

# Dielectric Analysis of Chlorinated Polyvinyl Chloride Stabilized with Di-*n*-octyltin Maleate

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**ABSTRACT:** Dielectric relaxation of chlorinated polyvinyl chloride stabilized with di-*n*-octyltin maleate has been studied in the frequency range 1 kHz–1 MHz at various temperatures between 300 and 450 K. A clear dielectric relaxation band ( $\alpha$ -type) associated with dipolar polarization has been observed in the studied range. The stabilizer molecules increase the segmental mobility of the polymer, and specific interaction occurs between both the C–Cl and

C=O polar groups. The temperature dependence of the relaxation process was analyzed by combining the critical free volume expression by Cohen and Turnbull with the Williams-Landel-Ferry (WLF) model of the thermal expansion of free and occupied volumes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 316–320, 2009

**Key words:** CPVC; di-*n*-octyltin maleate; dielectric relaxation

## INTRODUCTION

Chlorinated polyvinyl chloride (CPVC) is a popular engineering material because of its relatively low cost (0.5 €/kg), high glass transition temperature, high heat distortion temperature, chemical inertness, and flame and smoke properties. CPVC, which is produced by the postchlorination of polyvinyl chloride (PVC) resin, is used in a variety of industrial applications<sup>1–5</sup> where a high-functional temperature and resistance to corrosive chemicals are desirable. Besides pipe and fittings, it is used in pumps, valves, strainers, filters, tower packing, and duct, as well as sheet for fabrication into storage tanks, fume scrubbers, large diameter ducts, and tank lining. Because of its excellent corrosion resistance at elevated temperatures, CPVC is ideally suited for self-supporting constructions where temperatures up to 95°C are present.

It well known that CPVC cannot be processed without the addition of stabilizers. Commercial CPVC stabilizers are usually either basic lead salts,<sup>6</sup> which can trap the evolved hydrogen chloride gas, thus delaying the polymer degradation, or metallic soap esters,<sup>7</sup> whose stabilizing action occurs through displacement of the labile chlorine atoms on the polymer chains by the ester from the decomposed stabilizer. Recently, a new class of stabilizers of an organic nature has been developed.<sup>7</sup> These stabilizers trap the radical species in the degradation process by blocking

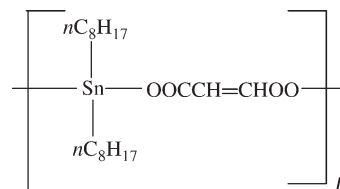
the newly formed radical sites on the polymeric chains and by absorption of the liberated HCl gas.

In this work, we investigate the effect of the addition of one of these new stabilizers on CPVC by means of dielectric relaxation spectroscopy, which is currently used in the study of molecular motions of polymers. According to this fact, these new stabilizers are needed to enhance the industrial applications of CPVC and create new applications.

## EXPERIMENTAL

CPVC used in this work was supplied by Weihai Jinhong Chemicals (Shandong, China), with chlorine content 65% and density 1.52 g/cm<sup>3</sup>.

CPVC (4 g) was dissolved in 20 mL of tetrahydrofuran (THF, Aldrich, Germany) and then mixed with 1.0 wt % of di-*n*-octyltin maleate (supplied by Argus, USA), which has the following chemical structure:



The obtained mixture was stirred rapidly for 15 min. The casting method was used to obtain films of 0.1-mm thick. Silver paste was used as metal electrodes on both sides of the specimen. The dielectric parameters (capacitance,  $C$ , and dielectric loss tangent,  $\tan \delta$ ) were measured with the help of a Hioki RLC meter, type 3531, over the frequency range 100 kHz–

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10 MHz and temperatures 300–450 K. The dielectric constant ( $\epsilon'$ ) and relative loss factor ( $\epsilon''$ ) were calculated using

$$\begin{aligned}\epsilon' &= C_f/C_o \\ \epsilon'' &= 1/R\omega C_o\end{aligned}\quad (1)$$

