The Dependence of the Dielectric Properties of Particulate Blend on the Step Crosslinking Process

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The dielectric properties of styrene butadiene rubber (SBR) loaded with fast extrusion furnace black (FEF) samples crosslinked with sulfur via step crosslinking process were studied. The measurements were performed in the frequency range from 10^2 to 10^5 Hz at room temperature, and macroscopic permittivity $\acute{\varepsilon}$ describing the dielectric properties of the samples was evaluated. Extension of logarithmic law of mixtures enables equations to be formulated which describe the dielectric behavior of particulate polymeric composite containing conductive particles. These equations give the dielectric constant and dielectric loss of the composite as a function of the dielectric constant of the polymeric matrix, the volume fraction and the aspect ratio of the inclusions, and the frequency of the applied field. Equations proposed by Tsangaris et al were tested and modified with the experimental data over a wide range of frequencies and the step crosslinking process. Satisfactory agreement was observed taking into account the variation of the aspect ratio with the volume fraction of the FEF black in the NR matrix and also with the partial time of vulcanization process.

1. Introduction:

The pace of research on dielectric properties of heterogeneous materials has accelerated in recent years. Industries such as the aerospace, electronics and others, have continuously provided the impetus pushing the development of new materials in a fascinating and rich variety of applications. Examples abound, ranging from shield enclosures to capacitive video disk to antistatic devices and electromagnetic absorbing materials [1-3]. The trend towards a wider variety of applications is almost certain to continue. At the same time, these materials hold general interest since they provide fundamental problems which are not completely answered, e.g. stochastic transport in disorder media [4] and metal-insulation transition[5].

The search for new materials having specific physical properties has been mainly empirical, because no exact theory is currently known that relates macroscopic properties of multiphase composites to their macroscopic properties. In fact, by now there is a rather extensive theoretical literature which is devoted to the analysis of the effective (average) dielectric permittivity of an inhomogeneous medium for different sample topologies [6-10].

The dielectric permittivity of composite materials consisting of a polymeric matrix and conductive or non-conductive fillers has been calculated by a variety of relationships that are valid for heterogeneous systems. They express the dielectric permittivity έ of the composite as a function of its components volume fractions and permittivities.

The calculation of permittivity of dielectric mixtures and the variety of proposed formulae have been reviewed by Reynolds and Hough [11], Van Beck[12], Boettcher and Bordewijk[13], Grosse and Graffe[14] Kraszewski.[13].

The size and shape of inclusions have not been considered in the above trials of the calculations of the permittivity of dielectric mixtures. Although experimental evidence [16] reflects the influence of these parameters on the dielectric permittivity values. Equations which take into account the inclusions characteristics, giving the dielectric permittivity and conductivity of a conductor loaded dielectric, have been proposed by Neelakanta[17].

Tsangaris et al [18] formulated suitable equations expressing the dielectric permittivity έ, and dielectric loss ε" of composite material in terms of the applied field frequency and the components characteristics as follows:

$$\varepsilon_{eff}^{\backslash} = \frac{\varepsilon_1^{\backslash}}{[(\varepsilon_1^{\backslash}-1)^y +1]}[[(\sigma/\omega\varepsilon_o)^{v_2}(\varepsilon_1^{\backslash}-1)^{1-v_2}\cos(\frac{\pi v_2}{2})]^y +1]...........................(1)$$

$$\varepsilon_{eff}^{\backslash\backslash} = \varepsilon_1^{\backslash}[[(\sigma/\omega\varepsilon_o)^{v_2-1}(\varepsilon_1^{\backslash}-1)^{1-v_2}\sin(\frac{\pi v_2}{2})]^y +1]..(2)$$

Where y is the depolarizing factor [19], which depends on the aspect ratio and orientation of the inclusions [20]. It is given by [21]:

$$y = \frac{1}{1-(\frac{a}{b})^2} - \frac{(\frac{a}{b})}{[1-(\frac{a}{b})^2]^{3/2}}\cos^{-1}(\frac{a}{b})..(3)$$

Where a/b is the aspect ratio of the inclusions, σ is the conductivity of conductive inclusions, V_2 its volume fraction, ω is the applied frequency, and ε_0 is the permittivity of free space.

The framework for development of rubber processes is set by the demands of customers for improved product performance and consistency, and by the unique nature of the industry in which the manufacturer often formulates a different rubber compound for each product. It is this in- house control of rubber compound composition which is, at the same time one of the industry's main strengths and one of its main problems. However, there is substantial scope for advances in the area of rubber processing. The most important effect of processing is to ensure scattering of the particles of filler through the rubber.

