Study of Dielectric Properties of Particulate Blends

S. ABD-EL GHANY,[1] M. H. ABD-EL SALAM,[2] G. M. NASR[3]

[1] Physics Department, Faculty of Science, Helwan University, Cairo, Egypt

[2] Physics Department, Faculty of Education, Ain Shams University, Egypt

[3] Physics Department, Faculty of Science, Cairo University, Cairo, Egypt

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ABSTRACT: The effect of the addition of high abrasion furnace (HAF) black on the dielectric properties of poly (ethylene-propylene-diene monomer) EPDM, polyethylene (PE) blend using both sulphur and peroxide vulcanizing systems was studied. It was observed that the increase in the permittivity is more pronounced with HAF black in the case of sulphur system than for the peroxide one. Many theories have been tested to calculate the effective permittivity of these particulate blends. The observed values of the permittivities are in close agreement with those calculated by Tsangaris's model, taking into account the variation of the aspect ratio (a/b) of the HAF black with the volume fraction of the HAF black in the matrix and type of the vulcanizing system.

Key words: particulate blends; polymer dielectrics; composites

INTRODUCTION

Electrical conductivity is important in many rubber and plastic compounds including antistatic applications and shielding against electromagnetic interference (EMI). Elastomers and plastics are insulators (dielectrics) to which conductivity is imparted by addition of a finely divided or colloidal filler of high intrinsic conductivity, such as carbon black. Over the years, a sizable body of information has developed regarding measurement of conductivity, and the factors, which affect it in such compounds or composites.[1,2]

Polymeric blends are well established in the field of high-temperature insulation due to their low cost, ease of availability, and their outstanding electrical, chemical, and high-temperature resistance properties. The electrical conduction properties of polymer-carbon black composites have been extensively reported, but only a small part of early works deal with ac conductivities.[3]

The effective permittivity and conductivity of a composite material composed of two or more components are dependent on the microgeometry of the components as well as on their permittivities and conductivities . Bergman and Dunn[4] and Milton[5] proved that the effective dielectric constants of a two-components composite material is a function of the ratio of the dielectric constants or conductivities of the components that can be described by a series of simple poles and residues, as was described by Liu and Wu.[6] The present work describes sulphur and peroxide cross-linked poly-(ethylene-propylene-diene monomer)/polyethylene (EPDM/PE)–high-abrasion furnace (HAF) black blends in relation to the behaviour of their dielectric properties as a function of both volume fraction of HAF black and frequency from 10^2 to 10^5 Hz. Experimental results show good agreement with the calculated values of the effective dielectric constants using different theories of heterogeneous dielectrics.

Correspondence to: S. Abd-El Ghani.

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EXPERIMENTAL PROCEDURE

Blends of EPDM, PE, and carbon black (HAF) containing two separate vulcanizing systems. These were sulphur and peroxide system (α, α'-bis(tetrabutyl peroxy)-m/p diisopropyl benzene mixed with calcium carbonate, having the trade name as (peroximon F40). The vulcanizing systems were compression molded at 153 ± 2°C and 40 Kg/cm^2 for 20 min. The conductive filler used was HAF. Carbon black concentrations in this work are always expressed by phr (part per hundred part of rubber by weight). The blend formulation—containing EPDM, 50 phr; PE, 50 phr; stearic acid, 1 phr; zinc oxide, 5 phr; processing oil, 20 phr; different concentrations of HAF black up to 70 phr—was vulcanized with sulphur system (2-mercapto benzthiozal [MBT], 0.7 phr; tetra methylthiuram disulphide [TMTD], 1 phr; sulphur, 1.5 phr). The second and third groups contained 4 phr peroxide and 10 phr peroxide, respectively, instead of sulphur system.

The dielectric properties were measured using a bridge (Type Philips PM 6304 programmable automatic RCL meter) in the frequency range of 10^2–10^5 Hz. The samples were in the form of discs 0.2 cm thick and 0.5 cm in radius.

