JOURNAL OF MATERIALS SCIENCE 26 (1991) 4130–4135

Dielectric-relaxation studies in polymethyl methacrylate-mica composites

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Dielectric properties have been studied in polymethyl methacrylate (PMMA) and composites of PMMA containing different weight ratios of mica at different temperatures and different frequencies. It has been observed that the dielectric constant (ε') and dielectric loss (ε'') increase with the increasing amount of mica in the composites up to a certain percentage of mica. The activation energy values have been calculated. The results have been explained on the basis of the space charge effect, dipolar orientation and increase in the free volume of PMMA with the addition of mica in it.

1. Introduction

Dielectric studies of polymer composites provide valuable information about molecular motion and their interactions in the composite materials. Mica reinforced thermo plastics are now becoming increasingly important because of their many advantages. The high strength and rigidity of mica along with its low density and low cost make it an ideal candidate as an alternate reinforcing agent in composites where strength to weight ratio are necessary requirements. Mica is a silicate mineral found in abundance in the form of flakes and usually in a thin sheet structure. A study on the effect of mica on the dielectric properties of PMMA is important from the practical point of view also because PMMA is used extensively in electric insulation as well as in applications where clarity is important.

Some investigations [1–4] have been published on the effect of plasticizers on the dielectric and mechanical properties of high polymers and their influence on glass transition temperature (T_g). The aim of this study is to investigate systematically the effect of adding increasing quantities of mica on the dielectric and thermal properties of PMMA.

2. Experimental procedure

The polymer samples were prepared by solution cast method using benzene as the solvent. PMMA in the form of granules was obtained from BDH (England). Mica in the form of sheets was ground and then sieved through 106 μm sieve. Mica loaded films were made by dispersing mica powder in PMMA solution in different weight ratios (3–30%). The films were dried in the solvent atmosphere and were later put in the oven at 60 °C for 48 h to remove all traces of solvent. The films were 50–150 μm in thickness. Aluminium electrodes were vacuum deposited on an area of 2 cm^2 on both sides of the films for dielectric measurements. Dielectric parameters such as capacitance and dissipation factor were measured by an impedance analyser (Hewlett-Packard model 4192A) at various frequencies (100 Hz–1 MHz) and temperatures (50–160 °C). The differential scanning calorimetric (DSC) thermograms were recorded on a Du Pont Thermal Analyser (model 1090) at a heating rate of 10 °C min^{-1}.

3. Results and discussion

Fig. 1a and b show the variation of permittivity (ε') and loss (ε'') with percentage of mica in the composites at different temperatures and at 1000 Hz. It can be seen that ε' and ε'' increase with the increasing amount of mica in the composite up to a certain percentage (10%) and then decrease slightly at each temperature before starting to increase again. These results indicate the diffusion of polymeric chains at the interface of PMMA and mica is taking place which is apparent from the higher value of T_g and the activation energy [5] for this composite sample (Table I). This will lead to an increase in ε' and ε''. At still higher percentages of mica, it acts predominantly as an intramolecular plasticizer where the mica molecules are distributed in the inter-aggregate space. This will hinder the polymer chain elongation and consequently may result in the decrease of ε' and ε''. It seems that at still higher percentages of mica, interfacial polarization along with the dipolar polarization of the polymer and the polarization of mica start playing a role. This may

TABLE I

Sample	Activation energy (k cal mol^{-1})	T_g (°C)
PMMA	21.4 (2)	89.3
PMMA + 10%mica	21.8 (8)	100.5
PMMA + 20% mica	14.0	82.5
PMMA + 30% mica	11.4	80.0

