

Effect of Fillers on Electrical Properties of Epoxy Composites

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Synopsis

The effect of fillers such as glass, ferrite, and carbon on the dielectric properties of epoxide resin along with conductivity has been studied as a function of frequency (1–100 kHz) and temperature (30–200°C). The glass transition temperature is not much affected by the presence of the fillers. The observed higher values of dielectric permittivity and loss in the case of filled polymers are attributed to Maxwell–Wagner–Sillars polarization.

INTRODUCTION

In recent years glass-fiber-reinforced epoxide and polyester composites have received increasing attention because of the combination of properties such as high strength and dimensional stability with low weight, corrosion and chemical resistance, and dielectric properties.^{1–3} Depending upon the application and the manufacturing process selected, a number of additives are often employed to provide specific products or end use properties.^{4–6} These include inert fillers, flame retardants, compounds to enhance surface finish, release agents, viscosity control materials, etc. These polymer composites have been studied mostly by mechanical methods and chemical analysis. The dielectric relaxation spectroscopic studies will reveal the extent of bonding between the binder and the filler and, in turn, the compatibility between the two; hence one can predict the mechanical and other properties of the composites. But relatively less attention has been paid^{5,7,8} to the application of the dielectric method to multicomponent polymeric systems.

The present work essentially deals with the effect of fillers such as glass fiber, ferrite, and carbon upon the dielectric properties of epoxide in a wide frequency range and temperature ranges. Further, the changes observed in the dielectric properties have been correlated with the dc conductivity studies on these composites.

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TABLE I
Composition of the Epoxide Composites

Sample	%Composition (w/w)			
	Epoxide	Glass	Ferrite	Carbon
A. Epoxide	100	—	—	—
B. Epoxide + glass	45	55	—	—
C. Epoxide + glass + ferrite	35	57	8	—
D. Epoxide + glass + carbon	41	54	—	5

EXPERIMENTAL

The epoxy resin polymer was commercial adhesive grade room temperature curable araldite LY 556 supplied by Ciba-Geigy (India) along with a curator, an aliphatic amine catalyst HY 951 in the ratio 10:1 for curing. The hand lay-up process was used to make the glass composites. The resin and the E-glass in the form of fabric were placed in the mold manually. Entrapped air was then removed with squeezers. Successive layers of glass and resin were added to build the composite of desired thickness and then cured at room temperature. The inorganic additives employed were nickel-zinc-manganese ferrite and activated carbon. The composition of the fillers in epoxide polymer is shown in Table I.

Dielectric permittivity (ϵ') and loss (ϵ'') were measured with General Radio Capacitance Bridge (Mode GR 1615) using three terminal cells⁹ in the frequency range 10^3 – 10^5 Hz and temperature range 30–200°C. The accuracy in ϵ' and ϵ'' is about 2 and 4%, respectively.

dc conductivity measurements were carried out by two electrode cell using a Keithley electrometer (Model 610C). The experiment involves the measurements of resistance of the sample to calculate dc conductivity and its variation with temperature. Resistance was measured 1 h after the stability of the temperature had been attained.

Samples were cut and polished to the size of $1.0 \times 0.6 \times 0.2$ cm, and their surfaces had been backed by thin aluminium foils to serve as electrodes. The temperature of the sample was controlled within $\pm 1^\circ\text{C}$.

In order to avoid any influence of moisture, the samples were stored in a vacuum desiccator in the presence of silica gel for 24 h before performing the experiment. The experiment was also carried out under the vacuum of 10^{-2} torr.

RESULTS AND DISCUSSION

Dielectric Studies

Fillers employed here are inorganic materials having no dielectric transitions in the range where the host polymer has. Thus, the results obtained here are due to the polymer in the presence of the filler.

The dielectric permittivity (ϵ') of the filled polymers (B, C, and D) and pure polymer (A) as a function of frequency at representative temperatures 30 and 180°C is shown in Figure 1. It is seen that the values of ϵ' are larger than

