# Dielectric Properties of Carbon Black Loaded EPDM Rubber Based Conductive Composites: Effect of Curing Method

**F.S. Shokr**

Faculty of Science for Girls, King Abdul–Aziz University, Jeddah, KSA
f.s.shokr@hotmail.com

**Abstract:** Different construction of high abrasion furnace black (HAF) have been dispersed in ethylene propleyene diene monomers (EPDM) composites and vulcanized by different methods. The dielectric properties of the elastomer crosslinked by gamma irradiation, laser beam irradiation and chemical vulcanization were compared. The frequency response of dielectric behavior has been studied for all prepared samples using LCR meter in the frequency range 100- $10^5$ Hz. The results are explained on the basis of proposed model. It is observed that the ac. conductivity increases with increase in HAF-bulk contents passing through a percolative threshold. The percolation threshold for EPDM– HAF black composites vulcanized by chemical or γ – irradiation dose and by laser beam was found to be around 20 phr. Both the quantum mechanical tunneling (QMT) of electrons through the barrier separating localized states and the classical happing over the same barrier were elucidated through the study of the frequency dependence of the ac. electrical conductivity of much EPDM composites.
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**Key words:** EPDM; Radiation; Dielectric Prosperities, Percolation threshold; Quantum mechanical tunneling.

## 1. Introduction

Composites materials, which are usually fabricated with an emphasis on properties such as mechanical strength, have also been used in electronic applications. One such class of composite materials is particulate- filled conductive polymer matrix composites. Then composites consist of polymer matrix in which a second phase, which is usually either a metal or carbon based filler, is dispersed, usually by conventional methods of polymer processing [1]. Conductive polymer composites have been used in a number of applications such as electromagnetic frequency interference (EMI) shield, antistatic devices and conducting coating [2- 4].

The dielectric properties of the composites depend on the volume fraction, size and shape of conducting fillers, and also on other factors such as, preparation method, curing method and interface and interaction between fillers and polymers [5, 6]. It is well established that the effective utilization of filled polymers depends strongly in the ability to dispraise the particle homogenously throughout the matrix [7].

Compared with the conventional chemical process such as peroxide or sulfur induced vulcanization used for cross-linking rubber, radiation cross-linking has some advantages. It results in the formation of a three-dimensional network through union of macro-radicals generated [6]. The process is very fast, clean and requires less energy.

The main object of this work is to study the ac dielectric properties of high abrasion furnace (HAF) carbon black loaded ethylene propleyene diene monomer rubber (EPDM) composites vulcanized by γ – irradiation or laser beam in the presence of ethylene glycol dimethacrylate monomer (EGDM) as a radiation sensitizer. The results were compared for those of EPDM vulcanized by chemical methods. The irradiation of polymeric materials involves the formation of crosslinks in the solid state and has got the ability to modify or cross-link polymers which are virtually resistant to chemical treatment. EGDM is generally used as a radiation sensitizer, which gives high yield of radicals under the influence of radiation, promotes the cross-linking at a much lower radiation dose and consequently improves the properties of the base polymer [8- 12] .

## 2. Experimental

### 2.1 Materials:

Ethylene-propylene diene monomer EPDM rubber (ethylene/ propylene ratio: 60/39; diene content: 5 wt.%) was supplied by Heliopolis chemicals company, Cairo, Egypt. Ethylene glycol dimethacrylate EGDM as radiation sensitizer was supplied by Sartomer Company, USA. Its molecular weight is 198. The filler used was HAF (N-330) having a particle size 30 nm and all ingredients were supplied by Transport and Engineering Company (TRENCO), Alex., Egypt.

### 2.2 Sample Preparation:

Rubber composites with a different filler loading were prepared by mastication of EPDM then mixing for a period of 20 min. with different ingredients in phr (part per hundred parts of rubber by weight). Mixing was done on a laboratory two- roll mill of 30 cm working distance and 15 cm diameter at a friction ratio of 1: 1.25. After rubber mastication, the compound ingredients such as activators, carbon black, processing oil, accelerators and vulcanizing agent were then added constituents in ratios as shown in Table (1). After compounding, the stocks were left for 24 h to mature. The vulcanization process (conventional method) was conducted at 140 $^{o}$C under a pressure of 40 kg/cm$^2$ for 30 min.

**Table (I):** Composition of HAF/ EPDM/ samples.

| Ingredient (phr) | Chemically vulcanized | | | | | Radiation curing | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| EPDM | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| HAF | 0 | 10 | 30 | 50 | 70 | 0 | 10 | 30 | 50 | 70 |
| Processing oil | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| EGDM | | | | | | 5 | 5 | 5 | 5 | 5 |
| MBTS[a] | 2 | 2 | 2 | 2 | 2 | | | | | |
| PβN[b] | 1 | 1 | 1 | 1 | 1 | | | | | |
| Sulfur | 2 | 2 | 2 | 2 | 2 | | | | | |

a) Dibenthiazyl disulfide. b) phenyl-□- napthylamine.

For gamma or laser curing, the mixes were compression moulded between smooth teflon sheets at a temperature of $110^0$C and a pressure of 5 MPa in an electrically heated press. In order to ensure predetermined sheet size, the hot pressed sheet was cold pressed afterward in another press at the same pressure and cooled with water. The moulded samples, in the form of thin sheets, have been irradiated. The vulcanization process via γ- irradiation or laser beam was conducted by using a laboratory gamma source or Nd – YAG laser source.

