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Open-Circuit Thermally Stimulated Discharge Currents Investigation in Polyethelene Terephthalate

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Abstract: Open-circuit thermally stimulated discharge currents in polyethylene terephthalate films have been investigation in the poling temperature range of 30-150°C. This material shows a negative TSDC intensity peak at approximately 80°C originated from dipolar process and another around 110°C (ρ-peak) attributed to the manifestation of space-charge effects. Since, this polymer is a commercially available and well known material, the main focus is set on the thermo-electrical properties. Therefore, the dependence of the polarization on the poling temperature has been utilized to look at the polarization which has been stored during the poling process. These measurements show an upper limit for the polarization.

Key words: Thermally Stimulated Discharge Currents (TSDC), PETP, corona poling, material, poling, temprature, Algeria

INTRODUCTION

Polyethylene Terphthalate (PETP) is a polycondensate. It can be synthesized from terephthalic acid and ethylene glycol under separation of water (Anderson, 2005). The repeating unit is made up of two different parts, ethylene glycol and terephthalic acid.

The produced polymer consists of long chains. Apart from the C=O groups, the main chain is totally symmetric. Since, the electronegativity of oxygen is higher than that of carbon, the double bond is polar. This means that the group forms a dipole and the polar properties of the materiel. There are several different brand names for PETP such as Mylar® (Dupont) and Hostaphan®(Heochst). These different brands differ in their properties like glass-transition temperature, crystallinity, impurities, etc.

The earlier mentioned C=O groups in the polymer are of special interest since they can be a effected using an electric field. The applied electric field causes changes within the material. This effect is called poling and the way how the field is applied is specified by the poling process (Van Turnhout, 1975). In the present research, the corona poling method is used. Resulting from the poling process, the electrical properties of the material can change. Thermally stimulated discharge currents method (Mano *et al*., 1999) is used to investigate the observed electrical process.

MATERIALS AND METHODS

Corona poling: For corona poling one or both surfaces of sample can be uncovered. This free surface is the one which will be exposed to the corona discharge. The other surface is connected to the grounded heating plate.

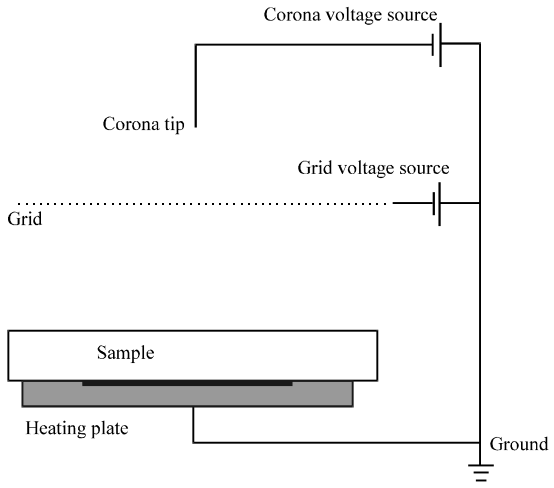

Fig. 1: Schematic corona poling setup

The effect of a corona discharge is produced in a gas atmosphere only. If a high electric field is applied to a needle or a sharp blade, the air at the tip or edge gets ionized. The ionized particles, charged at the same polarity as the tip are accelerated by the electric field towards the ground.

In an arrangement as shown in Fig. 1, this effect can be exploited to polarize a sample. The corona source is placed close to a grounded plate. On this plate, the sample is mounted. When the corona discharge starts the ions are deposited on the sample surface. If the sample is electrically insulating, the charges remain on its surface

and build up an electric field between surface and the grounded plate. Thus, a poling field is applied.

Open-circuit Thermally Stimulated Discharge Currents (TSDC): Open-circuit TSDC measurements consist in principle of a sample holder and a probing electrode below the holder. For the measurements the sample has to be flat which is proved by the sample holder. The construction of the setup provides a constant gap thickness between sample and lower electrode. A parallel plate arrangement as shown in Fig. 2 is built of the sample holder with sample and the probing electrode.

The insulation of the probing electrode is provided by quartz glass insulators. A screw which holds the lower electrode can be used to adjust the distance between the sample surface and the electrode. The thickness of this gap has an important influence on the measured signal. The sample and the probing electrode are shielded from electric fields using a metallic mesh and are insulated by quartz glass from the environment. For the temperature control the whole setup is placed inside a air circulation heating and drying oven. The temperature inside is controlled by a (BT 300/302 CLTS) temperature controller. The controller can adjust the temperature to stable values between room temperature and 500°C and to linear increasing temperature ramps. A decrease in the temperature in the temperature is possible for high temperatures only because the oven uses the surrounding air to cool it self. Due to the high heat capacity of the oven a more powerful cooling system would be needed for linear cooling ramps down to room temperature. For the electrical contacts quartz glass insulated tubes in a triaxial arrangement are used. This lead-through into the oven can be cooled with nitrogen gas to room temperature. Outside the oven, a KEITHLEY triax cable is used to connect a KEITHLEY 617 electrometer for low level current measurements. Inside the shielding cage a Ni/CrNi thermocouple (type K) is placed close to the sample.

