Indian Journal of Pure & Applied Physics
Vol. 46, August 2008, pp. 535-539

New approach for the measurement of glass transition temperature of polymer

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Received 19 February 2007; revised 16 January 2008; accepted 6 May 2008

Global thermally stimulated discharge current (TSDC) and partial thermally stimulated discharge current (PTSDC) spectra were recorded to investigate the molecular motions at glass transition temperature (T_g) level in both sided vacuum aluminized 30 μm thick poly (methyl methacrylate) samples. The calculated values of charge released, relaxation time and activation energy correspond to α and β relaxation processes. The TSDC peak occurred at a temperature, which is close to T_g of the polymer. This temperature is in agreement with the T_g determined using DSC technique.

Keywords: TSDC, DSC, PTSDC, α-relaxation, β-relaxation, Poly (methyl methacrylate), Glass transition temperature

1 Introduction

Polymers typically exhibit broad melting endotherms and glass transition as major analytical features associated with their properties. Additionally, charge storage and transport properties of polymers are also affected by T_g. Therefore, the study of T_g is very important for the selection of polymeric material used in insulating devices. The change in structure of polymer depends upon thermal, mechanical and electrical stress that can be studied precisely by means of TSDC on the basis of molecular relaxation processes. Several researchers have reported the change in behaviour of polymeric materials with the rise in temperature and studied dielectric properties using thermally stimulated discharge current techniques[1-5]. However, the application of TSDC technique to deduce T_g and understand macromolecular motion at T_g level is rarely reported.

There are mainly two types of experimental TSDC procedures depending upon the time taken for samples to get polarized. The TSDC is obtained when the sample is fully polarized (i.e. polarizing time is large enough); while PTSDC is obtained when sample is partially polarized (i.e. polarizing time is quite small). The glass transition strongly depends upon processing conditions, dispersion in structural and chemical properties of polymeric materials, which can be usually characterized either by differential scanning calorimetry (DSC) or by differential thermal analysis (DTA). The aim of the present study is to deduce T_g of PMMA using new experimental approach in terms of TSDC and PTSDC and investigate the molecular motion at T_g level.

2 Experimental Details

The circular samples of 30 μm thickness and 5 cm in diameter were used in the present study. The solution of particular concentration was prepared in a glass beaker by dissolving PMMA (5gm) in 100 ml toluene at room temperature (i.e.30°C). The solution was kept for 24 h at room temperature to yield a homogeneous and transparent solution. It was poured onto an optically plane glass plate floating on mercury pools and the solvent was then allowed to evaporate inside an oven at 40°C for 24h to yield the desired samples. The dried sample was subjected to room temperature out gassing at 10^{-5} torr for a further period of 24 h to remove any residual solvent. Both surfaces of the samples were vacuum aluminized over central circular area of diameter 3.6 cm. The samples were thermally polarized at 110°C (i.e. above T_g) with different values of poling field, because our intention is to study molecular relaxations at T_g level. The TSDC and PTSDC were recorded by means of digital electrometer (Scientific Instruments, Roorkee, India) at a linear heating rate of 3°C/min. In order to avoid the effect of ground loop and extraneous electrical noise, the electrometer was properly shielded and grounded. The T_g values of the samples were measured using temperature-modulated differential scanning calorimeter (TA instrument model 2910) at UGC-DAE Consortium, Indore (MP), India. Sample weighing 4-12 mg was heated at a rate of 3 °C/min. The experimental chamber consists of cell. The cell is flushed for a few minutes with purge gas at high flow rate to get rid of any minute impurities. The sample and the reference are placed on raised platforms cast on the thermoelectric constantan disk, which serves as the primary means of heat transfer to the sample and the reference from the temperature programmed furnace. The resulted heat flow to the sample is measured by area thermocouples fixed to the under side of disk platforms. All the observations were carried out with the accuracy of ± 5% experimental error and results are reproducible.

3 Results and Discussion

Fig.1 shows the global TSDC thermogram recorded at poling temperature of 110°C with different values of polarizing field (V_P). A significant change has been observed in the shape of TSDC thermograms with the increasing value of poling field. All the thermograms are characterized by two peaks: one at 55°C and other located around 90-105°C. PMMA has polar side group, which can rotate with the main chain. The co-operative motion with the main chain gives rise to first peak (i.e. β peak). It is supported by the fact that the linear relationship between field and peak intensity, which implies the dipolar origin of β peak[6]. The activation energy corresponding to these peaks is well within the limit as reported in literature [7].

