Electrical permittivity and conductivity of carbon black-polyvinyl chloride composites

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Electrical conductivity and permittivity of carbon black-polyvinyl chloride composites were studied over a wide frequency spectrum (dc, 1.3 GHz). Conductivity of the bulk composites increases with higher volume fraction of carbon black as expected. However, the functional dependence of the increasing conductivity with carbon black loading is different below and above the percolation threshold because of the different mechanisms involved. Bulk electric permittivity increases until the composite percolation is reached and then decreases to zero after fully connected conductive paths have been established. Such highly loaded composites showed a metal-like electrical behavior. Different electrical percolation threshold of the composites were found for different species of carbon black. Carbon blacks with the lowest packing efficiency reach the percolation threshold with the least volume fraction of carbon black loading. The percolation behavior of spherical carbon blacks showed good agreement with Bruggeman's effective-medium theory in terms of both the percolation threshold and frequency dependence of conductivity at percolation.

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I. INTRODUCTION

The electrical properties of conductor-insulator composite systems have been a subject of both theoretical and experimental interests for a long time. For the theoretical aspects of such systems, readers are referred to the summary by Landauer.[1] Many experimental studies on such systems were brought about by the increasing use of these materials in electromagnetic shielding applications.[2–5]

Polymer-carbon black composites, such as rubber-carbon black, is one of the most extensively studied systems because of its wide spread use in the automotive industry.[6] However, most of these studies were mainly focused on the mechanical aspects of the composites. Carbon black-thermoplastic composite systems are relatively new. Fox has reported conductivity of a carbon black-polyvinyl chloride (PVC) composite as a function of weight percent loading[7] and Sheng, Sichel, Gittleman, and coworkers[8] have investigated the dc resistivity of similar carbon black-PVC systems in the low temperature regime and discussed their conduction mechanism. Kawamoto *et al.* reported some ac-resistivity measurements which can be found in a recent review by Sichel *et al.*[9]

In this report, we will analyze the electrical conductivity and permittivity of carbon black-PVC composites over a wide frequency spectrum (dc, 1300 MHz). While the compound of PVC used was fixed, the carbon black structures have been varied drastically with four different species of commercially available carbon blacks.

The structural dependence of the electrical percolation threshold and the volumetric conductivity will be discussed in terms of effective-medium theory and conductive network considerations.

Even though carbon blacks are not as highly conductive as some of the metallic fillers, they do provide the uniqueness of being small and inert spherical conductors (150–750 Å). They also aggregate into chain-like structures with different overall aspect ratios. Studies of electrical permittivity and conductivity on composites with these fillers (especially at different frequencies) are useful for construction of similar conductive composites and also provide important data for comparison with theoretical models for such systems in general. Conductive composites of various kinds are being used in electromagnetic shieldings[4,5] for electrical components, disks for information storage,[7] as well as to avoid electrostatic buildup in general.

II. EXPERIMENTAL

The PVC compound (denoted as "*A*") used to load the different volume fractions of carbon blacks was similar to that described by Martin *et al.*[10] In order to evaluate the effect of the various components on the electrical properties of the compound, the simplified version (denoted as "*B*") was also prepared. The exact formulation is reported elsewhere.[11]

The various components in the PVC compound were first dry-blended to form a single batch of PVC formulation. This batch of PVC compound was then again dry blended with different weight percents of carbon black. The species of carbon blacks included the Regal SRF-S®, Mogul-L®, and XC-72® (Cabot Corp., U.S.A.), and also Ketjen Black® (Akzo Chemie, The Netherlands).

These dry blends were then melt blended in a Haake Rheometer at 200 °C for approximately 10 min, and then compression molded into plates approximately 1.5 mm thick. The plates were molded and annealed under pressure at 200 °C for approximately 2 min. This ensured an isotropic composite structure. They were then cooled rapidly (~ 50 °C/min) to room temperature.

Samples were prepared by machining the plates into disks of approximately 6.35-mm diameter. Gold was then vacuum deposited on the surfaces of the samples for electrical measurements. Four-point probe dc-conductivity mea-

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surements on the plates were also performed. They showed no observable deviation from the two-terminal measurement. Thus, data using the two-terminal technique is used for this report.

A Hewlett Packard Network Analyzer (Model 8505A) was used for ac-conductivity and permittivity measurement. In the experimental measurement, the complex composite conductivity σ_m^* is defined as

$$\sigma_m^*(\omega) = \sigma_m(\omega) + i\omega\epsilon_0\epsilon_m(\omega), \quad (1)$$

where $\sigma_m(\omega)$ is the real part of the composite conductivity, $\epsilon_m(\omega)$ is the dielectric constant at frequency ω, and ϵ_0 is the vacuum permittivity.