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

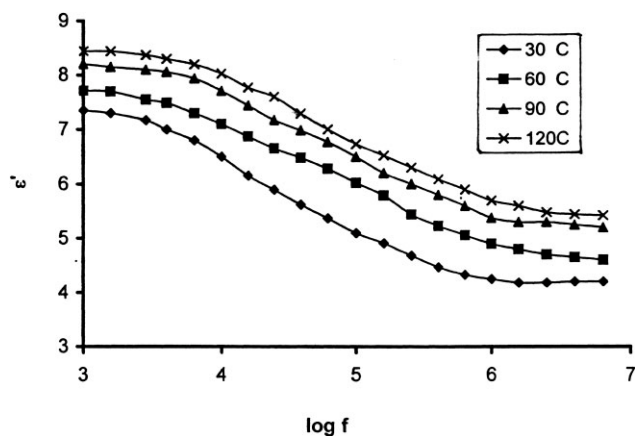
$$C_o = \pi r^2 \epsilon_o/d \quad (2)$$

where  $d$  is the perpendicular distance between the parallel electrodes,  $\epsilon_o$  is the vacuum permittivity, and  $r$  is the radius of the top electrode.

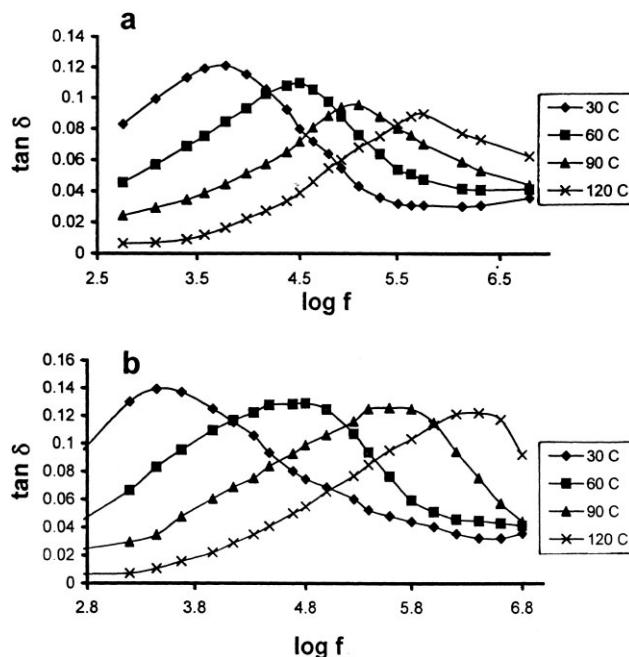
## RESULTS AND DISCUSSION

Relaxation phenomena in CPVC are associated with a frequency-dependent orientational polarization. At low frequency, the dipoles align themselves along with the field and contribute fully to the total polarization of the polymer.<sup>8,9</sup> At higher frequencies, the variation in the field is too rapid and polarization fails to keep up, so the dipolar contribution to the polarization and consequently to dielectric permittivity ( $\epsilon'$ ) becomes smaller at higher values of frequency. This is the reason for the observed decrease in  $\epsilon'$  with increasing frequency observed in Figure 1. From another point of view, this behavior can be explained according to the fact that both the heating and the external electric field cause an increase in the random motion of the polymer main chains. This will increase the free volume, i.e., separates the chains from each other that free the polymer polar groups, because of the separation between the chains that leads to the increase of  $\epsilon'$  values.

Dielectric loss results (Figs. 2 and 3) exhibit only one dispersion region, which give evidence of dipolar

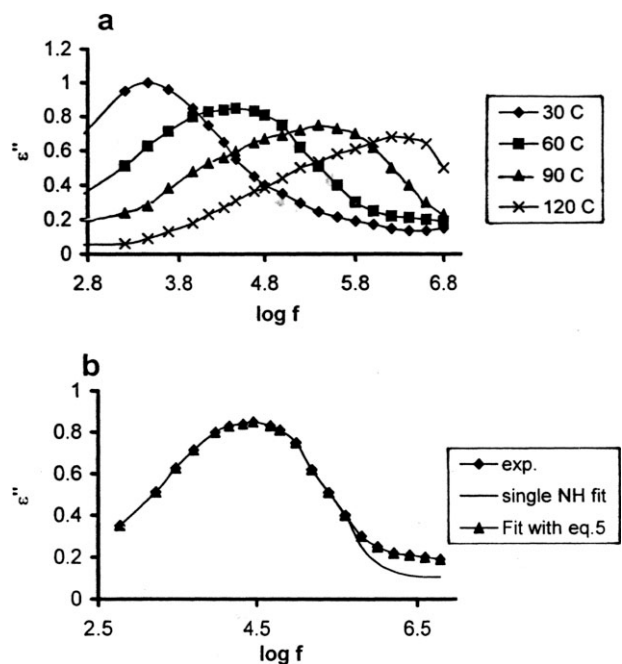


**Figure 1** Dependence of permittivity on frequency (dielectric dispersion) for CPVC stabilized with di-*n*-octyltin maleate.