Generally, the high temperature TSDC peak corresponds to glass transition temperature of polymeric material as observed by many researchers[8-10]. The α peak (i.e. second peak in Fig. 1) which occurs in glass transition region, attributed to space charge relaxation (α–relaxation) due to trapping of charge carriers injected from the metal electrodes in the vicinity of the polymer surface. This process is followed by the shift in peak temperature with field[11]. This observation is seen in our experiment; therefore, space charge relaxation may be the origin of the charge in TSDC of second peak. It is possible that the motion of main chain segment at different polarizing field is not uniform. This suggests that electric field polarizes a wide diversity of modes of motion in the glass transition region[12], associated with the TSDC. The activation energy of these peaks is the function of polarizing field. The increase of activation energy with field is related to relaxation processes in polymer. In fact, it is reasonable to consider that modes of motion varies with polarizing field in glass transition region, giving rise to increase of width of glass transition region as observed in TSDC thermogram (i.e. ranging from 90 to 105°C), however, T_g of polymers is characteristic value. In order to resolve the T_g of polymer from these peaks, the PTSDC is recorded.

Table 1 presents the parameters that correspond to TSDC peaks. Fig. 2 shows the PTSDC thermograms, which are characterized by single peak. The total charge released by each PTSDC peak is plotted as a function of V_p (Fig. 3). When dipolar relaxation is involved, then charge release is strictly proportional to the field strength[13].

The log τ versus V_p characteristics corresponding to TSDC is shown in Fig. 4. We conclude that τ has linear relation with V_p. In general, it is found that intensity of TSDC peak is subjected to V_p as observed in several TSDC thermograms. In the present study,

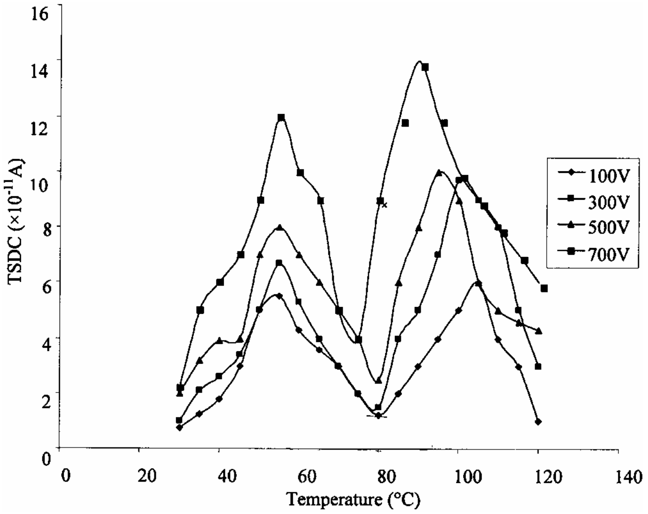

Fig. 1—TSDC thermograms at 110°C with different polarizing voltage and same charging time (i.e. 2.5h.)

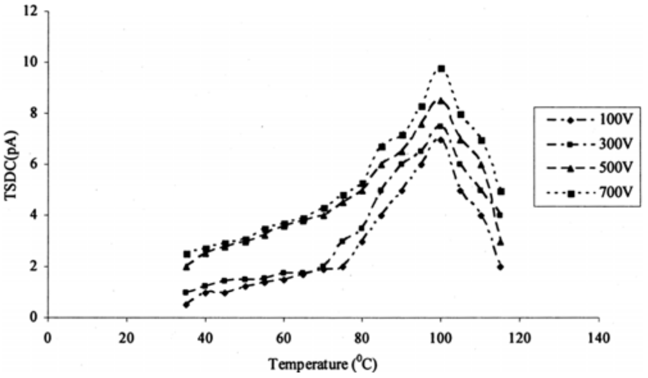

Fig. 2—PTSDC thermograms at 110°C with different polarizing voltage and same charging time (i.e. 300 sec.)

