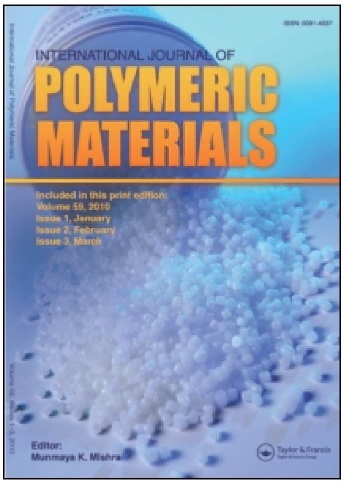

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DIELECTRIC RELAXATION OF POLY(VINYL CHLORIDE) STABILIZED WITH DIBUTYLTIN LAURATE-MALEATE

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The dipolar relaxation mechanisms of polyvinyl chloride stabilized with dibutyltin laurate-maleate have been studied by dielectric relaxation spectroscopy. The study was carried out in the frequency range 1 k–1 MHz at fixed temperatures above and below the glass transition temperature. The broadening of the loss peaks was considered because of the multiplicity of molecular conformations, which stablizer molecules can form. The results show a distinct broad relaxation process with activation energy of 0.5 eV. The dielectric strength increases with temperature and the origin of the relaxation was ascribed to the reorientation of the polar C–Cl and C=O groups.

Keywords: PVC, dielectric relaxation, dibutylin laurate-maleate

INTRODUCTION

Dielectric behavior studies provide information about the electric polarization and the relaxation time of molecules. The former is related to the dipole moment, and the latter is essentially a function of the molecular dimensions. An analysis of the data on these two parameters provides information about the molecular structure [1]. An investigation on the variation of different dielectric parameters with the temperature and frequency of polymers offers a suitable device to detect molecular motions. This includes whole molecule rotation and motion in the backbone or of side chain movements [2–3]. The relaxations arising from different modes have been assigned α, β, γ, and so on. Dielectric behavior studies of polymers have also revealed such multi relaxation processes [4–6].

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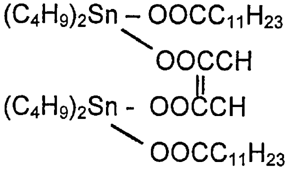
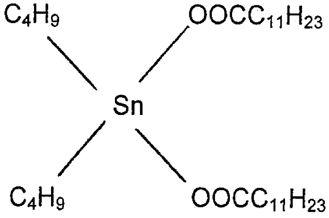
The stabilizer used in the present work is dibutyltin laurate-maleate of the chemical structure



SCHEME 1

with the trade name Thermolite 17 produced by M & T Chemicals. This stabilizer is composed of two well-known PVC stabilizers, which are dibutylin dilaurate, which has the structure



SCHEME 2

and dibutyltin maleate with chemical structure

$$[(C_4H_9)_2SnOOCCH = CHCOO]_n.$$

The interesting properties of dibutyltin laurate-maleate stabilizer are:

1. Does not initiate further degradation of the polymer.
2. There is no sudden, severe blackening, vigorous hydrogen chloride evolution, or almost total loss of physical properties occurring when the alkyl tin stabilizers are spent.
3. No co-stabilizers are required to absorb the chlorine preferentially.
4. It is completely soluble in PVC and almost every type of plasticizer.
5. Does not exhibit any tendency to water blush or fog when clear PVC composites containing this stabilizer are exposed to moisture or, alternatively, humidity for long periods.

6. It appears to lack response to most of the organic adjuvant or secondary stablizers so frequently employed with other metallic compounds stabilizers.

The aim of the present work is to contribute to a better understanding of the role of stabilizer in the dielectric behavior of PVC.

