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Ac conductivity, relative permittivity and loss tangent of PVC Paste/Graphite Electrode Waste Composites

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ABSTRACT

Ac conductivity (σ_{ac}), relative permittivity (ε'), and loss tangent ($\tan\delta$) of Polyvinyl Chloride Paste (PVC-P)/Graphite Electrode Waste (GEW) composites behaviour as a function of PVC-P wight fractions (5, 10, 15, 20,and 25) wt.%, temperature in the range (30-90)$^{\circ}$C and frequency in the range (100Hz-2MHz), were investigated and given a qualitative explanation. The relative permittivity was found to increase with the increase of GEW filler content, and was high in the low frequency range, but diminishes as the frequency increases. The permittivity was found to increase with the increase of temperature up to the transition temperature (Tg). Ac. conductivity and impedance of the composites behaviours as function of frequency and temperature have also been investigated.

Keywords: Ac conductivity, permittivity, Polyvinyl Chloride Paste, Graphite Electrode Waste

INTRODUCTION

Composites which are made of polymer with organic filler have been successfully used in electrical and electronic industries. These systems are considered heterogeneous and their electrical characteristics depend on several factors such as volume fraction, size, shape, and conductivity of the filler, the adhesion between the filler and the polymer and the method of processing. The advantage of such composites is that it can be produced to exhibit enhanced and compatible properties that the constituent materials may not exhibit(1-4) .

Filler can improve the mechanical, thermal and electrical (conductivity and permittivity) properties. It can lower the shrinking in addition to the price reduction consideration. In order to achieve both thermally conducting and electrically insulating polymer-matrix composites, fillers such as (diamond, boron nitride aluminum nitride, silicon carbide, alumina, fused SiO_2 and beryllium oxide), are used [5-8]. Metallic fillers, carbon black and graphite are used to enhance both electrical and thermal properties [8-10]. Non conductive fillers increase the dielectric permittivity due to interfacial polarization (Maxwell-Wagner-Sillars polarization). For con fillers, electrical conductivity and dielectric permittivity increase with increasing the filler volume fraction until drastic changes in these properties reach a critical range of filler concentration called percolation threshold. The effective use of composites strongly depends on the ability to disperse the fillers homogeneously throughout the material (11).

Graphite is a carbonaceous material; expanded graphite with a high aspect ratio and excellent electrical conductivity can be produced by exfoliating graphite intercalation compound through rapid heating in a furnace or microwave environment. Graphite electrode waste from electric arc furnace can substitute graphite synthetic as a reinforcement material for carbon composite.

Composites material has been used widely in industrial sectors as materials for antistatic, electromagnetic shielding, and electronic technology [12, 13]. In electronic technology, composites material has been used for a device with improved electromagnetic and energy storage system [14] or electrochemical energy storage systems [15]. In this study, (PVC-P as a matrix and GEW powder as a filler) composites were prepared and their dielectric properties were investigated as a function of filler weight fraction (5, 10, 15, 20 and 25 wt.%), temperature in the range (30-120°C) and frequency in the range

(100Hz-2MHz). A.C.conductivity and impedance were also studied.

EXPERIMENTAL

MATERIAL

A commercial LICHIDE PVC paste 717-21 heavy duty-clear (as received from market), with permittivity (ε'= 3.19), Volume Resistivity 5.4×10^{15} ohm/cm and density=1.42 gm/cm^{3}supplied by SWAN TRADING (L.L.C) were used as polymer matrices for the composites. GEW powder from Iron and steel factory is used as an additive, with particle size of ~ 75µm.

SAMPLE PREPARATION

In order to insure a good dispersion of the filler and to provide a homogenous composite, the GEW powders were added to the PVC-P in different weight percentages (5, 10, 15, 20 and 25 wt%) and suitably mixed at about 65°C for 7 minutes. The mixture then was casted as a thick film on clean Al substrates. The initial curing was carried out at room temperature for 24 hours, followed by post curing at 120°C for 2 hours. Circular disk shaped thin film Aluminum electrodes 6 mm in diameter were vacuum deposited on the upper side of the casted composites. A sandwich of Al/PVC-P:GEW/Al were finally made.

