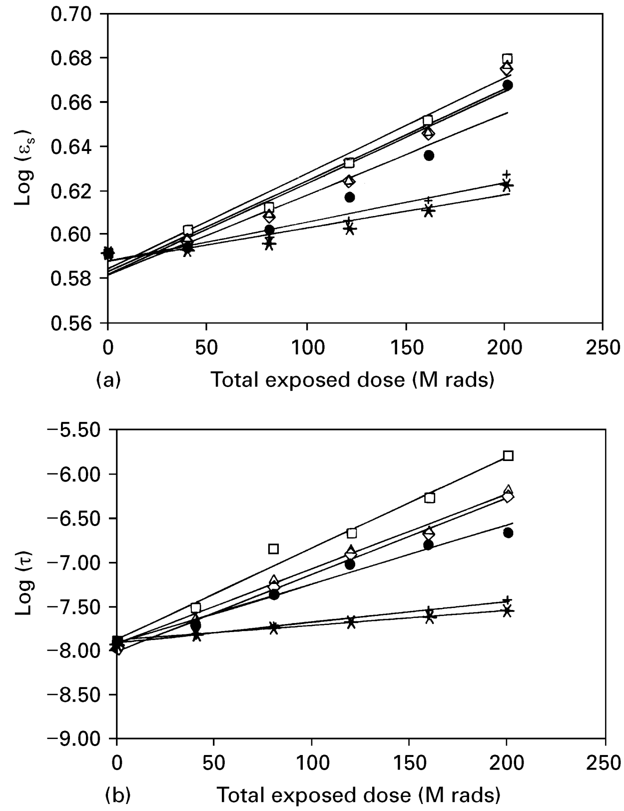

Figure 4 Variation in (a) static dielectric constant and (b) relaxation time parameter for EPDM vulcanizates with different doses of γ irradiation. Key, (□) control, (△) Ac, (◇) Py, (●) BrAc, (+) PAcSu and (∗) PPySu.

$$(RSI^{R}) = (Slope^{R})_{Control}/(Slope^{R})_{Antirad} \tag{8}$$

$$(RSI^{E}) = (Slope^{E})_{Control}/(Slope^{E})_{Antirad} \tag{9}$$

TABLE V Relative stability index from relaxation time parameter, static dielectric constant and equilibrium swelling measurements

Recipe name	(RSI^{R})	(RSI^{E})	(RSI^{S})
Control	1.00	1.00	1.00
Ac	1.18	1.03	1.60
BrAc	1.20	1.04	1.72
Py	1.53	1.17	2.72
PAcSu	4.31	2.32	4.70
PPySu	5.85	2.70	5.60

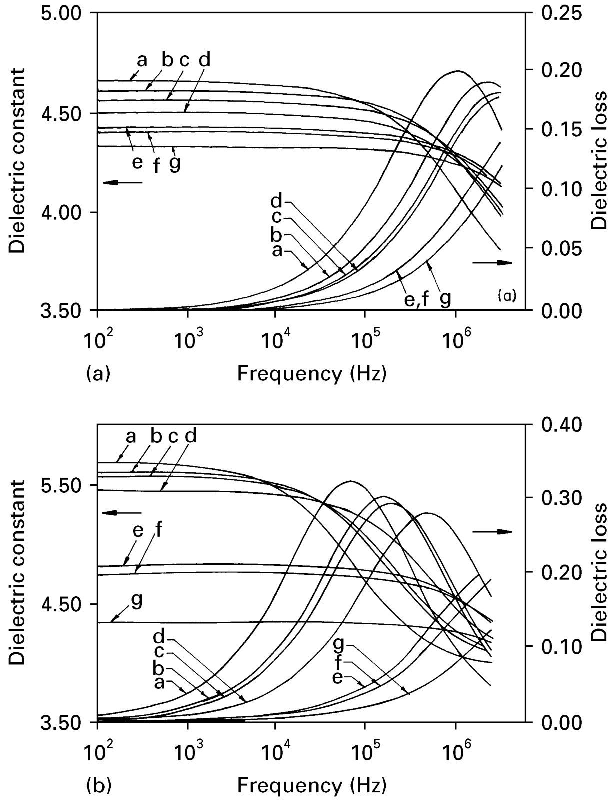

Figure 5 Frequency scan of dielectric constant and dielectric loss parameter for EPDM vulcanizates at (a) 80 MRads and (b) 200 MRads exposure of γ radiation. Key, (a) control, (b) Ac, (c) BrAc, (d) Py, (e) PAcSu, (f) PPySu and (g) unirradiated.

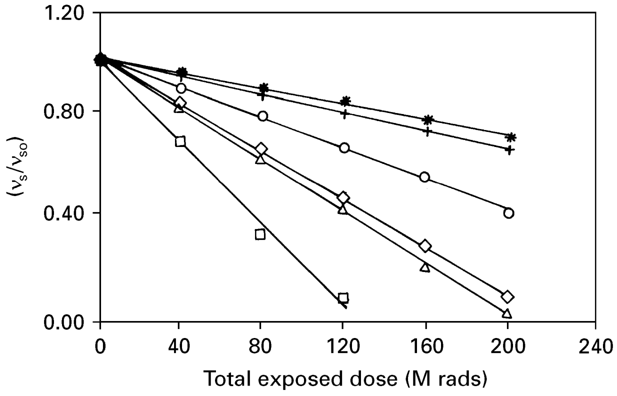

Figure 6 Variation in relative change in equilibrium swelling for EPDM vulcanizates with different doses of γ irradiation. Key, (□) control, (△) Ac, (◇) BrAc, (○) Py, (+) PAcSu and (∗) PPySu.