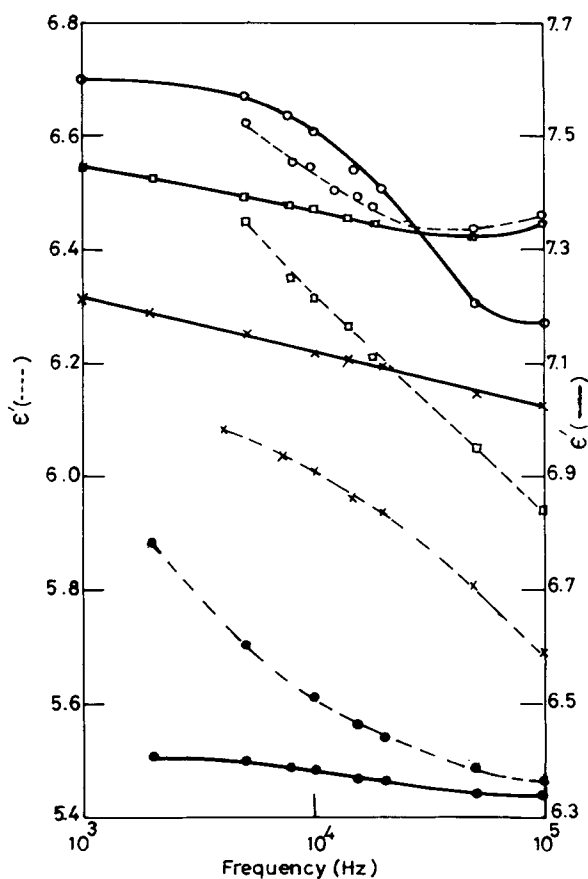


Fig. 1. Variation of ϵ' with frequency: (●) A; (×) B; (○) C; (□) D; (---) 30°C; (—) 180°C.

those of the pure polymer in the whole frequency range for both the temperatures. But ϵ' decreases with the increase of frequency for all the four samples. At any frequency with the increase of temperature, ϵ' is also seen to be increasing for all the samples.

Figure 2 shows the plot of ϵ'' as a function of temperature at 5 kHz for all the four samples. For sample A, there occurs two maxima, one around 70°C and the second one at 150°C. The low temperature peak is assigned to the β -relaxation process, and the high temperature peak to the α -relaxation process. It has been also shown¹⁰⁻¹⁴ that the α -relaxation process is associated with the segmental motion or glass transition process. The β -relaxation process is attributed to the relaxation of the glyceryl unit $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$. Introduction of glass (sample B) reduces the intensity of the α peak and increases the β peak intensity, and there occurs a small peak around 50°C probably corresponding to the γ -relaxation process, which may be ascribed to the enhanced rotation of the methyl group attached to the main chain and the presence of filler. It can be further noted that β peak occurs at a significantly higher temperature (90°C) and the α peak is shifted to lower temperature (130°C).