The laser used in this experimental was a Q–switched Nd: YAG laser type (continuum $Nd^{3+}$: YAG ny 81 – 300) utilize one basic head model, this is (711–06). The output powers were about 100, 50, 10 MW with the applied pulse width of a single shot equals 10 ns (FWHM), at the Infra red range. The laser source is located at laser research institute, Cairo University, Egypt.

The gamma irradiation of the composite sheets was carried out at room temperature using a $^{60}$Co gamma source model GB150 type B manufactured by the AEA of Canada and located at NCRRT, Egypt. Irradiation doses ranged from 50 to 200 kGy in air. Specifications of the gamma cell were reported elsewhere [13].

ac conductivity $\sigma_{ac}$ as a function of frequency is measured by precision LCR meter HP 4284 A at frequency range 100- $10^5$ Hz at room temperatures. The electrical contacts are made by silver paint. The complex dielectric constants are obtained from the measurements of capacitance (*C*) and dissipation factor (*d*). The real part of dielectric constant (ε`) is evaluated from the relation, $C = \varepsilon` b/t$, where *b* is the area of circles electrode with a diameter approximately 1cm and *t* the thickness of the sample. The dielectric loss is calculated from the dissipation factor, ε`` = *d*ε`. The ac conductivity $\sigma_{ac}$ (ω)= ω ε`` (ω) is investigated at room temperature with ω, angular frequency.

## 3. Results and Discussion

The dielectric properties of a polymer composite depend on several major factors: the properties of the constituent phases, such as the permittivity and conductivity, their relative volume fraction, and the morphology of the system. Percolating composites containing an increasing amount of conducting fillers exhibit significantly greater relative dielectric constant (ε`) and loss (ε``). Such systems, being heterogeneous, are also subjected to interfacial polarization or Maxwell-Wagner- Sillars (MWS) relaxation, which occurs at the interface of dissimilar materials [14, 15]. The free carries moving in the different phases of the composite are blocked at the interface between the media of different conductivities and permittivities. These immobile charges, being unable to discharge freely or accumulate at the electrode give rise to an overall field distortion. These phenomena results in a significant increase in the system capacitance and, consequently the appearance of an interfacial polarization peak.

### 3.1 Effect of Carbon Black Content:

The variation of the relative dielectric constant ($\varepsilon`/\varepsilon`_0$) vs. carbon black (CB) loading for EPDM (vulcanized by different methods) is shown in Figures (1-3) at a frequency of 1 kHz and at a temperature of 300 k. $\varepsilon`/\varepsilon`_0$ increase moderately with the CB concentration up to 20: 30 phr and exhibits an abrupt increase at polarization according to the vulcanizing method. This result suggests that the percolation threshold for the HAF/ EPDM composites vulcanized by chemical or γ- irradiation associated with laser beam occurs between 20 and 30 phr. This range is little lower than that determined from $\sigma_{ac}$ (30 phr) (paper under publication), properly become of the higher sensitivity of the dielectric measurement and because it takes into account the different loss- generating phenomena together. The dielectric response of systems with low CB contents is similar to the dielectric properties of the polymer matrix because at low concentrations, CB particles are widely dispersed. With increasing CB contents, the tendency of conductive chain formation increases through the aggregation of CB network, and the electrical filamentary conduction of the composite increases.

The increase of the relative dielectric constant is a result of the formation of a conducting CB network structure and is also due to the high interfacial polarization, which is clearly observed in samples vulcanized via laser shots with respect to the other mechanisms (C.F. Figures (1-3)).

