Thermally Stimulated Discharge Current Spectra and UV-vis Absorption in Polymethylmethacrylate Electret

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A B S T R A C T

The PMMA electrets were prepared by thermal polarization method. UV-vis absorption and thermally stimulated discharge current (TSDC) spectra have been recorded in PMMA electrets of 10 μm thickness. The PMMA electrets are polarized at 333 K with different polarizing fields. The observed TSDC and UV-vis spectra are the function of polarizing field. It has been found that absorption decreases with increasing field. The TSDC peak (α peak obtained at high temperature) is shifted towards lower temperature region with increasing field. The observed activation energy with the low temperature peak (β peak) is found to be varied between 0.21-0.55 eV, while for α peak it varies from 0.50 to 0.91 eV. The TSDC peaks are explained on the basis of theoretical predictions; however, the decrease in band gap energy of PMMA electret could be explained on the basis of UV-vis absorption peak. The configuration of UV-vis absorption in the region 200-900 nm gives the method of characterizing band gap energy. The dipolar and space charge polarizations are possible mechanisms to explain the TSDC in PMMA electrets. The optical micrographs distinguish the molecular structure of polarized and unpolarized (i.e., pristine) samples.

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INTRODUCTION

Electrical properties of insulating polymers are complicated because of their dependency on structure, additives, impurities, polarizing conditions, etc. Although many studies have been carried out, but electrical properties are still not completely understood. TSDC spectra have been extensively used to study the charge transport and charge storage in polymeric electrets, due to the relative simplicity of experimental process and the high resolution of the method [1]. Polymer electret represents a rapidly growing field of research due to their fundamental behaviour and their practical application [2,3].

In spite of continuous increasing attention, the mechanism of charge generation, its storage and transportation within the organic insulating polymer, and the effect of their structure on these processes are still to be studied. The study on the motion of charge on the surface is followed by a variety of capacitance probes, by optical microscopy or through the measur-

ment of surface charge density and thermally stimulated current [4-6]. This type of measurement also provides some insight into the conditions, which exist on the surface of a high voltage insulator after charging, either by field application and temperature or as a result of flashover [7]. 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 [8].

TSDC consisted of measuring with a certain heating rate, the current generated by the build up, and/or the release of polarized state in a solid dielectric sandwiched between two electrodes. Two theories for the origin of the TSDC have been proposed. In one of these, the residual polarization is attributed to dipole orientation; on the other hand it is attributed to charge carriers captured in traps associated with a definite energy of activation. It is also known that electrical polarization in polymers is caused by the dipole alignment, space charge injected into the polymer by surface breakdown, charge injection from the electrodes, rotation or motion of the main or segmental polymer chain, orientation of permanent dipole, etc [9-11]. The polarization in PMMA is the result of one or more of the above effective processes all together when it is subjected to heat and electric field [12-14]. But the basic problem is the nature of polarization in electret and variation of band gap energy after polarization is still less understood. The UV-vis spectrum is expected to understand the change in band gap energy after polarization of PMMA samples. PMMA is one of the promising classes of material, which can be used for the expanding applications of electrets in the field of energy sector [15-17]. It is an excellent material because it has simple structure and has the desired electrical properties. However, it has one limitation: its temperature stability is limited to 373 K due to its glass transition temperature of 378 K. The effect of the charging field and temperature on polymeric sample is well studied by optical micrograph. The optical micrographs of polymeric electrets represent the polarization history [18-21]. The present investigation provides the new information pertaining to systematic analysis and discussion of electret state in PMMA using TSDC and UV-vis absorption technique. The effect of the charging field and

temperature on polymeric sample can be well studied by optical micrograph.

