Preparation and Dielectric Properties of Bulk and Membrane Composites of Extra Fine Graphite Loaded Natural Rubber

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Abstract—**Composites of natural rubber (NR) loaded with micro–sized graphite using two different preparation methods; in bulk and membrane forms. The dielectric properties were studied in the frequency range 100 Hz - 200 kHz. dielectric constant and the AC conductivity were found to be described by the well-known percolation theory. The percolation threshold for both types of samples was found to be around 0.25. A deviation in the value of the percolation exponent form the universal value was found. Also, the conduction mechanisms operating in the composite were determined.**

Keywords—Dielectric properties, NR, Graphite, Percolation

*Introduction—*In this era of nanocomposites, much interests have been directed to the study of carbon based conducting polymer composites (CPC) mostly carbon nanotubes (CNTs) and to a certain limited extent graphite. However, using CNTs in nanocomposites is subjected to many difficulties such as processing, dispersion within the composite and mainly its high cost. For this reason, graphite is considered the favorable filler for tailoring a CPC with specific properties. Also, graphite-based CPC have a variety of applications such as sensors and energy storage systems [1-5].

However, incorporating graphite into CPC may requires a high loading level which may lead to composite redundancy and/or detrimental mechanical properties [1, 6, 7]. Several attempts have been devoted to reducing the percolation threshold for a variety of CPC as follows. Celzard *et al* [8], reported that epoxy/expanded graphite (EG) composites with a percolation threshold of 1.3 vol. % was attained. Also, several groups reported PMMA/EG, PS/G, nylon 6/exfoliated graphite, PS/PMMA/EG with low threshold values [9–14]. Tchmutin and coworkers [15] and Du *et al* [16] also researched the conductivity of PANI/ graphite composites, but the graphite was

natural expandable graphite, and the size was at micrometer and millimeter scales. Recently, Nano graphite was used to prepare PS/Nano G [17] and PMMA/Nano G [18] composites with very low values of percolation threshold, about 1.6 and 1.5 vol%, respectively.

The aim of the present work is to study the influence of the preparation method and the dimensions of the composites on the dielectric properties of NR loaded with micro-sized graphite.

Experimental work

Materials and Preparation

Table (1) shows the formulation used in this work. NR was supplied by TRENCO, Alexandria, Egypt, while fine powder extra pure graphite (50 μm) was supplied by Merck, Germany and both were used as received. Graphite properties are: Solubility (20 °C) insoluble; Molar mass 12.01 g/mol; Density 2.2 g/cm^3 (20 °C); pH value 5 - 6 (50 g/l, H_2O, 20 °C).

Table l Formulation of the rubber compounds

Ingredients		Quantity(phr[a])
Rubber	NR	100
Filler	Graphite	0,10,20,30,40,50,60,80,100
Plasticizer	Processing oil	10
Activators	Stearic acid	1.5
	Zinc oxide	5
Accelerator	MBTS[b]	1.5
Age resisters	PBN[c]	1
Vulcanizing Agents	Sulfur	2

Graphite content in each sample was calculated in phr as shown in table (1) then the true volume fraction of graphite was calculated using the formula

$$\varphi_{\text{true graphite}} = \frac{w_{\text{true graphite}} / \rho_{\text{true graphite}}}{\sum_i w_i / \rho_i} \qquad (1)$$

Where w_i and ρ_i are the weight fraction and the density of the ith phase, respectively.

