

Investigation of Electrical and Dielectric Properties of Prelocalized Graphite/Poly(vinyl chloride) Composites Near the Percolation Threshold

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ABSTRACT: Present article reports the effect of percolation threshold on the electrical and dielectric properties of prelocalized graphite-filled poly(vinyl chloride) composite. The variation of room temperature electrical conductivity, D-shore hardness, and relative permittivity as a function of graphite concentration has been studied below and above percolation concentration of the filler. The percolation threshold at which insulator to conductor transition takes place is estimated to be 0.0026 volume fraction of graphite. The current density-electric field characteristics of the composites having different filler concentrations are also studied. It has

been observed that the nonlinear electrical characteristics become linear when the composite undergoes insulator to conductor transition. The dielectric constant and dissipation factor are found to increase slowly up to the percolation concentration and beyond it, a sudden increase in its value is observed. The D-shore hardness is found to decrease by nearly 10% at the point of percolation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2027–2033, 2007

Key words: poly(vinyl chloride); dielectric properties; hardness; composites; conducting polymers

INTRODUCTION

Polymeric materials are usually insulators. Insulating polymers can be made conducting^{1–8} by mixing electrically conducting fillers. The conducting polymer composites can be easily shaped into various complicated forms by the traditional technique of extrusion and injection-molding. The commonly used conducting fillers are Al, Au, Cu,^{9,10} carbon black (CB),¹¹ and graphite¹² in powder form. Metallic powders generally suffer from oxidation, which deteriorate electrical properties of the composite due to the nonconducting nature of oxide layers. Conducting polymer composites^{13,14} have a wide range of industrial applications such as antistatic materials, self-regulating heaters,^{15,16} over current and over temperature protection devices,^{17,18} and materials for electromagnetic interference shielding.^{19,20}

The insulator-conductor transition observed in polymer composites is generally sharp and percolative in nature. Percolation threshold^{21–26} is that critical volume fraction of conducting filler below which the conductivity of the composite decreases by several order of magnitude. Many theoretical models of percolation threshold^{27–30} as well as the experimental confirmations^{31,32} of the percolation behavior in conducting

polymer composites have been reported in the last few decades. In addition, the structural properties are also expected to be modified at the point of insulator-conductor transition. By analyzing the experimental data, for electrical conductivity and dielectric properties, it is possible to understand the mechanism for the insulator-conductor transition of the composites. The current density–electric field (J – E) characteristics are reported^{12,33} to change from nonlinear to linear one when the composite undergoes from insulator to conductor transition. The introduction of conducting filler into polymer matrix also modifies the dielectric properties of the conducting composite. According to Mamunya et al.,³ the dielectric behavior of conducting polymer composites is subjected to Maxwell-Wagner's interfacial polarization for heterogeneous systems when one of the components of the composite has higher electrical conductivity when compared with the other.

This work deals with the effect of critical filler concentration on various physical properties of prelocalized graphite-filled poly(vinyl chloride) (PVC) composites. The variation of room temperature electrical conductivity and hardness with filler content is investigated below and above percolation concentration of the filler. The percolation concentration is estimated by using power law model of conductivity. The J – E data were analyzed using linear as well as second-order polynomial fit. Conduction mechanism has been discussed on the basis of J – E curves. The variation of dielectric constant, dissipation factor, and loss factor as a function of frequency and graphite content are studied at an ambient temperature.

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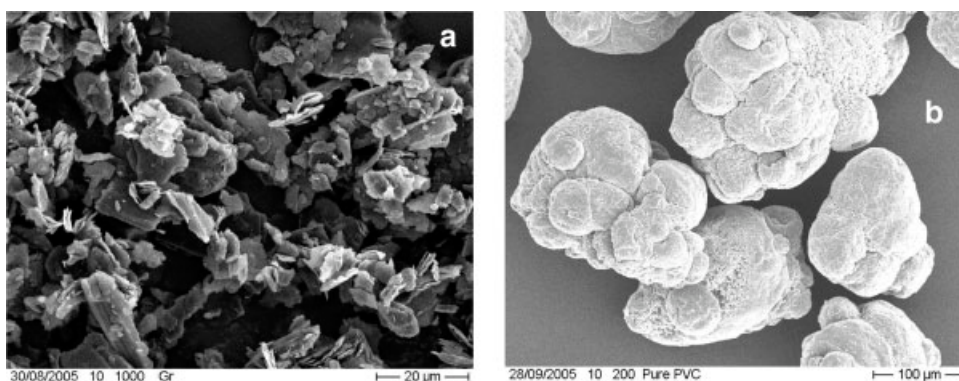


Figure 1 Scanning electron micrographs of (a) graphite flakes and (b) PVC powder.