RESULTS AND DISCUSSION

The frequency dependence of the dielectric permittivities for carbon-free samples vulcanized either by sulphur or peroxide system are presented in Figure 1. The dielectric permittivity shows a slightly increasing part, which is followed directly by a decreasing one, after a certain frequency. In the case of the 10 phr- peroxide vulcanizates, such frequency is lower than for either the 4 phr-peroxide vulcanizates or sulphur-vulcanizates.

Besides, the dielectric permittivity for the 10 phr-peroxide vulcanizates have the highest values. This can be ascribed to the different degrees and nature of vulcanization of PE in the presence of different vulcanizing systems. In fact, sulphur system is not able to enhance cross-links in PE, which can be easily cross-linked in the presence of peroxide.[7] The increase of the concentration of peroxide to 10 phr causes high content of cross-linking of (PE) compared with the 4-phr peroxide. Figure 2 represents the frequency dependence of the dielectric permittivity for EPDM/PE blends containing different concentrations of HAF carbon black and vulcanized either by sulphur or peroxide system.

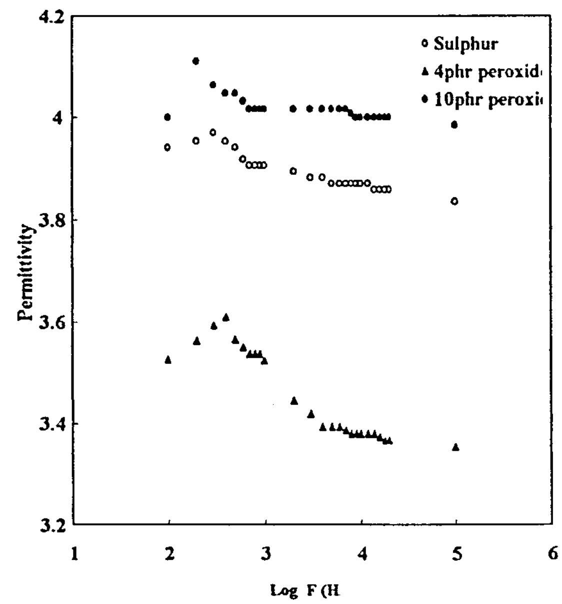

Figure 1 Frequency dependence of dielectric permittivity for carbon-free blends vulcanized either by sulphur or peroxide system.

The addition of carbon black clearly raises the dielectric permittivity. On the other hand, the dielectric permittivity gradually decreases as the frequency is increased. It is interesting that the dielectric permittivity for sulphur-vulcanized samples is higher than that of peroxide-vulcanized ones, probably because of the polar nature of the sulphur system.[5]

The dielectric permittivity of a composite dielectric containing more than one component may be expressed in the general form

$$F(\varepsilon_c') = \sum_i^m V_i F(\varepsilon_c') \qquad (1)$$

where $F(\varepsilon_c')$ is some function of the composite dielectric permittivity; V_i and ε_i are volume fraction* and dielectric permittivity for the ith component of the composite containing m number of components. For a two-component system, eq. (1) assumes the form

* The volume fraction has been derived from the weight fraction by simple calculation involving the densities of the constituents.