Table 1—TSDC parameters

Polarizing Voltage (V)	Relaxation peak	Peak Current I_m (× 10^{-11}A)	Activation energy A (eV)	Relaxation Time τ (sec)	Charge Released Q (Coul.)
100	β	5.5	0.29	$4.5\text{x}10^{-17}$	$2.9\text{x}10^{-11}$
	α	6	0.67	$2.9\text{x}10^{-21}$	$10.4\text{x}10^{-11}$
300	β	6.7	0.32	$1.1\text{x}10^{-17}$	$65\text{x}10^{-11}$
	α	9.7	0.72	$11\text{x } 10^{-21}$	$12.69\text{x}10^{-11}$
500	β	8	0.46	$5.2\text{x}10^{-7}$	$13\text{x}10^{-11}$
	α	10	0.73	$20\text{x}10^{-21}$	$15\text{x}10^{-11}$
700	β	12	0.51	$5.1\text{x}10^{-7}$	$16\text{x}10^{-11}$
	α	14	0.75	$24 \text{ x } 10^{-21}$	$19\text{x}10^{-11}$

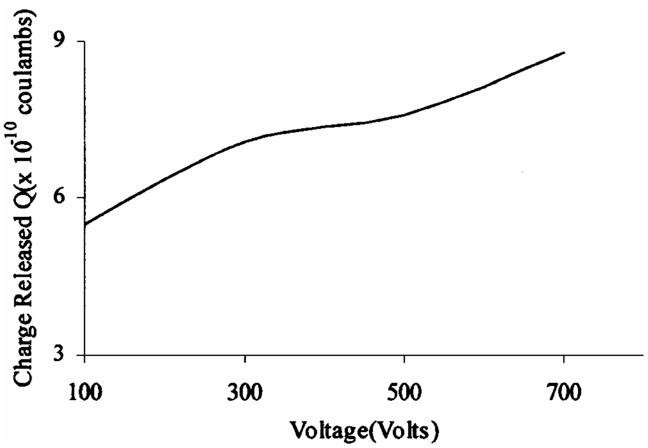

Fig. 3—Charge release versus polarizing voltage curve for PTSDC

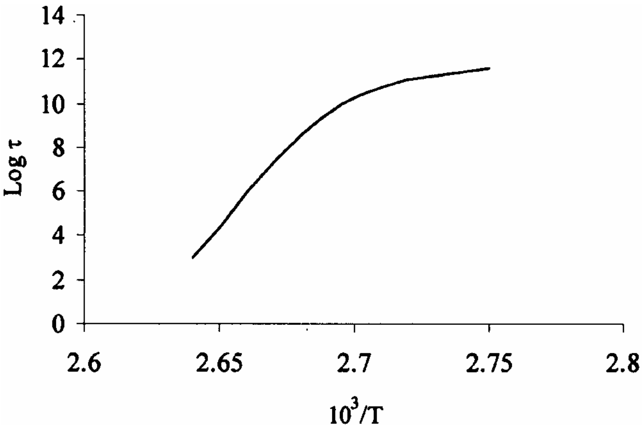

Fig. 4—Arrhenius plot of relaxation time

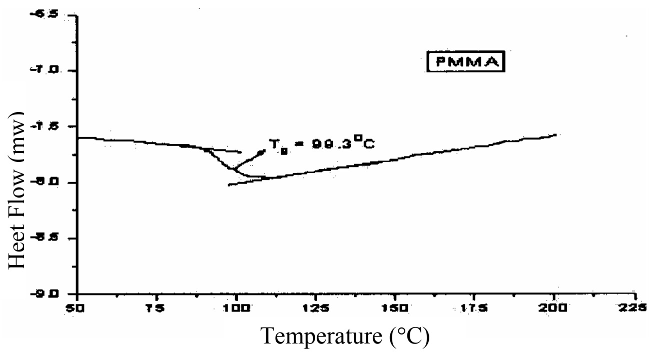

Fig. 5—DSC thermogram of PMMA sample

we discriminate the thermograms of TSDC and PTSDC in such a way that low temperature peak is disappeared in PTSDC. The position of α peak is the same in PTSDC, while different in TSDC. Because PTSDC peak is originated jointly due to dipolar and space charge relaxation processes and is not affected by charging conditions as reported in the literature[14,15]. It is a significant support with the dipolar and space charge relaxation peaks appeared separately in TSDC. The value of activation energy associated with the peak of PTSDC varies in the range 0.23-0.71 eV, which suggests the possibility of α and β relaxation processes. The calculated values of activation energy using initial rise method[11] for PTSDC peak indicate that disorientation of dipoles take place together with trapping of charge carriers near glass transition temperature. Fig. 5 shows the result of DSC for PMMA, which clearly shows the glass transition temperature of PMMA is 99.3°C.