**Figure 2** Plot of dielectric loss tangent against (a)  $\log f$  for pure CPVC and (b)  $\log f$  for CPVC stabilized with di-*n*-octyltin maleate.

lar polarization. Increasing temperature facilitates the orientation of these dipoles and increases the number and mobility of charge carriers. From dielectric loss data, Figures 2 and 3, it is clear that the



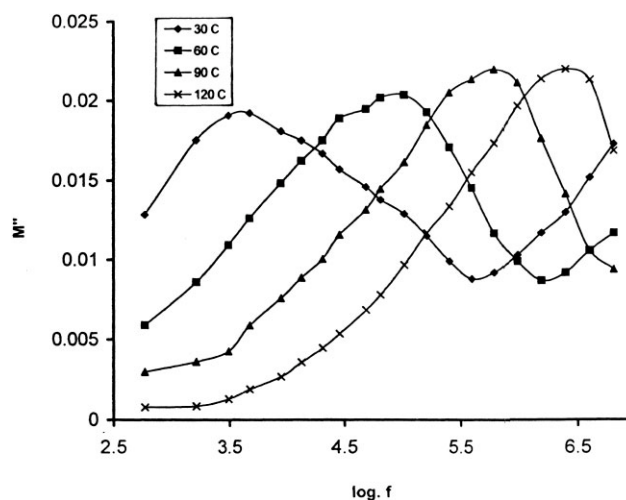
**Figure 3** a) The frequency dependence of the dielectric loss  $\epsilon''$  at various temperatures for CPVC stabilized with di-*n*-octyltin maleate; (b) the imaginary part of permittivity as a function of  $\log f$  at 60°C with 1-fitting with NH equation and 2-fitting with NH equation with the addition of the conductivity term.

dielectric loss peaks are shifted to higher frequencies and the broadening increase by the addition of the stabilizer in comparison with that of pure CPVC [Fig. 2(a)]. This behavior can be attributed to the fact that the stabilizer molecules increase the segmental mobility of the polymer. The mechanism of segmental mobility involves main-chain motion over large length scales. This intramolecular cooperativity requires intermolecular interaction, which might be represented in the description by the parameter of free volume. The number of polymers taking part in the molecular motion increases with the temperature because of the increase in free volume. There are some limited free volumes in the amorphous regions of CPVC where stabilizer molecules can enter as single molecules. These free volumes are filled with some stabilizer molecules. The remaining stabilizer molecules tend to aggregate. These gathered molecules cannot penetrate into CPVC chains. These stabilizer aggregates weaken the bonds between neighbor CPVC chains. This leads to the increase in the free volume in the amorphous region of the polymer.

The observed dielectric loss tangent ( $\tan \delta$ ) peaks for stabilized CPVC, Figure 2(b), are broader than that for pure CPVC, Figure 2(a) (except for 30°C sample, it is seemed to be the same). This broadening may be explained according to the fact that there are two main contributions to dielectric losses in stabilized CPVC. The first one ( $\alpha$ -type) is related to the thermal relaxation of freely rotating dipoles in which the thermal energy is of only one type of excitation. The second ( $\rho$ -type) occurs at higher temperatures, which increases with temperature and may be due to space charges. Overlapping of the two relaxations leads to a broader peak as that obtained.

The temperature and frequency dependence of the imaginary part of the dielectric constant in CPVC, Figure 3(a), show the presence of a relaxation peak, which lies in the glass transition temperature region of the polymer. This relaxation peak (denoted as  $\alpha$ -relaxation) is due to the reorientation of the polar segments of the polymer chain during the glass transition of the polymer, which leads to a uniform polarization.