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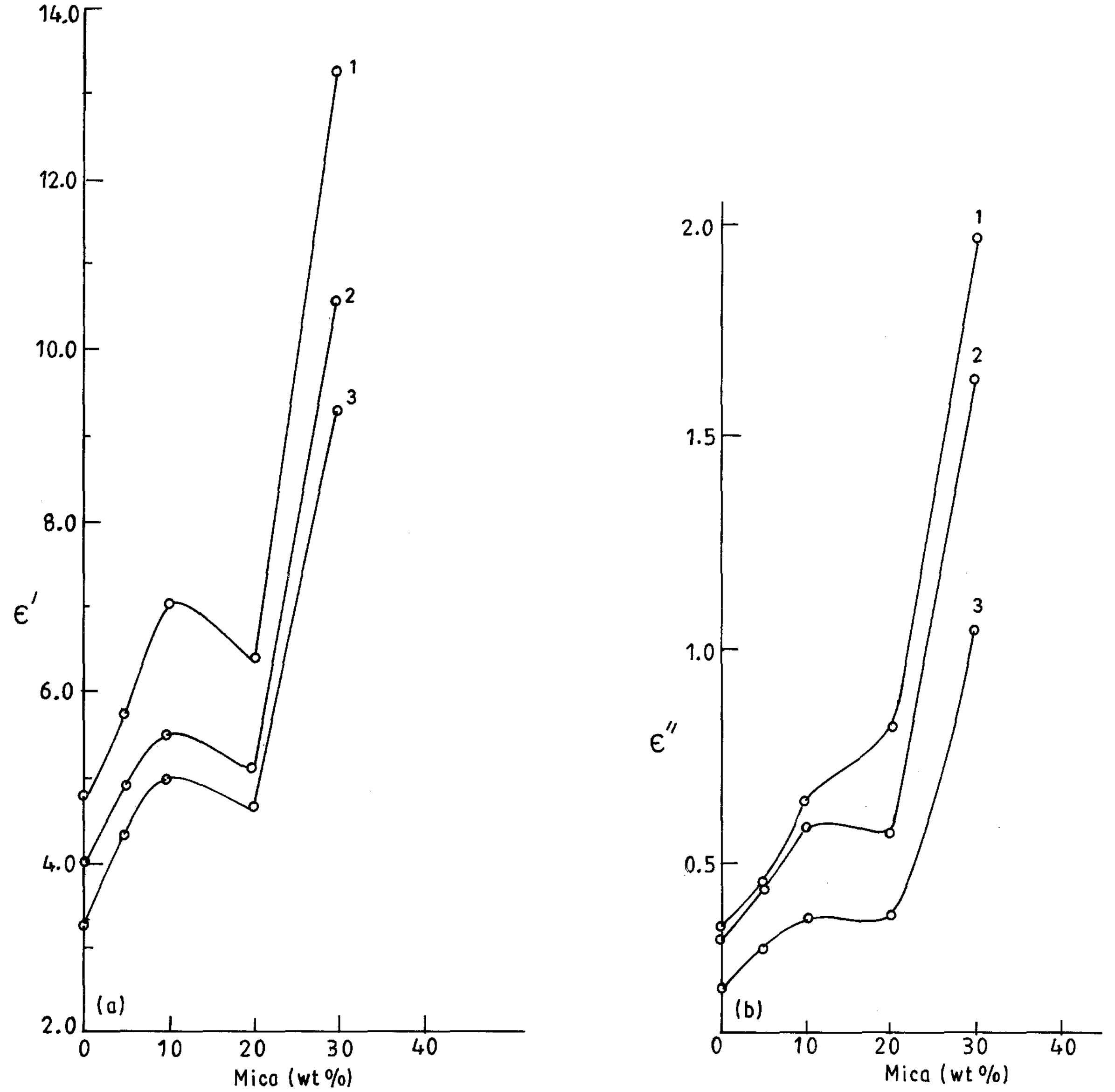

Figure 1 (a) Variation of ε' against percentage of mica at (1) 50, (2) 90, and (3) 130 °C, at fixed frequency 10^3 Hz; (b) variation of ε'' against percentage of mica at (1) 50, (2) 90, and (3) 130 °C, at fixed frequency 10^3 Hz.

