Research Paper

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Thermally Stimulated Discharge Current Studies on Storage Time of Liquid-Crystalline Random Copolyester, Vectra A

Material Science

KEYWORDS : Thermally Stimulated Discharge Current (TSDC); liquid-crystalline copolyester; Vectra A.

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ABSTRACT

We have investigated the thermally stimulated discharge current (TSDC) spectra in temperature range 15-250 oC for different storage time (ts) [2 hrs - 96 hrs] of Vectra A. The TSDC spectra of Vectra A consist of peaks namely β and α peaks located at temperature 25 oC and 110 oC respectively. The β and α are the dipolar peaks, β-peak arises due to the orientation of HNA group and α-peak is attributed due to the orientation of main chain and associated with the glass transition temperature of Vectra A. The peak value of depolarization current decreases with increase in storage time that agrees with the concept of free volume theory. Also, the location of peak temperature shifts towards higher temperature with increase in storage time confirming the existence of distributed polarization. The important dielectric relaxation parameters; activation energy, charge released and relaxation time are also determined.

Introduction:

Liquid crystal polymers (LCPs) are attracting attention of current material research as they possess useful structural material and unique combination of electrical, thermal, mechanical and chemical properties. As a result, LCPs are ideally suited for large applications that include high precision mouldings and high performance fibres. Liquid-crystalline copolyester composed of 27 % of HNA and 73% of HBA under the brand name of Vectra A is used as engineering plastics because of good processability [1]. Thermally Stimulated Discharge Current (TSDC) is a tool that sets criteria for making efficient technical electrets [2]. Also, research is devoted to the TSDC of Vectra A earlier. Alhaz –Mohammed et al. made dielectric measurements on two samples with different compositions of HBA/HNA in frequency range from 1 Hz to 10 kHz [3]. The TSDC papers on storage effect of liquid crystal polymers are limited. In the present paper we have studied the TSDC of thermograms of Vectra-A, prepared by varying storage time from 2hrs to 96 hrs.

Theory:

The polarization (P*)* stored in the dielectric decay with time and is given by,

$$\frac{dP}{dt} = -\frac{P}{\tau} \qquad (1)$$

Where τ is the dipolar relaxation time. When the dielectric is heated at a uniform rate, the solution of equation (1) is

$$P = P_0 \exp\left(-\int_0^t \frac{dt}{\tau}\right) \qquad (2)$$

An electric field (E_p) and temperature (T_p) is applied to the dielectric initially when its dipoles are oriented freely then

$$P_0 = \frac{N \mu^2 E_p}{3 k T_p} \qquad (3)$$

Where N = concentration of dipoles and μ = the dipole moment.

The rate of change of polarization or in other words depolarization current density is given by

$$i(T) = -\frac{dP}{dt} = \frac{P_0}{\tau} \exp\left(-\int_0^t \frac{dt}{\tau}\right) \qquad (4)$$

As the variation of time and temperature is in continuity, the current density is obtained by progressive decrease in polarization in thermally stimulated discharge current (TSDC) experiment and the new variable T can be introduced. So differentiation must be performed now in term of the new variable introduced. So assuming simple temperature program in which the temperature is linearly increasing from a temperature T_0.

$$T = T_0 + h\,t \qquad (5)$$

Here T_0 is initial temperature and h is the inverse heating rate i.e. h = dT / dt.

The Arrhenius equation for the variation of τ with temperature is given as

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

For uniform rate of heating $T=T_0+ht$, combining equations (3), (4) and (6), we get

$$i(T) = \frac{N \mu^2 E_p}{3kT_p \tau_0} \exp\left(\frac{-U}{kT} - \frac{1}{h\tau_0}\int_{T_0}^{T} \exp\left(\frac{-U}{kT}\right) dT\right) \qquad (7)$$

By making the use of equation (7) we get

$$\tau = \int_{t(T)}^{\infty} \frac{i(t)\,dt}{i(T)} \qquad (8)$$

The value relaxation time (at any temperature can be calculated accurately as

$$\tau(T) = \frac{\text{Area under the TSDC Curve between } T_0 \text{ and } T}{\text{Value of TSD current at temperature T}}$$

Equation (6) can be expressed as

$$\ln \tau = \ln \tau_o + \frac{U}{kT} \qquad (9)$$

A linear plot between ln ***(τ) and 1/T yields the activation energy (U) (***Bucci plot method) and the pre-exponential factor (τ_o) [4].

Material and method: Vectra A is a main-chain thermotropic liquid-crystalline random copolyester composed of 73% 4-hydroxybenzoic acid (HBA) and 27% 6-hydroxy-2-naphthoic acid (HNA), as shown in figure (1), commonly known as copoly(HBA/HNA).

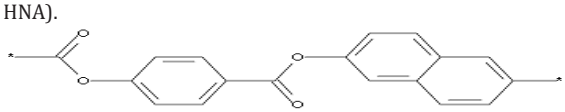


Figure1: Chemical structure of Vectra -A

Vectra A is procurred from from Good Fellow (UK). The Samples were prepared by cutting the rod in the form of pellets of thickness 1.3 mm.

The samples were metalized on both the surfaces by vaccum evaporation of Aluminium to form electrical contacts. The method of TSD is outlined in following figure (2).