In the present work, the proposed equation of Tsangaris et al is tested on a carbon black loaded rubber composites and a comparison made between the experimental and theoretical values. Moreover, the effect of step crosslinking process on the dielectric properties of styrene butadiene rubber loaded with different concentration of FEF black will be discussed.

2. Experimental Work:

The styrene butadiene rubber used throughout the investigation was from a single batch so as to avoid variation due to colony differences, method of preparation, and so on. A series of FEF/SBR composites was prepared in accordance with the ASTM D15-62T schedule; the different compositions are listed in Table (1).

Table (1): Mix formulation of the SBR loaded with FEF carbon carbon black Samples

Ingredients(phr)	
SBR	100
FEF	0-60
Processing oil	10
Stearic acid	2
MBTS[a]	2
PBN[b]	1
Zinc Oxide	5
Sulfur	2

Mixing was done on a laboratory- size two roll mixing mill (320 x 150 mm) at a friction ratio of 1:1.25. The natural rubber was masticated under controlled conditions of temperature (35-40 C), time, and nip gap.

The compounding ingredients were then added. After compounding, the stock was left for 24 h., to nature before vulcanization. The elastomer sheets (NR with different FEF filler content) were partially crosslinked by heating for a time t_1 (0, 3 min., group A and B respectively) at vulcanization temperature of 150 C and at a pressure of 4.5 MPa. between two-platen electrically heated hydraulic press (type David Bridge).The protective films were then removed and the elastomer sheet were exposed to a 30 % biaxial extension using an equibiaxial stressing frame, the elastomer sheet were then subjected to further crosslinking for a time t_2 at the vulcanization temperature. The total time $(t_1 + t_2)$ was chosen from rheometer curve to give essentially complete crosslinking (30 min.).

The dielectric properties were measured using a bridge (type Hi-tester 8084) working from 40Hz up to 5 MHz and sensitivity of 10^{-4} pF) 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 radius.

3. Results and Discussions:

At the beginning of the vulcanization of rubber, the carbon black structure has been broken by the final milling process and may be further broken by the flow occurring in the mould. The heating causes some of the structure to re-form, thus decreasing the resistivity. There may also be some further reaction of the carbon black with the free radicals produced either by the milling process (due to their increased mobility at vulcanization temperatures) or by thermal decomposition of reactive groups. Any free radicals scavengers present may reduce these effects markedly. As a result of these factors it is possible that the biaxial strain of the vulcanizate during curing affects appreciably the dielectric properties of the sample.

3.1. Volume Fraction Dependence

As the difference between the conductivities of the host polymer (SBR rubber) and the filler (FEF black) is extremely great, very strong effect (known as Maxwell-Wagner-Sillars effect)[22] is expected due to the incompatibility between rubber (soft phase) and carbon black (hard phase) in such systems. Consequently, dielectric permittivity,ε', increases with the volume fractions of FEF carbon black as shown in Figures (1,2) for both groups (A, B) respectively. The increase in $\acute{\varepsilon}$ is more pronounced at higher volume fractions of carbon black and slightly affected by the step crosslinking process.
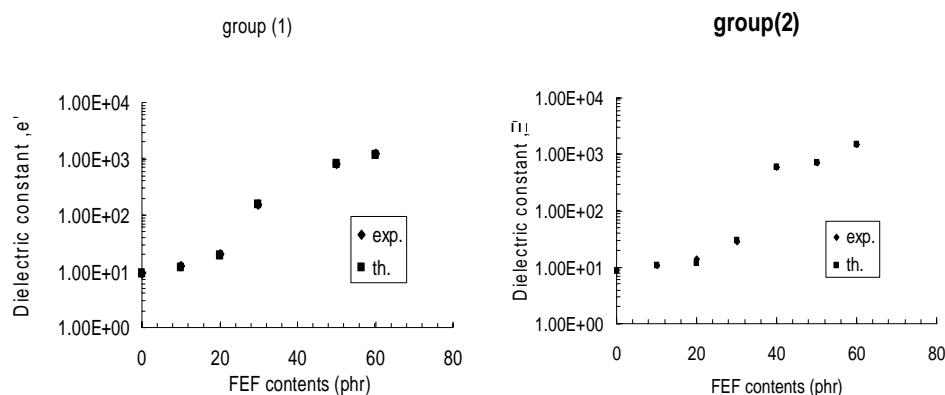
Fig.(1): Permittivity of composites versus weight fraction of HAF black at given frequency (1 KHz) for given temperature (30C): □ proposed Tsangaris et al model.
♦ experimental values.   (a) First group   (b) Second group

