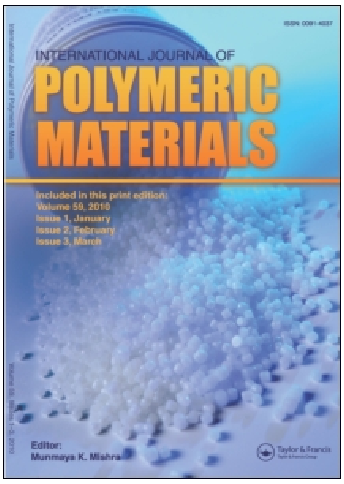

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Mahrous, Salah(2005) 'Transient Current and Dielectric Relaxation in PVC Stabilized with Di-N-Octyltin-β-Mercaptopropionate', International Journal of Polymeric Materials, 54: 3, 173 — 181

To link to this Article: DOI: 10.1080/00914030390214923

URL: http://dx.doi.org/10.1080/00914030390214923

International Journal of Polymeric Materials, 54:173–181, 2005
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ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030390214923

TRANSIENT CURRENT AND DIELECTRIC RELAXATION IN PVC STABILIZED WITH DI-N-OCTYLTIN-β-MERCAPTOPROPIONATE

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DC current technique has been used to calculate the dielectric losses in PVC stabilized with di-n-octyltin-β-mercaptopropionate using Hamon approximation. Both the shift factor and William-Landel-Ferry relation were used to determine the glass transition temperature of the prepared sample. It was found that the loss caused by the dielectric relaxation predominates below T_g whereas that caused by the dc conduction predominates at higher temperature. The obtained α-relaxation was attributed to the cooperative motion of the C−Cl dipoles (of the polymer) and the C=O (of the stabilizer).

Keywords: PVC, di-n-octyltin-β-mercaptopropionate, dc conduction, dielectric losses

INTRODUCTION

The European commission green paper on the environmental issues of PVC, published on 26 July 2000 in Brussels and the world summit on sustainable development in Johannesburg during September 2002 stated that PVC stabilizers containing lead or cadmium are dangerous to the environment. This article studies some physical properties of PVC stabilized with organotin mercaptides, which is less dangerous to both humans and the environment.

The mercaptides stabilizers have proved to be the most versatile type of stabilizer for rigid (unplasticized) poly(vinyl chloride) (PVC)

Received 1 April 2003; in final form 7 April 2003.

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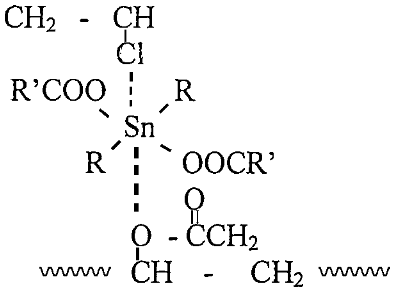
processing [1]. Industrially, PVC stabilized with mercaptides used for the production of pipes, electrical conduit, rigid bottles and containers, and siding and other building products. Unlike other types of PVC stabilizers, metallic or otherwise compounds that contain the $-S-Sn(R_2)-S-$grouping (and that are not polyfunctional) are unusual in that they permit the processing of these compositions at minimum melt viscosities [2] and without contributing to surface sticking or other processing difficulties. A tentative explanation for this is that in the processing of rigid PVC with metal carboxylate stabilizers, a rise in melt viscosities is due to bonds formed through the vacant *d* orbital of the metal employed as the stabilizer [3]. Coordination with *p* electrons of atoms in pendent substituents occurs, as is shown in Scheme 1 below, creating secondary crosslinks. This is true for a PVC molecule [4].

The search for PVC stabilized with organic compounds needs more information about the morphology of the obtained system. Therefore, much importance is attached to the problem of evaluating the structure of such systems both at molecular and supramolecualr level. Some information on the structure may be obtained by using direct methods, for example, study of the dielectric behavior of the polymer. 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 [5]. An investigation of 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 the side chain movements [6–8].



SCHEME 1 Creation of secondary crosslinks.

THEORY

The current obtained immediately after the application of a step function voltage is known in most cases to decay with time until a steady state current is achieved. This steady state current may be many orders of magnitude lower than the initial value of the transient current. The discharge current flowing on removal of the voltage is usually the mirror image of the charging current except that a steady state current does not occur. In many cases this transient current has been observed to decay as:

$$I(t) = A(T)t^{-n} \tag{1}$$

where I is the current, t the time after application or removal of the external voltage, $A(T)$ is a temperature dependence factor and $n \approx 1$.

