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Effect of mica on the dielectric relaxation of polyvinyl chloride (PVC) films

Part 1

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Dielectric constant (ε') and dielectric loss (ε'') have been measured on polyvinyl chloride (PVC) and PVCs containing different weight ratio of mica at different temperatures and frequencies. It has been found that the dielectric constant and dielectric loss increases with the increasing amount of mica in the composite until a certain percentage of mica. The activation energy values were calculated for these materials. It was observed that the activation energy values go on decreasing with the increasing amount of mica in the composites. The results have been explained on the basis of the space charge effect and increase in the free volume of PVC with the addition of mica in it.

1. Introduction

Mineral filled polymer composites, both thermoplastic and thermosetting, have become widely accepted in electrical and other applications. Mica is an attractive candidate as a filler in electrical applications as it has excellent insulating properties. Mica, when used as a reinforcing agent in plastics, offers many advantages including planer reinforcement, reduced creep, reduced wear of processing equipment, etc. [1, 2]. A study on the effect of mica on the dielectric properties of polyvinyl chloride (PVC) is important from the practical point of view also because PVC is used extensively as an electric insulation in many industrial applications.

Some investigations [3-9] 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 properties and T_g of PVC.

2. Experimental details

Solution cast films of PVC obtained from BDH India were made by dissolving it in tetrahydrofuran. Mica loaded films were prepared by dispersing mica powder (grain size 45 μm) in PVC solution in different weight ratios. The films were dried in the solvent atmosphere and were latter put in the oven at about 60° C for 48 h, to remove all traces of solvent. The films prepared were 50-300 μm thick. Aluminium electrodes were vacuum deposited on an area of 2 cm^2 on both sides of the films for dielectric constant and loss measurements. The dependence of dielectric constant and loss at various temperatures and frequencies were carried out with the help of 4192 LF impedence analyser (Hewlett Packard).

3. Results and discussion

The results obtained for the permittivity (ε') and loss (ε'') for samples with increasing mica content in PVC at different temperatures and at 10^5 Hz are shown in Fig. 1a and b respectively. It can be seen that ε' and ε'' increase with the increasing amount of mica in the composite until a certain percentage (about 10%) and then decrease slightly at each temperature before starting to increase again. These results indicate that up to about 10% of mica in polymer acts as an intermolecular plasticizer and is able to penetrate the molecular bundles of PVC, leading to chain separation. This will lead to an increase in $\varepsilon'$and ε''. At still higher percentage of mica, it acts predominantly as an intramolecular plasticizer, where the mica molecules are distributed in the interaggregate 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 percentage of mica, interfacial polarization along with the dipolar polarization of the polymer and the polarization of mica starts playing a role. This may increase the value of the composition (as mica has higher value of ε' not shown in Fig. 1).

Figure 2 shows the variation of ε' and ε'' with frequency at various fixed temperatures and with temperature at various fixed frequencies for the pure PVC samples used. These are the normal expected curves for a dipolar material. The sharp increase of ε' above 80° C (Fig. 2a and c) is indicative of the fact that the glass transition temperature of the PVC sample is about 80° C. This shift in the loss peak to higher frequency (Fig. 2d) with increasing temperature and to higher temperature (Fig. 2b) with increasing frequency are the clear indications that the dielectric relaxation in PVC is dipolar in nature [3].

The variation of ε' and loss with frequency and temperature for two representative PVC mica

