



Thermally Stimulated Depolarization Current and Dielectric Relaxation Spectroscopy in Poly(vinylidene fluoride) Samples

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ABSTRACT

Dielectric relaxation properties of solution grown foil samples of poly(vinylidene fluoride) (PVDF) of 20 μm thickness with similar (Al-Al) electrode combination have been studied in the low frequency range of 100 Hz to 10 kHz by varying the temperature from 30°C to 170°C. PVDF foil samples exhibit two dielectric loss maxima, one around 130 \pm 10°C and the other around 150 \pm 10°C. These peaks correspond to α - and α' -relaxation processes, respectively. The variation of permittivity with temperature is attributed to the thermal expansion, orientation of dipolar molecules and the chaotic random motion of molecules in the close vicinity of α and α' peaks, respectively. The thermally stimulated depolarization current (TSDC) spectra of PVDF foil sample are characterized by two current maximas, one at 70 \pm 10°C (β -peak) and the other centered at 135 \pm 10°C (α -peak). The first peak attributed to β -relaxation process was caused by local motions of side chain. However, α -relaxation peak appeared due to the formation of space charge at metal polymer interface. The peak position and activation energy do not change with the poling field (E_p), but it strongly depends upon the poling temperature (T_p). The location of the TSDC α -peak is found to be comparable with the α -peak obtained by dielectric relaxation spectroscopy.

Key Words:

permittivity;
dielectric loss;
TSDC;
 α - and β -relaxation;
dipole-orientation;
space charge;
glass transition temperature.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) best known as Kynar, is a polar, semi-crystalline polymer with exceptional mechanical and electrical properties. PVDF, for technical applications is popular mainly for its strong piezo and pyroelectric properties. Although the basic repeated unit is chemically simple

(-CH₂-CF₂-), the physical properties are to a great extent variable. Beside the non-crystalline phase, there are known three crystal forms designated as forms I, II and III, which are all stable at room temperature. Form I has orthorhombic, trans-trans conformation and form II has monoclinic with trans-gauche

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conformations, respectively. The amount of individual structural forms depends upon thermal, mechanical and electrical treatment of PVDF material. The structural studies reported some years ago have shown that the polar form I plays a significant role in the electrical responses [1-2]. Therefore, PVDF has attracted considerable attention due to its unique electroactive properties induced by high field exposure.

Several researchers have studied the charge storage and transport phenomena in polymer electrets by means of techniques based on thermal stimulation. The thermally stimulated depolarization current (TSDC) method was proposed by Bucci and Fieschi et al. in 1964. This technique is useful in understanding the dielectric relaxation and in elucidating molecular parameters such as charging processes, decay mechanisms, thermal stability, relaxation times, activation energies, etc. TSDC Technique has shown that the total charge stored in a polymer electret (electricity + magnet) and different mechanisms, which contribute to the storage of charges, are very sensitive to the structure of the electret material itself, because of the presence of different groups in the main molecular chain [3-4]. Thus, TSDC technique is proved to be a basic tool to identify and evaluate the dipole re-orientation processes, trapping and recombination levels in electrets [5].

Dielectric spectroscopy technique measures and analyzes the behaviour of the physical properties of the dielectric materials as a function of either the time they are exposed to a constant external electric field or the frequency of an external alternating electric field [6]. Dielectric properties of fluoro-polymers as PVDF are determined largely by the strong electric dipoles in the $\text{CH}_2\text{-CF}_2$ bond angle of the side group. Due to this feature in the molecular structure of the polymer, the dielectric spectroscopy can be advantageously used to study molecular motions in these polymers [7]. The dielectric behaviour of fluoro-polymeric films is of direct interest to both, the basic studies of electrical conduction through such films and their application as capacitors in microelectronics. The interpretation of the dielectric properties of PVDF foil samples in the present study is carried out by measuring simultaneously the permittivity and the dielectric loss over a wide range of temperatures and at increasing constant frequencies. The aim of the present investigation is

essentially to understand whether persistent polarization is due to alignment of dipoles or migration of charge carriers or a combination of both; and to study the low frequency dielectric properties of PVDF foil samples using dielectric constant and dielectric loss measurements.