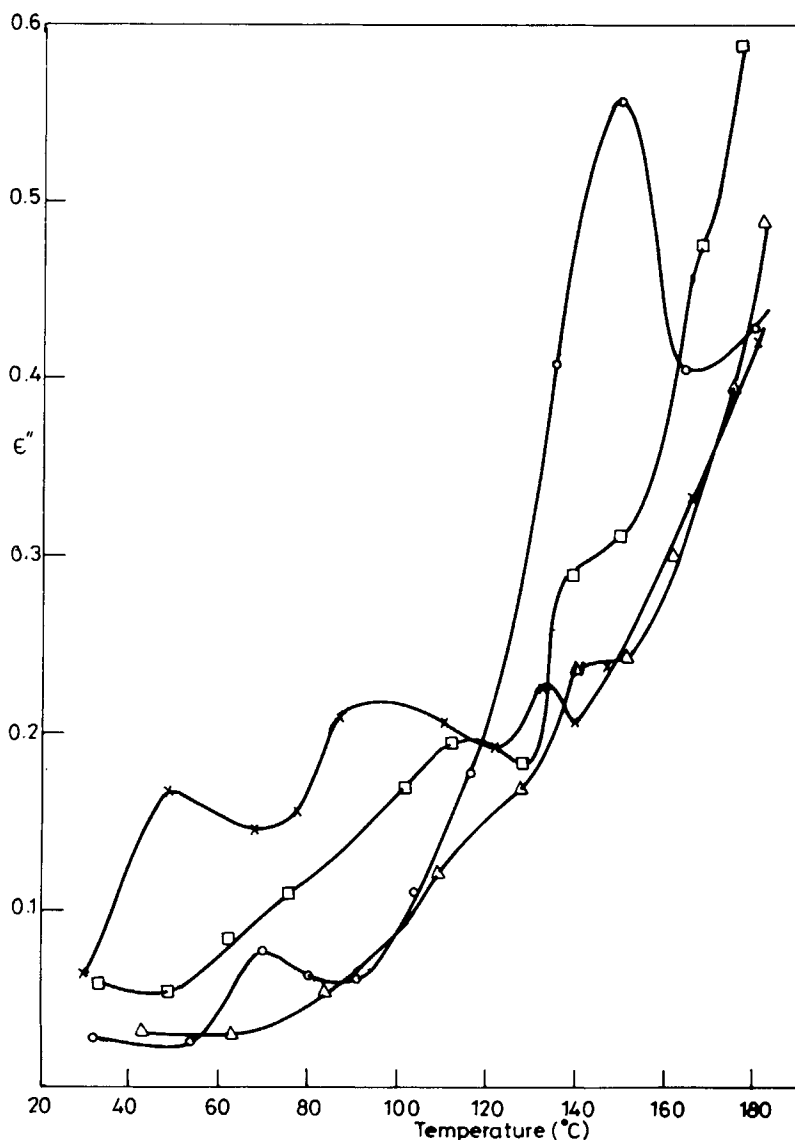


Fig. 2. ϵ'' vs. temperature at 5 kHz: (○) A; (×) B; (△) C; (□) D.

Incorporation of ferrite and glass into the epoxide matrix (sample C) suppresses the β peak completely and the α peak to a considerable extent, and only one peak is observed around 140°C. Such suppression may work out for a tendency of margin of both α and β peaks suggesting the $\alpha\beta$ interaction. It may be seen^{15,16} that similar $\alpha\beta$ interaction does exist in the case of polymers and also in the presence of additives.

In the presence of carbon (sample D) the β peak is shifted to the higher temperature (110°C) and the α peak to 140°C. The intensity of the α peak is suppressed, and that of the β peak is enhanced.

On the whole, it may be understood that the additives of fillers to the polymer has suppressed the intensity of the α peak occurring at a reasonably

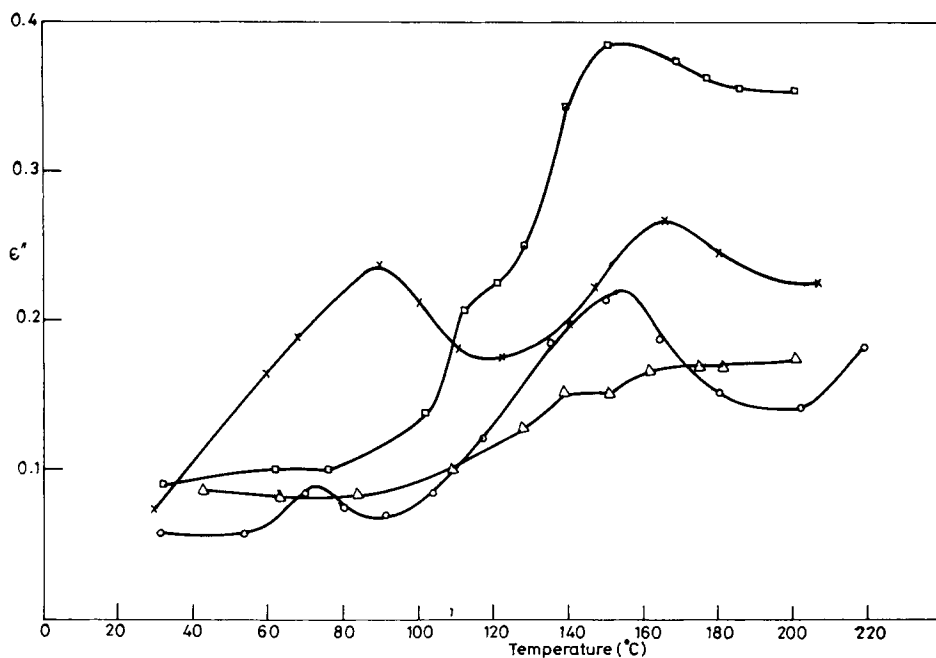


Fig. 3. ϵ'' as a function of temperature at 100 kHz: (○) A; (×) B; (△) C; (□) D.

constant temperature. However, β peaks occur in a scattered temperature range, which may be due to the direct or indirect influence of the γ peak.

Figure 3 presents the data of ϵ'' measured at 100 kHz as a function of temperature for all the four samples. They show the presence of both the α and β peaks occurring at relatively high temperatures when compared to the data at 5 kHz (Fig. 2). The peaks at 100 kHz are relatively weak for all the samples studied, and it is essential to note that γ peak has not been obtained as in the case of 5 kHz for sample B.