EXPERIMENTAL

The polyvinyl chloride (PVC) used in the present work was obtained from polymer Laboratories Ltd. The weight average molecular weight M_w was 2×10^5 and $M_w/M_n = 1.9$, where M_n is the number average molecular weight. The PVC was dissolved in tetrahydrofuran (THF, Aldrich) and then mixed with 10 wt% dibutyltin laurate-maleate. The obtained mixture was thoroughly stirred and then cast to obtain films with 0.1 mm thick. Gold was used as metal electrode on both sides of the specimen using the evaporation technique.

The dielectric parameters (capacitance, C, and dielectric loss tangent, $\tan\delta$) were measured with the help of Philips RLC meter type TM 6304 over the frequency range 1 k-1 MHz and temperatures of 50, 80, 100, and 120°C. The dielectric constant (ε') and relative loss factor (ε'') were calculated using:

$$\varepsilon' = C_f/C_o \tag{1}$$

$$\varepsilon'' = 1/R\omega C_o \tag{2}$$

where C_f is the capacitance of the sample-filled capacitor, ω is the angular frequency ($2\pi f$) and C_0 is the empty cell capacitance given by

$$C_o = \pi D^2 \varepsilon_o / 4d \tag{3}$$

where d is the perpendicular distance between the parallel electrodes, ε_o is the vacuum permittivity, and D is the diameter of the top electrode.

RESULTS AND DISCUSSION

The dielectric loss for the α-relaxation reflecting the micro-Brownian motion of polymer molecules is proportional to the number (N) of dipoles per unit volume. That is, the dependence of the dielectric loss is directly proportional to N. It reflects the orientational distribution of polymer chains in the amorphous region. The dependence of ε' on frequency (Figure 1) reflects the orientational distribution of polymer chains in the

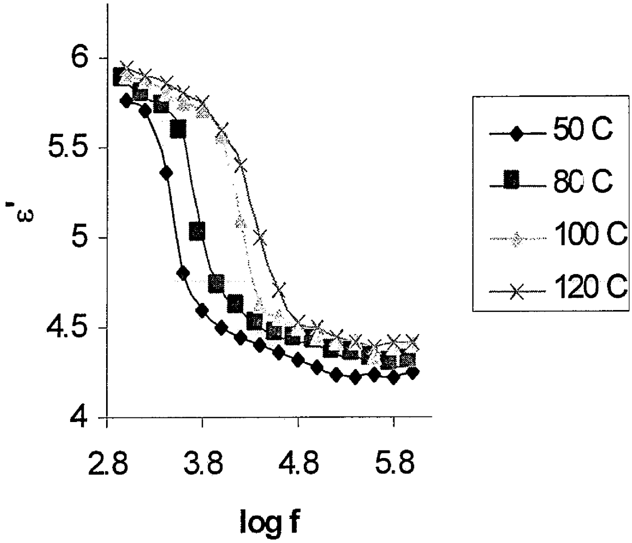


FIGURE 1 Variation of the dielectric contant, ε', with the frequency, f, at temperatures 50–120°C for PVC stabilized with dibutyltin laurate-maleate.

crystalline region as well as in the amorphous region [7]. The dielectric constant contains contributions from both amorphous and crystalline parts, which arise from dielectric relaxation due to the torsional motion of vinyl chloride repeat units. This leads to a change in dipole moment in the direction perpendicular to the PVC main chain [8].

The variation of the dielectric loss and loss tangent with frequency for PVC stabilized with dibutyltin laurate-maleate at temperatures below and above the glass transition temperature (50–120°C) is shown in Figures 2 and 3. The obtained relaxation peaks are broader than that of pure PVC [6, 9]. This broadening was considered to be caused by the multiplicity of molecular conformations that stabilizer molecules can form, causing separation of the PVC chains from each other's by stabilizer molecules. On the other hand, the stabilizer is not distributed homogeneously in the PVC matrix, that is some regions in the PVC are richer in stabilizer molecules than others [10, 11]. This is due to the heterogeneous phase structure that exists in PVC [11, 12]. This heterogeneity may be a result of the density fluctuations in the amorphous region or different degrees of crystallinity in PVC. This is considered to be the reason for the broadening of the relaxation peak.

