Computation of Dipole-Dipole Interaction Energy in Amorphous Polymers

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Abstract

In this work investigation of dipole-dipole interaction energy was made using (TSDC) experimental technique deconvoluted by Thermal sampling (TS) technique (TS-TSDC) the peaks were analyzed using a proposed model based on the dipole-dipole interaction concept (DDIM). The proposed model describes the (TS-TSDC) peaks and gives a significant peak parameters (i.e. Activation energy (E) and the pre-exponential factor (τ₀) in addition to the dipole-dipole interaction energy parameter (dᵢ). Application of this model to determine the peak parameters of polyvinyl chloride (PVC) amorphous polymer (TS-TSDC) data is presented. The results of the model was compared to a well known peak shape methods namely, the Initial rise, the half width, in addition to Cowell and Wood analysis.

Keywords: Dipole-dipole interaction, Relaxation, Modeling, TSDC, activation energy, PVC.

Introduction

Investigation of molecular motion in polymers grasping more attention, however, with the aid of modeling and experimentation we take an insight through the molecular motion. The well known study of molecular motion is the study relaxation processes take place inside the polymers during polarization / depolarization process. In these studies almost two techniques are used the first is dielectric spectroscopy (DS) and the other is the thermally stimulated depolarization current (TSDC) long with Thermal Sampling (TS). The polymer as a modeling system is very large and complicated molecular system which results in using the phenomenology of the relaxation process.

In this work a model was presented, which depend on the polarization phenomena, which take place in the relaxation process during the TSDC experiments,
in addition to the dipole-dipole interaction concept which take place between the oriented dipoles during the orientation process. The model provide a data to investigate the contribution of the dipole-dipole interaction to the TSDC curve.

Materials and Methods
Commercial pure amorphous PVC with average molecular weight, $M_w=100,000$ gm/mol, produced by BDH chemical Ltd, Poole, UK, were used in this work. Films were prepared by dissolving each component separately in tetrahydrofuran (THF), with continuous stirring for 48 hours, and then casting onto a flat glass substrate. The film was heated to 330 K and held for one week to remove all the traces of the solvent. The film thickness ranges from 50 to 60 $\mu$m, as measured by the digital micrometer (Mitutoyo No.293-521-30, Japan). Carbon past (Kontact-chemie, Germany) was used as a conducting electrode.

The experimental setup designed and built in our laboratory; TSDC measurements refer to references,[1,2] The TSDC measurements were performed using 3 Kmin$^{-1}$ heating rate. A Keithley 610C electrometer is connected in series to the sample in order to measure the depolarization current induced by the loss of the frozen-in polarization, which occurs as the temperature is increased. The resolution of the fine structure of the global TSDC spectra of PVC has been performed using the TS technique [3]. TS of the TSDC spectra is performed by polarizing the sample over a narrow temperature window ($\Delta T=5$K), then quenching, and then measuring the depolarization over a ~50K range.

TS of TSDC spectra was obtained by heating the sample to a polarizing temperature ($T_p$), then applying a polarization electric field for 15 min to polarize the dipolar entities, then cooling from $T_p$ to depolarizing temperature $T_d = T_p - 5$ K and then at $T_d$ the electric field was turned off, then the samples were depolarized for 15 min at $T_d$. The sample was then quenched to temperature of 50-60 K below $T_p$. Finally, the depolarization spectrum due to a narrow distribution of relaxations was then measured upon reheating rate of 3 Kmin$^{-1}$. By applying the TS technique at different polarizing temperature windows $\Delta T = T_p - T_d = 5$ K, sets of individual depolarization curves were obtained for every polarizing temperature which are subsets of that obtained from the global TSDC spectra. The signal for this TS spectrum is the result of the reorientation of the narrow packet relaxations, which were exited over the 5 K temperature around $T_p$.

Model and Calculations
The idea was to count for the dipole-dipole interaction during the depolarization process. The mathematical model made by assuming that the contribution of the dipole-dipole interaction affecting only the width of the TS-TSDC peak, which leads to assuming further that the energy contribution due to the dipole-dipole interaction to the TS-TSDC curve is distributed normally (i.e Gaussian distribution) on the whole curve. According to the local limit theorem [4] it is found that the contribution due to the dipole-dipole interaction is given by a correction factor:
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\[ C = \frac{1}{(d_i \sqrt{n})} \int_{-\infty}^{\infty} \exp \left( \frac{-(E-E_0)}{kT} \right) \exp \left( \frac{-(E-E_0)}{d_i^2} \right) \exp \left[ \left( \frac{-1}{\beta} \right) \int_{T_1}^{T_2} \left( \frac{1}{\tau_e} \right) \frac{dT}{\tau_e} \right] dE \]  

where, \((E_0)\) is the center of the energy distribution, \((d_i)\) is its width, \((\beta=dT/dt)\) is heating rate, \((E)\) is the activation energy and \(\tau (T)\) is the relaxation model.

Multiplying the correction factor (C) equation (1) with the TSDC curve model given by:

\[ I(T) = \left( \frac{AP_o}{\tau} \right) \exp \left( \left( \frac{-1}{\beta} \right) \int_{T_1}^{T_2} \left( \frac{1}{\tau} \right) dT \right) \]  

Where, \((A)\) is sample area, \((P_o)\) is the initial polarization and \(\tau (T)\) is the relaxation model used, gives the corrected TSDC curve given by:

\[ I_{th}(T) = C(T, \tau_o, E, d_i) I(T) \]  

The theoretical correction factor (C) is studied very intensively in order to get a complete picture about the correction factor behavior along with all variables and constants using MathCAD.