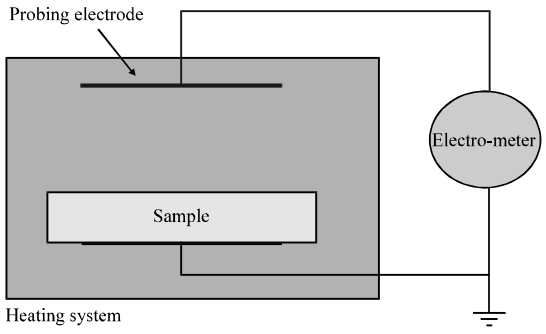

Fig. 2: Schematic open-circuit TSD setup

RESULTS

The open-circuit TSDC measurements were carried out as mentioned before. The size of the air gap g = 350±50 μm as well as the size of probing electrode A = 12.57 cm^2 have been the same for all measurements. Also, the corona poling parameters Utip = -10 kV and Tp = 20 min have been constant. In Fig. 3-5, a series of measurements on samples with increasing poling temperature Tp is shown.

The low-temperature noise seen in Fig. 3, is reduced significantly above 100°C. A possible reason for this noise which changes around 100°C is the surface potential of the sample.

Since, the heating system is working with a fan, it produces vibrations. If the probing electrode vibrates in the electric field of the surface charges noise is produced. Then, if the surface potential decreases the noise will decrease as well.

The high noise at temperatures above 120°C is caused by shrinking of the sample. Thus, the samples become wrinkled and get in contact with the probing electrode. Then, the charges move from the surface through the probing electrode and the electrometer to the ground. Since this happens discontinuously, the effect produces the noise at higher temperatures.

It can be seen that with increasing Tp, the position of the first (negative) peak is shifted to higher temperatures. The second (positive) peak remains almost stable at its initial temperature. For the whole experimental series with increasing poling temperature (Tp = 30….150°C), the peak positions are plotted in Fig. 6. It can be seen that the position of the negative peak reaches its maximum at a temperature of about 105°C. The positive peak does not clearly reveal a saturation in the peak temperature. However, there seems to be a limit around 125°C.

Furthermore, the area of the peaks changes with changing Tp. The negative, so-called α-peak, corresponds to the relaxation of oriented dipoles. A dipole relaxation with one relaxation time is described by the Debye-equation (Van Turnhout, 1980).

$$\frac{\partial P_s}{\partial t} + \alpha(T)P_s(x,t) = \varepsilon_0(\varepsilon_s - \varepsilon_\infty)\alpha(T)E(x,t) \qquad (1)$$

Where, P_s is the polarization of the dipoles. Due to the polarization forming process, there is no single dipole relaxation. The fast cooling produces a wide range of different relaxation frequencies due to the big free volume.

It was also found by other researchers (Devautour, 1997) that in addition to the Debye-equation a distribution function is needed to fit the α-maximum.