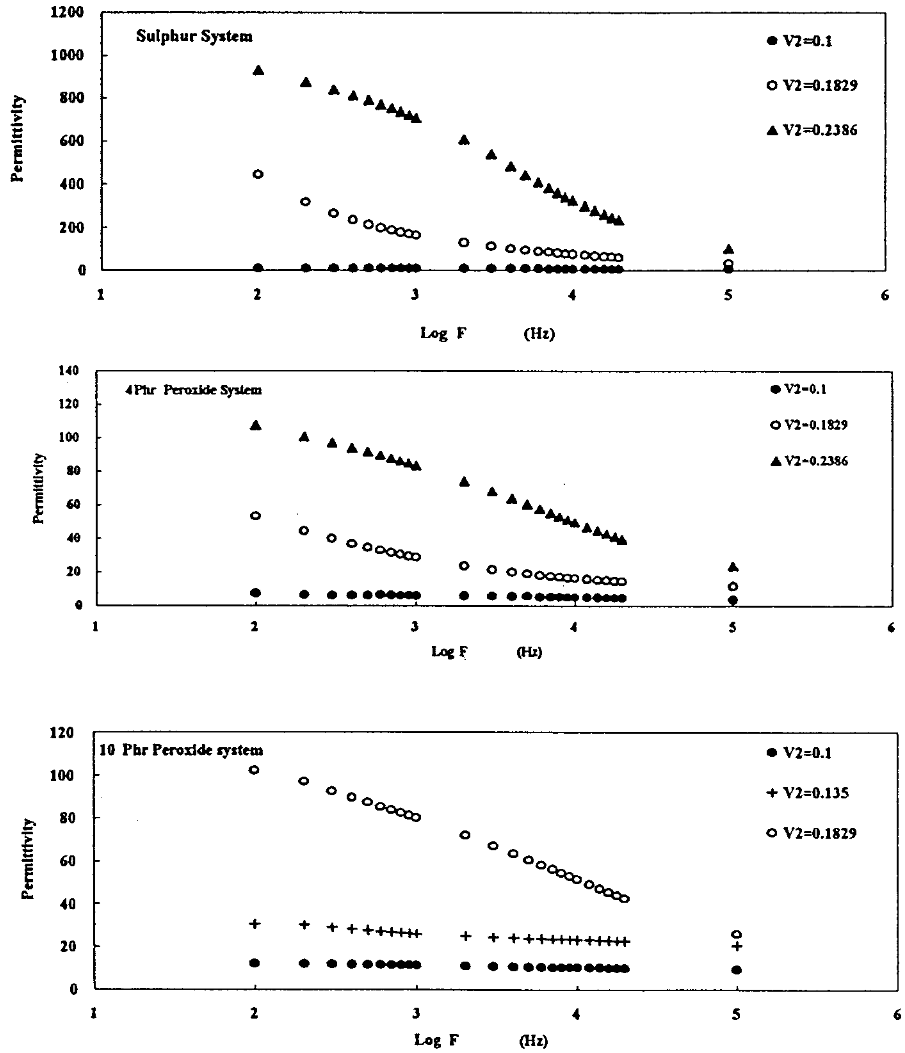

Figure 2 Frequency dependence of dielectric permittivity for blends containing different concentrations of HAF carbon black and vulcanized either by sulphur, 4 phr peroxide or 10 phr peroxide.

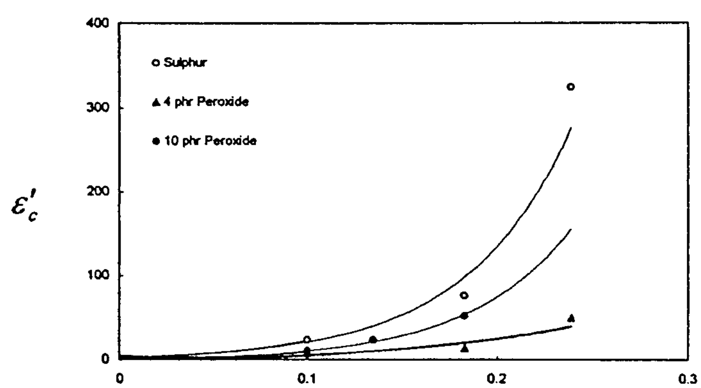

Figure 3 ε'_c vs. V_2, the volume fraction of carbon black, for both sulphur and peroxide systems.