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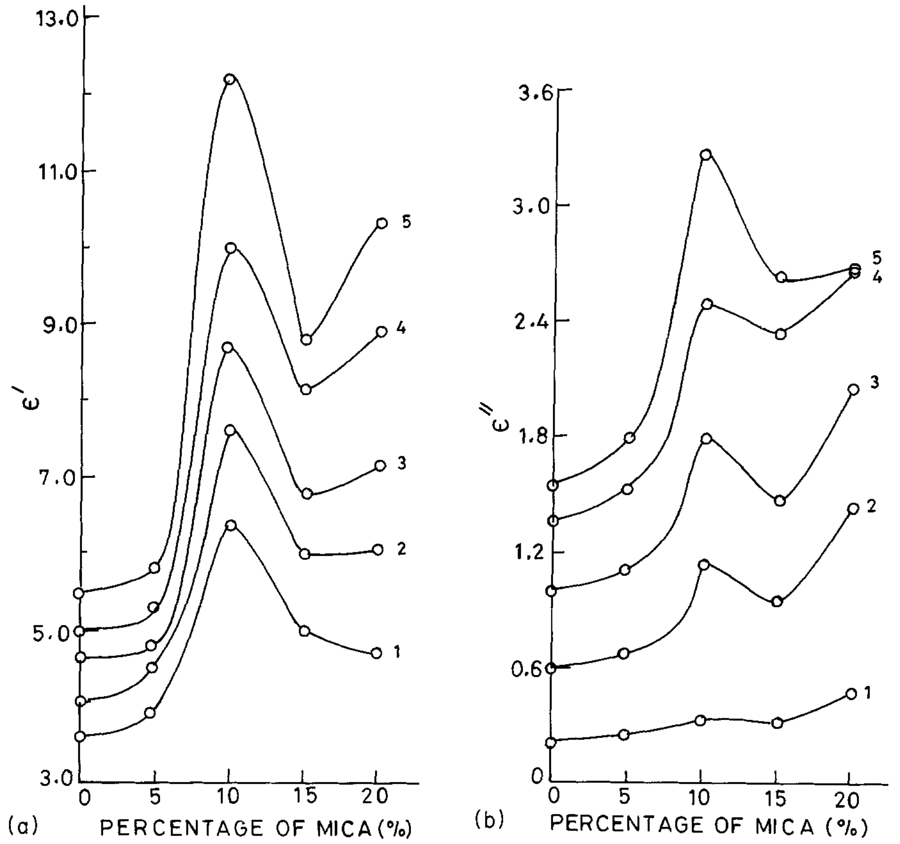

Figure 1 (a) Variation of dielectric constant ε' against percentage of mica at (1) 60° C (2) 80° C (3) 90° C (4) 100° C (5) 110° C at fixed frequency 10^5 Hz. (b) Variation of dielectric loss ε" against percentage of mica at (1) 60° C (2) 80° C (3) 90° C (4) 100° C (5) 110° C at fixed frequency 10^5 Hz.