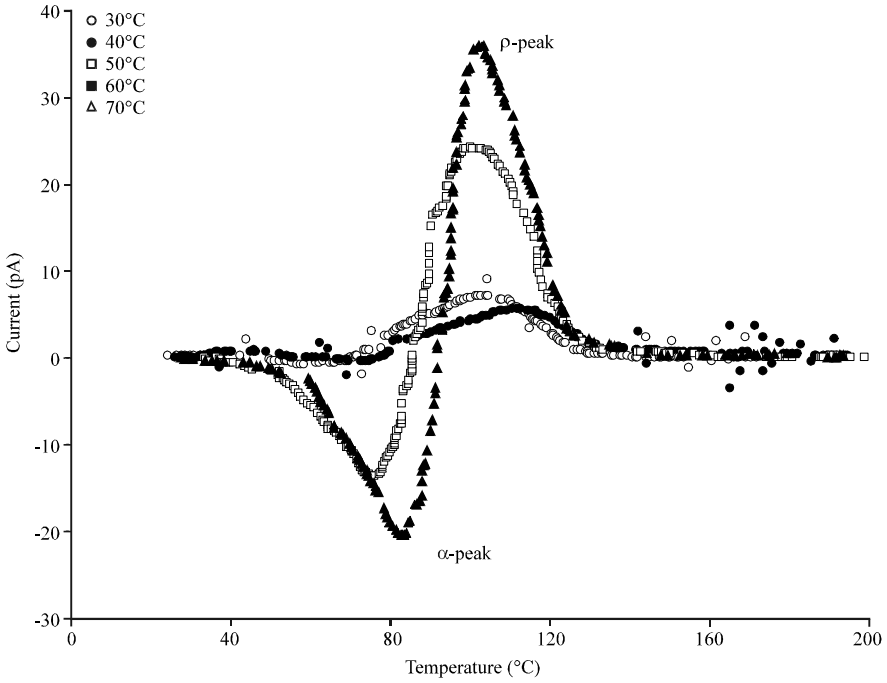

Fig. 3: Open-circuit TSD spectra: Samples are corona poled at different temperatures (30, 40, 50, 60, 70°C)

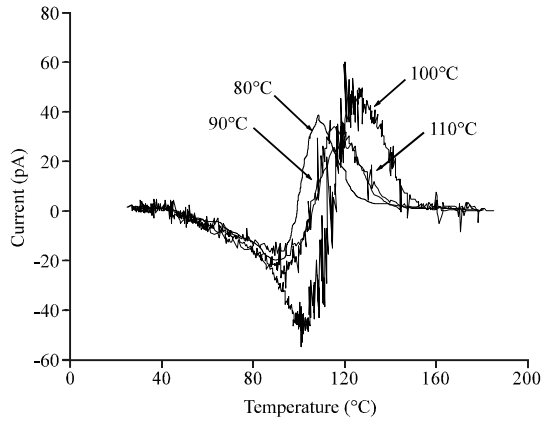

Fig. 4: Open-circuit TSD spectra: Samples are corona poled at different temperatures (80, 90, 100, 110°C)

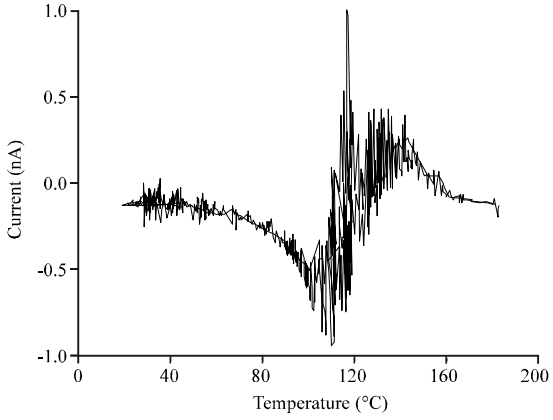

Fig. 5: Open-circuit TSD spectra: Samples are corona poled at different temperatures (120, 130, 140, 150°C)

Since, the relaxation frequency is not of interest in this study and the peaks are clearly separated, simple integration can be used to determine the dipole polarization. In Fig. 7, the peak area is plotted versus the poling temperature. The plot reveals that the dipole polarization increases with increasing Tp (Benrekaa *et al*., 2004, 2006) until Tp reaches 120°C. At higher poling temperatures, the polarization seems to be reduced but there is no clear dependency on Tp.

The second, so called ρ-peak corresponds to the detrapping of space changes (Gorokhovatsky *et al*., 1998; Neagu *et al*., 1997). Again, the area of the peak is used to indicate the behavior of the amount of stored space charges in dependence on the poling temperature. In Fig. 7, it is shown that the ρ-peak reveals a behavior similar to that of the α-peak.

For the interpretation of the open-circuit TSDC results it has to be regarded that there is a relatively large uncertainty included. Firstly, the cooling process is not very well defined since it is done manually. Secondly, also the determination of the peak position as well as the peak

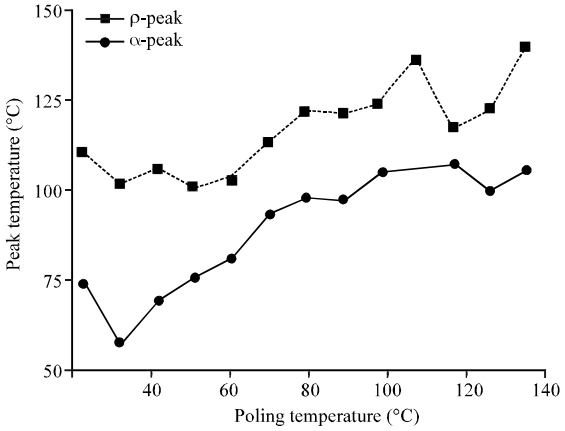

Fig. 6: Peak temperature of open circuit TSD spectra for poling experiments at different temperatures. The upper line corresponds to the ρ-peak and the lower line to the α-peak