From another point of view, the observed increase of the dielectric loss maximum with temperature, may be because [13] in semi crystalline polymers the dielectric strength, $\Delta\varepsilon$, of the α-relaxation can

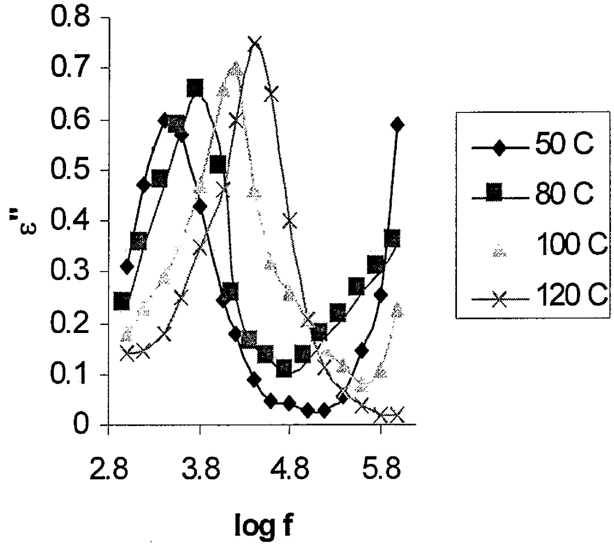


FIGURE 2 Experimental dielectric losses at several temperatures in the range 50–120°C for PVC stabilized with dibutyltin laurate-maleate.

increase with temperature indicating a progressive mobilization of the amorphous phase. Due to the fact that $\varepsilon''_{\max} \propto \Delta\varepsilon$, then an increase of $\varepsilon''_{\max}$ with temperature is expected.

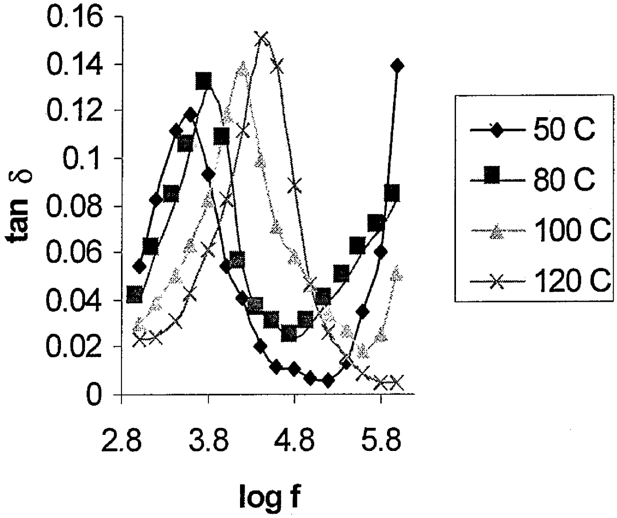


FIGURE 3 Variation of the dielectric loss tangent with frequency for PVC stabilized with dibutyltin laurate–maleate at different temperatures.

In order to compare with each other the peaks in ε'' and $\tan\delta$ plots Figures 2 and 3, of the dipolar relaxation mechanism, we use the following relation [14] for the peak frequencies f_{max}

$$\frac{f_{\max(\tan\,\delta)}}{f_{\max(\varepsilon'')}} = \sqrt{\frac{\varepsilon_r}{\varepsilon_u}} \tag{4}$$

where ε_r and ε_u are the low and high frequency limits of the real part of the dielectric function. From the $\varepsilon' - \log f$, Figure 1 plot is gotten $\varepsilon_r = 5.8$ and $\varepsilon_u = 4.2$ (at $T = 80^\circ C$) so that the theoretical values are $f_{\max(\tan\delta)}/f_{\max(\varepsilon'')} = 1.38$. The experimental values obtained from Figures 2 and 3 (at $T = 80^\circ C$) is $f_{\max(\tan\delta)}/f_{\max(\varepsilon'')} = 5$. This result shows that the maxima of the two functions occur in the right order, but shifted relative to each other more than expected for a Debye mechanism [15]. This result may be due to the modifications of the density function of the distribution of relaxation times of the α-relaxation due to the presence of the stabilizer in the PVC matrix.