EXPERIMENTAL

The matrix polymer used in this work is a commercial grade poly(vinyl chloride) (PVC) resin suspension (K 67-01) with particle size 105–150 μm (Reliance Industry, India). The conducting filler was natural graphite flakes (NFG) with average particle size of 10–20 μm supplied by Graphite India. Conductivity of the graphite flakes was 1.33×10^4 S/cm with density 1.75 g/cm³. Scanning electron micrographs (SEM) of graphite and PVC are shown in Figure 1(a,b), respectively. The flaky nature of graphite is clearly seen with size varying from 10 to 20 μm . The size of the PVC particles is also confirmed by the SEM micrograph. The samples of graphite-filled composite were prepared by tumble-mixing as described earlier.³⁴ In the mixing process, the surface of the PVC particles gets coated with graphite flakes because of the sticky nature of the latter. Such type of coating is referred as prelocalization of the conductive phase.^{35,36} Prolong mixing was done to achieve homogeneity of the spatial distribution of the conducting particles on PVC particles. The localized graphite flakes onto the PVC particles were compacted by hot compression molding in a piston cylinder assembly. The density and the glass transition temperature (T_g) of the compression-molded pure PVC pellet were found to be 1.12 g/cm³ and 80°C, respectively. Series of pellets of prelocalized graphite-filled PVC conductive composites with various concentrations from 0 to 0.033 volume fraction of graphite were prepared. The powder was pressed initially for 5 min at room temperature to eliminate any void formation within the pellet. The pellets were heat-treated thereafter above T_g up to 100°C under atmospheric pressure and cooled down to 70°C. Homogenized composites were then compression-molded into disk-shaped samples of diameter 1.01 cm and thickness ranging from 0.1 to 0.5 cm. The compression-molding operation was at 70°C first for 15 min at 105 MPa pressure (curing), and then at 100°C for 15 min at 35 MPa pressure (baking). Finally, the pellets were cooled down to room temperature under

atmospheric pressure. This procedure helps to improve the electrical properties, minimization of after-shrinkage, and enhancement in the quality and appearance by eliminating porosity, bubbles, or blisters. Both surfaces of the pellets were polished with sandpaper to remove the rich graphite surface layer and to eliminate surface irregularities. The conducting silver paint coatings were used as the electrical contact. Pellets were sealed in air free polyethylene bags prior to testing to avoid atmospheric and humidity effects. A digital multimeter was used for samples having electrical resistance lower than 200 M Ω . However, for the samples having resistance greater than 200 M Ω , a Keithley Pico ammeter (Model DPA III) was used. Current-voltage measurements were performed using Keithley 2400 source meter. The JEOL JSM 840 SEM was used for the analysis of surface morphology of the pure PVC and graphite flakes. Measurement of relative permittivity of the composites was carried out with an impedance analyzer (HP-4284 A) within the frequency range of 20 Hz to 1 MHz.

RESULTS AND DISCUSSION

Effect of graphite content on electrical conductivity

The electrical conductivity (σ) of graphite-filled PVC composites as a function of graphite volume fraction (ϕ) is illustrated in Figure 2. It is seen from the figure that σ increases by more than six-order when the graphite content reaches 0.0026 volume fraction (0.4 wt %) of graphite. The observed value (0.0026) of the critical volume fraction (ϕ_c) is very low as compared with other composites such as PE/PPY system³⁷ and blends of HDPE/PVDF³⁸ with conductive filler as CB. The observed low value of ϕ_c could be due to the prelocalization process used in the present work. Yacubowicz et al.³⁹ have also observed insulator to conductor transition in polyethylene/CB composite prepared via prelocalization of the filler particles onto the polymer matrix at volume fractions comparable to our data.