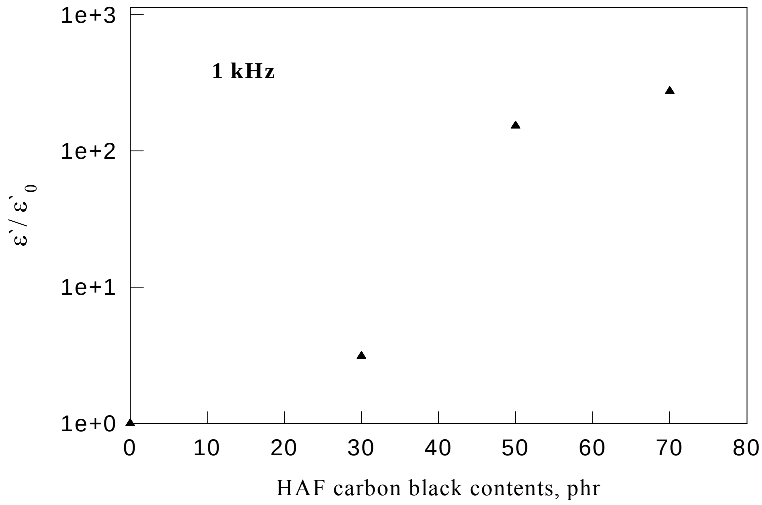


**Figure 1:** The dependence of ε`/ ε`$_0$ on HAF content, phr, for chemicaly vulcanized composites at 1 kHz frequency.

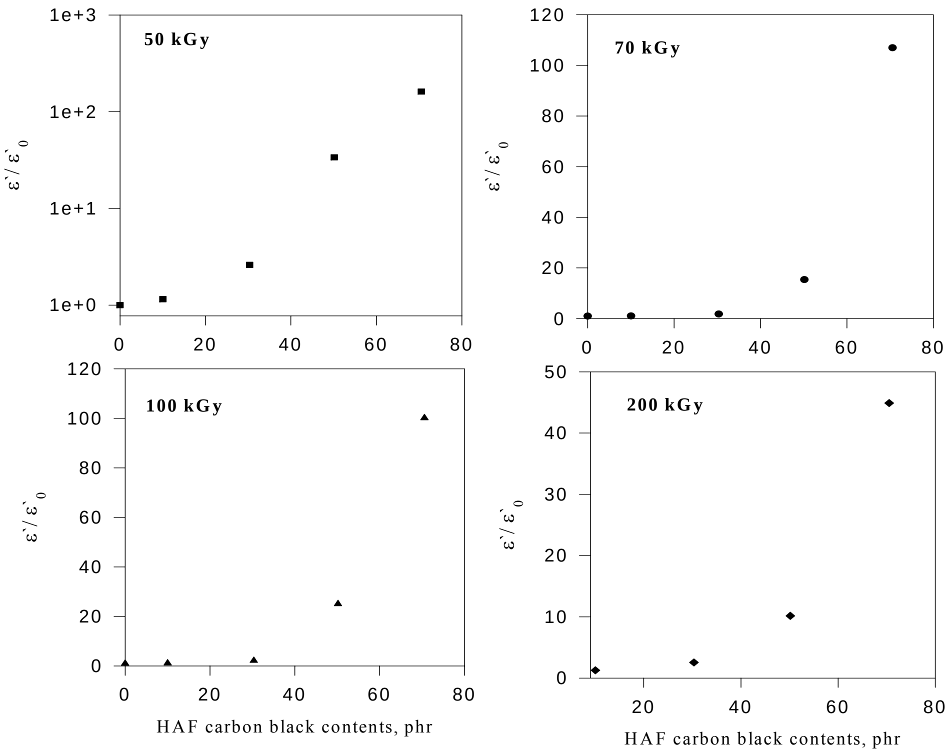


**Figure 2:** The dependence of ε`/ ε`$_0$ on HAF content, phr, for gamma vulcanized composites at 1 kHz frequency.

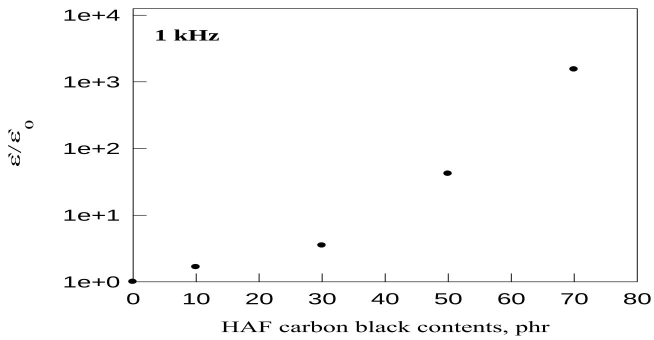


**Figure 3:** The dependence of ε`/ ε`$_0$ on HAF content, phr, for laser vulcanized composites at 1 kHz frequency.

The MWS (Maxwell- Wagner- Sillars) interfacial polarization effect can be estimated from some standard theoretical equations derived for a two- phase system of conductive particles distributed in an insulating matrix, which is very similar to the present CB/ EPDM system [16]. The theoretical values of the dielectric constant at different filler loading can be calculated with three different equations [17].

Equation (1) and (2) are used for the calculation of the dielectric constant for dispersed conducting spheres in an insulating matrix and equation (2) is used for calculating the dielectric constant of a conducting ellipsoid in an insulating matrix.

$$\varepsilon_c = t_1\left[\frac{1+2V_c}{1-2V_c}\right] \quad (1)$$

$$\varepsilon_c = \frac{\varepsilon_1}{1-3V_c} \quad (2)$$

$$\varepsilon_c = \frac{\varepsilon_1}{1-\frac{V_c}{3A}} \quad (3)$$

where $\varepsilon_1$ is the dielectric constant of EPDM matrix at 1 kHz at 300 K, (which corresponds to 11.9 for mechanically vulcanized samples, 6.05 for laser shots and 9.1 for 50 kGy, 7.95 for 70 kGy, 10.9 for 100 kGy, 7.48 for 200 kGy) [6], $V_c$ is the volume fraction of CB, and $\varepsilon_c$ is the dielectric constant of the composite.

The parameter *A* corresponds to the depolarization factor, which = 3 for spheres [18]. However, there is a well-known relation between ($\varepsilon_c/\varepsilon_1$) and the carbon black volume concentration in a mix from which the shape factor can be obtained as suggested by Lawindy and Abd El Nour [19] for CB reinforcing rubber given as:

$$\varepsilon_c = \varepsilon_1(1+0.67\varphi V_c + 1.62\phi^2 V_c^2) \quad (4)$$

where, $\phi$ is the shape factor of the carbon black particles.

The shape factor of HAF which gives a good fitting with the experimental data was found to be 6.0.

These theoretical predictions have been applied and presented with the experimental result, at room temperature and 1 kHz frequency, in Fig. 4 (a, b). We can see that none of these curves fit with the experimental result except Lawindy and Abd El Nour equation (equation 4).