EXPERIMENTAL

Preparation of Samples

The commercial PVDF (Solef 1015 PVDF powder, Solvay, Belgium) used in present study was procured from Solvay Corp. Ltd., Belgium and supplied by Redox Ltd. (India). Its weight-average molecular weight, $M_w = 261,000$, density = 1.78 g/cm^3 and viscosity (10% in *N*-methylpyrrolidone) = 1400. All samples were prepared by using the solution grown technique. These samples were outgassed in air at 60°C for 24 h, followed by room temperature outgassing at 10^{-4} torr for a further period of 24 h to remove any residual solvent.

Thickness Measurement and Electrode Coating

The samples thus prepared, were like circular discs of diameter 5 cm and approximately $20 \mu\text{m}$ thicknesses, calculated by measuring the capacitance by using the relation given in the literature [8]. Both the surfaces of the samples were vacuum aluminized using Hindhivac Vacuum coating unit with Penning and Pirani pressure gauges, ST-A6P3; over central circular area of diameter 3.5 cm for TSDC measurements. The square-shaped samples with metal-electrode area of dimensions $1 \times 1 \text{ cm}$ were used for dielectric measurements.

TSDC Techniques

The TSDC method consists of recording the thermally activated release of frozen-in polarization, which is the same as measuring dielectric losses versus temperature at low frequencies. A detailed description of the method is given in the literature [9]. The sample is sandwiched between the plates of the capacitor, made of aluminium, and polarized by the application of a high DC voltage power supply (Scientific Equipments, Roorkee, India, EHT-11). In present study, the samples are polarized at 30°C , 50°C , 75°C , and 100°C

with different values of polarizing field for a time t_p (total time of polarization) large compared with the relaxation time at T_p of the dispersion under consideration. With the electric field still applied the sample is cooled down to room temperature. The total time of polarization was 120 min. Afterwards the field was switched off and the sample was short circuited for 10 min to remove the frictional and stray charges. Then the sample is reheated at a constant heating rate of $3^\circ\text{C}/\text{min}$ from room temperature to 170°C . A discharge current is generated as a function of temperature, which is measured, with the help of a sensitive digital electrometer (Scientific Equipments, Roorkee, DPM-111), which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise. The analysis of the shape of the TSDC peak makes it possible to obtain the activation energy, E , the charge released, relaxation times etc. as shown in Table 1.

Alternate Current Dielectric Techniques

AC dielectric relaxation measurements for temperature range of $30\text{--}170^\circ\text{C}$ were performed using Agilent-Precision LCR meter (model: 4284A/20Hz-1MHz/Auto range/Bias-0V/Level-1V) over frequency range of 100 Hz-10 kHz. Dielectric tangential losses have been recorded for PVDF foil samples with a two-terminal electrode combination. The sample of $20\ \mu\text{m}$ thickness of dimension $2 \times 2\ \text{cm}$ and metal-electrode area of $1 \times 1\ \text{cm}$ was sandwiched between two brass plated stainless steel electrodes. The temperature of the electrode assembly along with the sample is controlled by means of a J-Type digital temperature controller (Pyrotron-TIC-3001) and a pre-calibrated thermocouple attached in close neighbourhood of the sample holder, which is being placed inside a furnace with temperature ranging from room temperature to 1000°C .