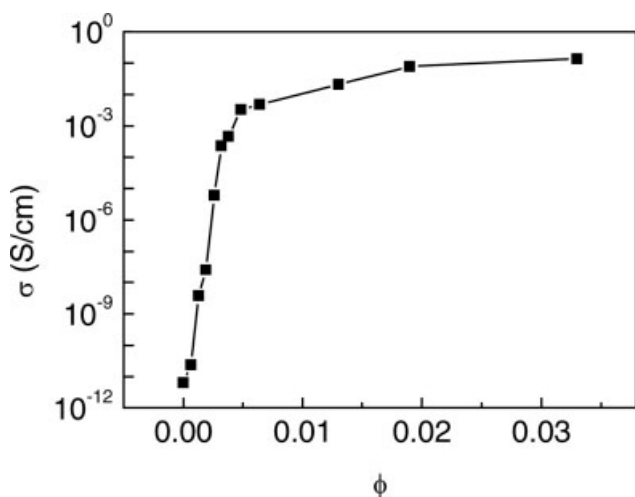


Figure 2 Variation of σ as a function of ϕ in prelocalized graphite-filled PVC composites.

Amorphous polymers possess a unique property of dispersion of conducting fillers uniformly within the polymer matrix; correspondingly, higher electrical conductivity may be achieved at the critical volume concentration of the filler in comparison to semicrystalline polymers.³ PVC is also a prominent member among amorphous polymers⁴⁰ and so in the present work on graphite/PVC composites, a high electrical conductivity ($\sim 10^{-5}$ S/cm) has been achieved at the percolation concentration.

Power law model

The variation of σ as a function of filler content is usually explained by power law model of conductivity,^{27,38,41} where σ is expressed as

$$\sigma = \sigma_0(\phi - \phi_c)^t \tag{1}$$

where t is the universal exponent determining the power of the electrical conductivity increase above ϕ_c and σ_0 is generally considered to be the conductivity of the conducting filler.^{24,38,41} However, Kirkpatrick²⁷ and Hsu et al.⁴² have argued that σ_0 may depend on the transport mechanism in the composite. From the best linear fit of the conductivity with excessive volume fraction of filler, both t and σ_0 can be obtained.

The plot of $\log \sigma$ versus \log of excessive volume fraction of graphite ($\phi - \phi_c$) is shown in Figure 3. The best linear fit with minimum standard deviation (0.15) has been obtained at $\phi_c = 0.0025$ (~ 0.4 wt %) volume fraction of graphite. The values of t and σ_0 as estimated from the slope and intercept of the line, respectively, (Fig. 3) are found to be 1.78 ± 0.05 and $87.2 \Omega \text{ cm}$. Various researchers^{24,25,27,41,43} have also predicted and obtained the value of t between 1.5 and 2.0. The value of σ_0 obtained in the work does not correspond to the conductivity of the graphite filler. It may be mentioned

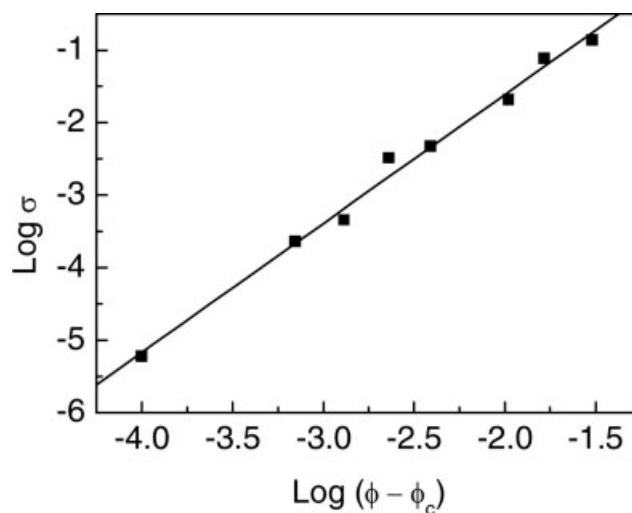


Figure 3 Plot of $\log \sigma$ vs. $\log (\phi - \phi_c)$ for prelocalized graphite-filled PVC composites.

that several researchers^{27,42,44} have considered σ_0 as a constant and obtained values which also generally do not correspond to the conductivity of the filler.