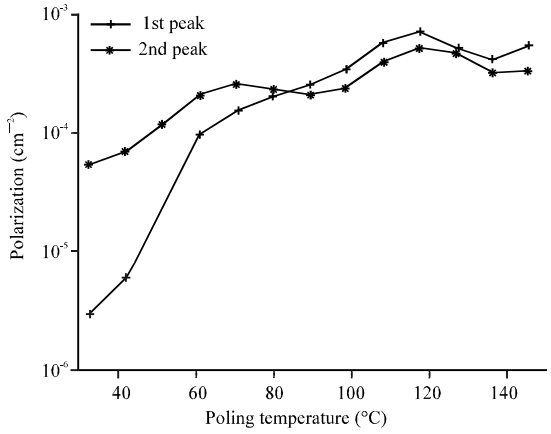

Fig. 7: Polarization of samples, poled at different temperatures and depolarization in open-circuit TSD experiment. The data marked with (+) and with (✱) correspond to the α-peak and the ρ-peak, respectively

area is not very exact. For the wide peaks at law poling temperatures the maximum position is not easy to find. At higher poling temperatures both the α and the ρ-peak are superimposed and thus, the maxima are shifted to lower temperatures. The same applies to the peaks areas because the peaks reducing each other by superposition. The saturation of the α-peak is caused by the saturating dipolar polarization. Thus, no further α-relaxations can be excited.

DISCUSSION

All samples were charged/polarized with the following corona parameters: Utip = -10 kV, Tp = 20 min, no grid. The varied parameter is the poling temperature Tp. Directly after poling the samples were cooled down is distilled water. At the same time, the surface potential of up to ≈ -5 kV is removed. This treatment has been chosen because a defined cooling was not possible and other shorting procedures caused breakdowns. About 90 min later, the samples were measured (open-circuit TSDC).

The open-circuit TSDC measurements show that the dipole polarizations as well as the amount of stored charges are increasing with higher poling temperatures (Fig. 7). Above Tp = 120°C both components are slightly reduced. This can be attributed to an increasing conductivity of the material and thus a reduced poling field inside the sample. The assumption is supported by the fact that around 110°C, the ρ-peak was found (Fig. 3). Another reason for the decrease at higher temperatures can be the stronger thermal vibration of the molecules inside the material (Das-Gupta, 1994). Thus, the alignments of the dipoles as well as the charge storage are reduced at higher poling temperatures. Finally, also the procedure of cooling can cause a reduced dipolar polarization and a reduced amount of stored charges. At higher temperatures relaxation processes take place faster whereas the time between switching the corona off and cooling is almost the same. Thus, both the dipole polarization and the amount of stored charges can decrease easier. To avoid this problem, a better temperature control system is needed for the cooling procedure.

For poling temperatures above 80°C, the ratio between the α-and ρ-peak is more or less constant. This may propose a charge-dipole interaction within the material. One possible model for this interaction is given by Schneider *et al.* (1983). It holds for amorphous and semi-crystalline materials which are charged at room temperature and describes quantitatively the effects poling and detrapping effects during a TSDC experiment, when the sample was charged previously. However, this model can not be applied within the present research because the poling procedure is not the same as by Schneider *et al.* (1983). There all samples were charged at room temperature whereas is here the charging was done at different temperatures.

The influence of the cooling process was investigated by Broemme *et al.* (1981) for 25 μm Hostaphan® foils. There is was found that for fast cooling the dipoles are mobile even at temperatures below the glass-transition temperature. Furthermore for a large free volume caused by fast cooling, the dipoles are fixed in their position due to the field of the space charges. This behavior was not found in the present research. In

contrast to the results by Broemme *et al.* (1981), the open-circuit TSDC shows a clear depolarization peak around Tg, even after fast cooling of the samples. These different results may be caused by different proprieties of Mylar® and Hostaphan®. For the investigation of the reduction of the free volume at room temperature, further experiments are necessary. Then, the time between the corona charging and the TSDC has to be varied.

CONCLUSION

The open-circuit TSDC experiments reveal an increasing dipolar polarization with increasing poling temperatures. Thus at higher temperatures, the dipoles align themselves better in the electric field. After the saturation at poling temperatures higher than the α-peak temperature the polarization reduces probably due to the thermal vibration of the molecules. The ρ-peak saturates also at Tp's higher than the peak temperature. The saturation proposes that all traps are filled with charge carriers for appropriate poling temperatures. Since, the trapping is a effected by molecular movements the higher ρ-peak temperature proposes another molecular mechanism at this temperature. Detailed investigations of the proposed mechanism can be done by using other methods such as differential scanning calometry.

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