RESULTS AND DISCUSSION

TSDC Measurements

The polarizing temperature and field-dependent TSDC thermograms are shown in Figures 1 and 2, respectively. Generally, these thermograms are characterized by two current maximas one at $70 \pm 10^\circ\text{C}$

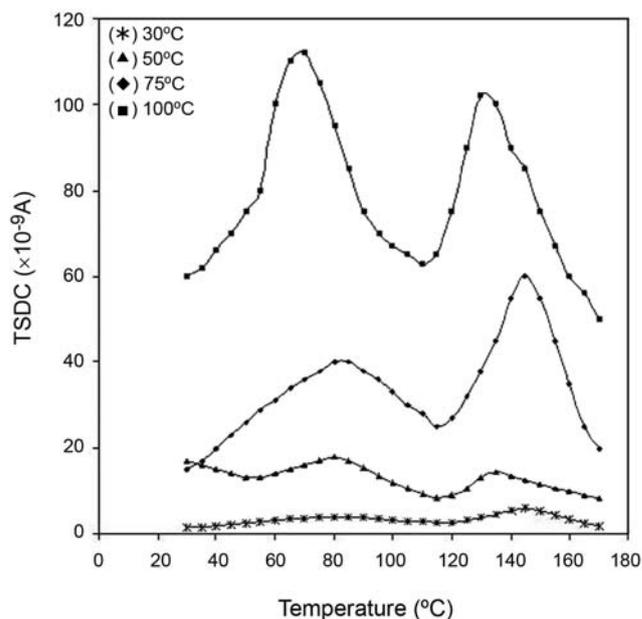


Figure 1. TSDC Thermograms of samples polarized with poling field (E_p) of $50\ \text{kV}/\text{cm}$ at poling temperature (T_p) of 30°C , 50°C , 75°C , and 100°C .

(β -peak) and the other centered at $\sim 135 \pm 10^\circ\text{C}$ (α -peak). The activation energy for all β -peaks is almost the same for field dependent TSDC thermograms (not shown in Table 1); while it varies for polarizing temperature-dependent TSDC thermograms (as shown in Table 1). The magnitude of peak currents has been found to increase with increase in

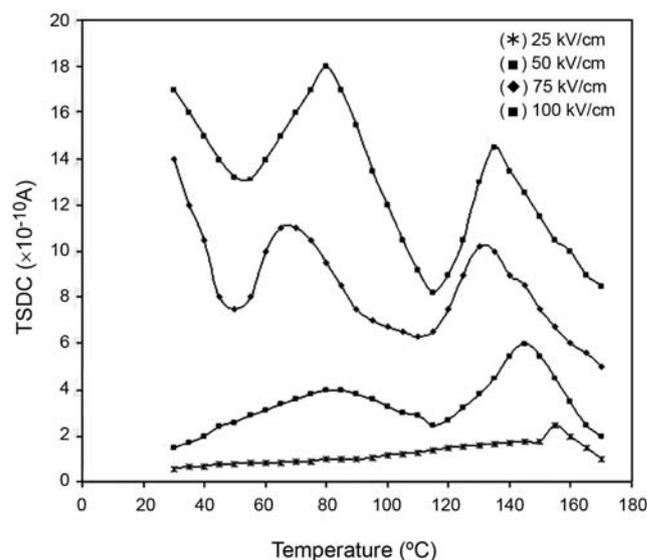


Figure 2. TSDC Thermograms of samples polarized at poling temperature (T_p) of 50°C with poling fields (E_p) of $25\ \text{kV}/\text{cm}$, $50\ \text{kV}/\text{cm}$, $75\ \text{kV}/\text{cm}$, and $100\ \text{kV}/\text{cm}$.

Table 1. TSDC Parameters.

Sample no	Polarizing field E_p (kV/cm)	Polarizing temperature T_p (°C)	Peaks	Peak temperature T_m (°C)	Activation energy E (eV)	Charge released Q ($\times 10^{-9}$ C)	Relaxation time τ ($\times 10^2$ s)	Peak current I_m ($\times 10^{-9}$ A)
1	50	30	β	-	-	-	-	-
			α	145	1.10	5.7	2.67	6
2	50	50	β	80	0.30	20.7	6.98	18
			α	135	0.97	15.3	2.93	14.5
3	50	75	β	85	0.16	65.3	13.09	40
			α	145	1.01	63.4	2.96	60
4	50	100	β	70	0.66	172.3	3.05	112
			α	130	1.02	117.6	2.72	102

polarizing fields and temperatures. The α -peak is shifted towards lower temperature side with increasing values of polarizing field and temperature.