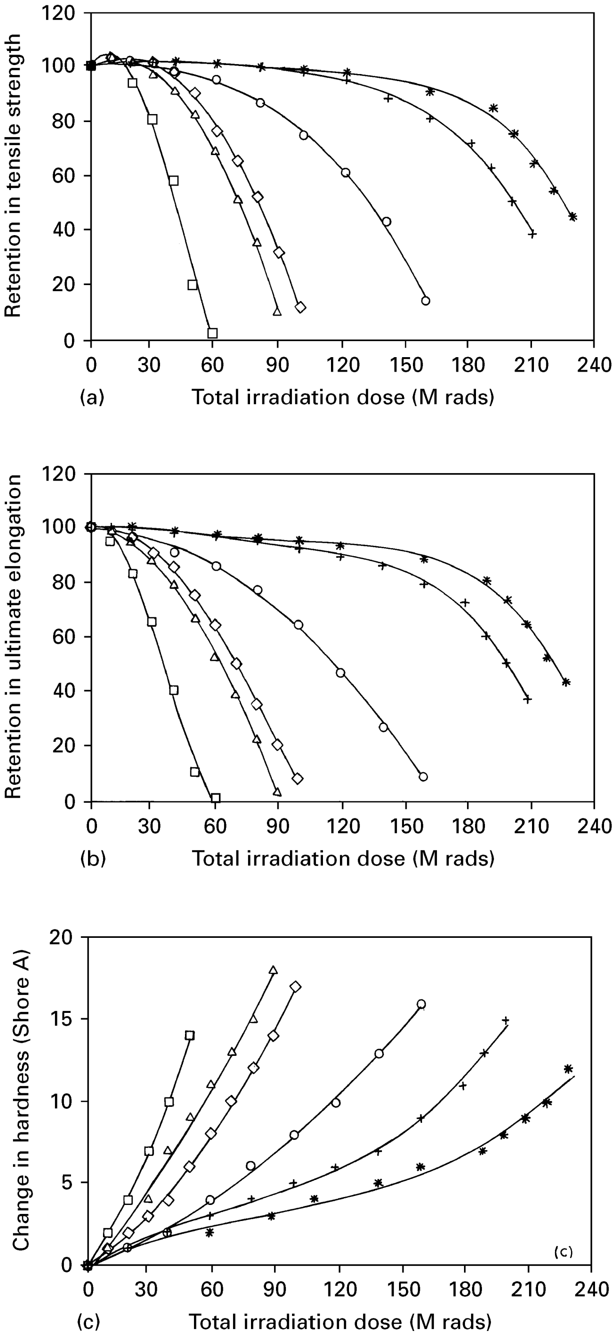

Figure 7 Effect of γ irradiation on relative change in (a) tensile strength, (b) percentage elongation at break and (c) hardness of EPDM vulcanizates. Key, (□) control, (△) Ac, (◇) BrAc, (○) Py, (+) PAcSu and (∗) PPySu.

where, $(Slope^{R})$ and $(Slope^{E})$ are obtained by linear least square fitting of the curves in the Log(τ) versus total exposed dose and Log(ε_s) versus total exposed dose plots respectively.

Since all the *RSI* are greater than 1.00 for antirads, the stabilizing action of these materials is confirmed. These values are representative of the rate and the extent of changes in the physico-chemical structure with respect to the total exposed dose, the comparative order of stabilization for different antirads can be listed as follows:

$$\text{Ac} < \text{BrAc} < \text{Py} < \text{PAcSu} < \text{PPySu}$$

The effect of different antirads is clearly seen from Fig. 5(a and b). The curves corresponding to PAcSu and PPySu do not show any relaxation behaviour in the frequency range studied even after a dose of 200 MRads of irradiation.

These inferences are further corroborated by the equilibrium swelling measurements (Fig. 6). The fractional solvent volume at equilibrium swelling linearly decreases with the increase in total exposed dose indicating a linear increase in the cross link density of the material. The trend for (RSI^s) values for antirads, computed using Equation 10 from the curves of (ν_s/ν_s^o) versus total exposed dose, closely agree with the (RSI^R) and (RSI^E) values,

$$(RSI^s) = (Slope^s)_{\text{Control}}/(Slope^s)_{\text{Antirad}} \qquad (10)$$

These values signify the relative rate of increase in the cross link density in the presence of an antirad to that in the absence of an antirad. The order of stabilizing efficiency for antirads, as compared from Table IV, can be given as follows:

$$\text{Control} < \text{Ac} < \text{BrAc} < \text{Py} < \text{PAcSu} < \text{PPySu}$$

This trend is similar to that found in the dielectric response studies discussed earlier. The decrease in percentage elongation at break and the tensile strength as shown in Fig. 7(a–c) also confirms the same trend and indicates that the deterioration in the bulk is a manifestation of a cross-linking reaction.

4. Conclusion

It has been demonstrated that dielectric spectroscopy can be employed as an analytical tool to quantitatively monitor the deterioration of a material. The comparative trend of stabilization efficiency obtained using the dielectric response and that obtained by equilibrium swelling are similar in nature. It is also concluded that antirads function as energy and charge scavengers and also guard against the attack of diffused oxygen when exposed to high energy γ radiation. The mechanism of deterioration in the ethylene propylene diene terpolymer vulcanizate was found to be predominantly a cross-linking reaction irrespective of the type and nature of the antirad used. It is also concluded from the dielectric response study, that in the presence of the antirads PPySu and PAcSu, deterioration is significantly less even up to exposures of 200 MRads.

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