**3.2 Frequency Dependence:**

The isothermal plots of ε` at 300 K against logarithm of the frequency are presented in Figures (5-7) for all groups, in which a sharp increase in ε` can be observed with an increase in the HAF constants beyond 20 phr. Moreover, ε` shows a very sharp increase (for EPDM loaded with CB > 30 phr) when the frequency is lower below 500 Hz. This behavior is mainly because at a relatively low frequency, there is always an increased contribution of interfacial polarization and $\sigma_{ac}$ toward a low factor.

Figures (8- 10) presents the variation of $\sigma_{ac}$ as a function of frequency for all three groups of HAF/ EPDM composites. It is evident from there figures that the ac conductivity $\sigma_{ac}$ (w) has a frequency dependence of the form:

$$s_{ac}(\omega)\,\alpha\,\omega^s \quad (5)$$

where the exponent *s* is seen to be a function of $\omega$. One determined the *s* value as a function of $\omega$ from the slope of the log $\sigma_{ac}$ ($\omega$) vs. log $\omega$ curve for various samples.

To obtain the *s* value, we fitted the log $\sigma_{ac}$ ($\omega$) vs. log $\omega$ data by a polynomial of the form:

$$\log\sigma_{ac}(\omega) = a + b\log(\omega) + c(\log(\omega))^2 \quad (6)$$

The slope at any $\omega$ was obtained from the equation:

$$s = \frac{d\log(\sigma_{ac})}{d\log(\omega)} \quad (7)$$

Using equations (6) and (7) we obtain

$$s = b + 2c\log(\omega) \quad (8)$$

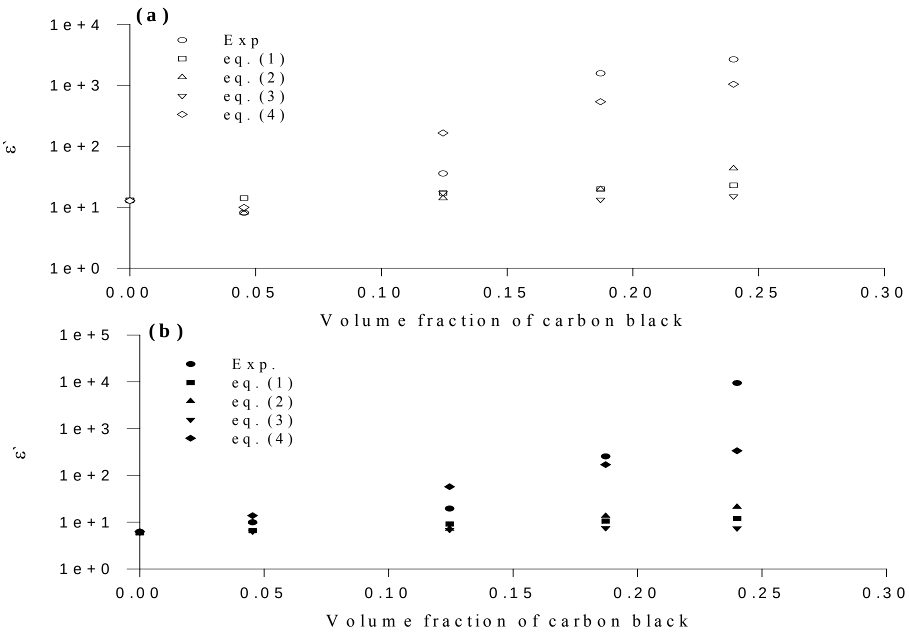


**Figure 4:** The dependence of dielectric permittivity (ε`) on volume fractin of filler for; (a) chemicaly vulcanized composites and (b) laser vulcanized composites.