J-E characteristics

J-E characteristics can be expressed³ as

$$J = KE^n \tag{2}$$

where K is a constant, which represents the conductivity of the composite, and n is the slope in the $\log J$ - $\log E$ plot. In eq. (2), when $n = 1$, then Ohm's law is fulfilled in the system. Figure 4 illustrates the $\log J$ - $\log E$ plots at room temperature of prelocalized graphite-filled PVC composites with different composition. The dependence of the exponent n with volume fraction ϕ is shown in Figure 5. It is found that n decreases from

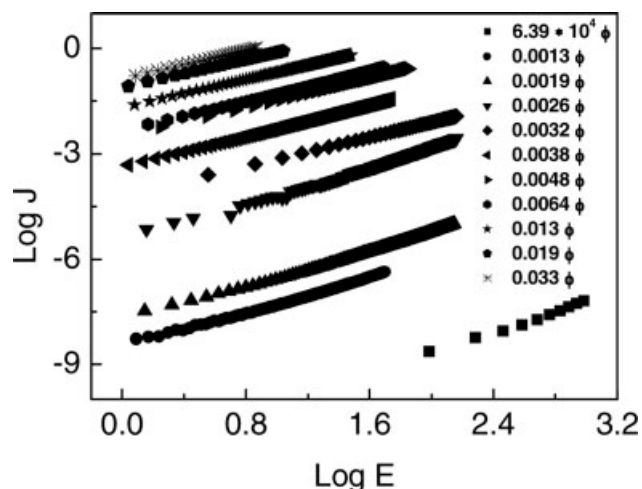


Figure 4 $\log J$ - $\log E$ plot of "prelocalized graphite-filled PVC composites" for various ϕ .

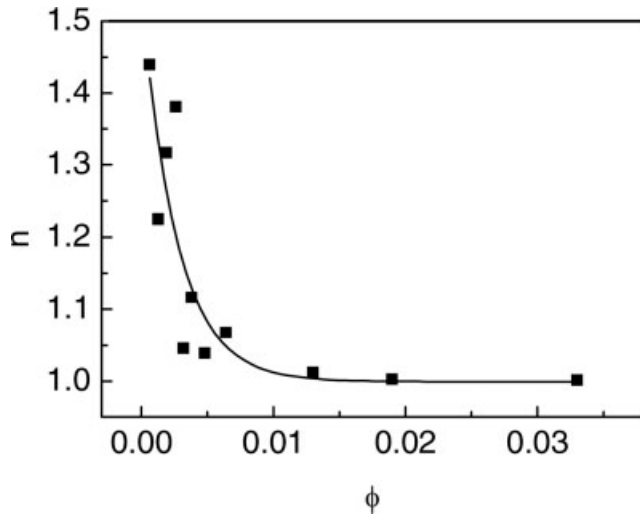


Figure 5 Plot of exponent n of eq. (3) vs. ϕ .

1.44 to ~ 1 with the increase in filler content. The transformation from nonlinear to linear behavior is observed near the percolation threshold. The variation of K and σ (experimental) with ϕ is shown in Figure 6. It is seen from the figure that both K and σ (experimental) closely match with each other.