Ingredients of the rubber composites were mixed using a 2-roll mill (mill specs were: 7 cm in diameter, working distance 30 cm, speed of slow roll being 24 rpm and gear ratio 1.4). The compounded rubber was divided into two parts. The first part was left for 24 hours before vulcanization that was performed at $153 \pm 2^{\circ}$C under a pressure of 150 bar for 15 minutes. By this way, bulk samples were prepared with average thickness 0.3 cm. The second part was dissolved in methylbenzene, which results in a highly concentrated solution and a homogeneous solution resulted after continuous stirring for 30 min. Next, the mixture was placed in a stainless-steel dish (of diameter 7 cm) and allowed to dry slowly that eventually resulted in a smooth and uniform thin membrane composite about 0.7 mm thick. Next, the resulting membrane samples were vulcanized under a pressure of 294 bar, at temperature of 153°C, for 30 minutes. The final membranes have average thickness 0.2 mm. Finally, all samples were aged at 70 $^{\circ}$C for 10 days to ensure stability of formation and the reproducibility of results.
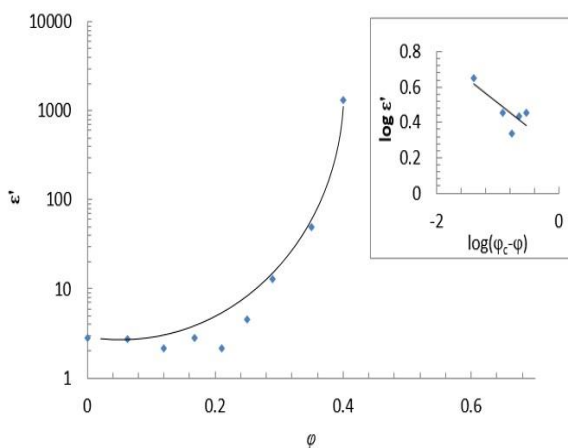
Measurements and Calculations

In general, the complex dielectric constant $\varepsilon^*(\omega)$ of CPC is frequency dependent and may be written as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\,\varepsilon''(\omega) \qquad (2)$$

Where the real part $\varepsilon'(\omega)$ represents the dielectric constant, and is calculated from

$$\varepsilon' = \frac{d}{\varepsilon_\circ A} C \qquad (3)$$

Where C is the measured capacitance, d and A are, thickness and the cross-sectional area of the sample respectively and $\varepsilon_o = 8.85 \times 10^{12}$ F/m , represents the permittivity of free space. In eq. (2), the imaginary part $\varepsilon''(\omega)$ accounts for the dielectric loss. The ratio $(\varepsilon'' / \varepsilon')$ is the "dissipation factor" which is denoted by $D = \tan \delta$. The dielectric loss ε'' was calculated using

$$\varepsilon'' = \varepsilon' \tan \delta = \varepsilon' D \qquad (4)$$

Where δ is called as the "loss angle" denoting the angle between the voltage and the charging current. Also, the AC conductivity was found from

$$\sigma_{AC} = \omega\,\varepsilon_\circ\,\varepsilon'' \qquad (5)$$

The dielectric properties were measured using a bridge with computer interface (type GM Instek LCR – 821 meter) in the frequency range 100 Hz-200 kHz.
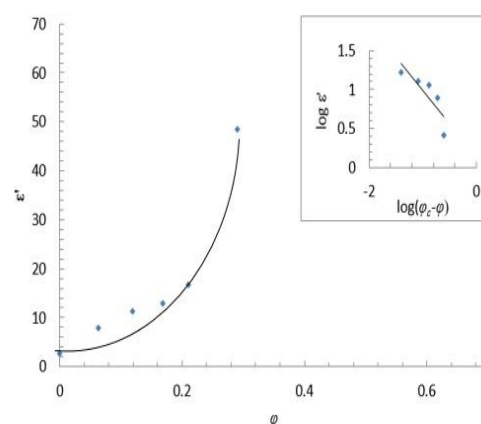