From another point of view, the current at time t after the application of a step function voltage V_o is given by the approximation [9].

$$I(t) = G_oV_o + C_\infty V_o\delta(t) + C_vV_o\phi(t) \tag{2}$$

where G_o is the dc conductivity, C_∞ the instantaneous capacity, $\delta(t)$ the δ-function, C_v the geometric capacity, and $\phi(t)$ is the decay function of the sample. The first term in the right-hand side of Eq. 2 denote the conduction, the second term denotes, the instantaneous charging, while the third one denotes the absorption current. G_o is given by:

$$G_o = \sigma\frac{S}{l} = 4\pi C_v\sigma \tag{3}$$

where S is the sample area, l the sample thickness, and σ is the specific dc conductivity. From Eqs. 2 and 3 one gets

$$\frac{tI(t)}{C_vV_o} = 4\pi\sigma\mathrm{t} + t\phi(t) \tag{4}$$

if $\phi(t)$ is represented by $At^{-n}(0.3 < n < 1.2)$, it is well known that loss permittivity at an angular frequency ω is related to the absorption current at a time t by the expressions [10].

$$\varepsilon_r''(\omega) = \frac{t\phi(t)}{0.63} \tag{5}$$

$$t = 0.63/\omega = 0.1/f \tag{6}$$

From these equations it can be said that the total loss permittivity is composed of the conduction and relaxation components,

$$\frac{tI(t)}{0.63C_vV_o} = \frac{4\pi\sigma t}{0.63} + \frac{t\phi(t)}{0.63} = \frac{4\pi\sigma}{\omega} + \varepsilon_r''\omega = \varepsilon''(\omega) \tag{7}$$

Generally $\varepsilon_r''(\omega)$ can be represented by introducing a dielectric relaxation spectrum $L_D(\tau)$ as [9].

$$\varepsilon_r''(\omega) = \int_{-\infty}^{\infty} \frac{L_D(\tau)}{1+\omega^2\tau^2}\, d\ \ln\tau \tag{8}$$

The data on $I(t)$ seem to be subject to the method of reduced variables. Therefore, the time-temperature reducibility may be assumed as

$$L_D(\tau, T) = cL_D\left(\frac{\tau}{a_T}, T_o\right) \tag{9}$$

and

$$\frac{\sigma(T_o)}{\sigma(T)} = ca_T \tag{10}$$

where c and a_T are vertical and horizontal shift factors as function of temperature T and an arbitrary reference temperature T_o. The reduction of the loss permittivity is given by [4].

$$\varepsilon_r''(\omega, T) = c\varepsilon''(\omega a_T, T_o) \tag{11}$$

EXPERIMENTAL WORK

Samples

The poly (vinyl chloride) (PVC) used in the present work was supplied by Polymer Laboratories Ltd. The weight average molecular weight M_w was 2×10^5 g/mol and M_w/M_n were 1.9, where M_n is the number average molecular weight. First, PVC was dissolved in tetrahydrofuran (THF, Aldrich) and then mixed with 10 wt% di-n-octyltin-β-mercaptopropionate. The obtained mixture was rapidly stirred. Casting method was used to obtain films with 0.1 mm thickness. Gold was used as metal electrode on both sides of the specimen using the evaporation technique.

Method

The samples were conditioned for 24 h by short-circuiting the electrodes at a temperature of 120°C to remove the electrical memory in the bulk of the sample. This precondition procedure improves the consistency of the results. A constant electric field was applied to the sample at constant temperatures (from 50–120°C) and the charging current monitored from 1 min after the application of the field up to 100 min. The field was then removed and the discharge current of the short-circuited sample was recorded over a similar period of time at constant temperatures. The current was measured using a Kiethly electrometer type 610 C.

RESULTS AND DISCUSSION

Figure 1 shows the current measured over a time period 1–100 min below and above the glass transition temperature (at 50 and 100°C). At, a temperature of 50°C the current obeys relation (1) with $n = 0.64 \pm 0.64$. At 100°C there is an increasing tendency toward stable currents within the observation period. The current response for increasing temperature (50–120°C) at constant field of 40 kV/cm is shown in Figure 2. The steady state current can be attributed to non-ohmic behavior, whereas the transient current was ohmic. This implies that the mechanisms for the two currents were different, which is in agreement with literature data [11, 12].