To confirm the transition from nonlinear to linear, J - E data have also been analyzed using second-order polynomial fit. The experimental nonlinear J - E curve can be represented as

$$J = \sigma_1 E + \sigma_2 E^2 \quad (3)$$

where σ_1 and σ_2 are the first- and second-order conductivity and assigned to linear and nonlinear part in the conduction process, respectively. Both σ_1 and σ_2 have been estimated from the polynomial fitting of the J - E data. The variation of σ_1 and σ_2 with respect to ϕ is

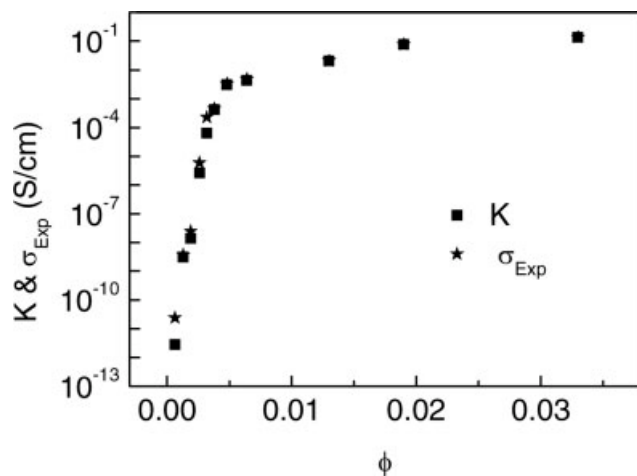


Figure 6 Plot of σ (Experimental) and constant K of eq. (3) vs. ϕ .

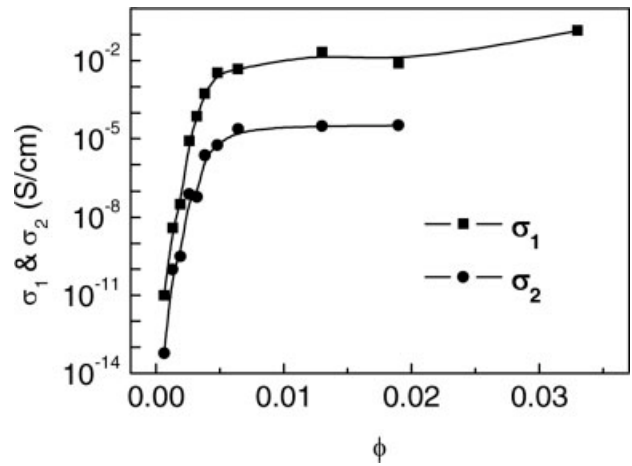


Figure 7 Variation of σ_2 and σ_1 as a function of ϕ for pre-localized graphite-filled PVC composites.

shown in Figure 7. It is evident from the figure that σ_1 and σ_2 increases sharply around ϕ_c and with further increase in filler content, their values gets saturated. The saturated value of σ_2 is about three-order smaller when compared with the saturated value of σ_1 .

The ratio of σ_2 to σ_1 with graphite content is illustrated in Figure 8. This ratio is found to decrease with the increase in filler content. Based on the ratio σ_2/σ_1 , the composites can be separated in two distinct regions namely, below and above ϕ_c , as shown by the vertical line in the figure. The contribution of σ_2 to J reduces to zero for higher concentration of graphite.

The conduction mechanism can well be understood by tunneling-hopping model. Initially, below ϕ_c , the filler particles are far apart and consequently very small current flows in the composite ($10^{-9} - 10^{-5}$ A). Hence, J - E characteristic below percolation threshold concentration of filler is non-Ohmic in nature as stated earlier. As the filler content approaches ϕ_c , the conductivity suddenly increases because of the filler particles

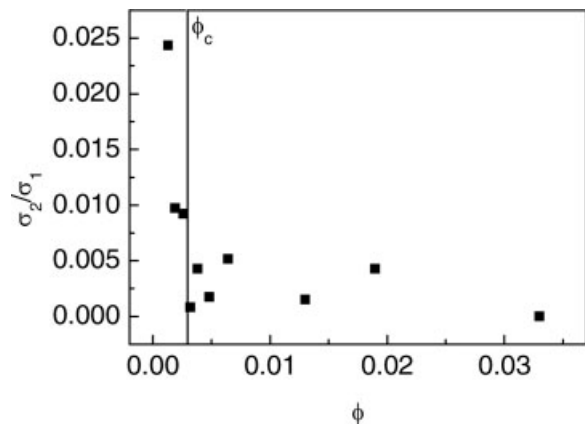


Figure 8 Variation of the ratio of σ_2 to σ_1 as a function of ϕ for pre-localized graphite-filled PVC composites.

