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Fractional polarization, a new technique of the thermally stimulated current method to study the physical and morphological structure of materials

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Segregation phenomena in copolymers are studied using thermally stimulated current method. The origin of the peaks observed with the thermally stimulated current technique can also be investigated; but molecular parameters such as the relaxation times, the free activation energy, the migration enthalpy and entropy, and the degree of disorder number in polymers are calculated analysing the relaxation map obtained by the fractional polarization method. This method represents an important technological advance with regard to the study of inner responses and characterization of the amorphous states of polymers.

1. Introduction

The thermal ionic current method was first introduced by Bucci and Fieschi in 1964 [1] to study the point defects in alkali halides. Later, for non-ionic compounds the technique was named as the thermally stimulated current (TSC) method. TSC is essentially a d.c. measurement with continuously varying temperature and is applicable in ranges of equivalent frequencies of 10^{-2} to 10^{-4} Hz. The sample under study is placed between two metal plates in a cryostat (Fig. 1) and is evacuated to about 1.33×10^{-4} Pa. A constant supply of He is maintained to avoid condensation of moisture which reduces surface resistance and increases the capacitance as well as dielectric loss. The relaxation of electric dipoles and mobile charges can be characterized by the current peaks of a previously polarized and cooled sample subjected to a slowly increasing temperature. TSC is uniquely suited for determining the influence of additives, dopants, plasticizers and water content. The fractional polarization method developed by Lacabanne [2] is ideal for the investigation of the fine structure of semicrystalline polymers, copolymers and blends, polymer complexes, and resins. It gives a true opportunity to study the physical and morphological structures of materials. When the polarization is due to a distribution of relaxation times then the technique of fractional polarization is used for experimental resolution of spectra and the production of the materials relaxation map. TSC using the technique of fractional polarization can be compared to the improvement of the electron microscope over the optical instrument. The electrometer in this TSC spectrometer is so sensitive that it measures current 10^6 times smaller than that measured in a tunnelling microscope. The technique is ideally suited to the investigation of the effects of molecular weight, chemical structure, internal stress, orientation, curing, crystallization, and thermodynamic history or individual relaxation modes.

2. Methodology

A widely used method for investigating the properties of dipolar complexes in dielectrics is to monitor the current arising from the relaxation of previously polarized dipoles during a linear increase in sample temperature. The sample to be studied is polarized by a static electric field at a certain high temperature to permit dipole orientation. The polarization thus acquired is congealed with electric field by lowering the temperature down to a certain temperature $T_0 \ll T_p$ so that τ_0 must be large. The sample is then short-circuited and connected to an electrometer. By increasing the temperature at a certain rate, the return of the previous oriented dipoles to equilibrium is stimulated.

The global spectrum (Fig. 2) gives the information about the number and the amplitude of the relaxations. In order to analyse the nature of relaxation, the complex spectrum of TSC can be resolved experimentally into elementary spectra by the fractional polarization method. The sequence of fractional polarization is shown in Fig. 3. The sample is polarized at temperature T_p during time t_p to make the alignment of the dipoles perfect. The temperature of the sample under field is lowered to $T_d = T_p - \Delta T$ (10 K). The sample is then short-circuited at temperature T_d for a period of t_d to remove any stray surface charges. The temperature is again lowered to 50 °C below the temperature T_d and the depolarization current is recorded. The values for the parameters T_p, t_p, T_d and t_d are so conveniently chosen that the oriented dipoles have practically the same value of relaxation time. Fig. 4 shows how the global spectrum is resolved experimentally into elementary spectra by

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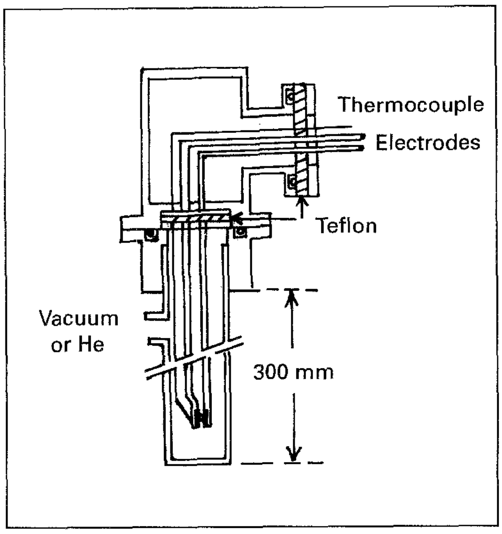

Figure 1 Schematic diagram of an experimental set-up.