The temperature dependence of the relaxation frequency is best shown in the so-called activation plot, log f_{max} vs $1/T$ in Figure 4. This plot may be approximated with a straight line, which means that the relaxation follows the Arrhenius law with activation energy $E_a = 0.35$ eV and pre-exponential factor (relaxation time formally at

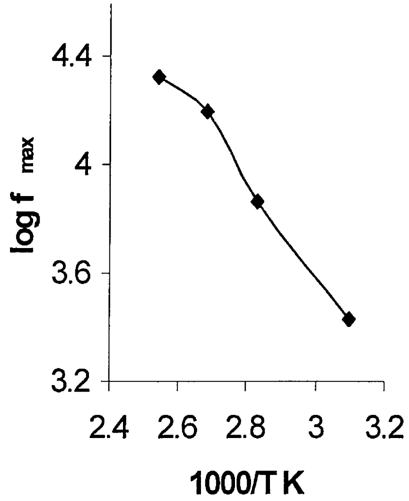


FIGURE 4 Arrhenius plot of peak frequency of the ε'' (f) peak for PVC stabilized with dibutyltin laurate-maleate.

infinite temperature) $\tau_o = 4.16 \times 10^{-6}$ s. The straight line suggests that the origin of the relaxation rests in individual rearrangements of single non-interacting dipoles rather than in collective behaviour of co-operating species, which is likely to correspond to the Vogel-Fulcher-Tamman law [16]

$$\tau(T) = \tau_\infty \exp[E_v / R(T - T_v)] \tag{5}$$

E_v, and T_v denote the Vogel activation energy, and the Vogel temperature.

As the rearrangements of dipole moments associated with the Polar C–Cl groups would necessitate a strong collective behavior, which in the activation plot is manifested as a bending curve approaching the Vogel-Fulcher-Tamman transition temperature T_o, the origin of the currently observed relaxation is due rather to the motion of the C–Cl as C=O groups, exhibiting much less co-operativity.

Study of the dielectric behavior of PVC stabilized with dibutyltin laurate-malate by a Cole-Cole plot (ε'' versus ε') is conventional, and provides valuable information about the dielectric relaxation process. Figure 5 shows the Cole-Cole representation where data points (ε'' vs. ε') form an arc when a dielectric relaxation occurs in the examined frequency interval. The obtained arcs are fitted to the Cole-Cole (C–C), Cole–Davidson (C–D), and Havriliak-Nagami (H–N) expressions for $\varepsilon''(\omega)$.

In the case of C–C[17]

$$\varepsilon''(\omega) = \Delta\varepsilon \frac{(\omega\tau_o)^{1-\alpha} \cos\left(\frac{\alpha\pi}{2}\right)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + (\omega\tau_o)^{2(1-\alpha)}} \tag{6}$$

in the case of C–D [18]

$$\varepsilon''(\omega) = \Delta\varepsilon(\cos\phi)^b \sin(b\phi) \tag{7}$$

while for H–N we have [19]

$$\varepsilon''(\omega) = \Delta\varepsilon \frac{\sin(b\phi)}{\left\langle 1 + 2(\omega\tau_o)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + (\omega\tau_o)^{2(1-\alpha)} \right\rangle^{b/2}} \tag{8}$$