The application of Eqn. (1) to calculate έ at constant frequency (1kHz) is shown by solid lines in Figures (1, 2). There is an approach between theoretical model and experimental values of the dielectric permittivity for SBR composites at low volume fraction of FEF carbon black particles for both groups (A, B). The depolarizing factor (y) for low FEF concentrations (<0.12) is substituted with a value that approximately indicates a spherical FEF inclusions (a/b ≈ 1) for both group A , B. Meanwhile, for higher FEF volume fractions, the depolarizing factor (y) increases with FEF contents which indicates that the carbon particles or aggregates takes the shapes of oblate ellipsoids with the minor axes (a) parallel to the applied frequency and this variation is more detected in group B . For more FEF contents (y) belongs to unity (as shown in Table 2), that is related to long rods perpendicular to the field .

Table (2): Represents the dependence of the depolarizing factor (y) on the FEF content for both group A and B (at 1000 Hz).

FEF volume fraction	y (Group A)	y (Group B)
0.044	0.5	0.4
0.085	0.5	0.4
0.122	0.5	0.5
0.156	1.37	1.37
0.188	1.25	0.25
0.217	0.9	0.9

FEF 10 phr

FEF 20 phr

FEF 30 phr

FEF 40 phr

FEF 50 phr

FEF 60 phr
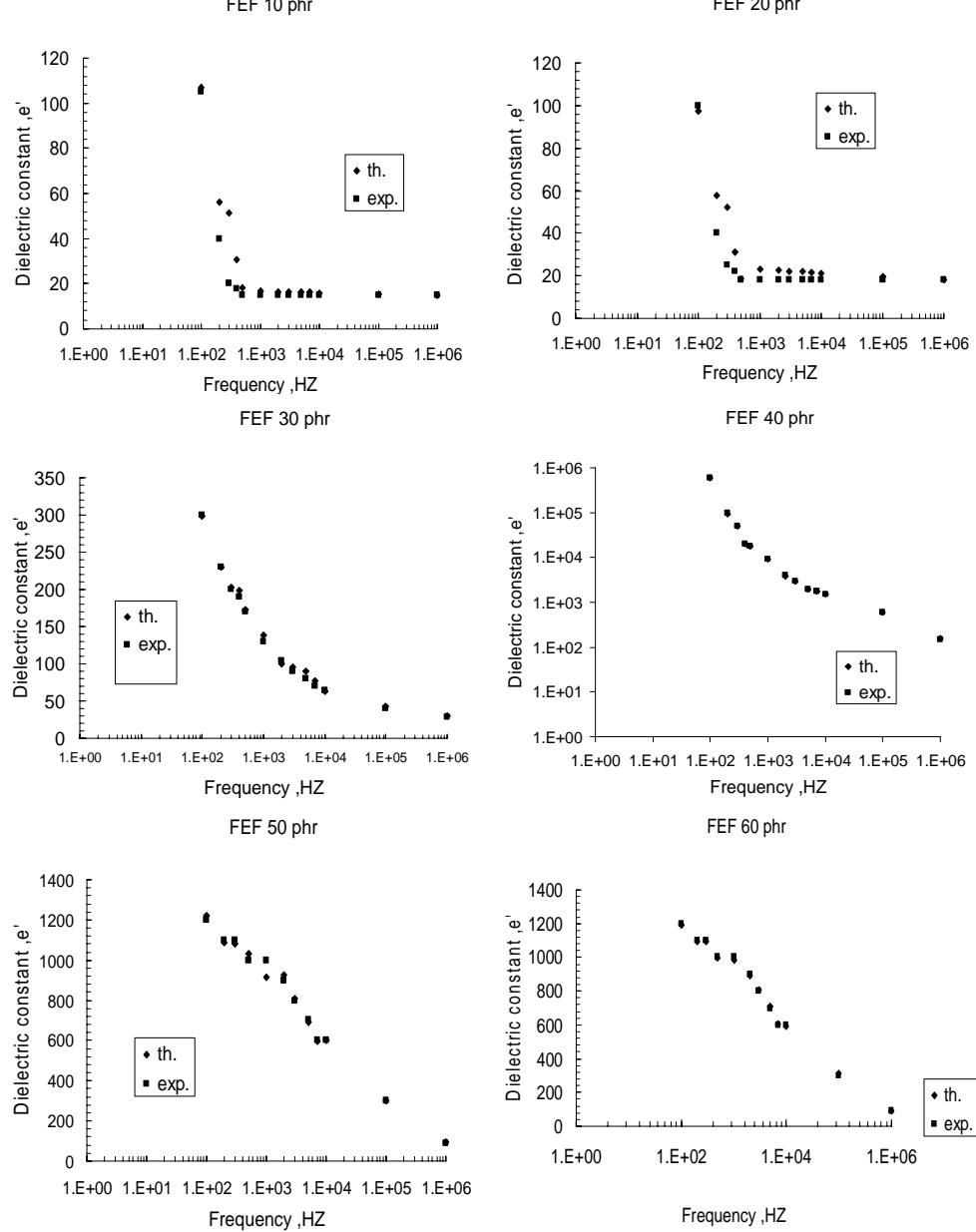
Fig.(2): Permittivity versus frequency of composites with given weight fraction of HAF black at given temperature (30C):