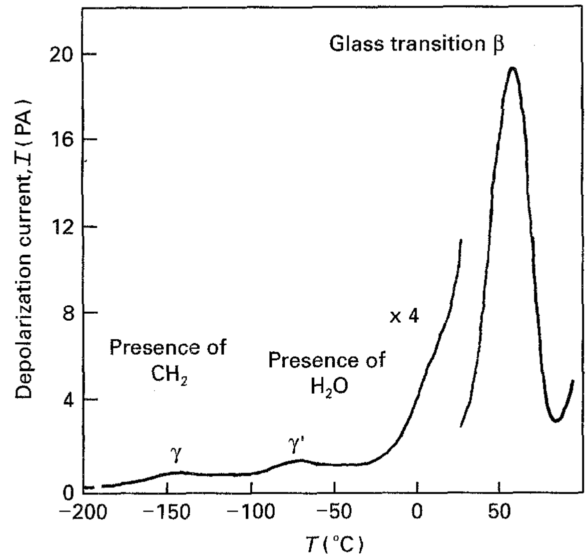

Figure 2 Global spectrum of a sample. $\bar{M}_n = 4000$; $T_p = 90\,°C$.

the fractional polarization method. The depolarization current has been measured with a Keithly 642 electrometer (lowest detectable current range 10^{-15} A) coupled to an x–y plotter and a pen recorder having two channels. The area bound by depolarization current $I(T)$ and temperature with linear rate $T(t)$ are recorded simultaneously by pen recorder (Fig. 5).

The relaxation time $\tau(s)$ at different temperatures can be calculated from the elementary spectrum curve recorded by pen recorder using the following equation

$$\tau_i = \frac{Q_i}{I_i} = \frac{S_i/v}{I_i}; \quad i = 1,2,3,\ldots,n \qquad (1)$$

where Q_i is the charge, I_i the depolarization current, S_i the area bound by the depolarization current and v is the temperature recording velocity. As $Q_i = S_i/v = \mathrm{cm}^2\,\mathrm{cm}^{-1}\,\mathrm{s}^{-1} = \mathrm{cm\,s}$; $\tau_i(s) = Q_i/I_i = \mathrm{cm\,s/cm} = \mathrm{s}$.

The calculation of the values of S_i at different temperatures for elementary spectrum 1 is shown below:

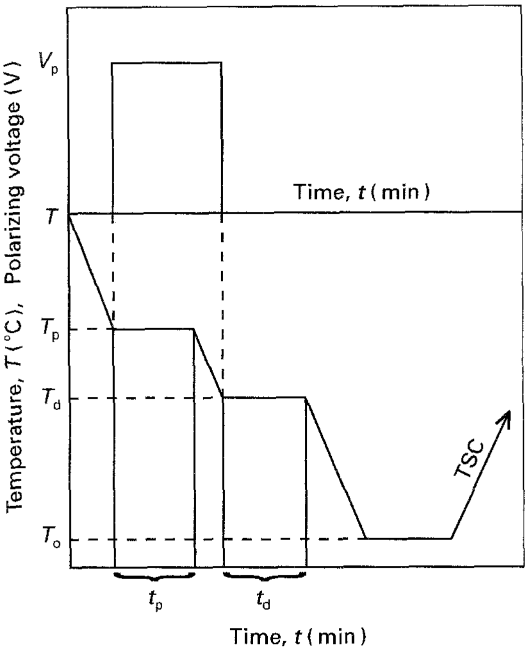

Figure 3 The sequence of fractional polarization.