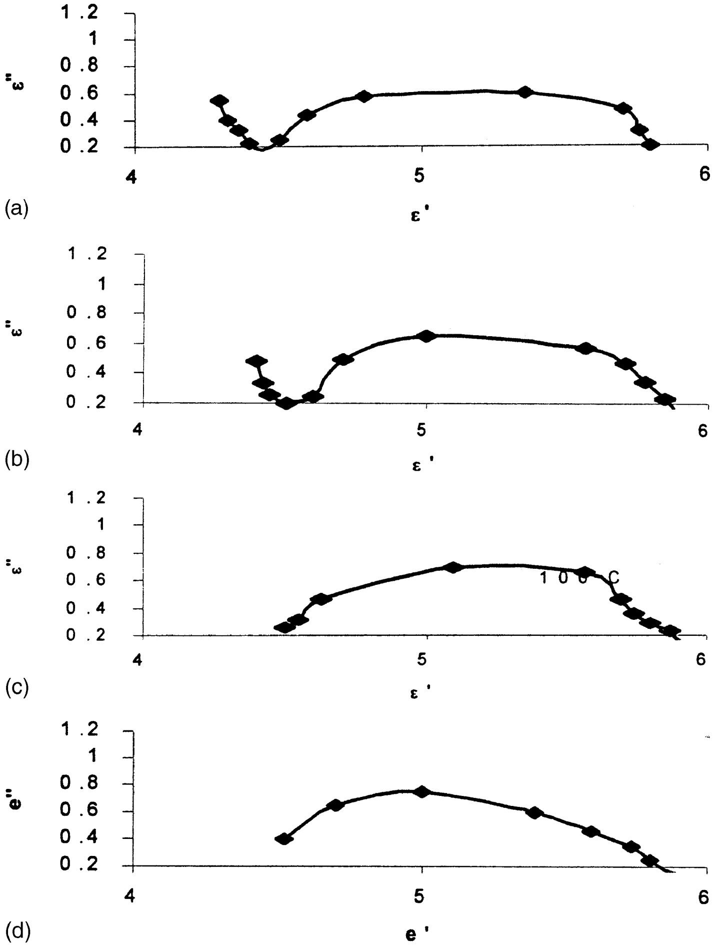


FIGURE 5 Cole-Cole plot of the α-relaxation process curve (a) at 50, (b) at 80, (c) at 100, and (d) at 120°C.

where $\phi = \arctan(\omega\tau_o)$, $\Delta\varepsilon = \varepsilon_r - \varepsilon_u$ and a, b are shape parameters. These equations reduce to the Debye form [20]

$$\varepsilon''(\omega) = (\varepsilon_u - \varepsilon_r)\frac{\omega\tau_D}{1+\omega^2\tau_D^2} \tag{9}$$

if $\alpha = 0$ (C–C), b = 1 (C–D), and $\alpha = 0$, b = 1 (H–N). The parameters obtained from best least-square fitting of Eqs. 5, 6, and 7 to the experimental data are listed in Table 1 and the fitting (not shown)

TABLE 1 Best Least-Square Fitting Parameters for the ε'' (f) Peak

	$\Delta\varepsilon$	A	b	$\tau_{o(s)}$	RMS dev.
Cole-Cole	1.24	0.12		2.4×10^{-7}	0.0025
Cole-Davidson	1.35		0.54	3.8×10^{-7}	0.0012
Havriliak-Negami	1.45	0.07	0.79	3.2×10^{-7}	0.0025

indicates that from the two one-shape parameter expressions the asymmetric C–D fits the data better than the asymmetric C–C. These results are in favor of a distribution of the short relaxation times. In terms of microscopic models for the shape of the dielectric response (e.g., cluster model) [19] this implies that short-range interactions dominate the relaxation processes.

The dielectric relaxation intensities, $\Delta\varepsilon$ have been obtained according to the circle intersection with the ε' axis in the Cole-Cole plot at different temperatures. The dielectric relaxation intensity as a function of temperature is shown in Figure 6. The α-relaxation intensity increases with an increase in temperature. An increase in molecular mobility causes the dipoles to reorient toward the alternating electric field, thereby resulting in an increase of the relative intensities for the α-relaxation. This observation implies that the net dipole moment increases as the vinyl chloride unit increases in length due to the attachment of the C=O dipoles of the stabilizer. An increase in the dipole moment favors a better reorientation of the molecular segments relative to the applied alternating electric field.