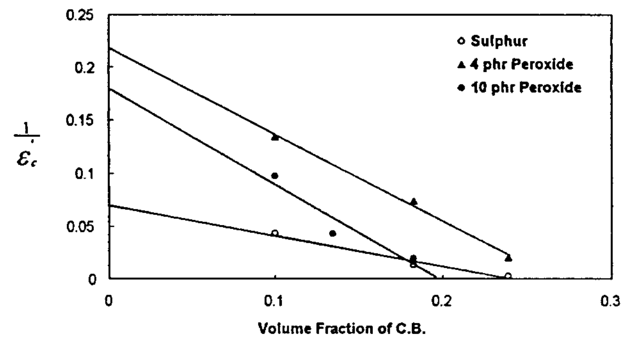

Figure 4 $1/\varepsilon_c'$ vs. V_2, the volume fraction of carbon black, for both sulphur and peroxide systems.

$$F(\varepsilon_c') = V_1\varepsilon_1' + \varepsilon_2'(1 - V_1) \quad (2)$$

where ε_1' and ε_1' are dielectric permittivities of components 1 and 2, respectively, and V_1 is the volume fraction of component 1.

Figures 3–5 illustrate the dielectric interaction pattern of mixed systems, with respect to composition. The dielectric permittivity ε_c' in these plots are those observed at a frequency of 10^4 Hz, where both dispersion and relaxation phenomena are most operative. The plot of ε_c' vs. V_2, the volume fraction of carbon black, for both sulphur and peroxide systems shows clear nonlinear (Fig. 3). However, plots of $1/\varepsilon_c'$ against V_2, which describes the law of harmonic mixture are linear, for both vulcanizing systems (Fig. 4). This would imply series combination of the blend constituents. Extrapolation of the plots to $V_2 = 0$ yields $1/\varepsilon_c' = 1/\varepsilon_1'$, where $1/\varepsilon_1'$ is the dielectric permittivity of vulcanized EPDM/PE blend without carbon black at f = 10^4 Hz. Graphically obtained ε_1' values for the sulphur vulcanizing system are in disagreement with the experimentally obtained values,

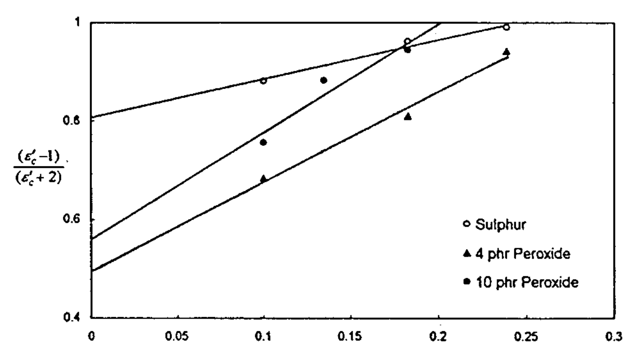

Figure 5 $[(\varepsilon_c' - 1)/(\varepsilon_c' + 2)]$ vs. V_2, the volume fraction of carbon black, for both sulphur and peroxide systems.

Table I Dielectric Permittivities of Vulcanized EPDM/PE Blend Without Carbon Black at $f = 10^4$ Hz

Values of ε_1'	Sulphur System	4 phr Peroxide	10 phr Peroxide
ε_1' observed	3.871	3.379	4.001
ε_1' calculated from Fig. 4	13.330	4.444	5.281

whereas a rough agreement is obtained in the case of peroxide system (Table I).

A trial was made to test the applicability of the Clausius–Mossotti equation for a mixture of dielectrics in the present systems. Slopes and intercepts obtained when the specific polarization $[(\varepsilon_c' - 1/(\varepsilon_c' + 2)]$ is plotted against V_2 (Fig. 5), are different for sulphur and peroxide rubber systems. The dielectric permittivity, ε_1' for vulcanized gum rubber can be theoretically obtained from the intercepts of these plots at $V_2 = 0$. The calculated values of the dielectric permittivities show some deviation from experimental ones.

On of the successful models is that due to Bruggman,[8] who considers spherical conductive inclusions. The Bruggman equation can be simplified by assuming that the permittivity of the conductive inclusions, tend to infinity, yielding eq. (3), which is often used, provided that the volume fraction of the inclusion is considerably less than unity ($V_2 \leq 1$).

$$\varepsilon_c' = \varepsilon_1'(1 + 3V_2) \quad (3)$$

Subscript (1) refers to the matrix and subscript (2) to the filler.