EXPERIMENTAL

The PMMA samples of 10 μm thickness used in the present study with weight average molecular weight, $\overline{M}_w$ = 145,000 g/mol, and having isotectic microstructure were supplied by Dupont India limited. The circular electrodes (i.e., 36 mm diameter) in both surfaces of samples were made by bismuth evaporated in vacuum for the preparation of electret. In the present study the samples were thermally poled at 333 K with polarizing field ranging from 20 to 100 kV/cm. The TSDC was recorded by means of electrometer (Scientific Roorkee, India) at a heating rate of 3ºC/min. In order to avoid the effect of ground loop and extraneous electrical noise the electrometer was carefully shielded and grounded. The detail of TSDC assembly is reported in literature [22]. The time of polarization (i.e., 2.5 h) was adjusted to be the same for all the samples. The bismuth electrodes could be removed easily after polarization of sample to permit optical measurement. The polarizing condition of samples was the same for measurement of TSDC and optical absorption. The UV-vis spectra between 200-900 nm were recorded by UV-vis-2800 Hitachi spectrophotometer. The optical micrographs of the samples were taken by the model inverted phase contrast, μ-scope, Nikon-Eclipse, TE-2000 μ & Nikon Digital camera DXM 1200F.
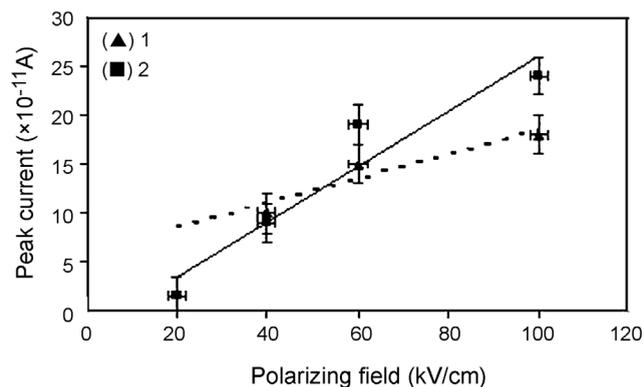
RESULTS AND DISCUSSION

Figure 1 shows the TSDC spectra of PMMA electrets polarized at 333 K with different values of polarizing field. Each themogram is characterized by two peaks. It has been observed that the TSDC is a function of polarizing field. The activation energy is calculated by using initial rise method. The activation energy lies between 0.2-0.5 eV for the first peak (i.e., low temperature peak), while for the second peak (i.e., high temperature peak) it lies between 0.5-0.9 eV. The activation energy is in good agreement with dipolar and space charge polarization in PMMA [23].
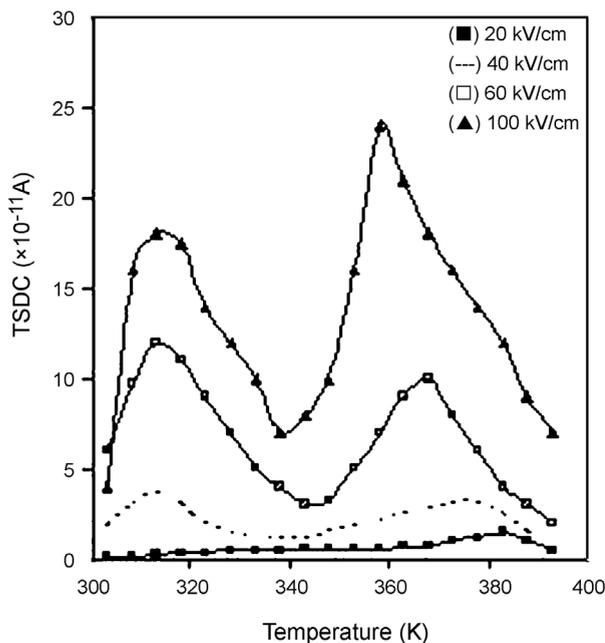
Figure 1. TSDC spectra of PMMA electret polarized at 333 K with different polarizing fields.

Figure 2. TSDC peak current is a linear function of polarizing fields (1: β peak and 2: α peak).