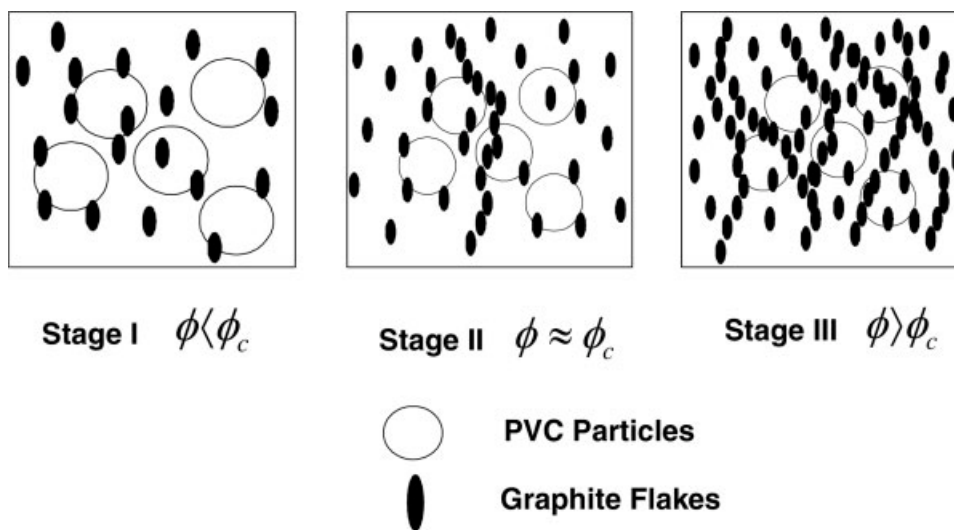


Figure 9 Different stages of polymer/graphite composite after compression molding at high temperature and pressure (a) $\phi < \phi_c$, (b) $\phi \approx \phi_c$, and (c) $\phi > \phi_c$.

coming together. The conduction mechanism now is done by hopping up of electrons. Again, with further increase in filler content, i.e., with $\phi > \phi_c$, filler particles either come in close contact or with a very small gap. In this case, the conduction process is done by tunneling up of electrons. The typical behavior of current from nonlinear to linear nature with increase in filler content causes a scaling factor in the J - E characteristics as given in eqs. (2) and (3) similar to the conductivity variation with excessive volume fraction of graphite in power law model. The formation of PVC/Gr composite by compression-molding of prelocalized PVC/Gr at elevated temperature is proposed in the schematic diagram in Figures 9(a-c).

Hardness

D-Shore hardness of prelocalized graphite-filled PVC composite with respect to ϕ is shown in Figure 10. D-Shore hardness tester (Model No. SRHT-501D by Scientico India) was used for hardness measurements. Pellets of ~ 0.5 -cm thickness have been taken for accurate and reliable results of hardness measurement. A relatively large decrease with increasing ϕ is observed when the filler concentration is roughly up to the percolation concentration. A moderate decrease in hardness however is observed beyond percolation threshold. The decrease in hardness with increase in filler content may be assumed to be due to the decreased particle to particle interaction among PVC particles because of the thick and relatively better coating of graphite particles within the composite.

Dielectric properties

The dielectric properties of a polymer composite mainly depend upon (a) permittivity and conductiv-

ity of the polymer composite and (b) the relative concentration of the conducting and insulating phases. The complex dielectric constant is defined by

$$\epsilon = \epsilon' - j\epsilon'' \tag{4}$$

The real part ϵ' is usually expressed as relative permittivity or dielectric constant, and imaginary part ϵ'' generally referred as loss factor. The dissipation factor $\tan \delta$ is expressed as the ratio of ϵ'' to ϵ' .

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \tag{5}$$

where angle δ is the loss angle.