CHARACTERIZATION AND MEASUREMENT

The samples capacitance and the loss tangent (tanδ) of composites were measured by (digital RCL bridge type MEGGER B131), at the frequencies 120Hz and 1kHz. For continuous frequencies in the range (120Hz -2MHz), RCL bridge type (METRAPOINT-RLC2 and ME 1634 FUNCTION GENERATOR) was used to measure the capacitance of the samples.

RESULT AND DISCUSSION

The electric permittivity, energy loss, and dielectric relaxation strength are important parameters for material science because these parameters are used to decide on the suitability for given application.

This experiment was meant to study the behaviour and dielectric properties of PVC-P/GEW composite. Figures (1) display the frequency dependence of dielectric properties. The variation of tanδ of GEW filled PVC-P composites as a function of frequency in the range (120Hz-2MHz) at room temperature. It is obvious that, tanδ increases as filler content increases for all frequency range studied. The increase in tanδ with increasing of filler contents may by an induced polarization which occurs at the polar ends of the particle by the applied electric field. Then charge carriers are efficiently transferred around the interface and become the conducting [16]. This will lead to a permittivity higher than the particle itself. It is interesting to find that there is a relaxation peak in about ~100000 Hz, indicating changes of the polymer molecular structure. GEW disrupt the original crystallization process of PVC-P, resulting in more free volume, while the poor interface also introduces more defects, the relaxation of the polymer occurs.

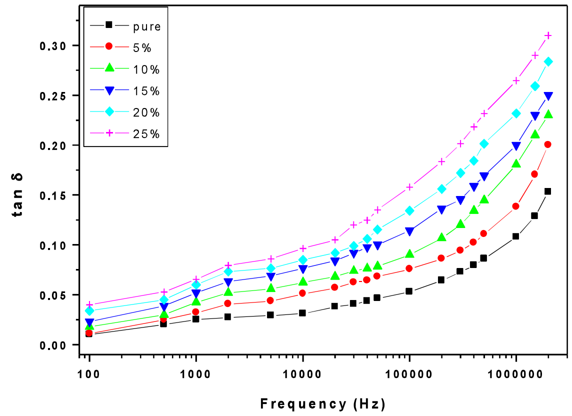


Figure (1). Frequency-dependence of the loss tangent of PVC-P/GEW composite.

Figure (2) shows the variation of tanδ as a function of temperature in the range 30-90°C at a constant frequency (1 kHz) for pure PVC-P and PVC-P/GEW composites (with different filler concentrations). It is observed that tanδ are increased in general as the filler content or temperature increases. The increase in tanδ with increasing of filler contents is related to the interfacial polarization, while that caused by increasing temperature may be related to the increase of segmental mobility and ionic conductivity. Since the rise in temperature (and the consequence drop in viscosity) exerts an effect on the amount of the losses due to the friction of the rotating dipoles, the degree of dipole orientation increases and ionic conduction increases, due to the thermal dissociation of molecule [17-21].

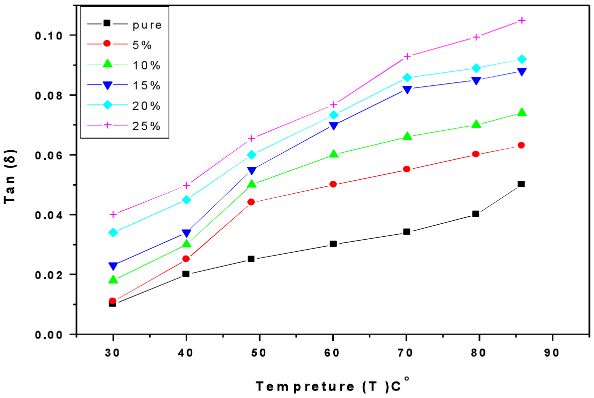


Figure 2. Temperature-dependence of the loss tangent of PVC-P/GEW composite.