Figure 1 shows ε' vs φ of the bulk composites at 100 kHz

Figure 2 ε' vs φ of the membrane composites at 100 kHz

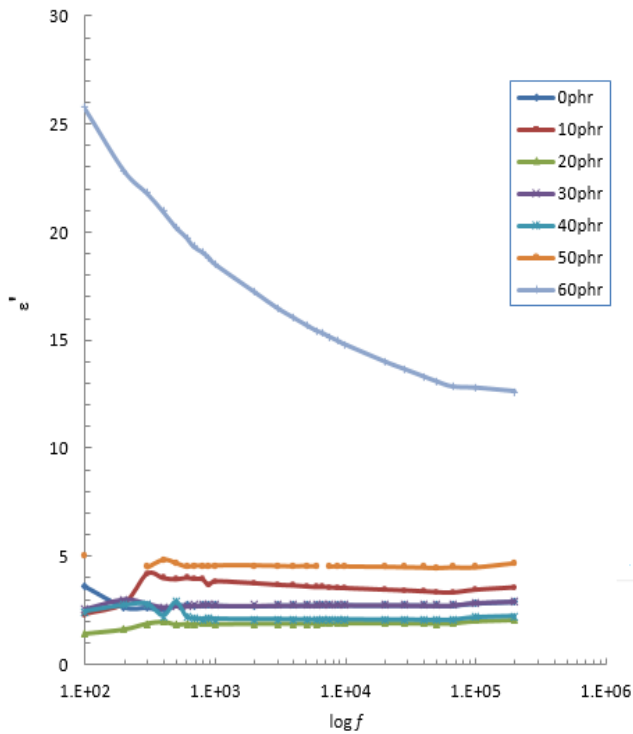**Figure 3** Frequency dependence of ε' of bulk composites

Figure 4 Frequency dependence of ε' of membrane composites

To ensure that Ohmic contacts exist at the electrodes, silver paste was used to paint the contact surface of each sample and allowed to dry fully before taking any measurements. A simple circuit was use for such measurements that consisted of a non-inductive hollow cylindrical oven in which a two - terminals sample holder was placed. The temperature of the oven was controlled manually through a variac and digital thermocouple.

Results and Discussion

Graphite content dependence

Figures (1-2) show the dependence of ε' on the loading level of graphite φ at a frequency 100 Hz and a temperature 27 C for both bulk and membrane forms respectively. Obviously, ε' increases gradually with φ up to the value $\varphi_c \approx 0.21$ for both composites, which is the percolation threshold for such composites. Above this value, ε' increases abruptly with a small increase in the filler loading. However, to explain this behavior, we notice that, for the region of small filler loading, ε' is the same as that of the insulating phase (NR) and the there is almost no apparent effect of the filler. But the percolation concentration $\varphi_c \approx 0.21$ is approached, a buildup of
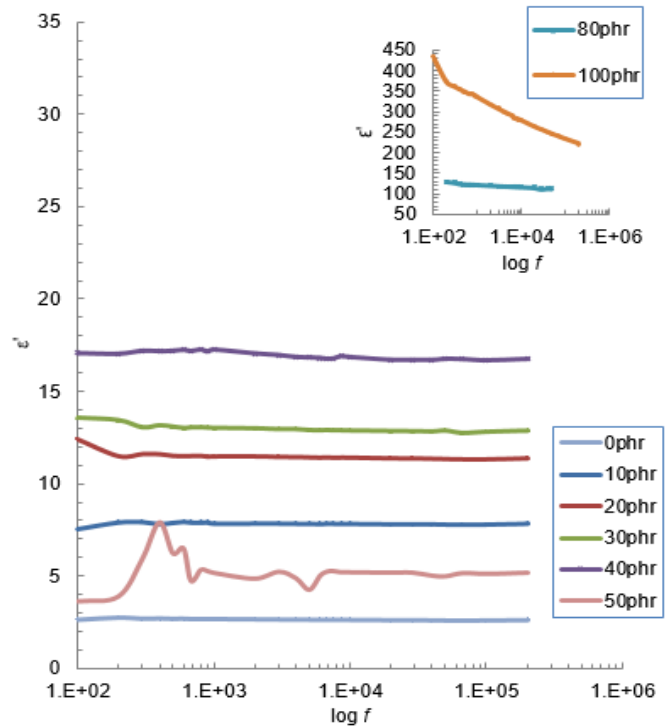
the charge carriers contributed by the added conducting phase (graphite) at the interface separating the phases increases the overall capacitance and the dielectric constant will increase also [19]. This process is known as Maxwell- Wagner polarization which originates in heterogeneous systems due to the incompatibility and the huge difference in the conductivities of the chemical species constituting the composites [20].