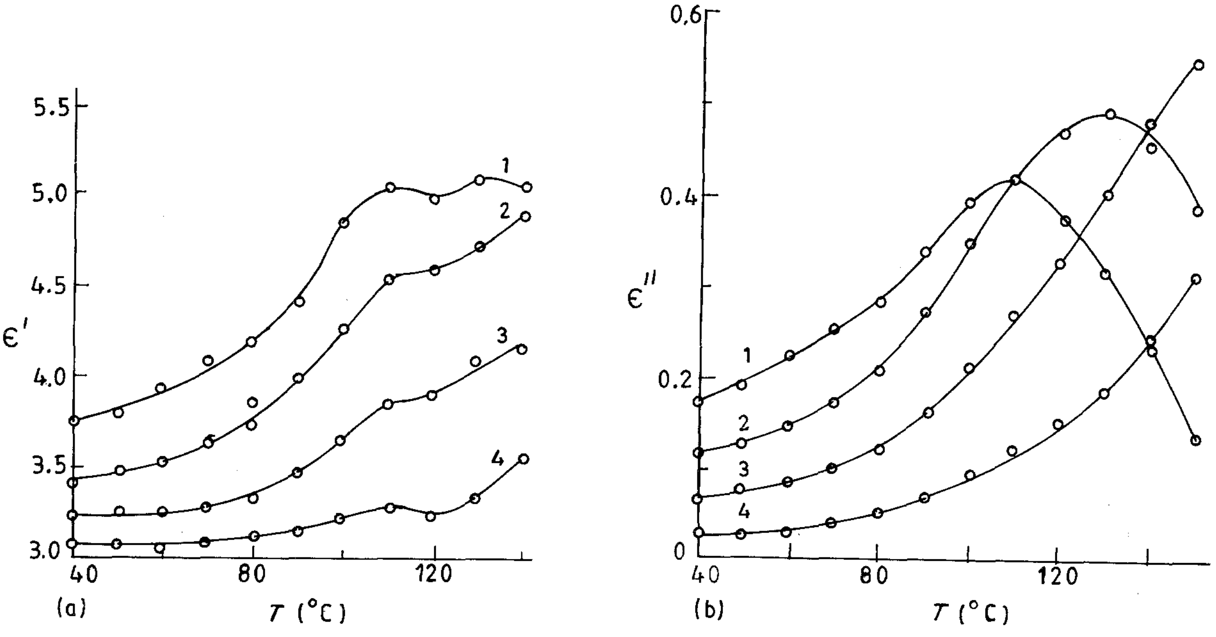

Figure 2 (a) Variation of ε' against temperature of pure PMMA at (1) 100, (2) 10^3 (3) 10^4 and (4) 10^5 Hz; (b) variation of ε'' against temperature of pure PMMA at (1) 10^3, (2) 10^4, (3) 10^5 and (4) 10^6 Hz.

increase the value of ε′ of the composite (as mica has higher value of ε′ (not shown)). This type of behaviour has also been observed in other polymer-mica composites [6].

Fig. 2a and b show the variation of ε′ and ε″ with temperature at various fixed frequencies for the pure PMMA samples used. ε″ shows a peak which shifts to higher frequencies with increasing temperature which clearly indicates the dipolar nature of the relaxation [7]. ε′ increases with temperature for the pure as well as the composite samples (Figs 2a, 3a and 4a) and this behaviour is more appreciable at lower frequencies. The increase of ε′ with temperature is due to an increase of the polarization arising from the facilitation of the molecular motion of polymer chain segments which allows orientation of dipolar units in the applied electric field. Trapped charge carriers are also expected to contribute to the total polarization as the polymer systems normally contain large numbers of trapping sites [8]. Polarization of trapped charge carriers is more significant at high temperatures and at low frequencies. Figs 3b and 4b show the loss thermograms for 10% and 20% composite samples. These curves also show the appearance of loss peaks which shift to higher temperatures with increase in frequency