The electrification of polymers takes place due to one or more of the following mechanisms operative simultaneously when it is subjected to dynamical, mechanical or thermal treatment with or without the static electric fields: (i) space charge injected into the dielectric by surface breakdown between the dielectric and the electrode; (ii) space charge injected from the electrodes; (iii) space charge caused by migration of charge carriers over microscopic distances; (iv) electronic or ionic dipoles caused by migration of charges over microscopic distances, and (v) orientation of permanent dipoles [10].

Broad peaks represent the presence of multiplicity of relaxation mechanism. The multiplicity of relaxation in PVDF may be because of the presence of trapping levels of different depths. Two peaks were reported for PVDF [11]. The first peak reported at 30°C (related to the charging temperature) and at 52°C due to the release of the charges trapped at crystalline/amorphous boundaries. PVDF is a polar polymer; contribution to the polarization may be due to the alignment of dipoles and formation of space charge/injection of charge carriers from metal electrode under the effect of the electric field.

β -Peak in polar polymers like PVDF mainly arises from localized rotational fluctuations of the dipoles and therefore, it is also referred to as dipolar relaxation process [12-14]. The molecular mechanism of β -relaxation has been discussed by many groups [15].

In PVDF β -relaxation can be associated to the dipole orientation of the polar side group. The occurrence of β -relaxation can be observed from certain characteristics of β -peak such as: (i) activation energy associated with this peak (as shown in Table 1) is very close to theoretically predicted value of E (i.e., ~ 0.30 - 0.60 eV) [16] and (ii) the peak position and activation energy do not change with poling field, but it strongly depends upon poling temperature.

The high temperature peak (α -peak) is due to the significant injection of charge carriers from the electrodes to the surface of the dielectric, which are frozen-in during the polarization of the specimen. It is also possible that PVDF contains a high number of impurity molecules prior to the field treatment and these molecules are dissociated into various ionic species. Therefore, it is reasonable to attribute the peaks appearing in high temperature region to space charge relaxation process (i.e., α -relaxation). α -Relaxation process occurs due to the injection of charge carriers from the electrodes at the metal polymer interface. The origin of α -relaxation process of this peak is confirmed by the facts: (i) peak current varies linearly with $V^{1/2}$ (not depicted) and (ii) the activation energy for this peak (i.e., 0.7 - 1.2 eV) does not differ much for activation energy values reported for α -relaxation in many polymers [17].

The charge trapping in a polymer takes place at the molecular chain, the side chain and at the interface of the crystalline and amorphous regions of the polymer [18]. The high field applied during electret formation may also produce some additional trapping sites. The

charge release from these traps occurs because of thermal excitation and motion of the molecular chain that cause the lowering of trap's depth. The released charge can recombine, retrapped in trapping sites, or may become discharged at the electrodes. The chance of retrapping of the released charge is high in PVDF having a large number of trapping sites and broad peaks can be explained by large distribution of the activation energies [19] and relaxation times as shown in Table 1. The high values of activation energies observed can only be associated with the ionic and electronic trapping [20]. The linear dependence of peak currents of β -peak and α -peak (for TSDC thermogram in Figure 2) versus poling field (not depicted) indicates that low temperature peak (β -peak) possesses dipolar nature and high temperature peak (α -peak) possesses the space charge phenomena [21]. In present study, at higher temperatures the charge-carrier injection increases, resulting in an increase in space charge and, hence, a rise in the current and since the polarizing field is kept constant the charge released from the impurity centres present in the sample does not neutralize the space charges thus yields increasing linear nature for peak currents of α -peak [22]. As reported, linear relationship between T_m and T_p in the temperature region of the α -peak, suggests that the peak is due to the bulk effects [23] whereas in the present study the dependence of peak temperatures T_m (temperature of current maximum) of thermally stimulated response for the α -peak of the TSDC thermogram on polarizing temperature T_p indicates diversion from the bulk effects (not depicted). The E increases with increasing T_m and then decreases (as shown in Table 1). This characteristic associated with the cooperative nature of the phase transition has been observed in several polymeric systems, and provides additional support that the peak is due to α -relaxation [24].