The dielectric losses,  $\epsilon''$ , Figure 3(a), and  $\tan \delta$ , Figure 2, under alternating field show a dielectric dispersion whose position and magnitude allows us to relate it to the main glass-rubber transition ( $\alpha$ -type) of the polymer. Support for this interpretation comes from the fact that this peak was also observed in pure CPVC (not included) at nearly the same temperature. With increasing temperature, the  $\alpha$ -relaxation peak shifts to higher frequency side. To describe the slight upturn at the highest frequencies for the 30°C curve, one can say that, at low temperatures and high frequencies the observed low values



**Figure 4** Variation of the dielectric modulus as a function of frequency for CPVC stabilized with di-*n*-octyltin maleate.

of  $\epsilon''$  do not refer to the bulk of the material. They are related to the so-called conductivity current relaxation.<sup>10,11</sup> By using the electric modulus formalism, we can suppress the large contribution of conductivity to the  $\epsilon''$  curves. The electric modulus  $M^*$ , introduced by analogy to the mechanical modulus, has the following form

$$M^* = 1/\epsilon^* = M' + iM''$$

where

$$\begin{aligned} M'(f, T) &= \frac{\epsilon'(f, T)}{\epsilon'^2(f, T) + \epsilon''^2(f, T)} \\ M''(f, T) &= \frac{\epsilon''(f, T)}{\epsilon'^2(f, T) + \epsilon''^2(f, T)} \end{aligned} \quad (3)$$

In Figure 4, we show  $M''(f)$  spectra obtained by transforming the data of Figure 3(a) to the  $M^*$  formalism in eq. (3). At the temperature  $T = 30^\circ\text{C}$ , we observe only the primary  $\alpha$ -relaxation of the polymer, which shifts to higher frequencies with increasing temperature. A new peak began to appear at high frequencies in Figure 4 and shifts to higher frequencies with increasing temperature. This peak contributes to the conductivity in  $\epsilon''$  plots, Figure 3(a). The shift of the frequency of the maximum  $M''$  with temperature corresponds to the conductivity current relaxation.<sup>12</sup> At each temperature, the region to the left of the conductivity current relaxation peak (low frequency side) is where the charge carriers are mobile over long distances, whereas the region to the right is where the charge carriers are spatially confined to their potential wells and consequently not moves to contribute to the conduction process.

The observed asymmetric  $\epsilon''$  peaks, Figure 3(a), are associated with intramolecular motion of an

isolated chain. Generally, asymmetric relaxation peaks are observed for chain molecules containing more than one type of polar groups.<sup>13</sup> The lowering of the temperature of the sample increases loss of the peaks because of the addition of di-*n*-octyltin maleate. Compared with that of pure CPVC [Fig. 2(b)], it is quite appreciable and is linked with the increase in free volume of the stabilized CPVC. The increase in  $\epsilon''$  peak width suggests an increase in the distribution of the  $\alpha$ -relaxation. The observed relaxation peak indicates that there is a cooperative main-chain motion.

The dielectric loss curves can be expressed in terms of the Havriliak-Negami<sup>14</sup> (HN) equation (the NH equation is an empirical equation, which includes the Cole-Cole and Davidson-Cole equations):

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{\left[1 + (i\omega_0\tau)^{1-\alpha}\right]^\beta} \quad (4)$$

Another form of HN equation, which includes a conductivity term, has the following form<sup>15</sup>:

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{\left[1 + (i\omega_0\tau)^{1-\alpha}\right]^\beta} - \frac{4\pi i\sigma_{dc}}{\omega} \quad (5)$$