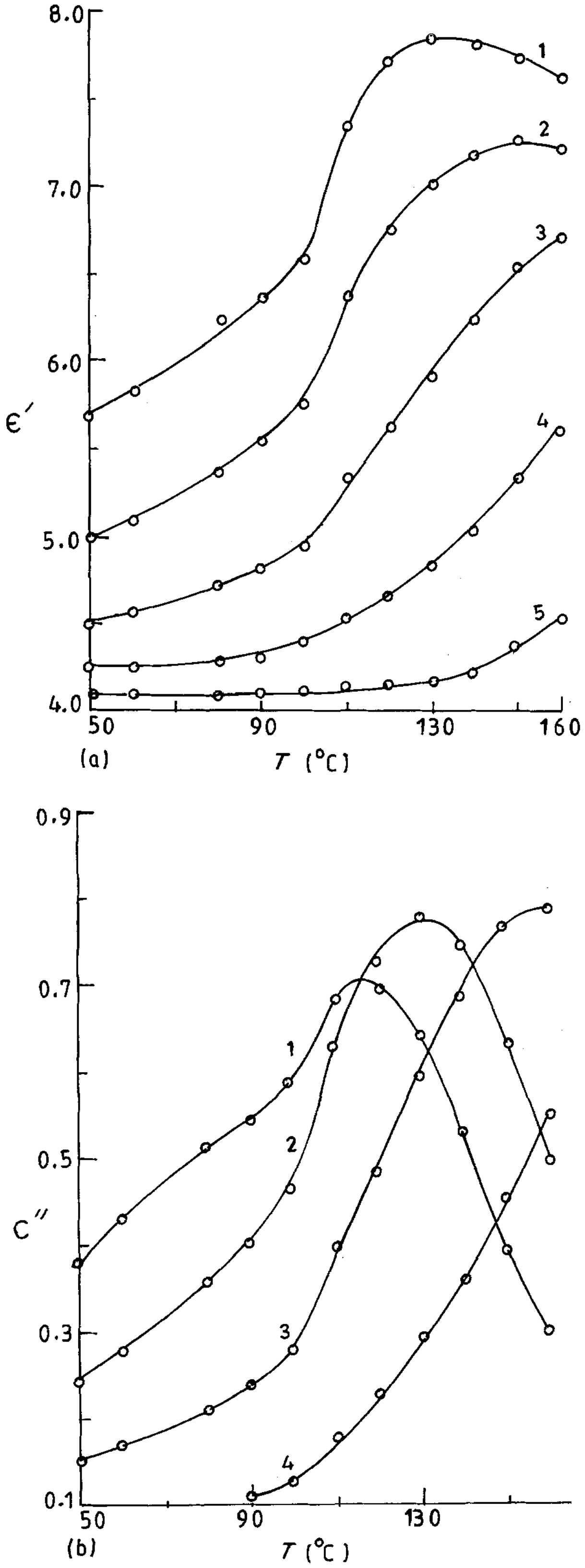

Figure 3 (a) Variation of ε′ against temperature of PMMA containing 10% mica at different frequencies (1) 100, (2) 10^3, (3) 10^4, (4) 10^5 and (5) 10^6 Hz; (b) variation of ε″ against temperature of PMMA containing 10% mica at different frequencies (1) 10^3, (2) 10^4, (3) 10^5 and (4) 10^6 Hz.

