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## Thermally Stimulated Discharge Current (TSDC) Study of 4:1 PVC PMMA Polyblend Thin Films doped with 10% Cinnamic Acid

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#### Abstract:

The 4:1, PVC PMMA polyblend thin films, with the doping of 10% of Cinnamic Acid, were prepared by using Isothermal Evaporation Technique. The TSDC study of these films were carried out at three different poling electric fields (Ep) 35 kV/cm, 50 kV/cm, 65 kV/cm at the constant poling temperature (Tp) 373 K. It has been observed that the peak Thermally Stimulated Discharge Current (TSDC) (Im) and peak temperature (Tm) increases with an increase in poling electric field.

**Keywords:** Polyvinyl Chloride (PVC), Poly Methylmethacrylate (PMMA), Thermally Stimulated Discharge Current (TSDC)

#### 1. Introduction

The TSDC is an effective tool for understanding the internal structure, molecular relaxations and decay of space charge due to trapping of charge carriers and their subsequent thermal release from traps in a polymer [1-4].

The TSDC technique for polyblends of PMMA and PVC has also been studied. The electrets behaviour of PVC and PMMA separately has been carried out by number of researchers. The TSDC study of polyblends of PVC and PMMA has been carried out and it has been reported that the TSD current increases with the increase in the poling electric fields (Ep). This effect of poling electric fields (Ep) after doping with 10% Cinnamic Acid on the charge storage properties of polyblend films was the main thrust of investigation.

#### 2. Experimental

#### 2.1 Sample Preparation

The Polyvinyl Chloride (PVC) of commercial grade supplied by Poly Chem., Mumbai and Poly Methylmethacrylate (PMMA) obtained from Otto Kemi were used for the present study. The two polymers PVC PMMA and Cinnamic Acid (CA) doped blend films have been prepared by taking CA in the weight percentage 10% were taken in the ratio 4:1 were dissolved in the common solvent Tetrahydrofuran (THF). The solution was kept for 3-4 days to allow polymers to dissolve completely to yield uniform solution. The solution mixture was then heated for 1 hour at 60°C to get completely homogeneous solution. A glass plate thoroughly cleaned with water and later with acetone was used as a substrate. To achieve perfect levelling (and uniformity in thickness of the films), a pool of mercury was used in a plastic tray. The solution was poured on the glass plate and was allowed to spread uniformly in all directions on the substrate. The solvent in the solution was thus allowed to evaporate completely and get air-dried. The film on the glass substrate was then removed and cut into small pieces of suitable sizes. In this way the films were prepared by isothermal evaporation technique. Further it was dried for 3 days to remove any traces of solvent. The thickness of the films was measured by digimatic micrometer (Mitutoyo Corporation, Japan).

#### 2.2 Measurement Technique



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Each film was metallised on both sides by applying silver paint and then the film was sandwiched between two brass electrodes of the sample holder. The Metal-Insulator-Metal system so formed was placed inside the furnace.

- i) The poling electric field Ep = 35 kV/cm) was applied across the sample at room temperature (30  $^{\circ}$ C) and the sample was heated at a nearly uniform rate (1.33  $^{\circ}$ C/min) till the system attained the constant poling temperature Tp = 373 K (100  $^{\circ}$ C). The charging current was measured with respect to the increasing temperature.
- ii) Keeping the applied field ON for one hour at the constant applied field Ep = 35 kV/cm, the charging current was measured with respect to time.
- iii) Keeping the field ON the sample was slowly cooled down to room temperature in another one hour. In this case also the charging current was measured with respect to decreasing temperature. Thus the total time of charging was adjusted to be 3 hours in each case.
- iv) At room temperature the electric field was removed and the sample was kept shorted for 15 minutes to remove the surface charges. In this way the thermoelectret has been prepared at (Ep = 35 kV/cm) and Tp = 373 K.
- v) Now the thermoelectret had been formed. It was then heated at the same heating rate and the discharging (TSD) current was measured as the function of temperature from 303 K 453 K ( $30 \, {}^{\circ}\text{C}$  180  ${}^{\circ}\text{C}$ ). The current was recorded after every 5  ${}^{\circ}\text{C}$  rise of temperature whenever it showed a significant change in its value.

The same procedure from steps (i) to (v) was followed, for preparing the thermoelectrets, at poling Fields (Ep = 50 kV/cm and 65 kV/cm) and at the same poling temperature Tp = 373 K.

#### 3. Results and Discussions

In this manuscript results have been presented in the form of representative graphs for all the poling (Ep = 50 kV/cm and 65 kV/cm) and constant poling temperature (Tp = 373 K). The variations of charging current with rising temperature are illustrated as in figure 1. It has been observed that the charging current increases with an increase in temperature.

#### 3.1 Measurements carried out:

After attending the constant poling temperature Tp = 373 K, the sample was charged at the constant applied field for the period of one hour. For this charging current has been recorded with respect to time at an interval of 5 minutes upto one hour. The charging current gradually decreases with the increase of time as shown in figure 2.

After charging the sample for one hour, the temperature was gradually decreased from 373 K to room temperature keeping the field ON. The charging current with decreasing temperature was recorded after every decrease of 5  $^{\circ}$ C. It has been noticed that the charging current decreases for the decrease in the temperature as illustrated in figure 3.

The electric field was removed and the thermoelectret sample was gradually heated at the average uniform heating rate of 1.33 <sup>o</sup>C/min. The TSD current has been recorded with respect to increase of temperature. The graphs were plotted between TSD current and Temperature (known as Thermograms) as shown in figure 4.