Generally, the intensity of the peak decreases with the increase of frequency and the peak is shifted to high temperatures at high frequencies. Figure 4 shows the typical plot of dielectric loss (ϵ'') values taken at different frequencies as a function of temperature for sample C. The data in the low frequency region show a large difference in the values of the filled (B, C, and D) and the unfilled polymer (A), those of the former being always larger, especially at high temperatures.

All these features can be explained on the basis of the heterogeneity of the filled epoxy resin, which causes the virtual electric charges to get concentrated at the interface of the heterogeneous system having different permittivity and conductivity. This gives rise to the polarization effect known as the Maxwell-Wagner-Sillars (MWS) polarization.^{16,17} The dielectric properties of the heterogeneous system are shown to obey the well-known Debye equation,¹⁸ and an arc plot can give some indications like the appearance of "tails" superimposed on Cole-Cole arc plots at low frequencies.¹⁶

Thus in Figure 5 giving the Cole-Cole plot for all the four samples studied around 150°C, sample A shows a gradual increase while a filled polymer indicates two types of relaxation mechanisms, namely, dipole orientational polarization and Maxwell-Wagner-Sillars (MWS) polarization. So, as a con-

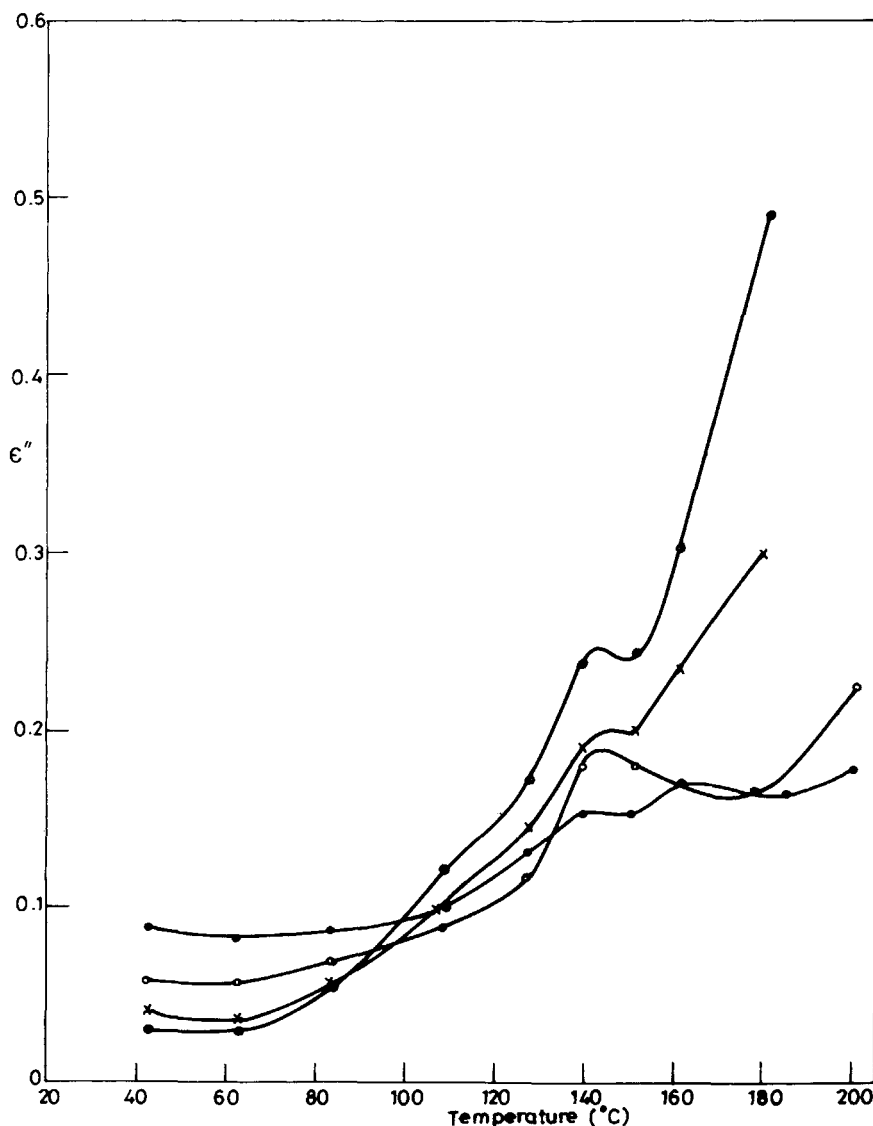


Fig. 4. ϵ'' vs. temperature at different frequencies for sample C: (●) 10^5 Hz; (○) 5×10^4 Hz; (×) 10^4 Hz; (●) 5×10^3 Hz.

sequence of MWS polarization, filled samples show higher values of permittivity and dielectric loss and a transition with a relaxation time larger than that due to a typical dipole orientation. The dynamic permittivity $\bar{\epsilon}_{\infty}$ for the MWS polarization effect of filled polymers can be had from the arc plot by extrapolating the MWS polarization curve towards the dielectric permittivity axis.