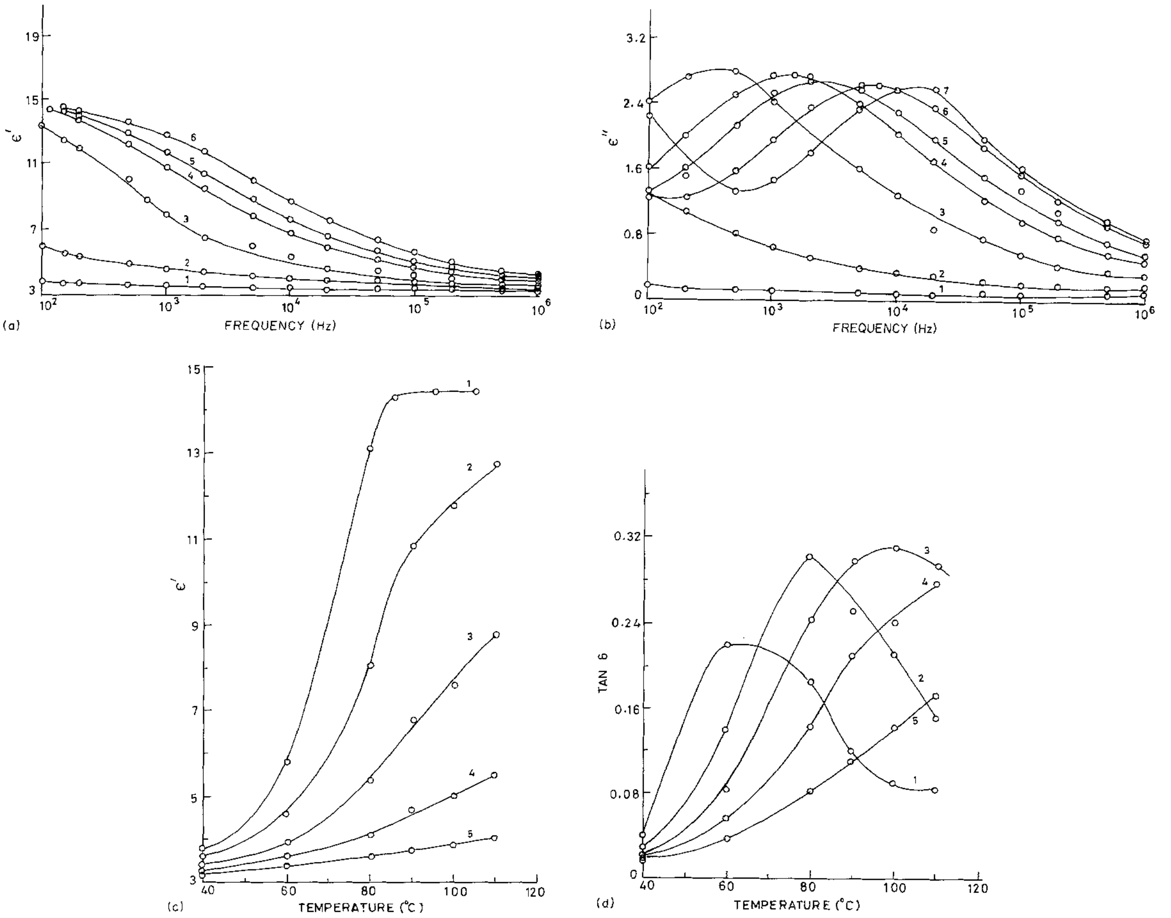

Figure 2 (a) Variation of dielectric constant ε' against frequency of pure PVC at (1) 40° C (2) 60° C (3) 80° C (4) 90° C (5) 100° C (8) 110° C. (b) Variation of dielectric loss ε" against frequency of pure PVC at (1) 40° C (2) 60° C (3) 80° C (4) 90° C (5) 100° C (6) 110° C (7) 120° C. (c) Variation of dielectric constant ε' against temperature of pure PVC at different frequencies: (1) 10^2 Hz (2) 10^3 Hz (3) 10^4 Hz (4) 10^5 Hz (5) 10^6 Hz. (d) Variation of tan δ against temperature of pure PVC at different frequencies: (1) 10^2 Hz (2) 10^3 Hz (3) 10^4 Hz (4) 10^5 Hz (5) 10^6 Hz.