In order to study the molecular relaxation at glass transition level, the poling conditions are chosen in such a way that it differentiate near T_g peak from the peaks reflected by different relaxation processes. PTSDC peak is considered to isolate high temperature TSDC peak near glass transition temperature region , is a good indication of deducing T_g of polymers. Bucci and Fieschi[16] proposed the TSDC method to study the electrical properties of insulating polymers, which is useful to understand the dielectric relaxation and molecular parameters[7]. The TSDC [I(T)] is recorded as a function of temperature and relaxation mechanism in materials that can be discussed on the basis of TSDC's peak position. The basic principle of

TSDC can be understood according to Deby's model. The decay of polarization[7] can be written as:

$$dP(t)/ dt = - dP(t)/ \tau (t) \qquad \ldots (1)$$

where τ(t) is single relaxation time. The temperature sweep[17] is defined as:

$$T(t) = T_0 + \beta t \qquad \ldots (2)$$

where T_0 is the initial temperature and β is heating rate.

After integration of Eq. (1) :

$$P(T) = P_0 \exp\left(-1/\beta \int_{T0}^{T} dT'/\tau(T') \right) \qquad \ldots (3)$$

The TSDC density is given as under:

$$I(T) = P_0 / \tau (T) \exp (-1/ \beta \int_{T0}^{T} dT'/\tau(T')) \qquad \ldots (4)$$

Eq. (4) describes the distribution of relaxation time; therefore, it is used to study the multiple relaxation process in material.

Since the observed relaxation is according to following relation[13]:

$$\tau (T) = \tau_0 \exp(A/ KT) \qquad \ldots (5)$$

where τ_0 is pre exponential factor (i.e. $\approx 10^{-16}$) and A (eV) is the activation energy.

The temperature at which TSDC peak appeared will follow the relation[2] :

$$\tau_0 A/KT_m^2 \exp (A/KT_m) = 1/\beta \qquad \ldots (6)$$

where T_m is the temperature at which the peak occurs, depends on A, τ_0 and β. Because TSDC peak characterizes relaxation process, therefore, relaxation parameters can be obtained by using relation given in Eq. (6). The charge released from TSDC peak has been calculated by the relation reported in literature [2].

The relaxation is associated with the glass transition phenomenon that, at a molecular level, remains an unsolved problem of condensed matter physics and chemistry. Fig. 4 shows the relaxation time temperature relationship according to Eq. (5). The temperature dependence of relaxation times was regarded as due to distribution of activation energies. We know that the existence of multiple relaxations could be explained by several relaxation mechanisms including dipole-dipole interaction and space charge. It is well accepted that the relaxation dynamics at the glass transition is associated with the Micro-Brownian segmental motion of chains, being cooperative in nature, which means that specific segment moves together with its environment. Therefore, α relaxation involves both intermolecular (i. e. connectivity with the main chain) and intramolecular (i. e. coordinated motion with the environment) interaction[18].

It is known for PMMA, the α and β relaxations are very strong, however, other relaxation processes are weaker [13,19]. The β relaxation is attributed to local motions such as hindered rotations of side group that can occur independently of the backbone movements, conformational changes in cyclic side groups[20] or limited motions within the main chain. The β relaxation is thermally activated process, therefore, the temperature dependence of Arrhenius-type is given in relation given in Eq. (5). The β relaxation is located at the low temperature; however, α process comes out at higher temperature. The change in the relaxation time at glass transition region could be interpretative as a change in the length scale of segmental motions that are in the origin of α relaxation[21,22]. In PMMA, the side group reorients rapidly and couples with the time scale of the processes resulted the high mobility of the side chain near T_g, which gives the TSDC peak. The position of TSDC peak was found to be at the temperature nearly equal to that of the DSC peak. The glass transition temperature observed by TSDC is located between 90-105°C, while 100°C by PTSD and 99.3°C by DSC. The reported glass transition temperature is 100±10°C, which corresponds to T_g observed by TSDC, PTSDC and DSC.

4 Conclusion

It has been concluded from the present study that TSDC and PTSDC peaks are originated due to α and β relaxation processes. The calculated value of activation energy for TSDC and PTSDC is in agreement with the relaxation processes. It is shown that the observed high temperature TSDC and PTSDC peak allows a simple determination of glass transition temperature of PMMA. The new approach of T_g study provides consistent result for glass transition phenomenon over the DSC.

Acknowledgement

We (M S Gaur and Prashant Shukla) gratefully acknowledge the financial support of the Uttar Pradesh Council of Science and Technology, Lucknow (U P) ,India. We are thankful to Dr S N Lall, Principal HCST Farah (Mathura) and Director

UGC-DAE Consortium, Indore (M. P.), to provide all necessary facilities for this work.

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