III. RESULTS AND DISCUSSION

A. Theory: Interfacial polarization and effective-medium theory

The Maxwell-Wagner-Sillars theory[12–14] is a classical theory used to explain the dielectric-loss due to the interfacial polarization of two-phase system when the volume fraction of the dispersion is small.[15] When the loading of conductor increases, the symmetric effective-medium theory of Bruggeman[16] is commonly used in accounting for the electrical properties of a conductor-insulator composite. When the phases in a binary-phase mixture are spherical, the Bruggeman's theory can be written[1] as

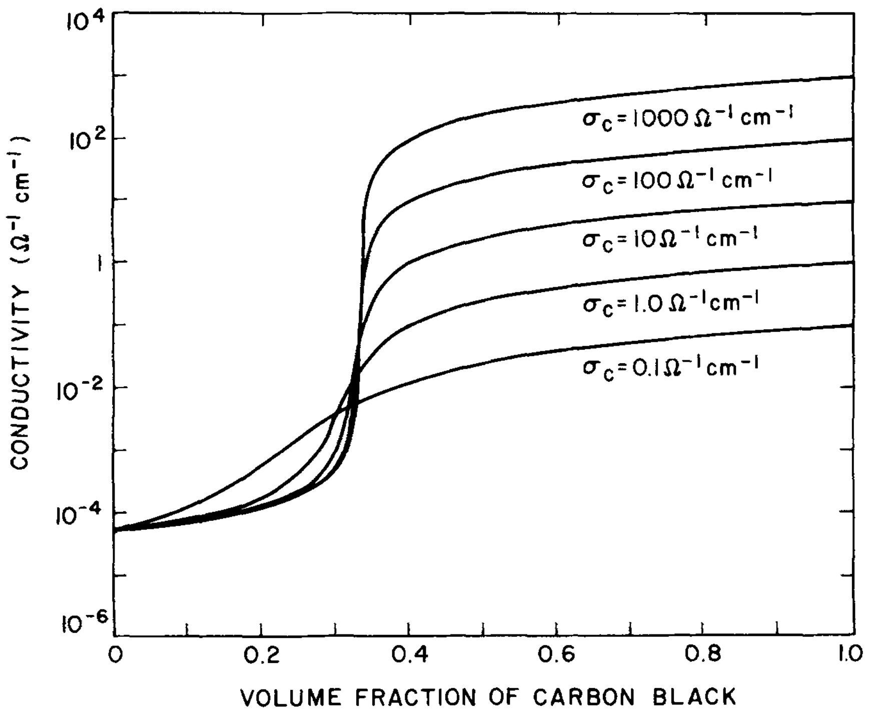

FIG. 1(a). Volumetric conductivity of carbon black-PVC composites as a function of carbon black loading at 915 MHz predicted by Bruggeman's effective medium theory. The parameters used for the calculation are the measured $\epsilon_p = 3.0, \sigma_p = 50\times10^{-6}\,\Omega^{-1}\,cm^{-1}$; ϵ_c is assumed to be zero while σ_c is assumed to possess values of 0.1 to 1000 $\Omega^{-1}\,cm^{-1}$.

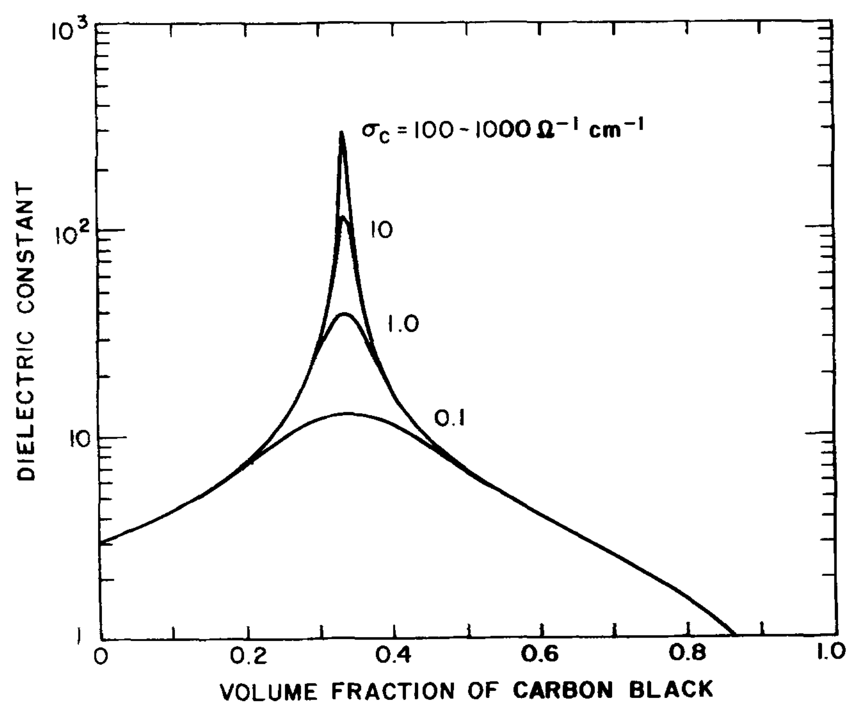

FIG. 1(b). The corresponding predicted bulk dielectric constants of carbon black-PVC composites under the same assumption used in calculating the volumetric conductivity.

$$\phi_c \frac{\epsilon_c^* - \epsilon_m^*}{\epsilon_c^* + 2\epsilon_m^*} = -(1-\phi_c)\frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*}, \quad (2)$$

where ϵ_c^*, ϵ_p^*, and ϵ_m^* are the complex dielectric constant of materials (in this case, carbon black, PVC, and the composite, respectively). If the volume fraction (ϕ_c), $\epsilon_c^*(\omega)$, and $\epsilon_p^*(\omega)$ are known, the real and imaginary part of ϵ_m^* as a function of loading can be readily calculated from Eq. (2).