On the basis of TSDC results we may assume that one part of the polarization is due to the segmental dipole orientation, which is responsible for the low temperature peak (i.e., β peak) and another part is jointly due to dipolar orientation and injection of charge carriers from electrode giving rise to high temperature peak (i.e., α peak) that appears below glass transition temperature (T_g) which is considered as an important characteristic of the polymer as reported in the literature [23-25]. To explain the origin of TSDC peak, the peak current has been plotted as a function of polarizing field, which corresponds to the temperature at which one expects to activate mainly the mechanism of β or α peaks. Figure 2 shows a linear relationship of peak current with polarizing field that gives rise to each polarization that is uniform. β peak is due to the orientation of molecular dipoles, so that a symmetric charge distribution is expected [26-27].

In the case of α peak the polarization combined dipolar and space charge mechanisms. The TSDC carried out at a temperature above 347 K, charge injection from both electrodes becomes increasingly important. In this case we assume that the charge injection from the cathode is more than anode and also that negative carriers diffuse through the sample

resulting an excess of negative carriers. The temperature at which this effect takes place ranges from 358 K to 383 K, which is in good agreement with the resistivity of PMMA and exhibits a remarkable decrease above this temperature [28]. Thus, we can understand that in PMMA the α peak is due to a background of dipolar polarization mechanism over which a free charge contribution becomes increasingly important with temperature as a result of the increasing carrier injection from electrodes and increasing conductivity. The possibility of the space charge cannot be ignored due to the linearity of the peak currents with polarizing fields and shifting of peak towards lower temperature [29,30]. The current maxima are supposed to have linear relation with initial polarization, P. One can understand that the following relation governs the charge density in PMMA electrets [31]:

$$\rho(x) = \rho_0 + \rho_1 = P(x) - dP_1(x)/dx \qquad (1)$$

where ρ_0 and ρ_1 are the free and bound charge densities. A small quantity of free charge may be comparable to the derivative of the polarization; however, its contribution to the total current shall be masked by the large contribution of dipoles to the depolarization current. This contradiction can be explained if we assume that the space charge contribution to the total TSDC is very small as compared to that of the dipole contribution. Our results are quite compatible as observed by Bernstein [32]; however, he has observed charge distribution profile in PMMA by the electrically stimulated acoustic wave method.

(a)

(c)

(b)