#### Gurukul International Multidisciplinary OURNA e-ISSN No. 2394-8426 Research Journal (GIMRJ) with **International Impact Factor 8.357 Monthly Issue** Peer Reviewed Journal **APR-2025** Issue-IV, Volume-XIII https://doi.org/10.69758/GIMRJ/2504I5VXIIIP0054 PVCPMMA CA(10) PVCPMMA CA(10) 4.5E-06 4.5E-06 4.0E-06 4.0E-06 Ep=65 kV/cm 3.5E-06 3.5E-06 -Ep=65 3.0E-06 "Ep=50 kV/cm 3.0E-06 kV/cm ₹ ₹ -Ep="50 kV/cm" 2.5E-06 2.5E-06 "Ep=35 Qurrent Current kV/cm 2.0E-06 Ep="35 2.0E-06 kV/cm" 1.5E-06 1.5E-06 1.0E-06 1.0E-06 5.0E-07 5.0E-07 0.0E+00 0.0E+00 310 320 330 340 350 370 380 0 10 20 30 40 50 60 Temperature (K) Time (min.) figure 1 figure 2 PVCPMMA CA(10) PVCPMMA CA(10) 4.5E-08 1.6E-06 4.0E-08 1.4E-06 Charging Current (A) 3.5E-08 1.2E-06 - Ep=35 Ep=65 kV/cm 3.0E-08 kV/cm 1.0E-06 ব Ep=50 2.5E-08 Ep=50 kV/cm 8.0E-07 kV/cm 2.0E-08 6.0E-07 Ep=65 Ep=35 kV/cm ß kV/cm 1 5E-08 4 0E-07 1.0E-08 2 0E-07



340 350

Temperature (K

330

figure 4

300

325

350

400

375

Temperature (K)

425

450

475

5.0E-09

0.0E+00

The prominent results can be summarized as follows,

360 370

- 1) At a given poling field *(while heating the samples)* the charging current was found to increase with the increase of temperature.
- 2) The charging current (while cooling the samples) was found to decrease with the decrease in temperature.
- 3) The charging current, in both the cases, was found higher at higher poling fields.

380

4) The thermograms showed single peaks at temperatures above 100°C. The current corresponding to the peak is known as peak TSD Current (I<sub>m</sub>).

#### 3.2 Discussion of Results

0.0E+00 310 320

In the present case we have used the two polymers PVC and PMMA doped with Cinnamic Acid. Among these, PVC is non polar, while PMMA is weakly polar with the dielectric constant 3.5 - 4 at  $10^3$  cps. The glass transition temperature of PS is Tg = 95°C (368 K), and for PMMA Tg =  $105^{\circ}$ C (378 K). Both of them are essentially insulation materials and number of free charge carriers is very small and their mobility is very low. In case of PVC PMMA polyblend, the conductivity undergoes almost similar variations with respect to temperature, voltage and dopant (Cinnamic Acid) concentration.

In electrets made from polar materials (such as PVC and PMMA), disorientation of dipoles play an important role. This disorientation tends to destroy the persistent dipole polarization by redistribution of all dipoles at random. The disorientation of dipoles takes place due to the rotation of a coupled pair of +ve and - ve charges. This requires certain energy (few eV per dipole in solids). Due to this reason, discharge by dipole disorientation is thermally activated. It can also be speeded up by heating the sample. The disorientation energy is not same for all the dipoles. Therefore, the dipole with low activation energy will disorient at higher temperature. If the differences in the various activation energies are not large, it is more

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appropriate to assume continuous distribution of activation energies, for which all individual peaks overlap and merge into a broad peak. In the present case, we have noticed such broad peaks, which may be result of the disorientation of polar side groups in polymers at low temperature. Another possible cause for the occurrence of broad peaks in the difference in the rotational mass. These differences occur, when polymer is heated to its softening temperature, where the dipoles are disoriented by the motion of main chain segments. In the present case, we have charged the sample at the temperature 373K. This temperature is quite closer to the glass transition temperature (softening temperature) of both PVC and PMMA. In this case dipoles disorientation is responsible for peak. In addition to dipoles, the electrets usually contain immobilized space charges. These are non-uniformly stored, often residing near the electrodes. During heating, they get immobilized, and neutralized either at electrodes, or in the sample, by recombination with charges of the opposite sign. This current may occur due to self-motion process that can be described in two ways.

- 1) If the changes are ions, they are generally considered to be free to move with thermally activated mobility. They can be seen as if hopping from one vacancy to another across a potential barrier equal to activation energy.
- 2) If the charges are electrons or holes, it is more appropriate to visualize them as if they are immobilized in local traps. The heating of the sample releases them in a band of energies in which they can freely diffuse to the electrodes. If the electronic carriers are trapped at single energy level, the TSD current will show one peak. If there is more than one peak, this indicates that the carrier occupy different energy levels. The increase in peak TSD current with the increase This results into the strong polarization under the influence of strong electric field. Therefore when the thermoelectrets poled at higher Ep is heated. It produces relatively larger TSD current.

At the given poling temperature (Tp) and the poling field (Ep), it has been noticed that the peak TSD current increases with the increase in the percentage of dopant cinnamic acid.

This can be understood by considering the effect of temperature on the dopant cinnamic

acid.



[Ideally the production of  $H^+$  ion (or proton) by heating CA should occur at 133°C when no other mode of activation or catalyst is applied]. The above reaction suggest that, the heating of CA releases proton ( $H^+$  ion) and therefore availability of ions at high temperature produces higher TSD current.

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