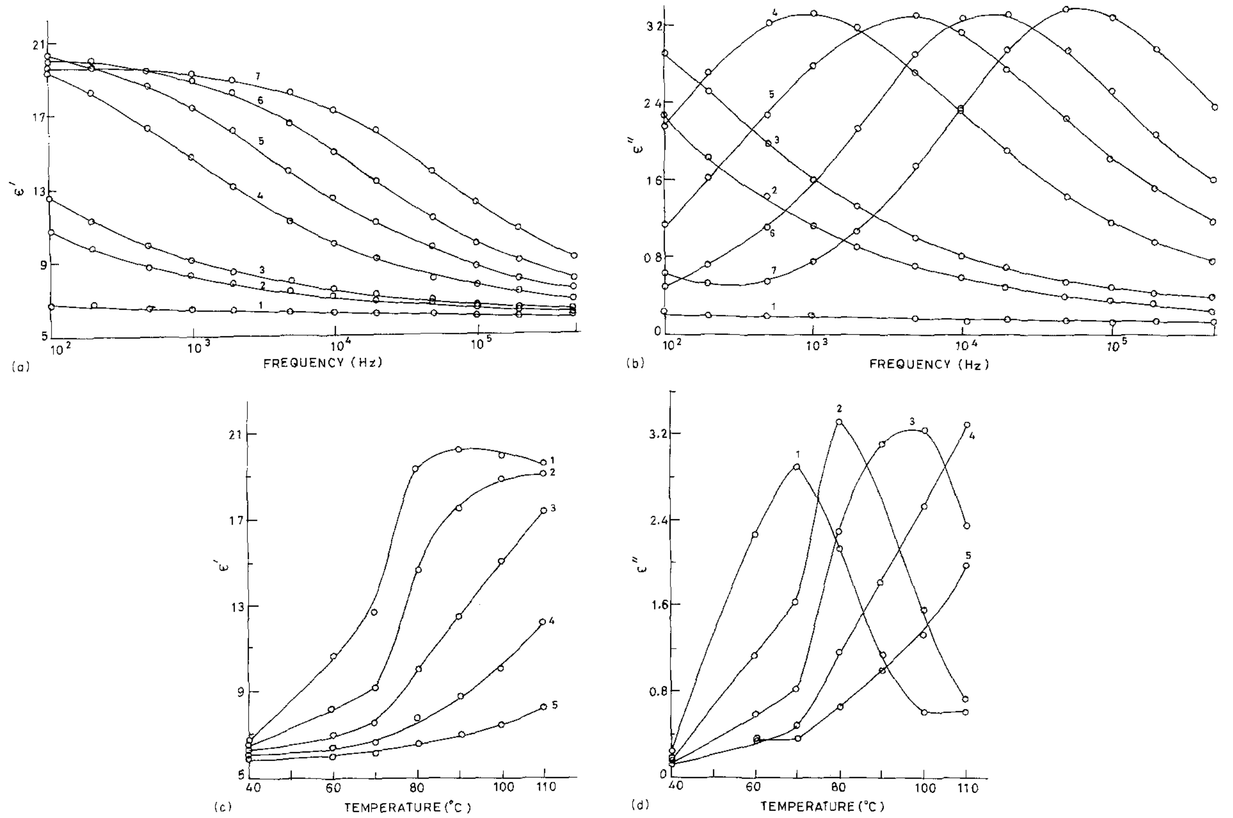

Figure 3 (a) Variation of dielectric constant ε' against frequency of PVC containing 10% mica at different temperatures (1) 40° C (2) 60° C (3) 70° C (4) 80° C (5) 90° C (6) 100° C (7) 110° C. (b) Variation of dielectric loss ε'' against frequency of PVC containing 10% mica at different temperatures (1) 40° C (2) 60° C (3) 70° C (4) 80° C (5) 90° C (6) 100° C (7) 110° C. (c) Variation of dielectric constant ε' against temperature of PVC containing 10% mica at different frequencies (1) 10^2 Hz (2) 10^3 Hz (3) 10^4 Hz (4) 10^5 Hz (5) 10^6 Hz. (d) Variation of dielectric loss ε'' against temperature of PVC containing 10% mica at different frequencies (1) 10^2 Hz (2) 10^3 Hz (3) 10^4 Hz (4) 10^5 Hz (5) 10^6 Hz.