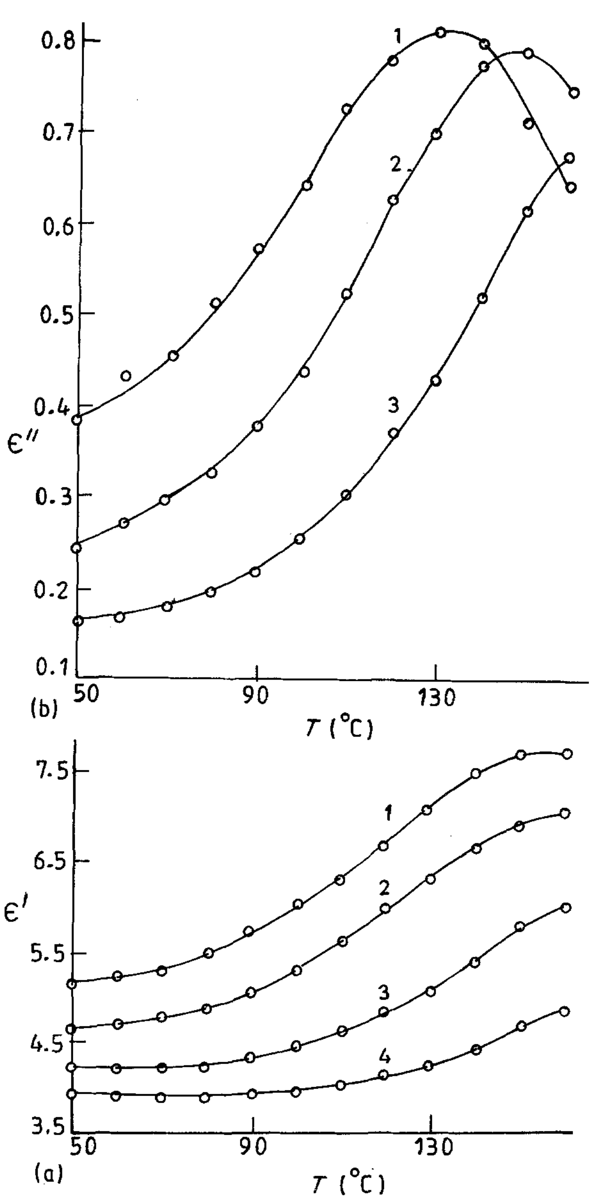

Figure 4 (a) Variation of ε′ against temperature of PMMA containing 20% mica at various frequencies (1) 200, (2) 10^3, (3) 10^4 and (4) 10^5 Hz; (b) variation of ε″ against temperature of PMMA containing 20% mica at various frequencies (1) 10^3, (2) 10^4 and (3) 10^5 Hz.

but the peak also shifts to higher temperature at a fixed frequency with the increase in the percentage of mica. This also shows the contribution of interfacial polarization to the total dielectric relaxation of the composite samples. This point becomes more clear from Fig. 5a and b for 3% and 30% of mica composite samples which show the variation of ε'' with frequency for various temperatures. Very distinct dipolar (although not Debye-type because they are broad showing distribution of relaxation times) peaks are observed in 3% composite while for 30% sample this characteristic is very much reduced which clearly shows the dominance of interfacial polarization mechanism in higher percentage mica composites.

Activation energies have been evaluated from the Arrhenius shift of the peak frequencies against temperatures (Fig. 6). Table I gives the activation energies for various samples. It is clear from the table that the activation energy increases up to 10% composite sample and then decreases. The higher value for 10% sample is in close agreement with the higher value of T_g for this sample as obtained from DSC studies