Alternate Current Dielectric Measurements

Figures 3 and 4 represent the permittivity (i.e., dielectric constant) and dielectric losses as a function of temperature varying from 30°C to 170°C at relatively low constant frequency varying in the range of 100 Hz-10 kHz for PVDF foil samples with similar (Al-Al) electrode combination. Dielectric loss exhibits two loss maximas; one around 130±10°C and the

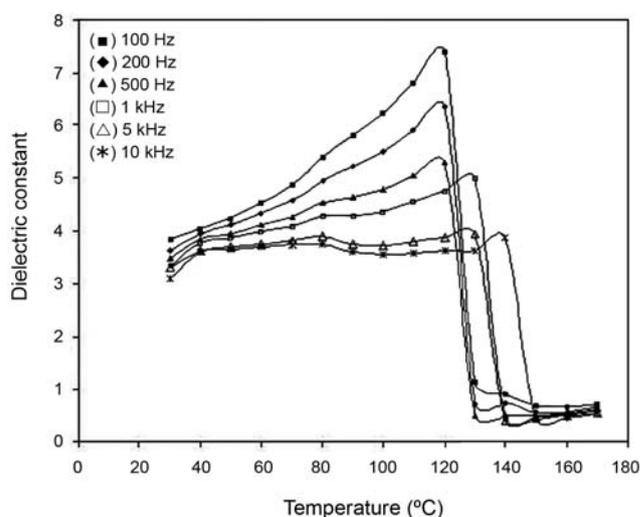


Figure 3. Dielectric constant versus temperature curve at constant frequencies varying from 100 Hz to 10 kHz.

other around 150±10°C. The first dielectric loss maximum at higher temperature (i.e., around 130°C) corresponds to the α -relaxation peak and the second dielectric loss maximum at slightly higher temperature (i.e., around 150°C) depicts α' -relaxation peak. The magnitude of both the loss and permittivity peaks were found to decrease as the frequency increases and dielectric peaks were found to shift towards higher temperature side. The permittivity of PVDF increases, with increasing temperature, but at still higher temperatures it drops down to minimum at 120±10°C for all frequencies from 100 Hz-10 kHz. This feature, which exhibits weak frequency dependence,

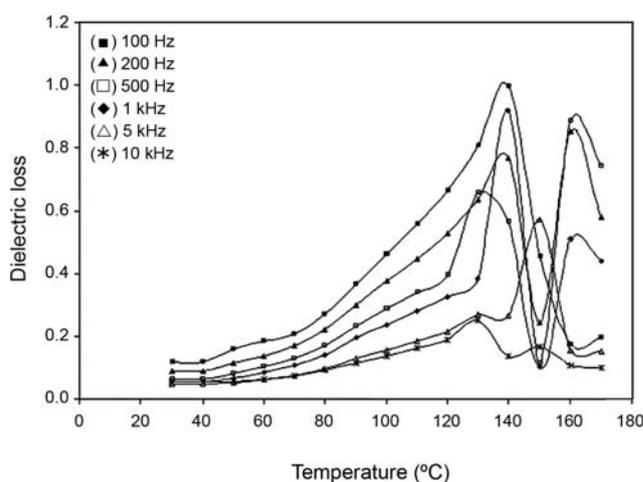


Figure 4. Dielectric loss versus temperature curve at constant frequencies varying from 100 Hz to 10 kHz.

corresponds to the dynamic melting temperature of the polymer [25]. Dielectric loss increases with increasing temperature for the entire frequency range till it drops down to minimum around $130 \pm 10^\circ\text{C}$ and then rises sharply to give its maximum at $150 \pm 10^\circ\text{C}$.