(d)
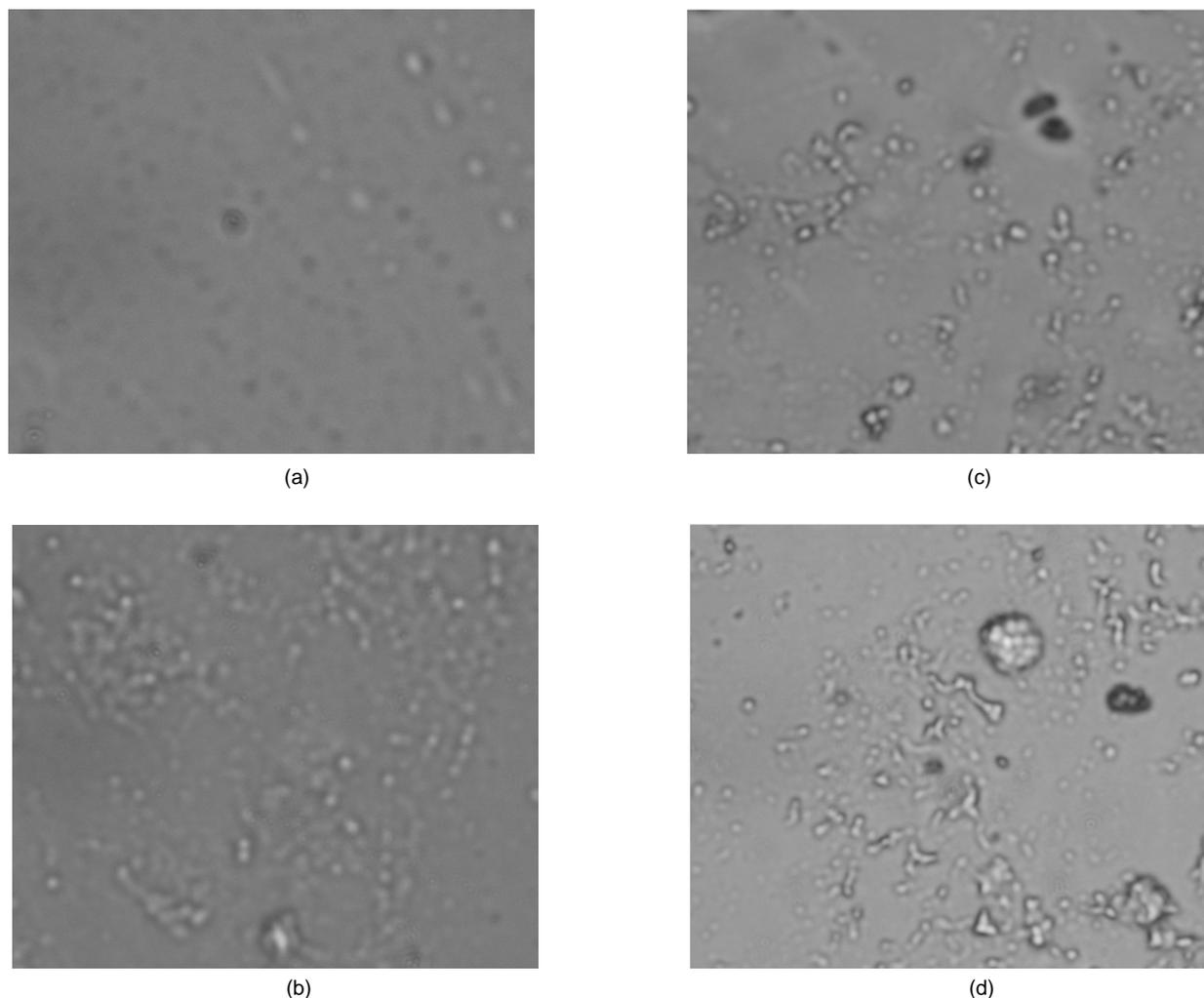
Figure 3. Optical micrographs of: (a) pristine PMMA sample, (b) PMMA electret charged with the field of 20 kV/cm, (c) PMMA electret charged with the field of 60 kV/cm, and (d) PMMA electret charged with the field of 100 kV/cm.

Figure 3a represents the optical micrograph of pristine PMMA sample, which shows the micro-structural morphology of PMMA before application of an electric field. It also shows the homogeneous morphology with flat shaped domains distributed in the polymer matrix.

Figures 3b, 3c, and 3d show the optical micro-graphs taken on PMMA electrets charged with the fields of 20 kV/cm, 60 kV/cm, and 100 kV/cm, respectively. These figures reveal the alignment of domains in regular shape as a structure. Since, in electret, dipole alignment occurs at the elevated temperature where the molecules or molecular chains are sufficiently mobile upon cooling; the aligned dipoles are frozen in, giving the dielectric a permanent polarization. When high field is applied,

the ions/charge carriers of two polarities drift towards opposite side, where they are trapped, and macroscopic dipoles are formed and confirm the polarization of trapped charges. This variation in morphology of pristine PMMA is in an agreement with polarization process [13]. The micrographs were recorded at ×100 magnification.

Figures 4a and 4b show the absorption spectra of pristine PMMA and PMMA samples polarized at 337 K with polarizing fields of 20, 60, and 100 kV/cm. The absorption of light energy by polymeric material in the UV-visible regions is related to promotion of electrons in σ, π, and n orbital from the ground state to higher energy states which are discussed by molecular orbital theory [33].