The calculated values of ε_c' for both vulcanizing systems are given in Table II. The disagreement between the calculated and the experimental values was observed.

In all the above formulae the dielectric permittivity is supposed to be independent of both the applied frequency and the components characteristics. This was taken care of by Tsangaris et al.,[9] who proposed a new model with suitable equations formulated to expressing dielectric permittivity ε_c' and dielectric loss ε_c' of a composite material as a function of the applied frequency and the component characteristics. These equations are as follows:

Table II Dielectric Permittivities of Vulcanized EPDM/PE Blend Loaded with Different Concentrations of Carbon Black, Calculated from Eq. (3) at $f = 10^4$ Hz

	Sulphur System			4 phr Peroxide			10 phr Peroxide		
V_2	0.10	0.18	0.24	0.10	0.18	0.24	0.10	0.14	0.18
ε' observed	7.91	75.80	324.2	5.2	16.47	49.71	10	23.33	51.64
ε' calculated	5.03	5.996	6.64	4.3	5.23	5.79	5.2	5.62	6.19

$$\varepsilon'_c = \frac{\varepsilon'_1}{[(\varepsilon'_1 - 1)^Y +]} \times \left\{ \left[\left(\frac{\sigma}{\omega \varepsilon_o} \right)^{V_2} (\varepsilon'_1 - 1)^{1-V_2} \cos \frac{\pi V_2}{2} \right]^Y + 1 \right\} \quad (4)$$

where Y is the depolarizing factor given by[10]

$$Y = \frac{1}{1 - (a/b)^2} - \frac{a/b}{[1 - (a/b)^2]^{3/2}} \cos^{-1} \frac{a}{b} \quad (5)$$