A trial was made to fit the experimental data using the universal power law [21-22] about φ_c, which could be written as
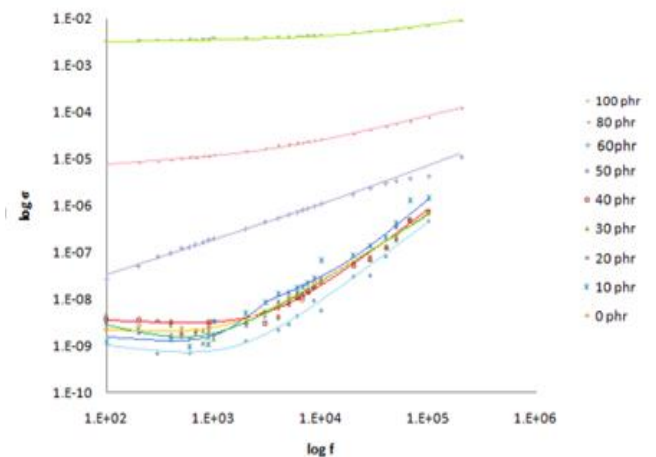

Figure 5 Frequency dependence of σ_{ac} of the bulk composites

$$\varepsilon' \propto (\varphi_c - \varphi)^{-k} \qquad (6)$$

Where k is a critical exponent. The insets of the Fig.(1-2) show the log-log plot of Eq. (3) the linear fitting of this plots gives the values $\varphi_c \approx 0.25$ for both and $k = 0.27$ and 0.84 for bulk and membrane forms respectively. However, these values differ significantly from those predicted by the percolation theory [23]. However, similar deviations from the universal value of k (~ 2) were reported earlier [24-27]. However, these deviations could be attributed to two reasons. The first is that, the theory didn't take the interaction between filler particles and the host matrix into account [24-25], while the second is that, if tunneling mechanism is possible as a conduction mechanism, non-universal values of k could be obtained [26-27].

Frequency dependence of ε'

Figures (3-4) show the frequency dependence of ε' for all composites at 30 C. For composites loaded with $\varphi < \varphi_c$, ε' exhibit a weak frequency dependence in the entire frequency range. However, when $\varphi \geq \varphi_c$, ε' shows a strong dependence on the frequency that could be attributed to the high leakage current resulting from the highly conductive filler. Also, for those composites at low frequency, ε' has a high value and decreases with the increase of the frequency of the applied field which could be explained simply as the frequency of the applied field is small, the polarization could follow well the applied field and the contribution to ε' is
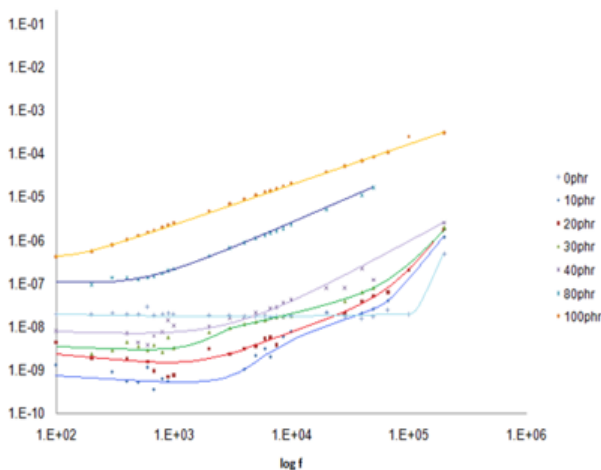

Figure 6 Frequency dependence of σ_{ac} of membrane composites
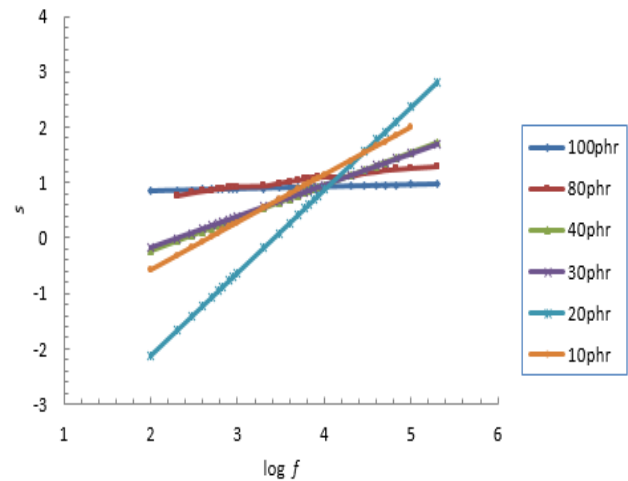

