Low temperature dielectric relaxation of poly (L-lactic acid) (PLLA) by Thermally Stimulated Depolarization Current

Manju Mishra Patidar1*, Deepi Jain2, R Nath1 and V Ganesan1

1UGC-DAE Consortium for Scientific Research, Indore, MP - 452001, India
2MITS, Gole ka Mandir, Gwalior, MP-474005, India

*E-mail: manjumishra.iuc@gmail.com

Abstract. Poly (L-lactic acid) (PLLA) is a biodegradable and biocompatible polyester that can be produced by renewable resources, like corn. Being non-toxic to human body, PLLA is used in biomedical applications, like surgical sutures, bone fixation devices, or controlled drug delivery. Besides its application studies, very few experiments have been done to study its dielectric relaxation in the low temperature region. Keeping this in mind we have performed a low temperature thermally stimulated depolarization current (TSDC) studies over the temperature range of 80K - 400K to understand the relaxation phenomena of PLLA. We could observe a multi modal broad relaxation of small but significant intensity at low temperatures while a sharp and high intense peak around glass transition temperature, Tg~ 333K, of PLLA has appeared. The fine structure of the low temperature TSDC peak may be attributed to the spherulites formation of crystallite regions inter twinned with the polymer as seen in AFM and appear to be produced due to an isothermal crystallization process. XRD analysis also confirms the semicrystalline nature of the PLLA film.

1. Introduction
Chemical structure of Poly (L-lactic acid) (PLLA) can be given by the formula (C3H4O2)n. Among the well known biodegradable polyesters, PLLA has attracted much attention in medical and industrial field due to its combined biocompatibility and degradation character. Being a prominent candidate of polymer industry, we could find only a few measurements on its low temperature dielectric relaxation [1]. Present paper attempt to probe it by employing thermally stimulated depolarization current (TSDC) technique. It measures the thermally stimulated release of the polarization frozen in during a previous application of an electric field during rapid cooling. During subsequent TSDC, the aligned dipoles randomly disorient at a rate proportional to the number of dipoles still aligned. TSDC spectra show peaks corresponding to different relaxations. Shape and location of peak are characteristic of mechanism by which polymers store their charges [2, 3].

2. Experimental Techniques
Solvant cast PLLA film of 15 mm diameter and 0.11 mm thickness is used as a sandwich between metallic copper electrodes for TSDC measurements using a homemade but versatile setup [4]. The PLLA film has been poled at temperature, Tp=350K. Tp is chosen well above the glass transition temperature, Tg~ 333K of PLLA, so that maximum number of dipoles are available that aligned in the direction of poling field, Ep= 2.7MV/m. In the presence of Ep, sample has been cooled down to the freezing temperature, Tf ~80K, which restrict the disorientation of aligned dipoles. Upon reaching the
desired freezing temperature film has been short circuited for 10min to remove effect of stray surface charge. Global TSDC spectrum of PLLA has been recorded with the Keithley 617 electrometer over the temperature range of 80K-400K by maintaining the linear heating rate of 5 K/min using Lakeshore DRC93CA in the vacuum of $10^{-3}$ mbar. X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) measurements have been used for the structural and morphological studies of the sample.

### 3. Result and Discussion

XRD pattern (Figure 1) of PLLA is showing the semi crystalline (~ 25% of crystallinity) nature of the film. Broad background is due to the amorphous contribution, while sharp peaks reflect the crystallized nature of the film. XRD analysis reveals that the film is in orthorhombic in nature and carries $P2_12_12_1$ space group symmetry. Lattice parameters calculated for the film are $a=10.584$ Å, $b=6.247$ Å and $c=28.806$ Å.

The morphology of freshly prepared PLLA film was studied by AFM Model Nanoscope E in contact mode (figure 2). AFM images clearly show emerged crystallites of PLLA from an amorphous background region due to iso-thermal crystallization and has a characteristic spherulite structures similar to those observed through a polarized optical microscope by Yasuniwa et al [5]. The AFM results support the XRD results, where the semicrystalline nature of the film has been depicted.

**Figure 1.** XRD shows the semicrystalline nature of PLLA film. **Figure 2.** AFM scan shows the spherulite kind of crystallised region in the film.

**Figure 3.** Global TSDC spectrum of PLLA poled at $T_p=350K$ and $E_p=2.7$MV/m.Inset shows the protocol opted for the measurement. **Figure 4.** Low temperature β relaxation of the TSDC spectra of PLLA along with constituent peaks a, b, c and d.
Figure 3 shows the global TSDC spectrum of PLLA. Inset of the figure representing the protocol opted for the TSDC measurement followed by \( T_p \) poling route. One can use the same protocol but followed by different poling temperature route according to the systems demand and the range of relaxation desired to be studied. Two prominent features can easily be identified in the global TSDC curve. A broad and low intensity peak has been observed at low temperature which covers the temperature range of 100-290K called as \( \beta \) peak whereas a sharp and high intense peak, named as \( \alpha \), appears in the range 300K-400K. \( \alpha \) peak gives an insight into the relaxation around the glass transition temperature \( T_g \sim 333K \) and has one order higher intensity than the low temperature \( \beta \) peak. The high temperature relaxation peak around \( T_g \) is considered due to the segmental mode of relaxation. During the TSDC process, the aligned dipoles will randomly disorient at a rate proportional to the number of dipoles still aligned.