Measurement of AC electrical properties of the composite materials sample employed following formula. The frequency dependence complex dielectric permittivity $\varepsilon^*(\omega)$ is given by

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega) \qquad (1)$$

Here, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary part of complex dielectric permittivity. PVC-P/ GEW as a function of frequencies at room temperature is shown in figure (3). As expected, the variation tendency of dielectric constant with frequency is inversely proportional to electrical conductivity (σ). The ε' attains high value at low frequency and decreases exponentially with increasing frequency. High values ε' in the low frequency range, are attributed to the process of interfacial polarization and the polarization induced by segmental mobility in the polymer which appears more effective at low frequency and high temperature respectively [18-22]. The dipoles responsible of these two polarizations have less time to orient themselves in the direction of the alternating field at high frequencies.

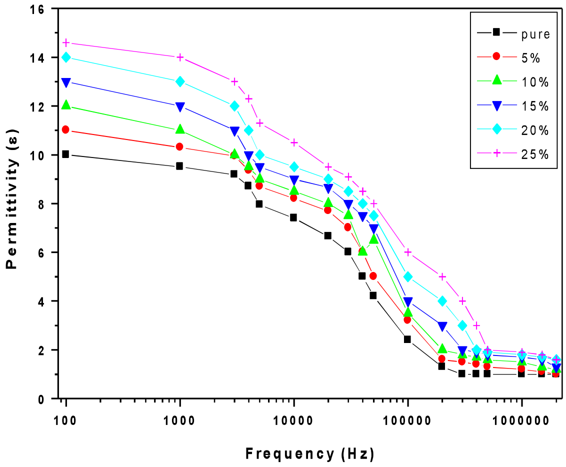


Figure 3. Frequency-dependence of the dielectric permittivity of PVC-P/GEW composite.

Figure (4) shows the variation of dielectric permittivity (ε') of PVC-P/GEW composite as a function of temperature in the range (30-90)˚C for different filler concentrations. Pure PVC-P was also included in the figure for comparison. It can be seen that in all cases ε' increases with increasing temperature up to a maximum where further increase in temperature would lead to decreasing the ε' value. Here, since there is no significant change in the filler permittivity with increasing temperature; the dielectric response of the composites may be related to: Firstly, the segmental mobility of polymer which increases with increasing temperature; this mechanism should increase the dielectric constant due to greater freedom of movement of the dipole molecular chains within the polymer at high temperature [23], Secondly, the disruption of contacts between filler particles caused by the thermal expansion of polymer and filer; this mechanism should decrease dielectric constant [23-26].

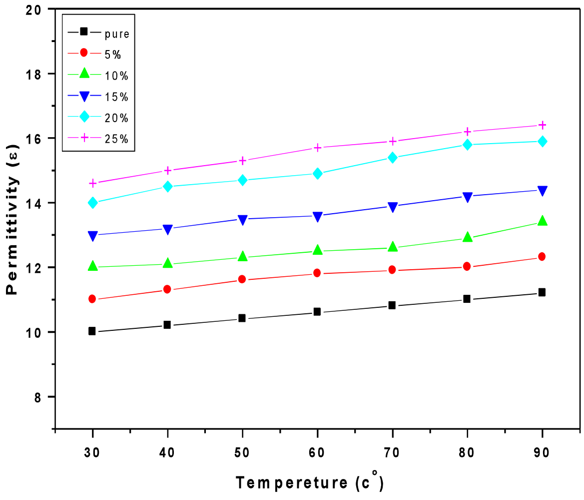


Figure 4. Temperature-dependence of real dielectric permittivity of PVC-P/GEW composite.