Conductivity Studies

Identifying glass transition temperature (T_g) from dc conductivity measurements widely used because the conductivity steeply rises above T_g^{19} due to the considerable increase in the ionic mobility. The variation of dc conductivity

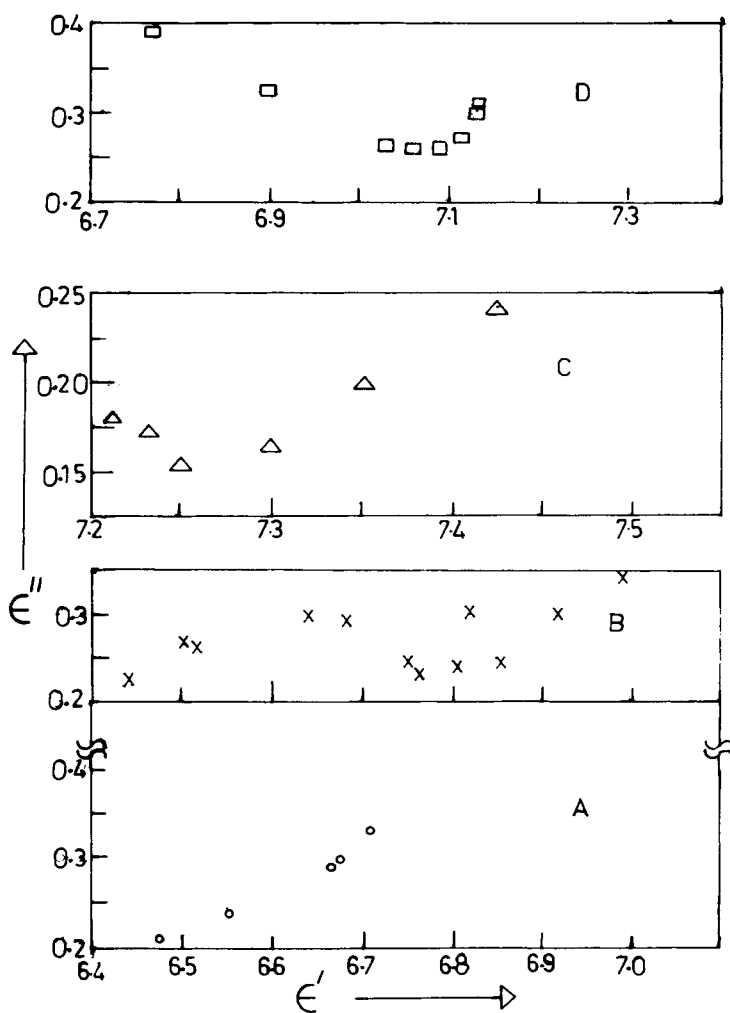


Fig. 5. The Cole-Cole plot.

with temperature is shown in Figure 6 for all the four samples. It is clear from the graph that the transition around 130°C corresponds to the glass transition temperature and epoxide composites B, C, and D have relatively low conductivity in comparison with the epoxide A.

The activation energy (E) calculations were made at the rubbery region (above T_g) using the relation, $\sigma_{dc} = A \exp(-E/kT)$, where the parameters have the usual significance and the results are inserted in Table II. It may be noted that only a slight difference exists among the values of T_g and, further, that the activation energy is almost the same. This is due to the fact that the glass transition temperature T_g depends only on the motion of segments of the macromolecules in the amorphous phase which are similar for all the four samples and are only hindered by the filler. Further, it gives us an understanding that there is a poor bonding present between the polymer matrix and the fillers.