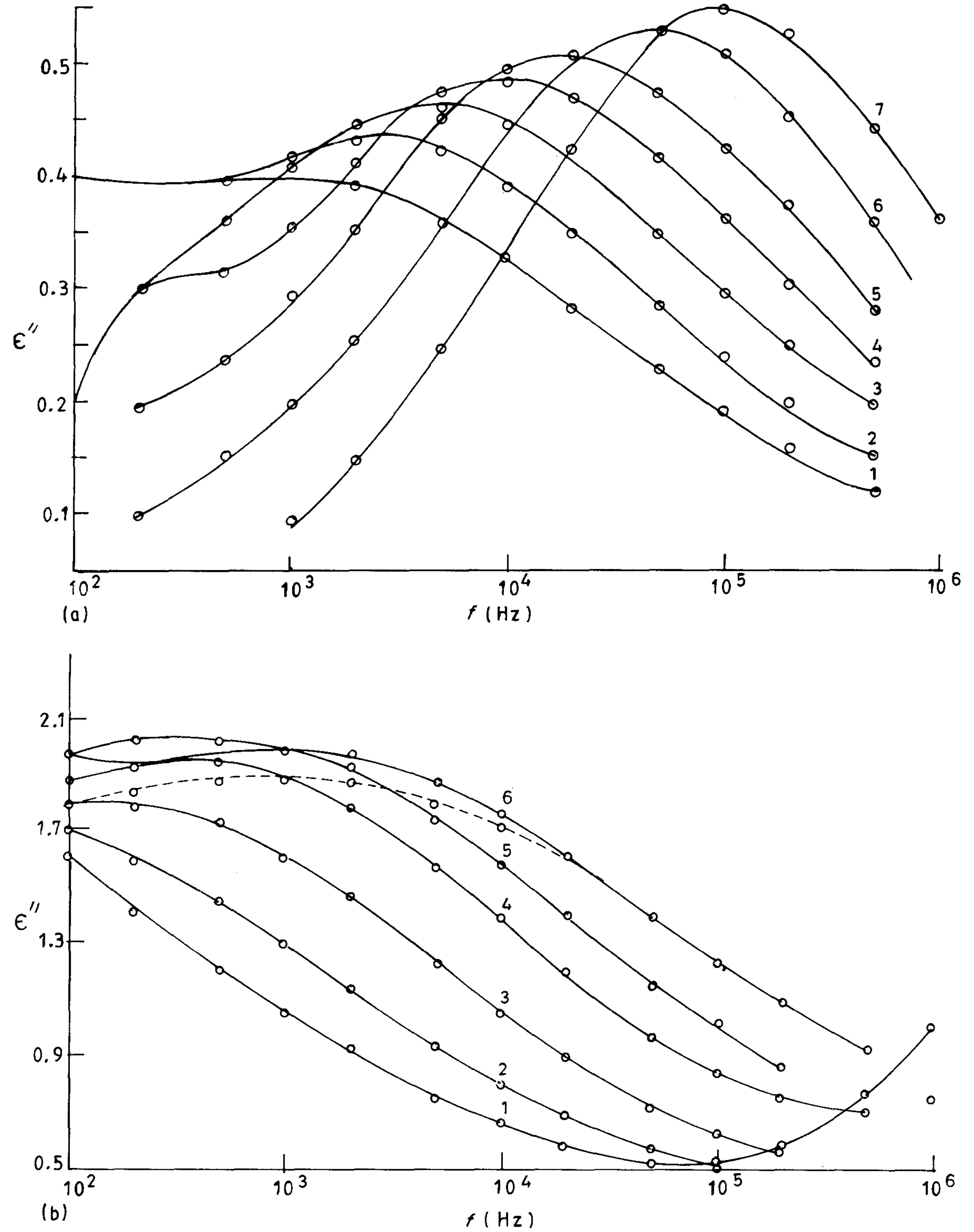

Figure 5 (a) Variation of ε'' against frequency of PMMA containing 3% mica at different temperatures (1) 90, (2) 100, (3) 110, (4) 120, (5) 130, (6) 140 and (7) 150 °C; (b) variation of ε'' against frequency of PMMA containing 30% mica at different temperatures (1) 50, (2) 70, (3) 90, (4) 110, (5) 120, (6) 130 and (7) 140 °C.

(Table I). The segmental motion requires higher energy and therefore T_g and activation energy both increase in value. The decrease in activation energy and T_g for higher percentage mica composites may be due to the change in internal viscosity of the samples at higher percentages of mica where chains are separated and free volume increases which facilitates both dipolar orientation and interfacial polarization but as the number of dipoles in higher percentages of mica composites reduces, the interfacial mechanism becomes more dominant. Fig. 7 shows the Cole–Cole plots for PMMA and 3%, 15% and 30% composite samples at 140 °C. The plots are not circular arcs and are characteristic of distributed relaxation. The dielectric increment Δε values for pure PMMA and different composite samples are shown in Table II. Δε increases with measuring temperature (3%) and also with increasing percentage of mica. The comparatively large dielectric increment in 30% mica composite cannot be explained by dipole-orientation polarization. Such behaviour may be attributed to be characteristic of interfacial polarization [9]. The slight decrease in Δε for 3% composite as compared to its value for PMMA may be explained as being due to the hindrance of PMMA dipoles in the composites because of the presence of mica.