♦ Theoretical model

□ Experimental values Represent experimental values (for first group)

a: weight fraction 10 phr   b: weight fraction 20 phr

c: weight fraction 30 phr   d: weight fraction 40 phr

 e: weight fraction 50 phr   f: weight fraction 60 phr

3.2. Frequency Dependence:

The application of equation (1) which gives the dielectric permittivity of the composites as a function of frequency for various volume fractions of FEF carbon black and for the two groups (A, B) is shown in Figures (3, 4) , together with experimental values at room temperature (30 C). The proposed model by Tsangaris et al approaches the experimental values more closely, for a low FEF volume fraction (for both groups). It shows the expected decrease in $\acute{\epsilon}$ with increasing frequency, which occurs as the interfacial polarization which dominates in the low frequency region (23, 24) gradually diminishes to zero at high frequencies. It also shows an increase in the dielectric permittivity (for both groups) with FEF contents as the composites becomes more conductive. The deviation from experimental values, especially for higher FEF loading ($\geq$ 40 phr) is attributed to the intrinsic weakness of the logarithmic law of mixtures on which Tsangaris et al model is based. However, these discrepancies may be due also to the dependence of the depolarizing factor (y) on the frequencies that was not taking into account by the author.

Table (3): Represents the dependence of the depolarizing factor (y) on the FEF content for both group A and B at different frequencies.