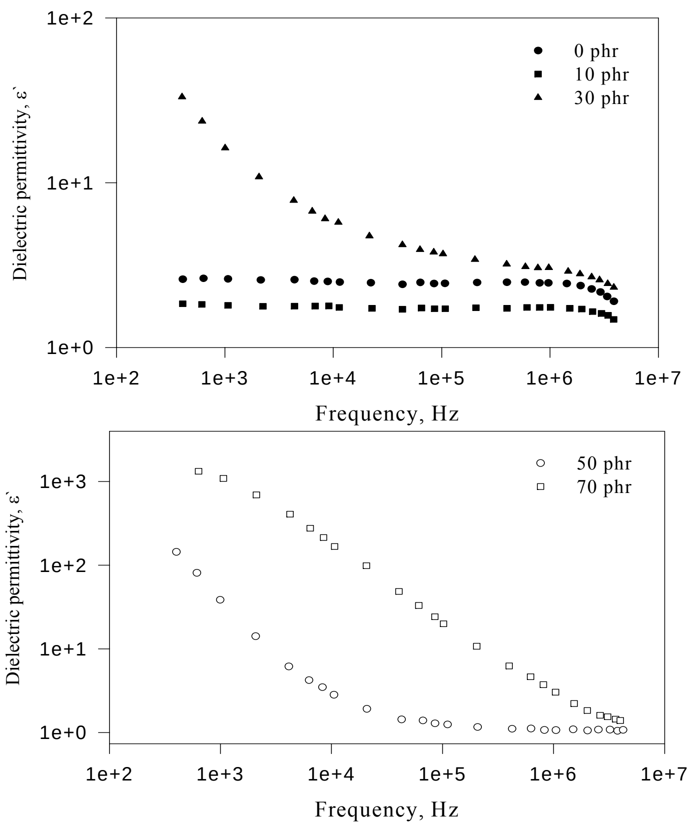


**Figure 5:** The frequency dependence of dielectric permittivity (ε`) for chemicaly vulcanized composites at 300 K.

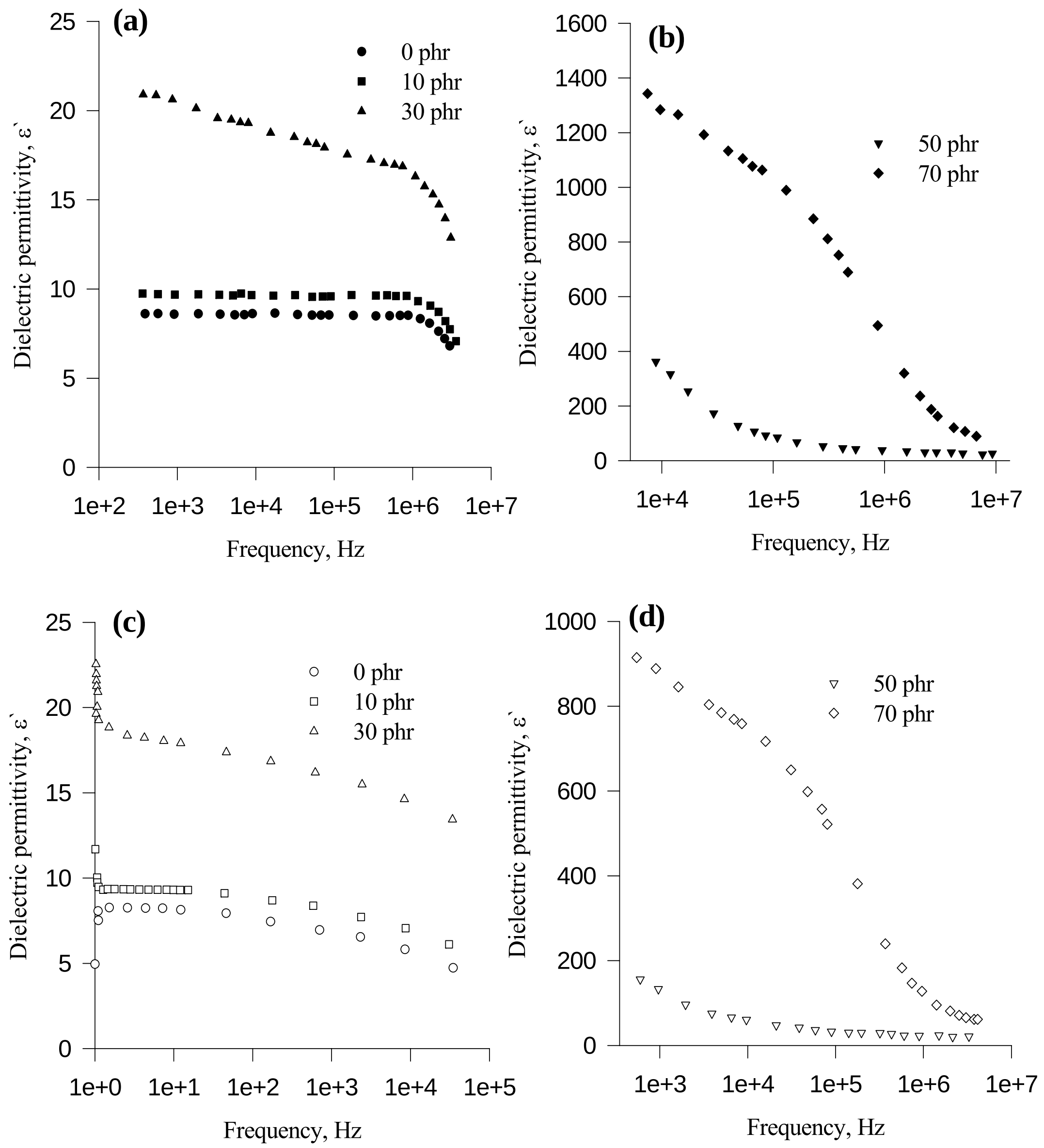


**Figure 6:** The frequency dependence of dielectric permittivity (ε`) for laser vulcanized composites at 300 K; (a, b): 50 kGy and (c, d): 70 kGy.