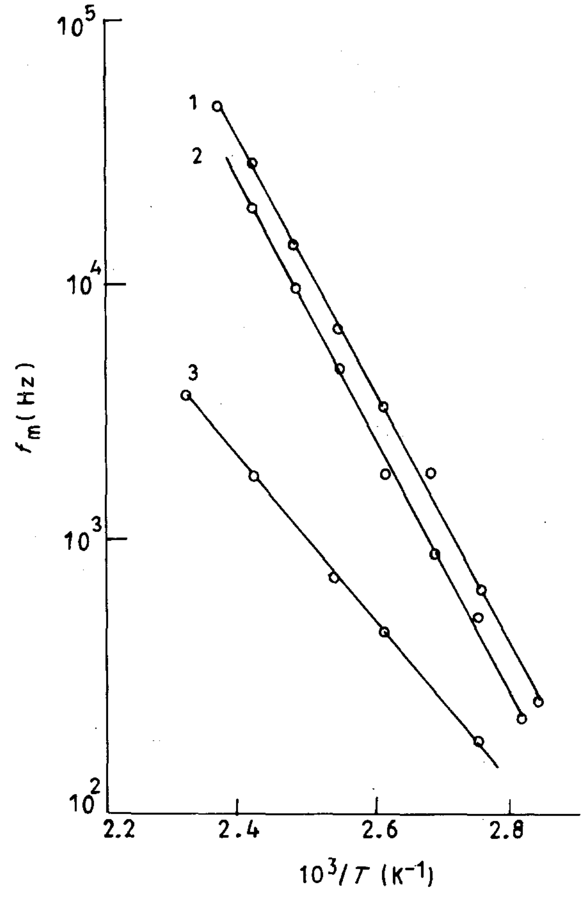

Figure 6 Plot of log f_{max} against $10^3/T$ for pure PMMA and composites. (1) PMMA, (2) 10% mica and (3) 20% mica.

4. Conclusions

Interfacial polarization plays a dominant role in higher percentage mica composites. It can be conclu-

TABLE II

Sample	T (°C)	Δε
PMMA	140	2.36
PMMA + 3% mica	80	1.45
PMMA + 3% mica	140	2.20
PMMA + 15% mica	140	2.80
PMMA + 30% mica	140	13.55

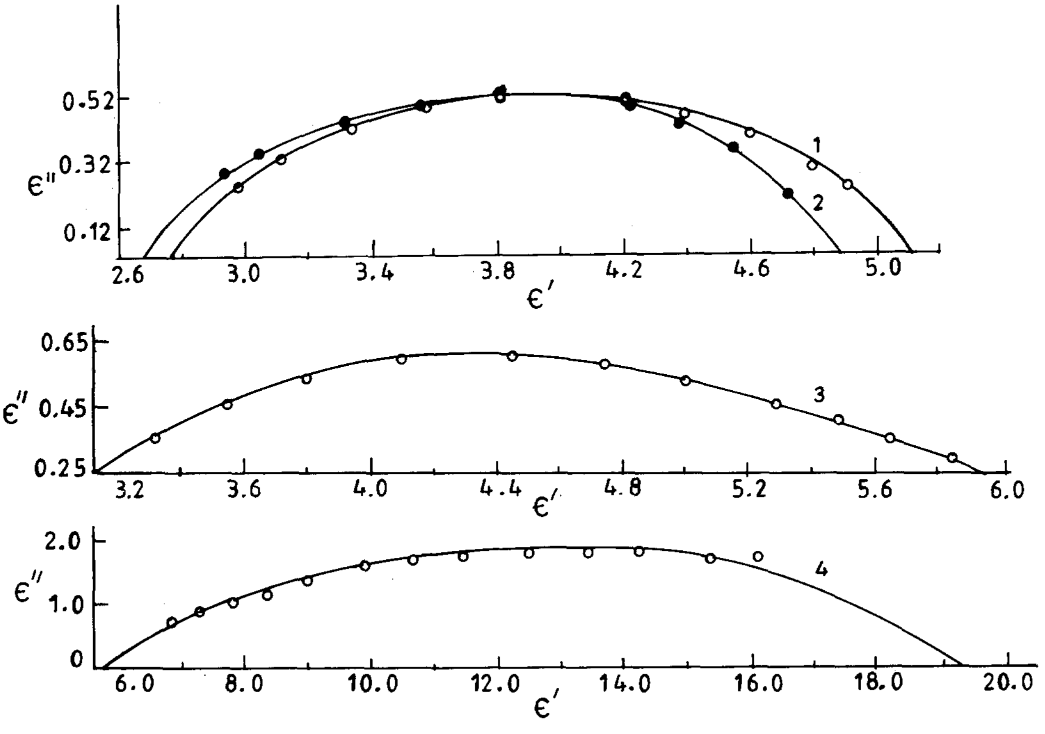

Figure 7 Cole–Cole plots for pure PMMA and composites at 140 °C. (1) PMMA, (2) 3% mica, (3) 15% mica and (4) 30% mica.

ded from the above results that the composite containing 10% mica shows better dielectric and thermal properties.

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Received 22 January
and accepted 30 November 1990