It is intrinsic in the formulation that such a three-dimensional random system exhibit its electrical percolation (insulator-metal transition) at the volume fraction of one-third. Springett[17] applied such theory to account for the frequency dependence in a dielectric constant and loss in an conductor-insulator composite system. It was shown that the bulk composite dielectric constant reached maximum at $\phi_c = 1/3$. The magnitude of $\epsilon_m^{\max}$ depends on both the frequency as well as ϵ_c^* and ϵ_p^* of the components involved. The more conductive spherical dispersions will exhibit higher maxima in ϵ_m at the percolation threshold. It was also demonstrated that, at percolation, both the conductivity and dielectric constants exhibit a sigmoidal-shape change at some characteristic frequency (ω_c), which is a function of the complex dielectric constants (ϵ_c^* and ϵ_p^*) of the components.

We use Eq. (2) to calculate the volume fraction dependence in the complex dielectric constant of carbon black-PVC composite. Figures 1(a) and 1(b) are the plots of the bulk ac-conductivity and dielectric constant at 915 MHz. The different curves corresponded to the wide range of assumed carbon black conductivity ($\sigma_c = 0.1$ to $1000\ \Omega^{-1}\ \text{cm}^{-1}$).

Theoretically, inside a single spherical carbon black, if the outer shell is graphitic and continuous, then the conductivity of the carbon will be similar to those of a perfect graphite ($\sigma_{\parallel} \simeq 3\times 10^4 \Omega^{-1}\ \text{cm}^{-1}$). However, the various deviations from a perfect graphitic structure will affect the intrinsic conductivity of the specific carbon species. If the electron transport inside a carbon black (simple or highly structured) has to jump across adjacent shells of graphitic planes due to some discontinuity of the graphitic planes in such particles, the carbon black conductivity might be influenced by the tunneling conductivity between the graphitic stackings ($\sigma_{\perp} \simeq 1.0\ \Omega^{-1}\ \text{cm}^{-1}$, depending on the d_{002} spacing of the carbon black).

It is interesting also, to note that, for a fixed ϵ_c/ϵ_p, the dielectric maxima ($\epsilon_m^{\max}$) at percolation reaches an asymptotic value of around 300 for $\sigma_c > 100 \Omega^{-1}\ \text{cm}^{-1}$. However, when the loading of the conductive component exceeds the percolation threshold, metal-like conductive paths will be established. At such level of loading, the composite will again be expected to exhibit a single-phase-like behavior in conductivity and dielectric loss. Additional loading of the conductive component will simply increase the number of conductive paths in a geometric manner and thus increase the bulk conductivity correspondingly.

When the loading of carbon black is below the percolation threshold, the conductivity between the grains of carbon black is expected to be primarily via hopping and tunneling mechanisms. In this mode of conduction, the electron transport may still couple strongly with the molecular and ionic processes in the insulating matrix such as PVC. Thus, when the loading increases, the conductivity is increased mainly by virture of the narrowing of tunneling gaps between the conductive grains. Thus, one can visualize the bulk conductivity to be described by functions such as

$$\sigma_m = f(\phi_c) e^{-X(\phi_c)}, \quad (3)$$

where $f(\phi_c)$ if a function representing the geometric network of the conductive path and $X(\phi_c)$ represents the average tunneling gap between the grains of carbon black which is being reduced with increased loading. For spherical conductors, when $\phi_c \ll 1/3$, the spatial distance between grains is large so that tunneling is negligible and thus conduction is mainly due to the interfacial polarization effect. When ϕ_c approaches 1/3, the conducting phase becomes connected and the tunneling term becomes important and enhances the conductivity in an exponential manner.

When the loading exceeds the percolation threshold, the gap between the grains might be governed by the inter-particle interaction (cohesion by the continuous matrix phase and the repulsion between the the particles) and is not expected to decrease drastically. Thus, one may expect the tunneling gap $X(\phi_c)$ to reach a critical value, and the additional conductive particles will only help the conductivity by geometrically increasing the conductive paths. The conductivity of the composite is expected to increase gradually to the asymptote when the conductivity of a random close-packed condition is reached.

B. Morphology of carbon black: Packing efficiency and percolation threshold

The SRF-S® and Mogul-L® carbon blacks are known

TABLE I. Summary of the essential features in the carbon blacks used for this study.

	Carbon black structures			
	SRF-S®	Mogul-L®	XC-72®	Ketjen Black®
Aspect ratio (structure)	spherical	spherical	medium	high
Primary particle size	600 Å	240 Å	300 Å	300 Å
Microstructure	graphite	graphitic	graphitic planes shared with neighboring particles	graphitic planes shared with neighboring particles