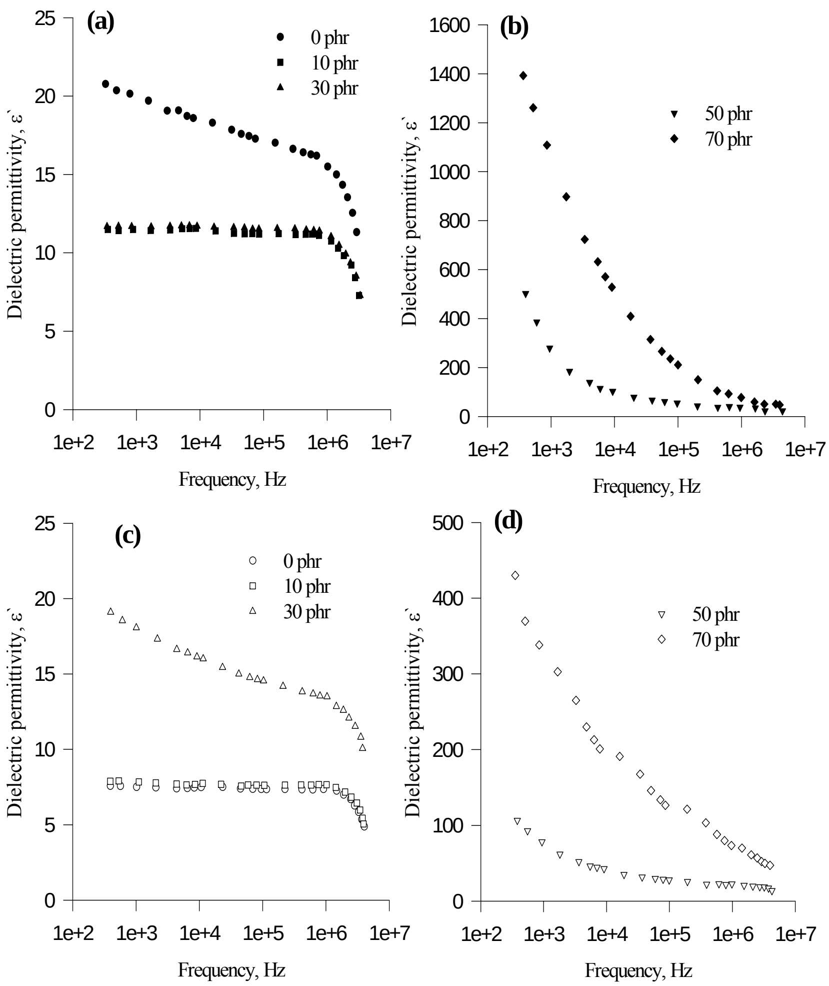


**Figure 7:** The frequency dependence of dielectric permittivity (ε`) for gamma vulcanized composites at 300 K; (a, b): 100 kGy and (c, d): 200 kGy.