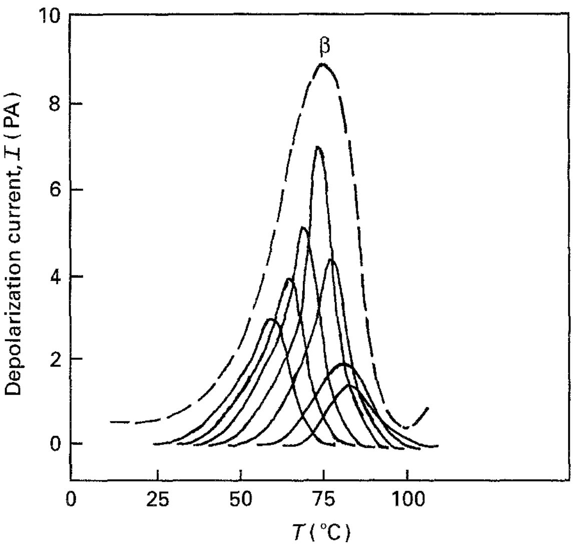

Figure 4 Global (–––) spectrum resolved into elementary (——) spectra. $\bar{M}_n = 16\,800$; $T_p = 90\,°C$; $T_g = 74\,°C$; $T_c = 105\,°C$; $\tau_c = 2.5\times10^{-2}$ s; $\Delta H_{max} = 2.8$ eV; $\sigma = 17.64\times10^{-14}\ \mathrm{S\,m^{-1}}$; DOD = 19.99.

S_0 = Total area of the curve measured by planimeter.

$$S_1 = S_0 - \left(\frac{I_0 + I_1}{2}\right) \times l, \quad \text{at } T_1$$

$$S_2 = S_1 - \left(\frac{I_1 + I_2}{2}\right) \times l, \quad \text{at } T_2$$

$$S_3 = S_2 - \left(\frac{I_2 + I_3}{2}\right) \times l, \quad \text{at } T_3$$

where l = distance between I_1 and I_0 or I_2 and I_1, or I_3 and I_2.

In general

$$S_i = S_{i-1} - \left(\frac{I_{i-1} + I_i}{2}\right) \times l \qquad (2)$$

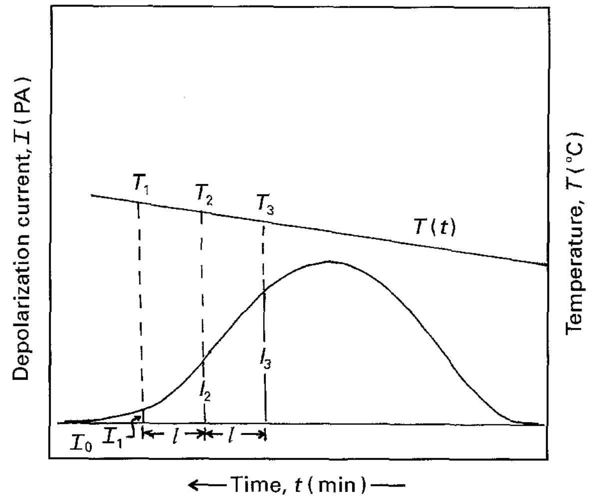

Figure 5 Relaxation time and Gibbs free energy calculation technique. See text for details.

Thus $\tau_1(s)$ at T_1, $\tau_2(s)$ at T_2, $\tau_3(s)$ at T_3 ... for elementary spectrum 1 are calculated. Similarly for each spectrum (2, 3, 4, ... , n) the values of $\tau_1(s)$ at T_1, $\tau_2(s)$ at T_2, $\tau_3(s)$ at T_3 ... are calculated.