The optical spectra of thermally charged electrets

show some interesting features. The PMMA electrets are characterized with three maxima located at different wavelengths, while pristine PMMA sample is characterized by single maxima only. The first maxima is the characteristic of material, while others arise due to thermal polarization. The height of absorption peak decreases with polarizing fields. There is a complete change in the properties of pristine PMMA samples after charging. We have never observed such a strange behaviour in the
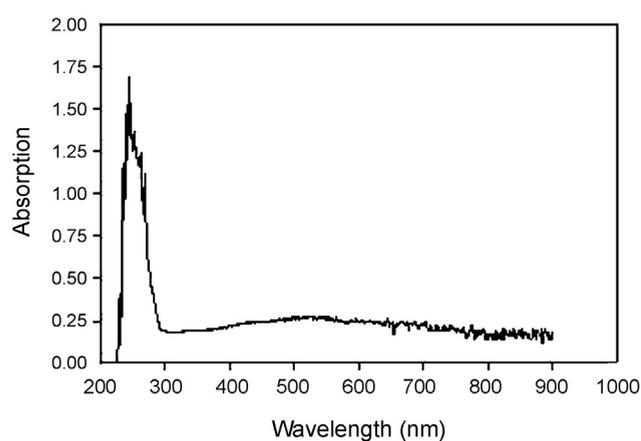
(a)
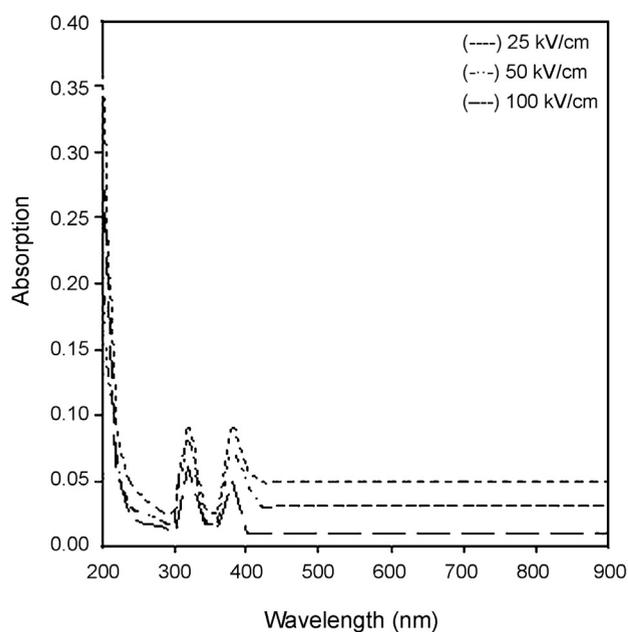
(b)

Figure 4. UV-vis absorption spectra of: (a) pristine PMMA and (b) PMMA electret polarized at 333 K with polarizing fields of 20, 60, and 100 kV/cm.

polymer studies. This can be understood in terms of energy bands in insulating polymers. The gap between conduction band and valance band decreases due to polarization, therefore, absorption decreases with increase in polarizing field. The optical band gaps in pristine and thermally charged PMMA were estimated by extrapolating the linear portion of curves resulting from $\alpha^2 h^2 \nu^2$ and $h\nu$ to zero absorption, where α, h, and ν are defined as the absorption coefficient, Planck's constant, and photon frequency, respectively [34,35]. The energy obtained for pristine PMMA sample is 4.54 eV and for charged samples are 5.32, 5.41, 5.61, and 5.73 eV. The increase in energy indicates that decrease in absorption due to change in molecular structure of material under the application of electric field and temperature. The change in structure can be easily observed in micrographs.

The intensity of absorption spectra is observed as the function of polarizing field. The absorption intensity decreases with increase of polarizing fields. In the range of 200-400 nm we can see the bond π-π^* transition away to the formation of double bond group of C=C bonds. The above-mentioned distinction is due to the polarization history of PMMA electrets. The behaviour of UV-vis spectra for PMMA electrets is not reported in literature. We have repeated the experiments many times and found a similar behaviour. The effect of charging on UV-vis spectra of polymers needs further investigation.

CONCLUSION

The TSDC results of PMMA electret are obeying the dipolar and space charge polarization. Optical micrograph shows that the structure of pristine PMMA has been modified to become a cluster of domains depending on the polarization at different fields. The increase in size of the tiny round-shaped domains in PMMA electrets has been observed with increase in applied field and this confirms the polarization process in the various electrets. UV-vis absorption spectra revealed that the optical band gap energies of the PMMA electret are lower than those of pristine samples due to the electrical charging of samples, which reduces the band gap of polymer.

ACKNOWLEDGEMENT

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