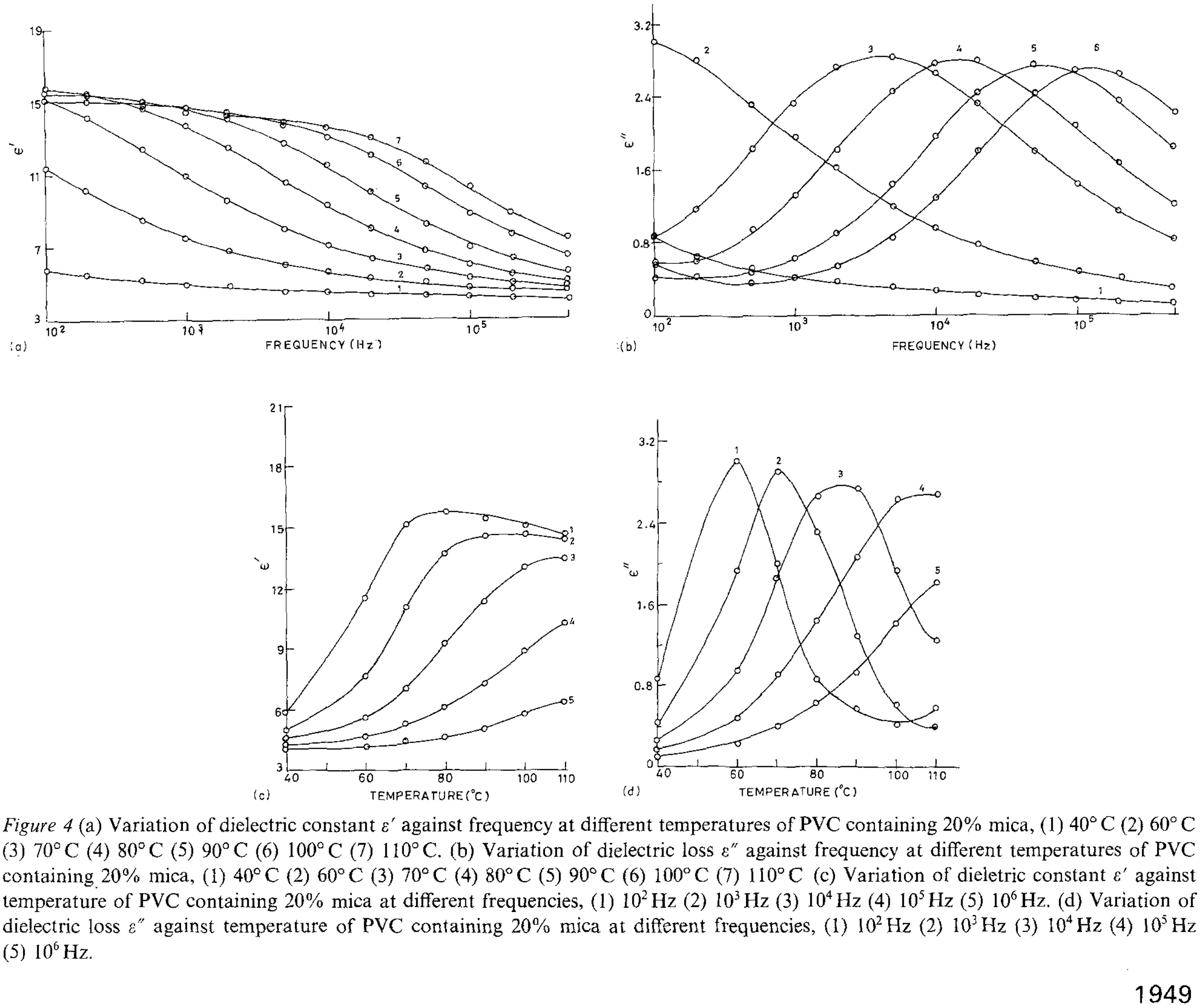

Figure 4 (a) Variation of dielectric constant ε' against frequency at different temperatures of PVC containing 20% mica, (1) 40° C (2) 60° C (3) 70° C (4) 80° C (5) 90° C (6) 100° C (7) 110° C. (b) Variation of dielectric loss ε'' against frequency at different temperatures of PVC containing 20% mica, (1) 40° C (2) 60° C (3) 70° C (4) 80° C (5) 90° C (6) 100° C (7) 110° C (c) Variation of dieletric constant ε' against temperature of PVC containing 20% mica at different frequencies, (1) 10^2 Hz (2) 10^3 Hz (3) 10^4 Hz (4) 10^5 Hz (5) 10^6 Hz. (d) Variation of dielectric loss ε'' against temperature of PVC containing 20% mica at different frequencies, (1) 10^2 Hz (2) 10^3 Hz (3) 10^4 Hz (4) 10^5 Hz (5) 10^6 Hz.

composites are shown in Figs 3 and 4. Fig. 3a and c and Fig. 4a and c show the normal dependence of ε' on frequency and temperature; the sharp increase in the values of ε' for lower frequencies at higher temperatures i.e. above 70° C for 10% mica composite and above 60° C for 20% mica, respectively. The increase in ε' at respective temperatures may be due to the lowering of the glass transition temperature due to addition of mica in PVC. The lowering of the glass transition temperature of polymers on addition of plasticizers in them has been observed in other polymers also [9].

The decrease in ε' at higher temperatures may be due to thermal agitation which will not allow the dipoles to orient. But at the same time, the contribution of interfacial polarization giving rise to space charge cannot be ruled out completely as this lowering of ε' with temperature has not been observed in pure PVC sample. Moreover this lowering is observed only at lower frequencies where the effect of space charge polarization can be felt [10].