Figure 7 Variation of s as a function of log f for bulk composites

maximum and the dielectric loss is minimum but when the frequency increases the polarization loses its ability to follow the field and field leads the polarization by a certain phase angle that will cause an increase in the dielectric loss and decreases its contribution to ε' [28].

Frequency dependence of σ_{AC}

The frequency dependence of the AC electrical conductivity σ_{AC} at 30 C for both bulk and membrane composites are shown in Fig. (5-6). Obviously, the log σ_{AC} - log ω for all composites consists in general of two regions; a frequency independent plateau up to a certain critical frequency above which the conductivity shows a strong dependence on the frequency. The value of the critical frequency increases with the concentration of the filler.

However. If the DC conductivity is small enough to be neglected, the AC conductivity could be represented well by the universal power law [29]

$$\sigma_{AC} = A \omega^s \qquad (7)$$

Where A is a temperature dependent constant, and s (≤ 1) is known as the frequency exponent and it is frequency – dependent. The value of s could be determined from the slope of log σ_{ac} (ω) - log (ω) at different frequencies for various samples [30] and this is shown in Fig. (7-8) for all composites.
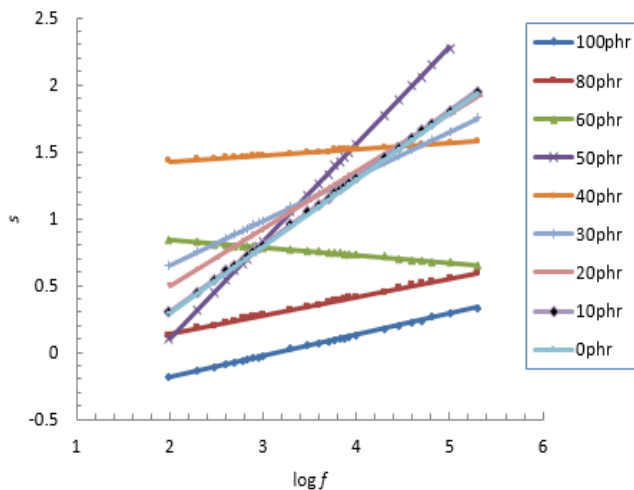
Figure 8 Variation of s as a function of log f for membrane composites

In composite materials, there are mainly two conduction mechanisms that could take place. The first is the correlated barrier hopping (CBH) mechanism [21, 31, and 34]. In this model, the conductivity was found to be temperature independent while the frequency exponent s was found to increase with the frequency according to the equation

$$s = 1 + \frac{6\,k\,T}{\left[W_m - k\,T \ \ln\left(\dfrac{1}{\omega\,\tau_0} \right) \right]} \qquad (8)$$

Where W_m is maximum barrier height and τ_0 is the characteristic relaxation time for the composite. The second is the quantum mechanical tunneling (QMT) mechanism [15, 32] in which the AC conductivity changes linearly with temperature, while s was found from

$$s = 1 + \frac{4}{\ln\left(\dfrac{1}{\omega\tau_0} \right)} \qquad (9)$$

Obviously, s decreases with the frequency.

From Figures (7-8) it is evident that only the composite loaded with 60 phr in the bulk form exhibits a decrease in the value of s with the frequency indicating that QMT is operative in this composite while all other composite show that CBH is the one that dominates within it.

Conclusion

Incorporating graphite as a reinforcing filler within a polymer matrix didn't alter the percolation threshold for the membrane composite than the bulk one, but the dielectric constant of the membrane composite is lower by several orders of magnitude than the bulk composite. Also, the AC conductivity and the conduction was found to be affected slightly by the preparation method and the dimensions of the final composite.

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