where  $\epsilon_\infty$  and  $\epsilon_0$  are the unrelaxed and completely relaxed (static) permittivities, respectively,  $\tau$  is the characteristic relaxation time ( $\tau = 1/2\pi f_{HN}$ ), which is closely related to the peak frequency,  $\omega_0 = 2\pi f_0$ ,  $f_0$  is the characteristic frequency related to the frequency of the maximum loss, and  $\alpha$  and  $\lambda$  are shape parameters describing the slope of the  $\epsilon''(\omega)$  curve below and above the frequency of the peak ( $0 \leq \alpha < 1.0 < \beta \leq 1$ ). The NH function could be fitted to the experimental  $\epsilon''(\omega)$  with parameters  $\alpha = 0.35$ – $0.3$  and  $\lambda = 0.45$ – $0.4$  over the temperature range 60–90°C. The conductivity term  $\frac{4\pi i\sigma_{dc}}{\omega}$  was added to the fitting function to account for the drift of charge carriers.<sup>16,17</sup> However, the conductivity,  $\sigma$ , is generally extracted by fitting separately the low-frequency data of  $\epsilon''$ . This is because the conductivity effect is well separated from the polarization one, particularly for the highest temperatures of the measuring interval. The difference between the two types of fitting, the one based on a single HN relaxation function [eq. (4)] and that based on eq. (5) are shown in Figure 3(b). From the analysis of the loss peaks by eq. (5), the obtained information are  $\Delta\epsilon = 7.23$ ,  $(1-\alpha) = 0.89$ ,  $\lambda = 0.59$ . On the other hand,  $\lambda$  is preferably quantified in terms of the Kohlrausch-Williams-Watts (KWW) parameter  $\lambda_{KWW}$ , obtained by the approximate equation<sup>18</sup>:

$$\beta = \frac{1.14}{w} \quad (6)$$

where  $w$  is the full width at half maximum and 1.14 that of a single Debye peak. The obtained value of  $\lambda$  is 0.53, which is in quite good agreement with the value obtained from eq. (5).

The number of dipoles associated in the relaxation process ( $N$ ) and the dipole moment ( $\mu$ ) for the prepared sample can be easily calculated using the Kirkwood expression<sup>19</sup>

$$\epsilon = \frac{7(n^2 + 2)^2 g \mu^2 N}{54\epsilon_0 kT} \quad (7)$$

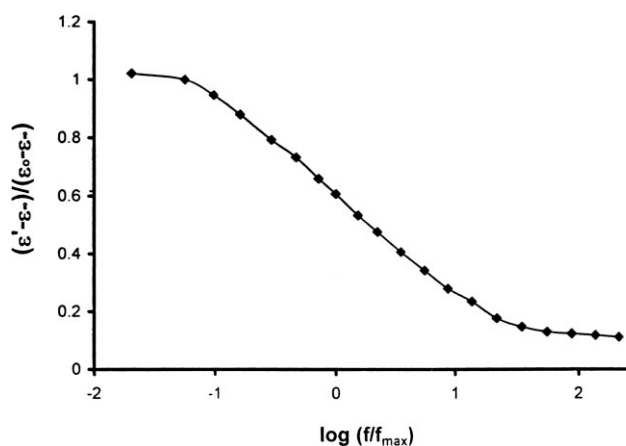
where  $n$  is the refractive index ( $\epsilon \gg n^2$ ),  $g$  is the Kirkwood orientation correlation parameter which is equal to 2.28.<sup>20</sup> The obtained values are  $N = \frac{N_{Avo}}{M_w \rho} = 3.35 \times 10^{28} \text{ cm}^{-3}$  (where  $N_{Avo}$  is the Avogadro's number,  $M_w$  is the polymer molecular weight, and  $\rho$  is the density), and the dipole moment is  $\mu = 2.74 \text{ D}$ . This value of dipole moment is greater than that of both the C–Cl (1.47 D) and C=O (2.3 D) groups separately. This indicates that both polar groups are participating in the sample polarization.

The activation energy of the relaxation process was calculated using the Vogel-Flucher-Tamman (VFT) equation,<sup>21</sup> which is characteristic for cooperative  $\alpha$ -relaxations:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k(T - T_0)}\right) = A \exp\left(\frac{B}{T - T_0}\right) \quad (8)$$