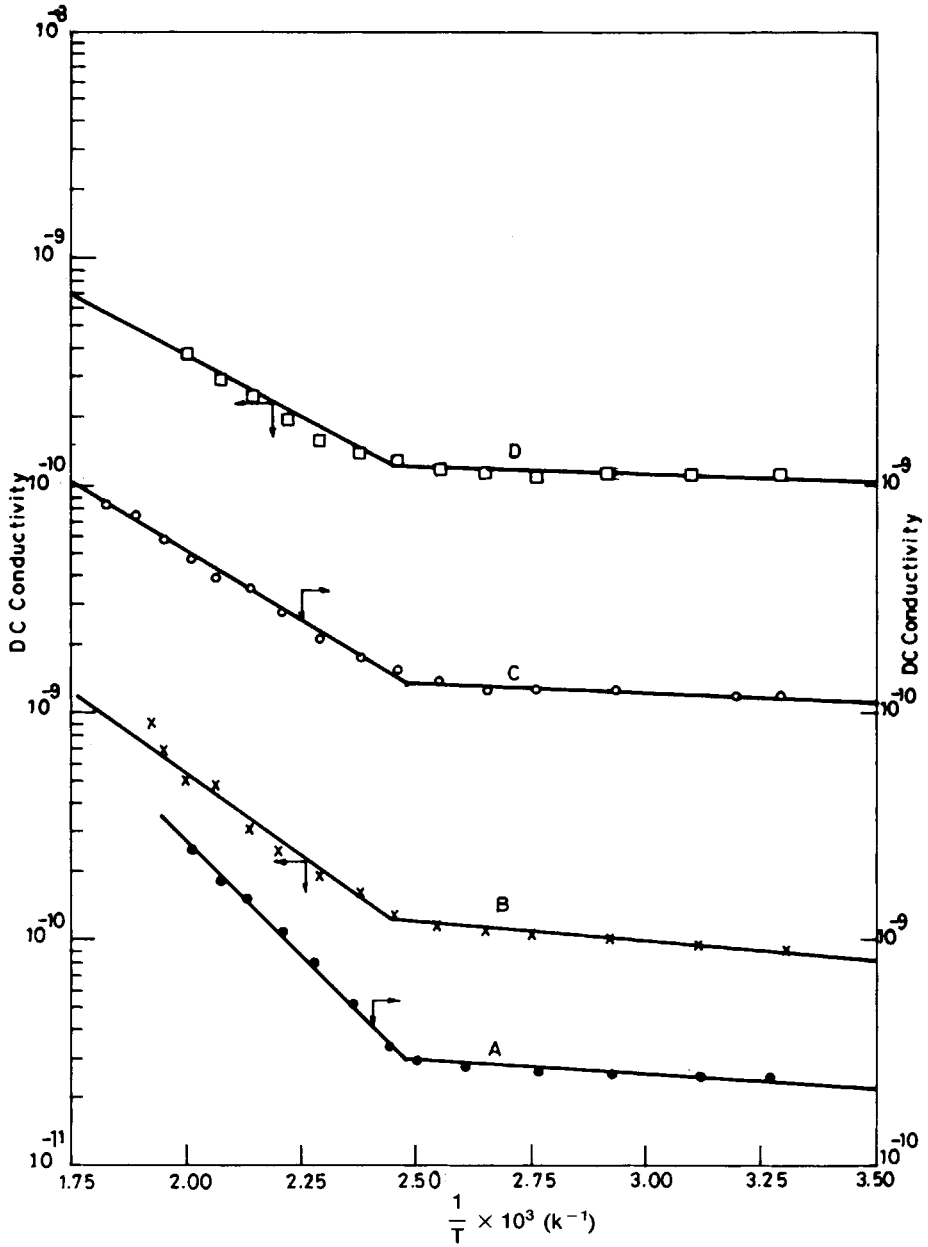


Fig. 6. dc conductivity vs. $1/T$.

TABLE II
Glass Transition Temperature and Activation Energy Data

Sample	Glass transition temperature (T_g) (°C)	Activation energy (E) (eV)
A	131	0.40
B	135	0.28
C	131	0.22
D	135	0.22

The glass transition temperature from dc conductivity data is not affected by the presence of filler while the maxima (at high temperatures) in the $\epsilon''-T$ curves is observed at higher than T_g obtained from conductivity data. This difference, however, exists as the ac activation energy is also frequency-dependent^{20,21} by way of differences of effective frequencies.²²

From the present investigations on epoxy composites it may be concluded that the α -relaxation process, which depends only on the segmental motion, is not very much affected while the β -relaxation process, which is caused by the motion of small groups, is strongly influenced by the MWS polarization effect due to the presence of fillers.

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