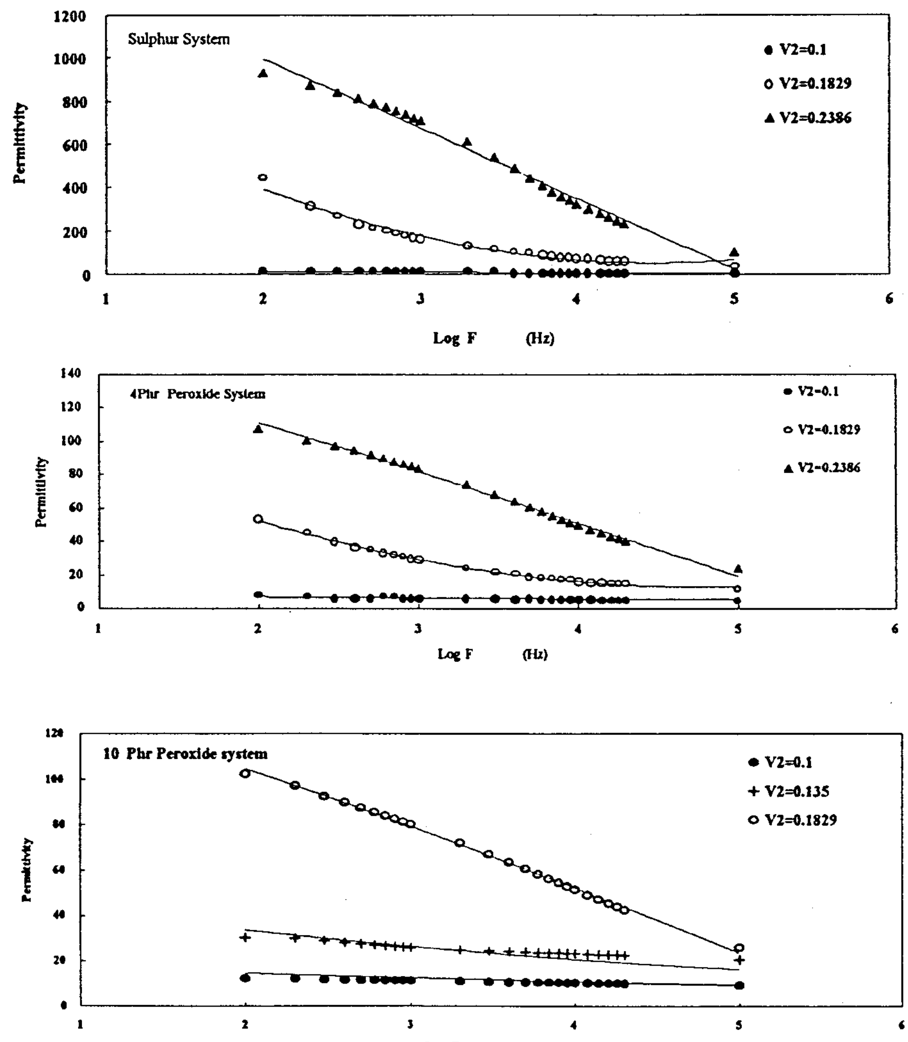

Figure 6 Frequency dependence of dielectric permittivity for blends containing different concentrations of HAF carboblack and vulcanized either by sulphur, 4 phr peroxide, or 10 phr peroxide; continuous lines represent values given by model, symbols represent experimental values.

Table III Values of the Aspect Ratio *a/b*, and the Depolarizing Factor (*Y*) That Makes Good Fitting of the Calculated Permittivities with the Experimental Ones

	Sulphur System			4 phr Peroxide			10 phr Peroxide		
V_2	0.10	0.18	0.24	0.10	0.18	0.24	0.10	0.14	0.18
a/b	0.47	0.03	0	0.73	0.27	0.23	0.25	0.15	0.08
Y	0.54	0.95	1	0.42	0.68	0.72	0.70	0.80	0.88

where ω is the frequency, σ is the conductivity of the filler, $\varepsilon_o$is the permittivity of free space, ε_1' is dielectric permittivity of the matrix, and a/b is the aspect ratio of the filler (a and b are the principal axes).

The shape of carbon black may be transformed from spherical to ellipsoidal or even to a long rod shape according to the volume fraction of carbon black within the matrix. The aspect ratio a/b of carbon black particles and thus the depolarizing factor (Y) are assumed to vary with the variation of the carbon black content within the matrix. Also, it is assumed that the aspect ratio depends upon the type of vulcanizing system used. Taking into account these assumptions, and knowing the conductivity $\sigma(\cong 10^2 \Omega^{-1} m^{-1})$[11] of HAF black, and the observed dielectric permittivities ε_1' of the unfilled blends for the different vulcanizing systems. The effective dielectric permittivities can be calculated using eq. (4). The obtained values at different frequencies for different vulcanizing systems and/or volume fraction of HAF black are shown by continuous lines in Figure 6, which are in agreement with the experimental points.

Values of the aspect ratio a/b, which were chosen to fit the calculated permittivities with the experimental ones, are tabulated in Table III. It is clear that values of the aspect ratio a/b depend on both of the volume fraction of carbon black and type of the vulcanizing system. Besides, the values of a/b for 10 phr peroxide vulcanizates are higher than those for the corresponding vulcanizates containing either 4 phr peroxide or sulphur systems. This due to the different nature of cross-linking from one system of vulcanization to another.

Figure 6 shows the expected decrease in ε_c' with increasing frequency, which occurs because the interfacial polarization that dominants in the low frequency region gradually, diminishes to zero at high frequencies.[12] It also shows an increase in ε_c' with HAF content, as the blend becomes more conductive.

CONCLUSION

We have studied the effect of addition of HAF black and two different vulcanizing systems, (a) sulphur system and (b) peroxide system, on the effective dielectric permittivity of vulcanized EPDM/PE blends. It has been observed that the dielectric permittivity increases by the addition of carbon black. This increase is in the sulphur system is more pronounced than for the peroxide system. This can be readily understood by taking into account the variation of the aspect ratio a/b of carbon black particles and thus the depolarizing factor (Y) with carbon black content and/or with the type of vulcanizing system used. The observed values of the dielectric permittivities are in close agreement with the calculated ones obtained by using Tsangaris's model.

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