Dielectric properties also depend on the orientation of the structure in the material. Dielectric loss of permittivity can be calculated from the measured loss tangent and capacitance:

$$V_\theta = V_T \sin(\pi - \varphi) \qquad (2)$$

$$\tan\delta = (V_T^2 - V_\theta^2)^{1/2} / V_\theta \qquad (3)$$

The variation of A.C conductivity (σ_{ac}) at room temperature with frequency for different filler content (pure PVC-P and PVC-P/GEW) of composites is shown in figure (5) at room temperature. Using dry mixing method, the electrical conductivity is fairly constant when the GEW load the content. Such composite materials generally exhibit non-linear increase of the electrical conductivity as a function of the filler concentration. The two parameters, electrical conductivity and percolation threshold, are together associated with. At a certain filler loading fraction, known as the percolation threshold, the fillers form a network leading to a sudden rise in the electrical conductivity of the composites.

The addition of a very low amount of conducting particles can make filler contact to form effective conducting paths and thus making the whole composite conductive. These specimens show a typical insulating behaviour with a frequency-dependent conductivity. However, the higher GEW loading in the polymer composite can cause serious GEW aggregation, and the electrical conductivity will lower or even decrease. The influence of temperature on $\sigma_{a.c.}$can be explained by considering that the charge carriers such as weakly bound ions in PVC-P, and polymer segmental chains, that would increase dramatically with increasing temperature [18,19,26]. A.C. Conductivity ($\sigma_{a.c}$) was calculated according to the relation:

$$\varepsilon'(\omega) = C\, d / \varepsilon_o A \qquad (4)$$

$$\varepsilon''(\omega) = \varepsilon' \tan\delta \qquad (5)$$

Where, d is separation distance between two electrodes, A is electrodes area, ε_o is the permittivity of the free space, (ε_o =8.85×10-12 F/m).

$$\sigma_{ac} = \varepsilon_o\, \omega\, \varepsilon'' \qquad (6)$$

Where $\omega = 2\pi f$ is the angular frequency.

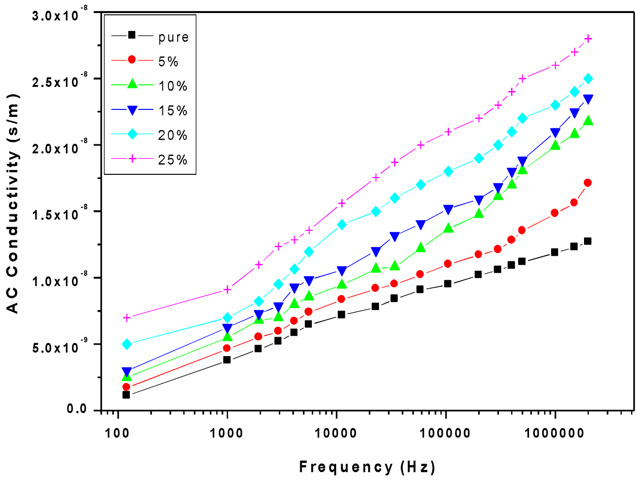


Figure (5). Plot of frequency-dependence of Ac conductivity of PVC-P/GEW composite.

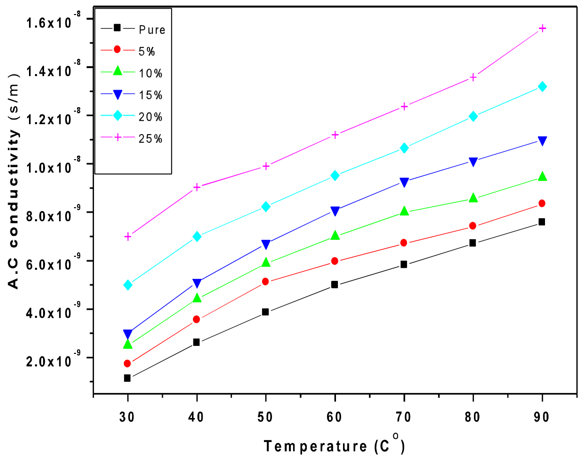


Figure (6). Plot of temperature -dependence of Ac conductivity of PVC-P/GEW composite.