Therefore in the primitive form, the TSDC is expected to follow the Debye rate equation

\[
dP(t)/dt + P(t)/\tau(T) = 0, \tag{1}
\]

Where \( P(t) \) is the polarization at time \( t \) and \( \tau(T) \) is the relaxation time.

Various parameters, as tabulated in table 1, like activation energy \( E_g \) and relaxation time \( \tau_0 \) of the PLLA polymer have been calculated by adopting BFG (Bucci-Fieschi-Guidi) or initial rise method applicable for Debye like single relaxations of dipoles [2] and using single Arrhenius relaxation time equation

\[
\tau = \tau_0 \exp(E_g/kT) \tag{2}
\]

Figure 4 shows the multiple constituent peaks fitted in low temperature part of TSDC spectra, which is helpful to understand more about the low temperature relaxation behavior of the macromolecules present in the PLLA polymer. One can see that a broad relaxation peak is composition of a number of small elementary peaks. These low temperature relaxations seem to be due to the small amplitude local motion in the amorphous phase. Parameters which are shown in table 2 are helpful to understand more about the low temperature relaxation behavior of the macromolecules present in the PLLA polymer. Discussion on broad peak ‘d’ is beyond the scope the present work due to its unusually broad nature.

The fine structures of the low temperature TSDC \( \beta \) peak may be attributed to the spherulites formation of crystallite regions, already observed in XRD and AFM results, as they are inter twinned with the

| Table 1. Parameters of high temperature \( \alpha \)-peak |
|-----|-----|-----|-----|-----|-----|
| \( T_m \) (K) | \( I_m \) (A) | \( P_0 \) (Cm\(^{-2}\)) | \( J_0 \) (Am\(^{-2}\)) | \( E_g \) (eV) | \( \tau_0 \) (ns) |
| 358 | 8.7E-12 | 8.3E-10 | 1.2E-08 | 0.49 | 0.89 |

| Table 2. Parameters of the low temperature \( \beta \)-relaxation peaks |
|-----|-----|-----|-----|-----|-----|
| Peak | \( T_m \) (K) | \( I_m \) (A) | \( P_0 \) (Cm\(^{-2}\)) | \( J_0 \) (Am\(^{-2}\)) | \( E_g \) (meV) | \( \tau_0 \) (ns) |
| a | 167.6 | 9.2E-13 | 6.6E-11 | 2E-09 | 7.58 | 34.2 |
| b | 216.6 | 8.7E-13 | 2.8E-11 | 4E-09 | 22.28 | 7.0 |
| c | 255.8 | 7.5E-13 | 5.1E-11 | 2E-09 | 14.33 | 2.6 |
| d | 288.4 | 9.0E-13 | 7.1E-10 | 3E-09 | 22.55 | 235.7 |
polymer and are expected to yield broken segments of varying lengths and degrees of crystallization. Hence sharpness appears in an otherwise broad β relaxation, which is a slow process called ‘Reptation’ that resembles a reptile motion of side chains of the polymers [6].

4. Conclusion
Low temperature dielectric relaxation of PLLA film has been studied by TSDC technique. Two features named β (100-290K) and α (300K-400K) are clearly observed in global TSDC spectrum. Various parameters are also calculated for β as well as α peak. The prominent change in the parameters signifies the different origin responsible for the β and α relaxation. XRD and AFM analysis shows the semicrystalline nature of the film. The fine structures of the β peak may be recognized due to the crystallization of the film.

Acknowledgment
The authors are thankful to Dr. A. K. Sinha, Director, UGC-DAE CSR, Indore for his encouragement and members of Low Temperature and Cryogenic laboratories for their help in cryogens. Authors thank Dr. M. Gupta for XRD measurements. The authors are also grateful to the DST, Govt. of India, New Delhi for providing research grant in the form of major research project SR/S2/CMP-005/2009 with fellowship to MMP and honorarium to RN.

References
[1] Laredo E, Prutsky N, Bello A, Grimau M, Castillo R, Muller A J and Dubois Ph 2007 Eur. Phys. J. E. 23 295
[2] Turnhout J V 1975 Thermally Stimulated Discharges of Polymer Electrets (Amsterdam: Elsevier)
[3] Sessler G M 1980 Electrets (Springer-Verlag Berlin Heidelberg New York)
[4] Jain D, Sharath Chandra L S, Nath R and Ganesan V 2012 Meas. Sci. Technol. 23 025603
[5] Yasuniwa M, Tsubakihara S, Lura K, Ono Y, Dan Y and Takahashi K 2006 Polymers 47 7554
[6] Das-Gupta DK, 2001 J. Electrostat 51-52 159-66