Frequency (Hz)	y (30 phr) Group A	y (60 phr) Group A	y (30 phr) Group B	y (60 phr) Group B
100	0.7	0.76	0.37	0.94
200	0.65	0.655	0.4	1.095
300	0.65	0.825	----	----
400	-----	----	0.45	0.9
500	1.0	1.04	----	----
600	----	----	0.55	0.9
1000	1.1	1.16	0.5	0.9
2000	1.0	1.18	0.55	0.9
3000	1.0	1.18	0.55	0.9
5000	1.0	1.18	----	----
7000	0.95	1.16	----	----
10000	0.87	1.18	0.65	0.9
1E+05	0.8	1.16	0.73	0.9
1E+06	0.7	0.9	0.85	1
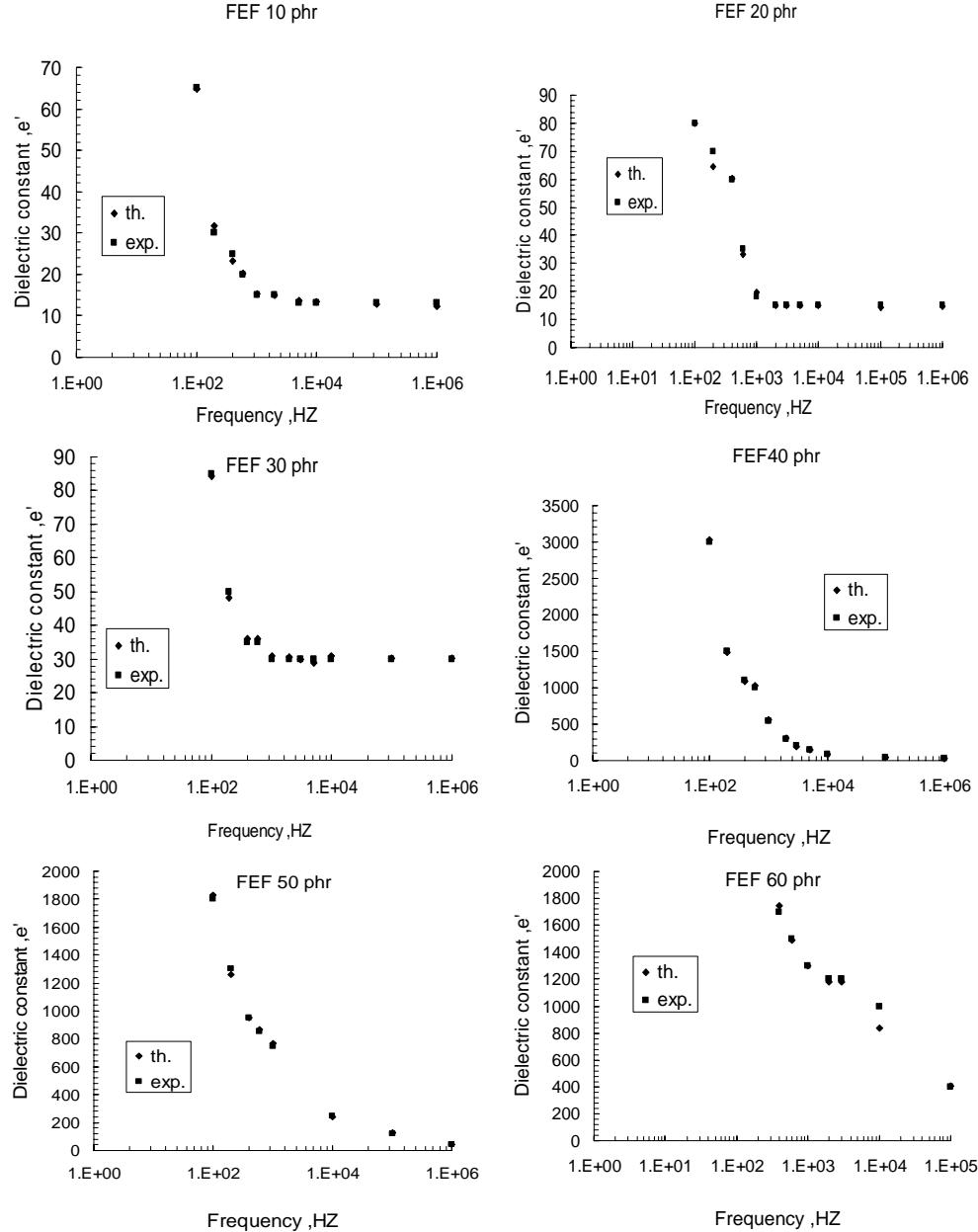
Fig. (3): Permittivity versus frequency of composites with given weight fraction of HAF black at given temperature (30C):

♦ Theoretical model

□ Experimental values Represent experimental values (for second group)

a: weight fraction 10 phr   b: weight fraction 20 phr

c: weight fraction 30 phr   d: weight fraction 40 phr

e: weight fraction 50 phr   f: weight fraction 60 phr

The shape of carbon black particles may be transformed from spherical to ellipsoidal or even to a long rod shape according to the volume fraction and the step crosslinking process of the rubber matrix (as clearly detected from Table 2). Also, it is assumed that the depolarizing factor (y) depends upon the applied frequencies and temperature. Taking into account these assumptions, values of (y) were chosen to fit the calculated permittivity with the experimental ones and tabulated (for 30 and 60 phr samples) in (Table 3). It is clear from Figures (5,6) that values of the aspect ratio and the depolarizing factor depend on the applied frequency for high FEF contents and the theoretical value of ε' is in a good agreement with the experimental values for both group A and B. Moreover, the step crosslinking process increases the depolarizing factor (y) reflex the rod like shape of the FEF black particles.

4. Conclusions:

We have studied the effect of both the step crosslinking process and the addition of FEF black on the effective dielectric permittivity of vulcanized SBR samples. It has been observed that the dielectric permittivity increases by the addition of FEF black and this behavior is more pronounced by the step crosslinking process. This can be readily understood by taking into account the variation of the aspect ratio (a/b) of the carbon black particles and thus the depolarizing factor (y) with carbon black contents and/or step crosslinking process. The observed values of the dielectric permittivity are in close agreement with the calculated ones obtained by using Tsangaris's model.

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