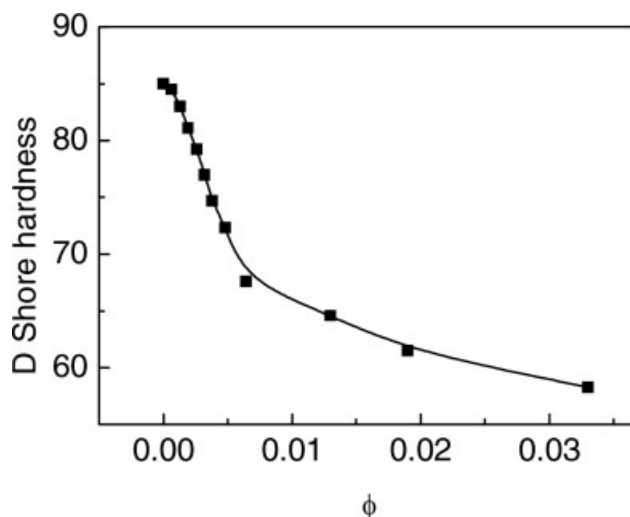


Figure 10 D-shore hardness as a function of ϕ for prelocalized graphite-filled PVC composites.

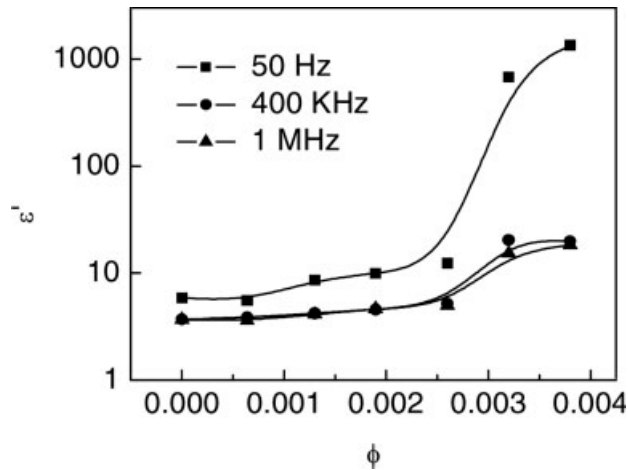


Figure 11 Variation of ϵ' as a function of ϕ at 50 Hz, 400 KHz, and 1 MHz for prelocalized graphite-filled PVC composites.

Capacitance and dissipation factor were measured directly using impedance analyzer. ϵ' was calculated using relation

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (6)$$

where d is the thickness, C is the capacitance, and a is the area of cross section of the pellet.

Figure 11 shows the variation of ϵ' with graphite concentration at three different frequencies: 50 Hz, 400 KHz, and 1 MHz. At the low frequency (50 Hz), a sudden increase in ϵ' has been observed with filler concentration beyond ϕ_c . At higher frequencies, there is a perceptible increase in ϵ' after ϕ_c . A distinct percolative behavior in ϵ' has been observed. High values of dielectric constant beyond ϕ_c could be

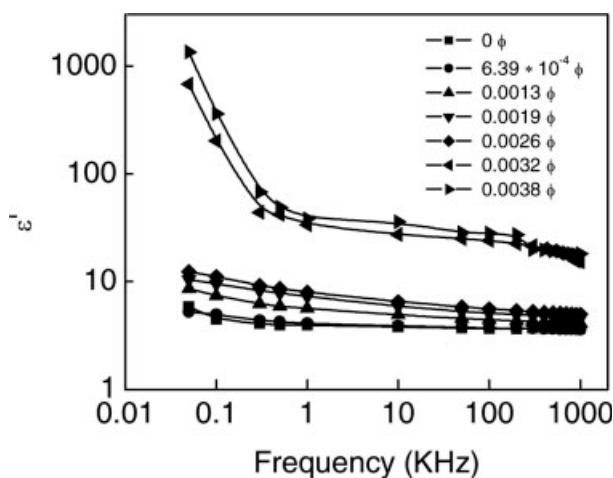


Figure 12 Variation of ϵ' as a function of frequency for various ϕ for prelocalized graphite-filled PVC composites.