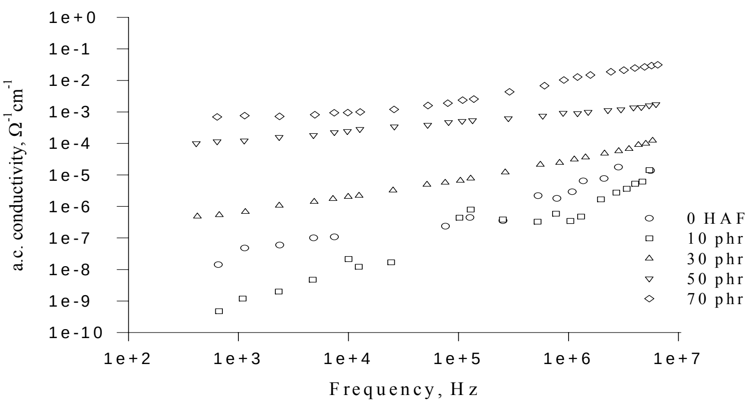


**Figure 8:** The frequency dependence of a.c. conductivity for chemically vulcanized composites at 300 K.

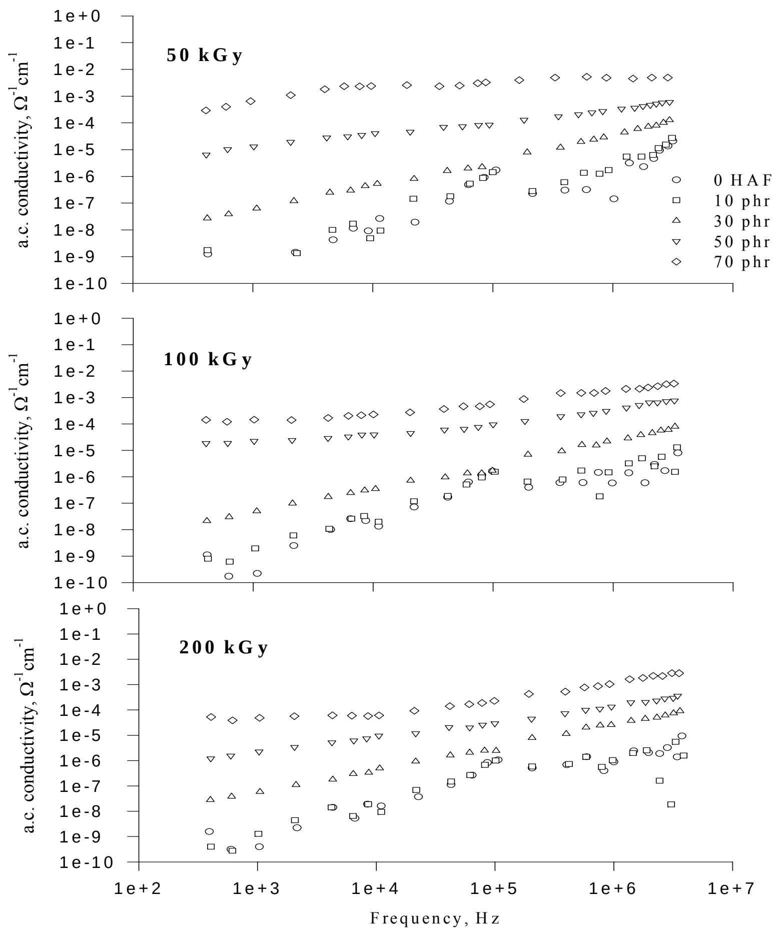


**Figure 9:** The frequency dependence of a.c. conductivity for gamma irradiation vulcanized composites at 300 K.

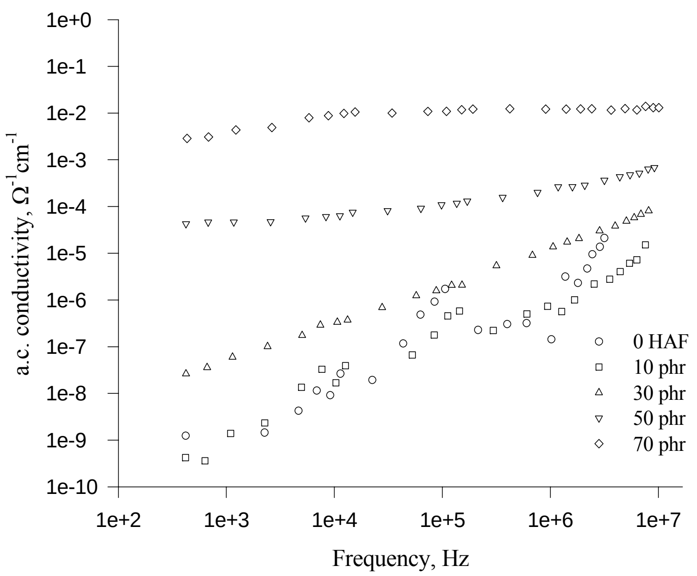


**Figure 10:** The frequency dependence of a.c. conductivity for laser irradiation vulcanized composites at 300 K.

Figure (11) shows a typical fitting of data, for EPDM loaded with 30 phr CB sample as an example which vulcanized by chemical method. The fitting parameters are indicated on the figure, the points represent the experimental data, and the solid line is the fitted curve. The parameter *s* were detected for all studied compositions and presented in Figures (12- 14) as a function of log $\omega$. It is evident from Figures (12- 14) that the fitting parameter *s* decreases as a function of frequency for samples loaded with HAF < 10 phr beside sample loaded with 70 phr of HAF and vulcanized by 5 Mrad – γ dose. This suggests that the variation follows the equation:

$$s = 1 - \frac{4}{\ln\left(\frac{1}{\omega t_0}\right)} \qquad (9)$$

where $t_0$ is the characteristic relaxation time and this equation describes the quantum mechanical tunneling (QMT) of electron through the barrier separating localized stated [20]. So, a QMT mechanism is operative in these samples.

For EPDM samples loaded with HAF > 10 phr (for all groups), Figures (12-14) show an increase in *s* as a function of *w*. This is consistent with the following equation, indicating the presence of a classical happing over the same barrier (correlated barrier happing CBH model proposed by pike) [21].

$$s = 1 - \frac{6\,KT}{w_M - KT\,\ln(\frac{1}{\omega t_0})^2} \qquad (10)$$

By substituting a value of $t_0 = 10^{-13}$ for unloaded EPDM, where $w_M$ is the maximum barrier height, K is the Boltzmann constant. The extracted values of $w_M$ and $t_0$ are summarized in table (2). These values for loaded EPDM samples (50, 70 phr) are consistent with those observed for amorphous semiconductor [22].

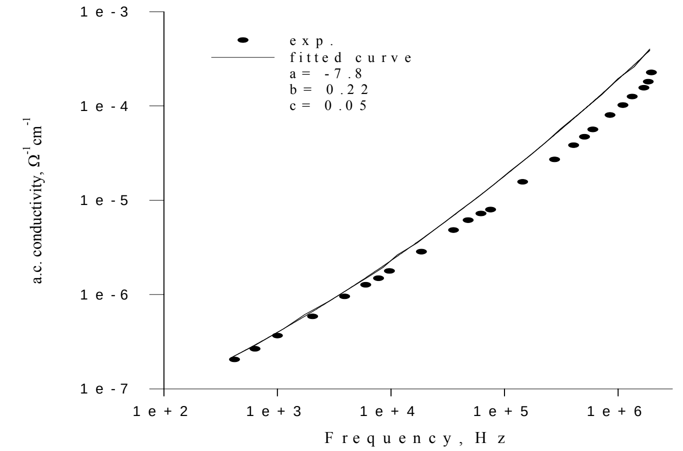


**Figure 11:** a.c. conductivity vs. frequency for rubber composite with 30 phr of carbon black. The solid lines are fits of Eqs. (6, 7 and 8).