A Fortran 95 program was made in order to compute the equation (3). The integral over \(T\) was calculated using the Simpson Composite method [5] where it is found to be more accurate for the exponential function. Then, The improper integral over the energy \((E)\) was approximated [6] The fitting was made using the three parameters least square technique [7] between the experimental data and the model data to calculate the three fitting parameters \(E, \tau_o, d_i\), in addition to the new parameter \(d_i\).

Results and Discussion

In order to investigate the work of dipole-dipole interaction model the Arrhenius model of relaxation is considered, shall call it DDIMA, and an experimental data peaks obtained from Poly(vinyl chloride)PVC, using the thermal sampling technique was used. Furthermore, to compare the model calculated peak parameters (i.e. the energy \((E)\) and pre-exponential factor \((\tau_o)\)) two known peak shape methods was used; the initial rise method (IR) [8,9], the half width method (HW) [10] in addition to the Cowell- Woods method(CW) [11].

Figure 1, shows the global TSDC experimental data along with the thermal sampling peaks obtained experimentally fitted with the (DDIMA) model. In this figure one can see the quality of fitting of the dipole-dipole interaction model (DDIMA) with the experimental data.

Figure2. shows the fitting of the experimental data and the calculated data using Cowell-Wood (CW) method. It shows the poor fitting specially in the high and low temperature sides. Figure3 shows the fitting of experimental data and the calculated data using dipole-dipole interaction model (DDIMA). It shows that the fitting is much more correlated to the experimental data which indicate that the dipole-dipole interaction process is affecting the TS-TSDC current peak, which was neglected before in the analysis of the TSDC current peak.

Table1. shows the dipole-dipole interaction model (DDIMA) calculated peak
parameters (i.e., the activation energy (E), the pre-exponential factor (τ₀), in addition to the dipole-dipole interaction strength parameter (dᵢ)). Both the activation energy (E) and dipole-dipole interaction strength (dᵢ) are introduced as (KJ/mole) and the pre-exponential factor (τ₀) is introduced in seconds for PVC polymer material.

The model calculated results show that the dipole-dipole interaction model data gives a significant figure for the pre-exponential factor (τ₀) while the initial rise (IR) method, the half width (HW) and Cowell-Wood (CW) methods give non significant figures. This gives an indication that the dipole-dipole interaction model gives more correction to the calculated relaxation time. Furthermore, the calculated activation energy (E_a) using the dipole-dipole interaction model (DDIMA) is less in magnitude than those calculated using the other methods which gives more significant values for the activation energy. Figure 4 shows a comparison of the calculated activation energy using the four different methods, IR, HW, CW, and DDIA respectively. In this figure it is found that the activation energies calculated using the IR method and DDIA are closely correlated except in TS peak no. 6, the calculated activation energy using the IR method gives a very high value 298 KJ/mole, whereas the DDIA model gives a more significant value 203 KJ/mole. These results indicate that the DDIA model corrects the errors in the peak shape methods (IR, HW) and also gives more correct values than the CW method. On the other hand, it is found that the CW method is much correlated to the HW method except in TS peak 3 and 5, they give much far values.

Figure 5 shows the dipole-dipole interaction parameter (dᵢ) against the maximum temperature (T_m) which shows that this parameter depends linearly on the maximum temperature in a manner that if the maximum temperature increases, it decreases linearly, except TS peak no. 4, it is not correlated to the line.

**Figure 1:** Windowing polarization of the -peak of PVC at different polarizing parameters, T_p as indicated in the figure. The intensity of the polarizing field E_p = 1x10⁷ Vm⁻¹, the polarizing time was t_p = 10 min, the width of the polarizing window T = 5 K, The heating rate was ω = 3 Kmin⁻¹. The conditions of the envelope (curve 10): E_p = 1x10⁷ Vm⁻¹, and T_p = 363 K. Dots, is the experimental data; lines, is, calculated data, numerically computed using the DDIMA model.
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Figure 2: The fitting of Cowell-Wood method and the experimental Thermal Sampling data for peak no. 4 in table 1.

Figure 3: The fitting of DDIMA model and the experimental Thermal Sampling data for the TS peak no. 4 in table 1.

Figure 4: The activation energy ($E_a$) values obtained using the three different methods IR, HW, CW, and DDIMA model.

Figure 5: The relationship between the calculated dipole-dipole interaction parameter ($d_i$) and the maximum temperature ($T_m$).

Table 1: The calculated thermal sampling peak parameters using the dipole-dipole interaction model in Arrhenius mode (DDIMA) in addition to the initial rise (IR) method, half width (HW) method, ad Cowell-Wood (CW) method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ts. No</th>
<th>$T_m$ (K)</th>
<th>$E_a$ (Kj/mol)</th>
<th>$\tau_f$ (sec.)</th>
<th>$E_a$ (Kj/mol)</th>
<th>$\tau_f$ (sec.)</th>
<th>$E_a$ (Kj/mol)</th>
<th>$\tau_f$ (sec.)</th>
<th>$d_i$ (Kj/mol)</th>
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Conclusions

The dipole-dipole interaction model correct the high and low temperature sides disagreement between experimental data and the calculated data using the CW method. Which mean that the dipole-dipole interaction affect the TSDC peak by increasing its width.

The dipole-dipole interaction model in Arrhenius mode DDIMA give more significant peak parameters values than the other methods used especially in the calculation of the per-exponential factor ($\tau_0$).

Using the dipole-dipole interaction model in Arrhenius mode DDIMA lead to computation of the dipole-dipole interaction parameter ($d_i$) which give an indication for the magnitude of this parameter in polymers. Finally its found that the dipole-dipole interaction depend linearly on the maximum temperature ($T_m$).

References