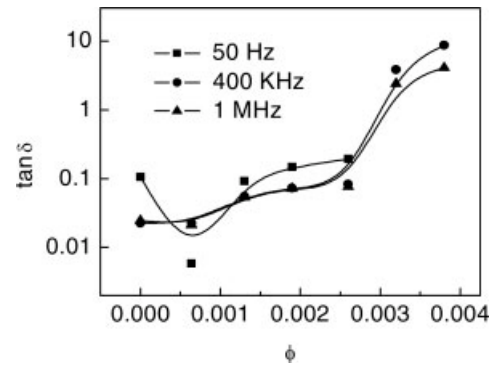


Figure 13 Variation of $\tan \delta$ as a function of ϕ at 50 Hz, 400 KHz, and 1 MHz for prelocalized graphite-filled PVC composites.

attributed to Maxwell-Wagner's⁴⁵ interfacial polarization in heterogeneous composite systems. Because of the interfacial polarization, large local fields are generated within the composite, which results in the large value of dielectric constant. In the present work, on heterogeneous type of prelocalized graphite-filled PVC composite structure, a large value of ϵ' (~ 1000) has been observed at low frequency. However, in homogeneous system,⁴⁶ the dielectric constant values are generally reported in the range of 2–150.

The variation of ϵ' with respect to frequency is shown in Figure 12. Continuous decreasing pattern has been observed for each composite irrespective of filler content. However, a significant fall up to 1 KHz has been found in samples having graphite concentration above percolation threshold. No sudden increase in ϵ' has been observed up to ϕ_c , indicating no accumulation of interfacial charge within the composite. As soon as the percolation process takes place within the

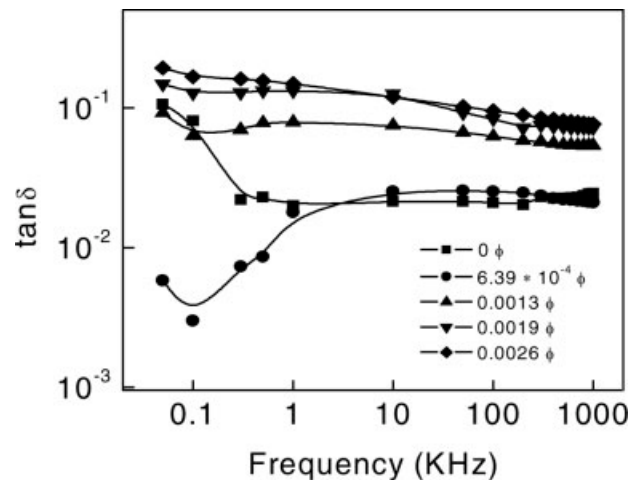


Figure 14 Variation of $\tan \delta$ as a function of frequency for various ϕ for prelocalized graphite-filled PVC composites.

composite, Maxwell-Wagner's interfacial polarization causes an increase in ϵ' at lower frequencies.

The effect of graphite content on $\tan \delta$ is shown in Figure 13 at three different frequencies: 50 Hz, 400 KHz, and 1 MHz. The dissipation factor is moderately increases roughly up to ϕ_c similar to that of the dielectric constant. Beyond the percolation threshold, $\tan \delta$ increases at a faster pace at 400 KHz and 1 MHz. At 50 Hz, $\tan \delta$ could not be measured in the samples having filler concentration greater than the percolation concentration due to the increased conductivity of these samples.

Figure 14 illustrates the variation of $\tan \delta$ with frequency. This variation is similar to the variation of ϵ' with some scattering at lower frequencies for lower content of filler. For concentrations of the filler beyond ϕ_c , the high value of $\tan \delta$ could not be measured because of the increased conductivity of the composites. The high value of $\tan \delta$ above ϕ_c could also be a consequence of Maxwell-Wagner's interfacial polarization.

CONCLUSIONS

The signature of percolation threshold is distinctly seen in the electrical conductivity, permittivity, and D-shore hardness data of the prelocalized graphite-filled PVC composites. The prelocalization process has resulted in a low threshold value of volume fraction of graphite and high conductivity of the composite at and above percolation. The electrical transport is by hopping below percolation threshold, which changes to tunneling process beyond percolation. The dielectric constant and dissipation factor were found to increase suddenly as the filler content crosses the percolation threshold because of Maxwell-Wagner's interfacial polarization phenomenon. The mechanical strength in terms of D-shore hardness is deteriorated by only 10% near the percolation threshold.

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