The dependence of dielectric loss (ε'') on temperature for selected composites at fixed frequencies is shown in Fig. 3d and Fig. 4d, while the dependence of ε'' on frequencies at fixed temperatures is shown in Fig. 3b and 4b. It is clear from these curves that a loss maximum is observed both with temperature and frequency and its position shifts towards higher temperature at fixed frequency and towards higher frequency at fixed temperature. This shows that the dielectric relaxation in the composites is mainly due to PVC dipoles. The shift in the dipolar maximum towards lower temperature at various fixed frequencies and at higher frequencies at various fixed temperatures with the increasing amount of mica may be due to the lowering of the transition temperature of PVC. A similar effect in PVC doped with Dioctylphthalate has been observed by Bishai *et al.* [11].

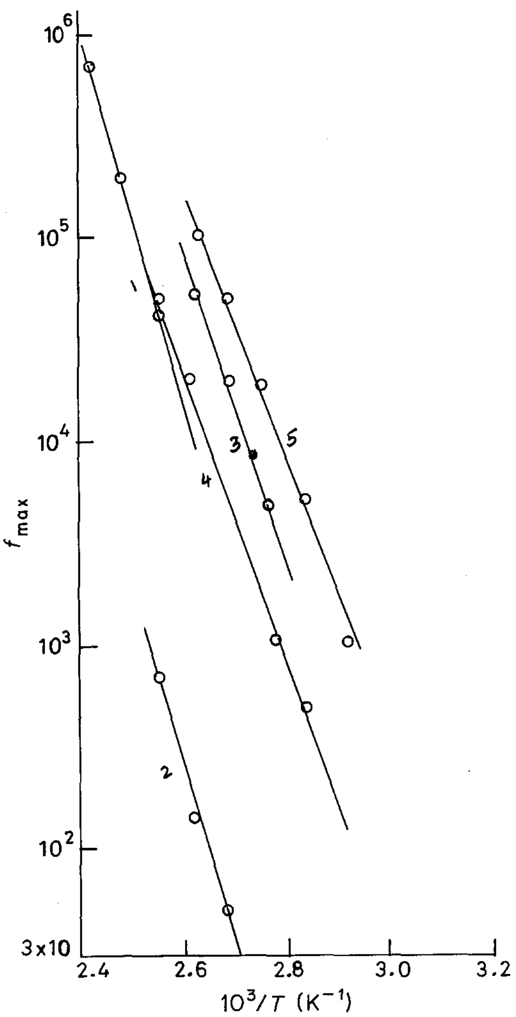

Figure 5 Plot of logf_{max} against $1000/T$ for pure PVC and composites. (1) PVC (2) +5% mica (3) +10% mica (4) +15% mica (5) +20% mica.

TABLE I

Sample	Activation energy (kcal mol^{-1})
PVC	43.13
PVC + 5% mica	38.36
PVC + 10% mica	34.05
PVC + 15% mica	31.33
PVC + 20% mica	29.06

To calculate the apparent activation energy for samples the logarithm of the frequency corresponding to ε''_{max} was plotted against the reciprocal of the absolute temperature. This is shown in Fig. 5, where a straight line was obtained for each concentration. From the slope of the straight line, the apparent activation energy was calculated using the equation

$$T = A \exp\left[-(\Delta H/RT)\right] \qquad (1)$$

Where $T = 1/(2\pi f_{max})$ is the relaxation time at the frequency of maximum loss, R is the gas constant and T is the absolute temperature. The activation energy ΔH obtained for samples having concentration from 5 to 20% mica was found to have a value from 38 to 29 kcal mol^{-1}. The activation energy values involved in the dielectric relaxation process of the pure PVC and composite materials are tabulated in Table I. It was observed that the activation energy goes on decreasing with the increasing amount of mica in the composite; such decrease was observed earlier also [12, 13] and ~~may be~~ attributed to the change in the internal viscosity of the medium [14]. On increasing the amount of mica the free volume increases and hence rotation of dipoles is more easy. This certainly reduces the activation energies. The work on still higher percentage of mica-containing PVC composites is still in progress.

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