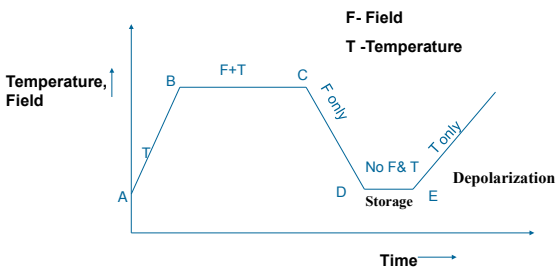
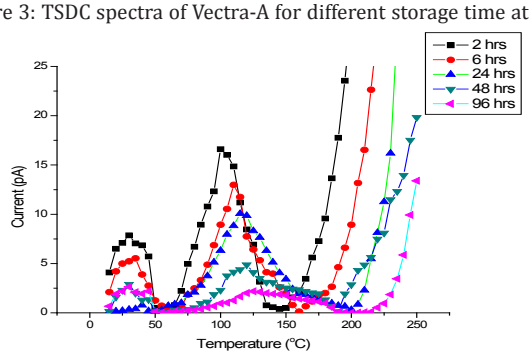


Figure 2: Charging and field programme during charging, storage and TSD

Samples of Vectra-A were kept inside the specially designed temperature controlled furnace and heated up to 75°C i.e. only temperature is provided to the sample (A to B). The thermo electrets were prepared by subjecting them to both dc field 11.5 kV/cm and constant temperature (B to C) for 1 hour. The samples were cooled to room temperature in the presence of electric field (C to D) with the help of blower. Then they were short-circuited and no field and temperature is provided for 2 hrs, 6 hrs, 24 hrs, 48 hrs and 92 hrs to five thermograms respectively (D to E) mentioned as storage time and reheated at linear rate of 2 °C/minute (E onwards). The discharge current generated was measured with sensitive Keithley electrometer 6514.

Results and discussion: Figure (3) illustrates the effect of various storage times (t_s) ranging from 2hrs to 96 hrs on TSDC spectra of Vectra A samples polarized at temperature (T_p) 75°C and polarizing field provided is 11.5 kV/cm.

Figure 3: TSDC spectra of Vectra-A for different storage time at



E_p = 11.5 kV/cm and T_p = 75 °C.

The TSDC spectra of Vectra A for different storage time's exhibits three peaks namely β and α peaks located at temperature 25 °C and 110 °C respectively. The β-peak obtained at room temperature i.e. 25 °C is due to the localized motion of HNA group. The peak at the same position is observed by Boresma during dielectric investigations of Vectra B [5]. The α-peak located around 110 °C is due to the orientation of main chain and associated with the glass transition temperature of Vectra A [6], [7]. This peak is associated with the phase transition from glassy to nematic phase. It is observed that the current maxima of TSDC spectra of Vectra A are markedly influenced by different storage times. The current maxima of TSDC peak decrease with increase in storage times and the location of current maxima shifts towards higher temperature. According to free-volume theory during the storage time that happens below the glass-rubber transition of a polymer leads to vitrification that further results in reduction of free space available for molecular motions and hence increases the relaxation times [8],[9].

Storage time is criteria to decide whether the TSD peak is arising from single dipolar relaxation or from distributed relaxation. Actually the shape and position of current of TSD peak of single relaxation time is independent of storage time conditions. On other hand if TSD peak arise from distributed relaxations they strongly depend upon storage time. The reason of strong dependence of distributed polarization on storage time is presence of fast moving and slow moving dipoles and these dipoles respond differently to short storage time and long storage time. It is evident from TSD spectra of Vectra A the location of current maxima of TSDC spectra shifts towards higher temperature with increase in storage time. It is confirmed that TSD spectra of Vectra A arises from distributed relaxation. Also, there is broadening in the peak with increase in storage times owing to the fact that all the dipoles, fast as well as slow, orient at increased storage time [10]. The analysis of TSD peaks have been performed by calculating important parameters, activation energy, relaxation strength and pre-exponential factor listed in Table 1.

	For β-peak			For α-peak		
Storage time t_s (hrs)	Activation Energy U (eV)	Relaxation Strength	Pre-exponential Factor (Sec)	Activation Energy U (eV)	Relaxation Strength	Pre-exponential Factor (Sec)
2	0.01474	0.00215	5.0×10^{-3}	0.10306	0.02909	9.02×10^{-1}
6	0.01549	0.01463	5.3×10^{-3}	0.11479	0.00630	3.28×10^{-1}
24	0.02551	0.01258	19.19×10^{-3}	0.33948	0.09588	2.8×10^{-8}
48	0.01910	0.01143	9.81×10^{-3}	0.14835	2.20135	2.7971×10^{-1}
96	0.00940	0.01157	14.88×10^{-3}	0.21234	0.03291	1.0153×10^{-2}

Table 1: Activation Energy, relaxation strength and pre-exponential factor for Vectra-A for different storage time at E_p = 11.5 kV/cm and T_p = 75 °C.

Owing to the different conformations, the rotation of different dipoles does not proceed in the same environment and therefore does not require the same activation energy.

Conclusion:

The present work aimed to study the TSD spectra of Vectra A with different storage time. It has been found that TSD peaks of Vectra A are strongly dependent on storage time confirming their origin from distributed relaxations. The calculated values activation energy, relaxation strength and pre-exponential factor also confirm the presence of multi-conformations in Vectra A.

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