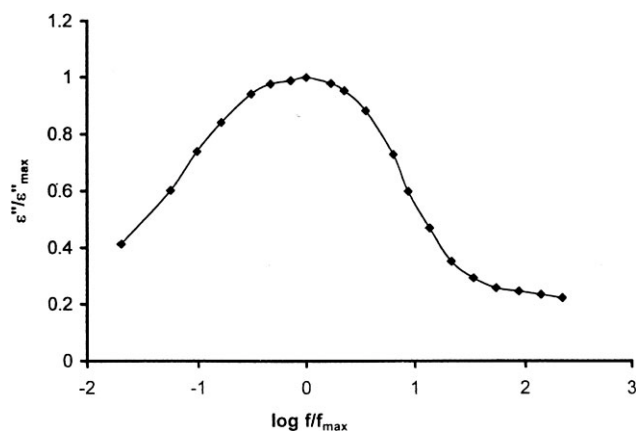
where  $\tau_0$  is the reciprocal of an attempt frequency is (the relaxation time at very high temperatures),  $T_0$  is the Vogel temperature which is equal 119 K, and  $E_a$  is a parameter related to the orientational energy barrier. The fitting parameters are  $\tau_0 = 5.48 \times 10^{-9} \text{ s}$ , which is close to that obtained from the HN equation. The glass transition temperature  $T_g$  calculated using eq. (8) for  $\tau = 100 \text{ s}$  and  $E_a = 1.02 \text{ eV}$  was 93.2°C. This value of  $T_g$  is in good agreement with the literature value 95°C.

Figure 5 displays the Arrhenius plot for the corresponding relaxation process, i.e.,  $\log f_{\max}$  vs.  $1/T$ ,



**Figure 5** Plot of  $\log f_{\max}$  against the reciprocal of the absolute temperature.





**Figure 6** Variation of the frequency shift factor  $a_T$  against  $1/(T_2 - T_1)$ .

where  $f_{\max}$  is the frequency at the  $\epsilon''$  maximum. The obtained curve is nonlinear and consequently cannot be fitted to the Arrhenius relation; this non-Arrhenius behavior indicates a micro-Brownian polymer chain motion. When the line of Arrhenius plot exhibits some curvature, it means that the molecular motion depends on the free volume. The VFT equation (8) is more suitable to fit Figure 5. The quality of the fits is good, and the resulting values obtained were  $f_0 = 2.23 \times 10^9$  Hz,  $B = 0.72$  eV, and  $(T - T_0) = 80$  K.

The interpretation of the temperature dependence of the relaxation process can be made by combining the critical-free volume expression by Cohen and Turnbull<sup>22</sup> with the Williams-Landel-Ferry (WLF)<sup>23</sup> picture of the thermal expansion of free and occupied volumes. The result gives the ratio of the critical free volume required for the dipolar movement ( $V_c$ ) to the occupied volume ( $V_o$ ) at a reference temperature ( $T_V$ ). Here,  $T_V$  is the temperature at which the total volume-temperature line, extrapolated from above the glass transition, intersects the occupied volume-temperature line, using the following relation<sup>24</sup>:

$$(\log a_T)^{-1} = \frac{2.3\Delta\zeta V_o}{\gamma V_c} \left\{ (T_1 - T_V) + \frac{(T_1 - T_V)^2}{(T_2 - T_1)} \right\} \quad (9)$$

where  $a_T$  is the frequency shift factor from constant  $T_1$  to  $T_2$ ,  $\Delta\zeta$  is the change in the expansion coefficient at the glass transition temperature and  $\gamma : 1$  allows for overlap of free volume. By plotting a relation between  $1/(\log a_T)$  vs.  $1/(T_2 - T_1)$ , Figure 6, one can calculate the value of  $V_c/V_o$ . For CPVC stabilized with di-*n*-octyltin maleate  $V_c/V_o$  was found to be equal 0.6 compared with the value 0.8 for the  $\alpha$ -relaxation in PVC.<sup>25</sup> The obtained value of the free volume is enough for the  $\alpha$ -transition to occur and there is no doubt that the obtained relaxation process is equivalent to the  $\alpha$ -transition in the polymer chain backbone. This is because the calculated value of the free

volume for PVC using the positron annihilation lifetime spectroscopy technique<sup>26</sup> is  $73.6 \pm 4.4\text{\AA}^3$ , which is the enough volume for dipoles to rotate.

## CONCLUSIONS

The dielectric investigation of CPVC stabilized with di-*n*-octyltin maleate revealed two relaxation processes namely  $\alpha$  and  $\rho$ . The results indicates that with increasing temperature, the  $\alpha$ -relaxation peak shifts to higher frequencies for stabilized and pure CPVC samples. The lowering of the loss peaks for stabilized sample because of the addition of the stabilizer is linked with the increase in free volume. The obtained value of the free volume is enough for the  $\alpha$ -transition to occur.

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