The complex impedance (Z^*) can be expressed as follws:

$$Z^* = Z + iZ \qquad (7)$$

where, Z and iZ are real and imaginary parts of impedance, respectively Figure (7) Shows the variation of impedance Z with frequency for PVC-P:GEW composites . It was noticed that the phase angle was always negative, indicating that the composites were capacitive and could be represented by parallel RC networks (lumped circuit) connected in series. Impedance values decrease with increasing frequency and increasing GEW concentration. The observed decrease in impedance with GEW content is due to the protonic migration transporting and impurities existing in the GEW filler. This motion leads to higher electrical conduction in the filled composites [21]. As can be seen, there is an exponential decrease in the impedance with the increase in frequency for all filler volume fraction, and the decrease is greater for high filler contents composites [22].

Figure (8) Shows the temperature dependency of impedance Z of PVC-P:GEW composites. There is an obvious decrease in Z, with the increasing of filler volume fraction due to the increased interfacial polarization, and with the rise in temperature. The impedance Z decreases with the temperature rise which is accompanied by clear dips near (90°C) temperature for all cases in which filler were added. This decrease in Z may relate to the increased mobility of segmental molecules as the temperature increased. The dips may be related to the glass transition temperature region where the segmental mobility is increased. As a consequence, these dips may refer to the glass transition temperature for all composites.

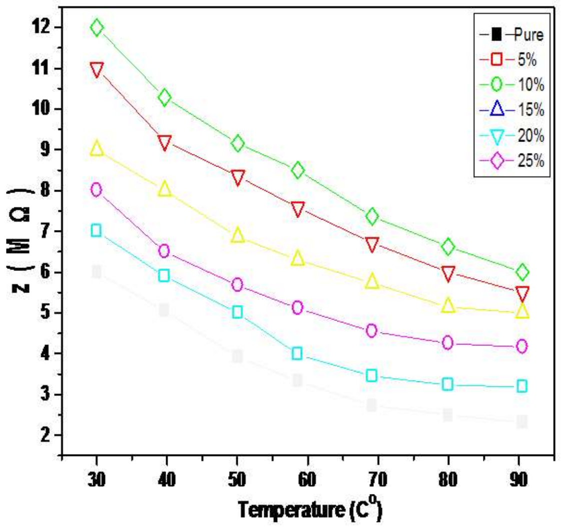
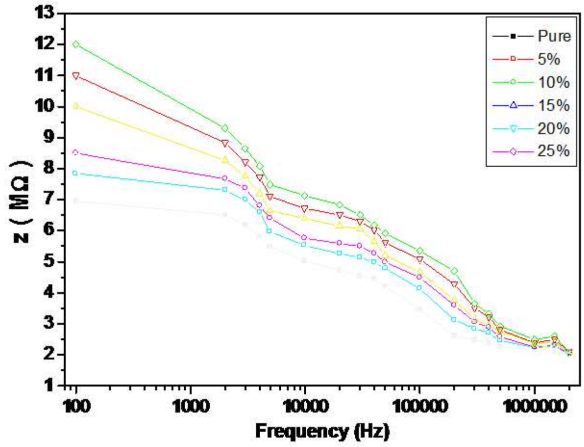


Figure (7). Plot of temperature -dependence of impedance of PVC-P/GEW composite.



Figure(8). Plot of frequency -dependence of impedance of PVC-P/GEW composite

Conclusion

It is found that the permittivity, dielectric loss and loss tangent for all composites increase with increasing the GEW filler content, or temperature which has been attributed to interfacial polarization and segmental mobility of the polymer molecules, respectively. The permittivity decreases with the increasing of frequency because interfacial and segmental mobility polarizations cannot keep up orientation in the direction of the alternating field. The impedance *Z* of the composite decreases with the increase of filler volume content, frequency and temperature.

Acknowledgements

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