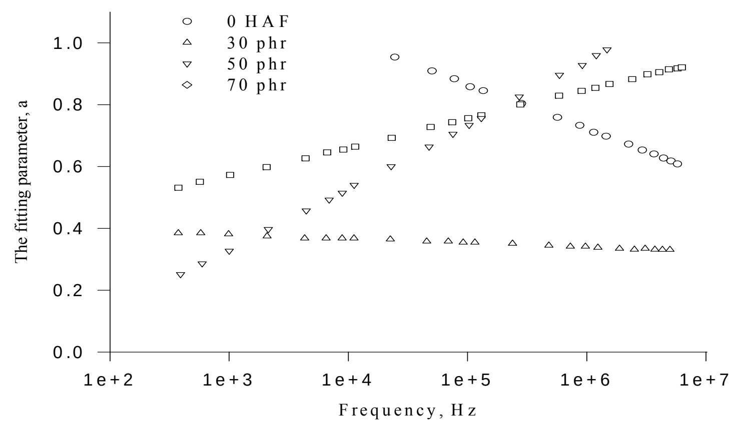


**Figure 12:** The dependence of the fitting parameter, *a*, on the frequency for chemically vulcanized composites.

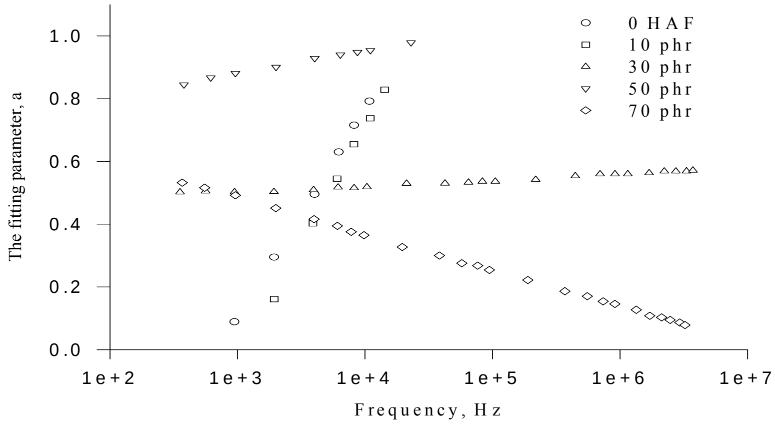


**Figure 13:** The dependence of the fitting parameter, *a*, on the frequency for gamma irradiation (50 kGy) vulcanized composites.

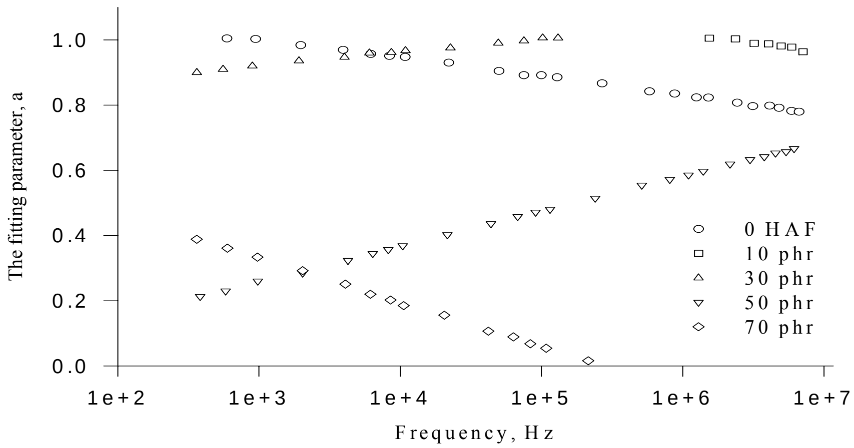


**Figure 14:** The dependence of the fitting parameter, *a*, on the frequency for laser vulcanized composites.

**Table (2):** The extracted values of $w_M$ and $t_0$ from equation (10).

| **Samples** | **$t_0$ (s)** | | | **$w_M$ (eV)** | | |
|---|---|---|---|---|---|---|
| **Chemical Vulcanization** | | | | | | |
| 0 | $3.03 \times 10^{-13}$ | | | - | | |
| 30 | - | | | 0.2 | | |
| 50 | $2.11 \times 10^{-11}$ | | | - | | |
| 70 | - | | | 0.1 | | |
| **Laser Irradiated** | | | | | | |
| 0 | $1.8 \times 10^{-13}$ | | | - | | |
| 30 | - | | | 1.55 | | |
| 50 | - | | | 0.04 | | |
| 70 | $3.8 \times 10^{-11}$ | | | - | | |
| **Gamma Irradiated** | | | | | | |
| | **5 Mard** | **10 Mard** | **20 Mard** | **5 Mard** | **10 Mard** | **20 Mard** |
| 0 | - | $2.7\text{x } 10^{-12}$ | $6.6\text{x } 10^{-11}$ | 0.35 | - | - |
| 10 | - | $1.1\text{x } 10^{-12}$ | $3\text{x } 10^{-11}$ | 0.32 | - | - |
| 30 | - | - | - | 1.77 | 0.96 | 1.24 |
| 50 | - | - | - | 0.5 | 0.1 | 0.53 |
| 70 | $1.3\text{x } 10^{-11}$ | - | - | - | 0.06 | 0.39 |

**5. Conclusions:**

Frequency dependence of dielectric constant ε` and ac conductivity $\sigma_{ac}$ of EPDM– HAF black composite with different HAF content has been studied in the frequency range 100 Hz– $10^5$ Hz and for different vulcanization methods. The experimental result indicates that ε` and $\sigma_{ac}$ increased with addition of HAF black in EPDM matrix.

A sharp increase in ε` is detected for EPDM loaded with HAF – black > 30 Phr. The percolation threshold is affected by the vulcanizing methods, where the samples vulcanized by 5 and 10 laser shots show minimum value for the percolation threshold. A modified empirical formula was successfully suggested to calculate the effective dielectric constant in terms of the dielectric constant of the constituent and the filler volume fraction.

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