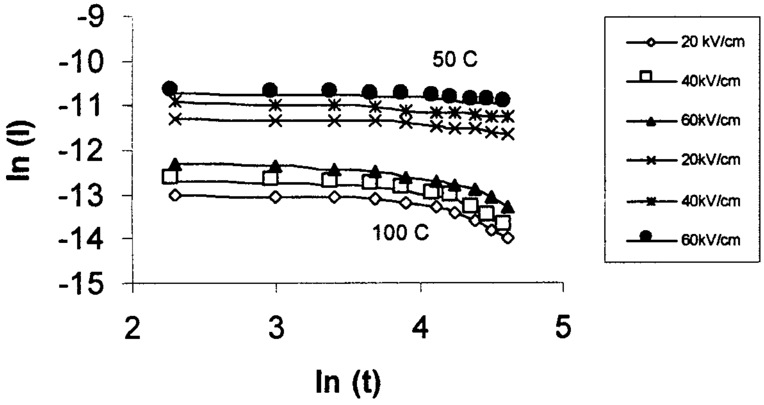


FIGURE 1 Decay current in PVC stabilized with di-n-octyltin-β-mercaptopropionate after applying various fields at a temperatures below and above T_g.

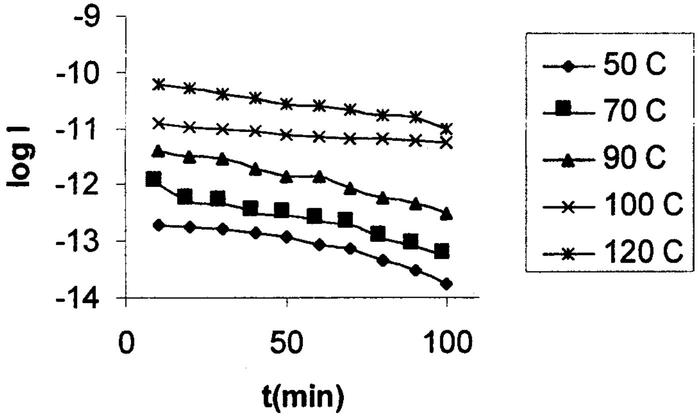


FIGURE 2 Current response in PVC stabilized with di-n-octyltin-β-mercaptopropionate to temperature increase at a constant applied field of 40 kV/cm.

Because the width of the crystalline regions in PVC increases when the material is held above the glass-transition temperature (T_g) for any length of time, it is possible that this structural change is responsible for the improved current stability at 120°C. The steady state values so obtained become more meaningful if presented as Arrhenius plot according to the relation

$$I = I_o \exp(E_a/kT) \tag{12}$$

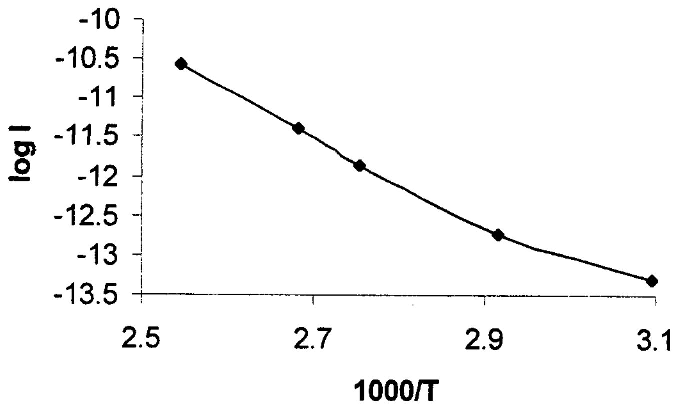


FIGURE 3 Arrhenius plot of steady current against (temperature)$^{-1}$.

from which activation energy E_a can be obtained. The plot (Figure 3) is reasonably linear, indicating single activation energy of 0.73 eV.