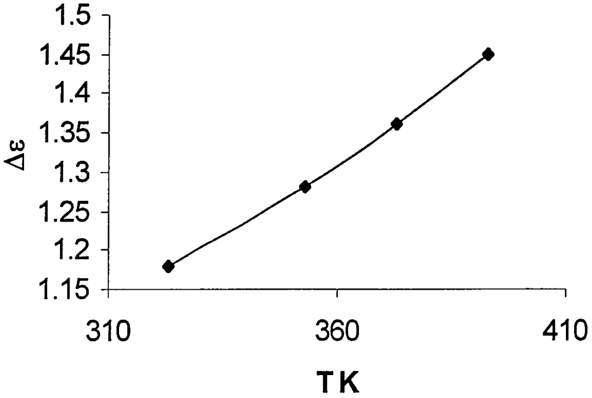


FIGURE 6 The relaxation intensity as a function of temperature for the α-relaxation of PVC stabilized with dibutyltin laurate-maleate.

For the dielectric strength ($\Delta\epsilon$), if the relaxation is dipolar by nature, a decrease would be expected with increasing temperature according to Curie's law ($\Delta\varepsilon \sim 1/T$)[20], which is contrary to the dependence observed, (Figure 6). A possible explanation is that the magnitude of $\Delta\varepsilon$ is proportional to not only the dipole concentration and dipole moment, but also is governed by the inter-chain interactions between adjacent chains, possibly due to hydrogen bonds. These interactions become weaker with increasing temperature so that the decrease of the effective dipole moment due to Curie's law is more than balanced by the diminishing inter-chain constraints, which effectively hindered reorientations of the C–Cl and C=O groups. Consequently, a moderate net increase of $\Delta\varepsilon$ with increasing temperature is seen.

The relaxation time is a measure of the rate at which equilibrium is restored after being distributed by an electric field. It needs not correspond to the rate of individual molecular fluctuations. The temperature dependence of the relaxation time, Figure 7, is considered as an essential basis for the assignment of relaxation processes. The relaxation time–temperature relation either obeys an Arrhenius law

$$\tau(T) = \tau_\infty \exp(E_a/RT) \tag{10}$$

or, in the case of cooperative segmental (α) relaxations, the Vogel-Fulcher-Tammann (VTF) expression, Eq. 5. From the data of Figure 7, it is apparent that the experimental values of τ(T) conform

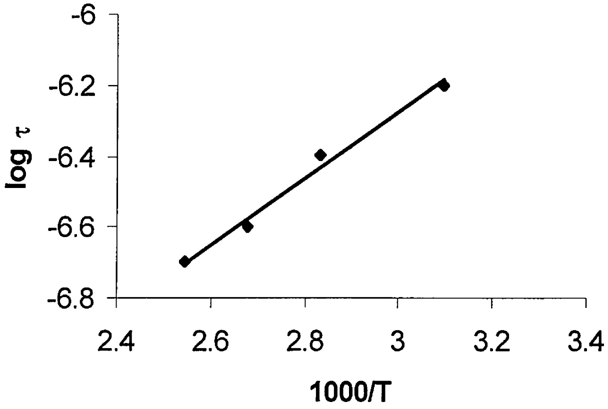


FIGURE 7 Temperature dependence of the relaxation time against the reciprocal temperature. The points correspond to the experimental data, whereas the solid line stands for VTF fits.

approximately to the VTF law. However, small deviations are observed at low temperatures. Several modifications of the VTF equation have been reported in the literature [21–23] based on different models to account for deviations of the $\tau(T)$ behavior from the VTF law near T_g. However, because the deviations observed are close to the experimental points, the author has preferred not to introduce additional parameters in the fitting procedure and to assume that the VTF equation remains valid as a good description of the equilibrium behavior of $\tau(T)$.

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