The important characteristic of the glassy state is the coupling between the different modes of relaxation responsible for the internal flow mechanism. This often results in a linear relationship between the enthalpy and entropy of activation for the processes involved. For a given relaxation mode isolated by polarizing at T_p, the relaxation time takes the form

$$\begin{aligned}\ln(\tau_i)_p &= \ln(\tau_0)_p + \Delta G_p/kT \\ &= -\ln kT/h + \Delta G_p/kT \qquad (3)\end{aligned}$$

Therefore

$$\tau_i = h/kT \exp(-\Delta S_p/k)\exp(\Delta H_p/kT) \qquad (4)$$

where h = Planck's constant and k = Boltzmann's constant

with

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

where ΔH_p and ΔS_p are the mean enthalpy and entropy of activation. Calculating the value of ΔG_p at each temperature ΔG_p versus T can be plotted. The slope of the spectral lines is equal to the entropy of the activation and the intercept is the enthalpy (Fig. 6), and the mean activation entropy ΔS_p is a linear function of the mean enthalpy ΔH.

An Arrhenius diagram of relaxation time isolated in polymer can be obtained by plotting of $\log\tau$ against T^{-1}. The variation of $\log\tau$ is a linear function of T^{-1} for each elementary spectrum (Fig. 7). The slope of the straight line giving the activation energy ΔH, can be calculated from the relation

$$\Delta H = \frac{\ln(\tau_1/\tau_2)}{(T_1^{-1}) - (T_2^{-1})} \times 8.62 \times 10^{-5}\,\text{eV} \qquad (5)$$

and the value of the pre-exponential factor of the relaxation time τ_0, can be obtained from the following equation

$$\tau_0 = \tau \exp\left(-\frac{\Delta H}{kT}\right) \qquad (6)$$

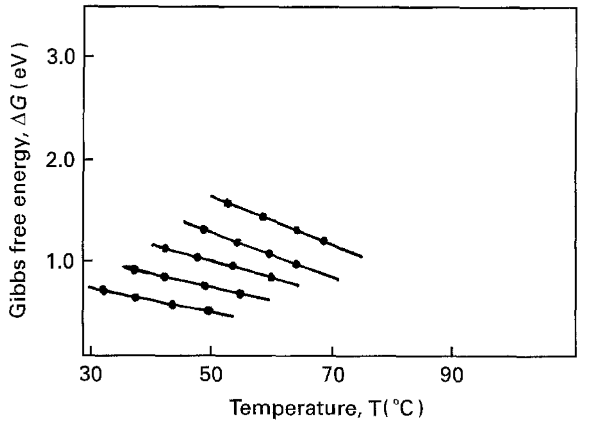

Figure 6 Relaxation map for the data obtained from elementary spectra plotted in the ΔG versus T plane. Intercept = ΔH_p, slope = ΔS_p.

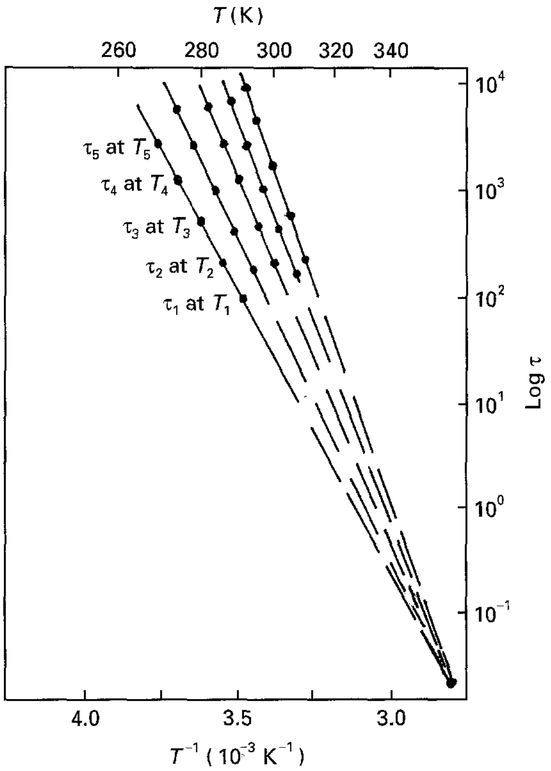

Figure 7 An Arrhenius diagram of relaxation time isolated in an amorphous material.

Similarly, for each elementary spectrum the values of ΔH and τ_0 are calculated.