The loss permittivity as a function of time (for PVC stabilized with di-n-octyltin-β-mercaptopropionate), which was obtained from the data on the current using Eq. 8 is shown in Figure 4. The variation of ε'' with frequencys Figure 5, obtained using the data of Figure 4 and the Hamon approximation [13] (f = 0.1/t). Figures 4 and 5 indicate that the loss caused by the dielectric relaxation predominates at lower

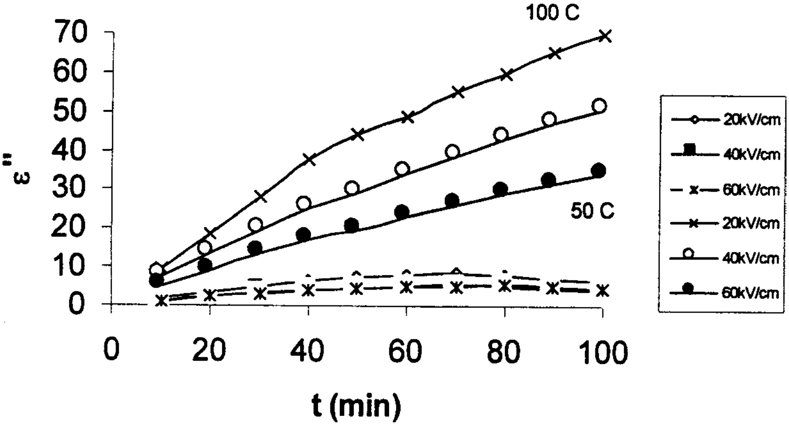


FIGURE 4 Time dependence of loss permittivity calculated from dc current data at 50, 100°C at different fields.

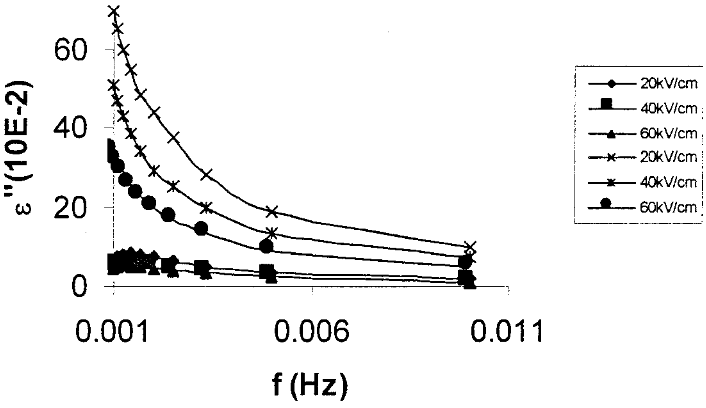


FIGURE 5 Frequency dependence of ε'' calculated using Hamon approximation f = 0.1/t.

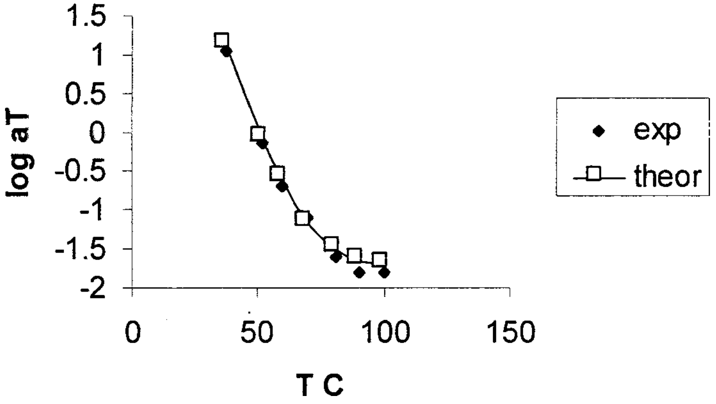


FIGURE 6 Temperature dependence of the shift factor (points), the solid curve calculated from the WLF equation with appropriate parameters.

temperatures whereas that caused by the dc conduction predominates at the higher temperatures. The relaxation is attributed to the cooperative motion of the main chain segments of the PVC containing the stabilizer.

The vertical shift factor, Eqs. 10 and 11 is approximately equal to unity. The horizontal shift factor is plotted against temperature in Figure 6. The solid curve is calculated by the William-Landel Ferry (WLF) equation [14]:

$$\log a_T = -C_1(T - T_o)/(C_2 + T - T_o) \qquad (13)$$

with $C_1 = 15$, $C_2 = -85°C$, T_o is a reference temperature = 70°C. The comparison between the experimental and calculated values indicates that the molecular process responsible for the α-relaxation and dc conduction loss corresponds to a glass transition [3]. The glass transition temperature, T_g, could be estimated as the temperature where the experimental values for the shift factor begin to become lower than the WLF curve (i.e., 82°C).

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