The distribution of relaxation time will have only one value following a process called the compensation phenomenon. During this compensation process the extrapolated straight lines in the Arrhenius diagram meet at a common point. The temperature and relaxation time at this point are called compensation temperature T_c and compensation relaxation time τ_c. The co-ordinates of the compensation point, (T_c and $\log\tau_c$), are related to fundamental properties of the state of the polymer, as influenced by its surroundings. Compensation phenomena determine the degree of coupling between the coupled relaxation modes which determine the thermokinetic state of this amorphous phase of polymer. For amorphous

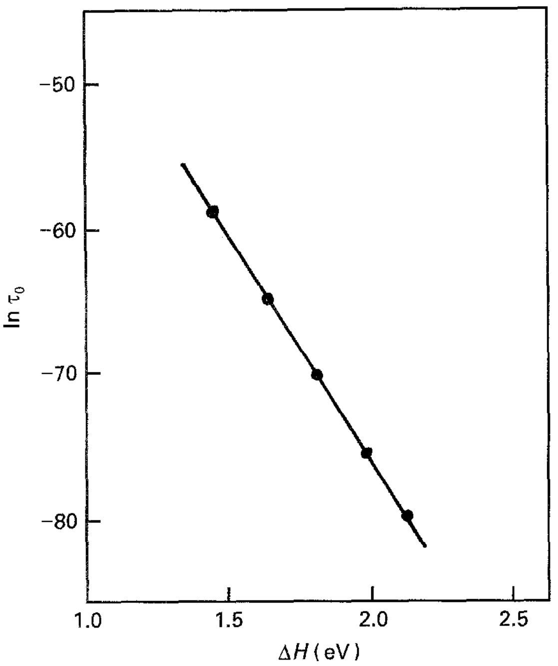

Figure 8 The variation of $\ln \tau_0$ as a function of ΔH for the relaxation times isolated in an amorphous material.

material or amorphous region in semicrystalline polymers the compensation phenomenon will take place, and the relationship between In τ_0 and ΔH will be linear (Fig. 8). T_c and τ_c can also be calculated by the following expressions

$$T_c^{-1} = \frac{\ln \tau_{01} - \ln \tau_{02}}{\Delta H_2 - \Delta H_1} \times 8.62 \times 10^{-5} \qquad (7)$$

and

$$\tau_c = \tau_0 \exp\left(\frac{\Delta H}{kT_c}\right) \qquad (8)$$

For a given relaxation mode isolated by polarizing at T_p, $\Delta H = \Delta G_p$. Putting the value of τ_0 from Equation 3 into Equation 8, the compensation phenomenon in the Arrhenius plane can be expressed in a general form by the following equation

$$\ln(\tau/\tau_c) = (\Delta G_p/k)(T^{-1} - T_c^{-1}) \qquad (9)$$

which puts the emphasis on the co-ordinates of the compensation point.

3. Superiority of the technique

Several techniques already exist to analyse the inner responses of materials to specific physical or chemical inputs for determining performance, or for checking quality. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are widely used both in the laboratory and on the production site along with thermal mechanical analysis (TMA), thermal expansion coefficient devices, and dielectric constant analysis. But none of these techniques has the power of analysis, the conclusive impact and the control over production quality that TSC techniques now provide. DSC and DMA both present several shortcomings which prevent them from being used extensively for quality control. DSC cannot be used to (i) characterize the differences in the amorphous state of the materials, (ii) determine T_g of a 40 μm fibre, (iii) distinguish tacky materials with different creep properties, (iv) differentiate specimens with different orientation. A DMA cannot be used to obtain the degree of disorder (DOD). The determination of the DOD number tells one how to compare the quality of interpenetration of the phases in block copolymers, blends and composite matrixes. The DOD number is directly related to the amount of internal stress induced by the speed of cooling. Careful measurements on oriented and pressurized specimens can be analysed using fractional polarization method. The free volume parameters can be determined from the Vogel equation, as well as the DOD from the compensation behaviour. DOD numbers can be compared for cured and uncured coatings to determine a quantitative scale for the degree of curing. The TSC technique's superior sensitivity allows detection of transition excellently which other techniques cannot see. Techniques such as DSC, DMA and DEA (Dielectric analyser) have no access to true thermokinetic functions. Besides this, only TSC can work directly with sample substrates, determine compatibility of polymer blends, evaluate adhesion of coatings to real substrates and compare adhesive properties of elastomers. In detail, the fractional polarization technique leads to the understanding of interactive coupling kinetics between the conformers belonging to the macromolecules and this method determines the respective contribution to the entropy of the electronic and atomic vibrations.

4. Experimental results

The thermally stimulated current technique is becoming more popular for investigating the molecular interaction in a compact phase of macromolecules. The following characteristics of a material are generally studied by TSC:

(i) Glassy state of a polymer – exhibited by relaxation peak resulting from molecular motion [3, 4];
(ii) the occurrence of dipolar relaxation process – indicated by the shift in peak temperature with the change in heating;
(iii) the presence of ions and space charge – investigated by slow cooling TSC [5, 6];
(iv) peaks due to water molecules – detected by putting the sample in a vacuum under different conditions;
(v) the mechanical properties of a copolymer attributed to the segregation of phases can be followed by observation of glass transition [7, 8] ;
(vi) the thermal properties of the materials – by heat treatment such as annealing and recrystallization of the sample after fusion [6, 8] ;
(vii) The conductivity of the material measured by the relation

$$\sigma = \frac{J}{E} = \frac{Id}{SV_p} \ (\mathrm{S\,m^{-1}}) \qquad (10)$$

where J = current density in Amp/m^2; E = dielectric field in Volt/m; I = depolarizing current in Amp; d = thickness of specimen in m; S = Surface area of specimen in m^2 and V_p = d.c. polarizing voltage in Volt.

(viii) Micro-Brownian motion in a polymer and MWS (Maxwell-Wagner-Sillers) effect in a phase separated copolymer – performing the experiment with different sample compositions:

(a) Micro-Brownian motion [9] – the intensity of glass transition is not a monotonically increasing function of the sample composition owing to the simultaneous variation in the degree of crystallinity.

(b) MWS effect [10] – the variation of peak amplitude as a function of sample composition shows the successive increase and decrease of active interfaces when passing from a continuous one phase to a continuous other phase and progressive decrease of the number of available ionic carriers for decreasing concentration in one segment, on the other.

5. Analytical results

The experimental results can be analysed to get the following inner responses of materials:

(i) The linearity in the plots of the charge released and the peak current versus the applied field suggests charge detrapping process.

(ii) A straight line obtained by the plot of peak current versus the square root of the polarizing field indicates charge injection from the electrodes.

(iii) The activation enthalpy, the activation entropy and the relaxation times at different temperatures can be calculated by analysing the spectra obtained by the fractional polarization method.

(iv) For amorphous polymers or for the amorphous region in semicrystalline polymers, the behaviour at T_g is characterized by at least one compensation phenomenon [11]. The compensation temperature can be determined by Arrhenius diagram or by plotting $\ln \tau_0$ against ΔH.

(v) The value of $T_c - T_g$ is significant in representing the internal state of the glass below T_g. The less internally stressed is the structure when the value of $T_c - T_g$ is larger.

(vi) The activated entropy calculated from the Eyring equation gives an indication of the degree of disorder (DOD) of the structure. A higher DOD corresponds to a better interpretation. The value found for the entropy of activation at $\Delta H = 0$ is shifted by an arbitrary amount, 100, to make DOD (in cal/°C) positive but a better physical meaning is actually achieved if 72 is used instead of 100 to obtain the true atomic entropic term [12, 13]. So, the DOD is expressed as

$$\text{DOD} = 72 - 2[\ln \tau_c + \ln T_c + \ln(k/h)] \quad (11)$$

6. Conclusions

The entire spectrum of depolarization current is the result of the interactive co-operation between various molecular motions. In previous work, the TSC output consisted of unresolved broad peaks representing a number of depolarization current modes. In this method a decisive step of submitting the polarized specimen to a different treatment is taken. This innovative concept makes possible the isolation of elementary Debye-type depolarization current within a complex system. Thus, it becomes easier to study the inner responses of the amorphous materials.

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