The dielectric dispersion appearing at high temperature is generally admitted to be due to the rotatory diffusional motion of the molecules from one quasi-stable position to another around the skeletal bond involving large scale conformational rearrangement of the main chain and is generally known as α -relaxation [26]. The small loss peak designated as α' -relaxation peak at much higher temperature is arising due to molecular motions in the folds on the surface of the crystallite. The low temperature dielectric dispersion is attributed to the dielectric response of the side groups, which are considered to be more mobile; or the small displacement of the dipoles near the frozen-in position and is generally known as β -relaxation [27]. The increase in permittivity above the room temperature may be due to increase in molecular mobility and also may be partly due to the expansion of the lattice [28] and partly due to the excitation of charge carriers, which are likely to be present inside the specimen at the imperfection sites. At lower temperature, molecules are immobile and therefore, the number of dipoles, which facilitate to orient with the field will be lower. Increase in temperature would increase the molecular mobility and therefore, higher number of dipoles orientate themselves in the field direction. The amorphous-crystalline interphases in PVDF foil sample behave as trapping centre for carriers. The molecular chains with different mobilities for the amorphous-crystalline regions try to adjust themselves in such a way as to add to the polarization of the system [29]. This molecular alignment of chains may cause the observed increase in the permittivity.

The variation in permittivity and dielectric loss, suggests the net effect of some internal field within the polymer along with the external AC field. The dipole-dipole interactions between the different groups or many body interactions suggest the lower losses with higher frequency range. The dependence of the permittivity on frequency can be determined from the literature [30] that permittivity should diminish with increasing frequency. The greater losses at lower frequencies as shown in Figure 4 could be asso-

ciated with the polarization of the trapped charge carriers [31]. In a semi-crystalline polymer as PVDF having amorphous-crystalline interphases trapping of charge carriers is quite possible. With the increase in frequency, polarization decreases and becomes vanishingly small at higher frequencies. The smaller losses with frequency also seems to show the decrease in the number of charges and delay in settling of dipoles due to the availability of very short time in one half cycle of alternating voltage [32].

This is very well reported in the literature [33] that TSDC is an isothermal, ultra low frequency (10^{-2} - 10^{-4} Hz) technique employing high DC field for polarizing samples whereas AC frequencies employed for the AC dielectric relaxation measurements at different temperatures.

In the present AC dielectric relaxation study frequencies are relatively higher (100 Hz-10 kHz) than the frequency calculated from the TSDC data [34], thus the dielectric loss peak is shifted to higher temperatures with respect to the TSDC α -peak.

The non-Debye TSDC α -peak indicated that there was a broad distribution of relaxation time. The same process gives rise to the peak at the frequency dependence of the dielectric constant and dielectric losses during AC dielectric measurements. Therefore, dielectric constant and dielectric loss curves over a wide range of temperature and at different frequencies show good resemblance with the shape and temperature position of the TSDC α -peak.

CONCLUSION

The present study reveals that both interfacial phenomena as well as space charge properties are known to play important role in the electrical behaviour of PVDF polymer. The amorphous-crystalline interface acts as a charge-carrier trapping site in PVDF. Shape and size of TSDC thermograms strongly depend upon poling temperature as well as poling field. Dielectric constant and dielectric loss of PVDF depend many folds on temperature and AC frequency at which the specimen is being placed. TSDC technique and low frequency dielectric spectroscopy are found to be simple enough to characterize PVDF, a dielectric material on the basis of various dielectric relaxation modes.

TSDC spectra can be correlated with the conventional AC dielectric spectroscopy, to obtain temperature-dependent dipolar relaxation information. Finally, the individual TSDC relaxation peaks can also be used to obtain various numerical estimates of relaxation parameters. In conclusion, it would appear from our work that TSDC and dielectric spectroscopy are excellent complementary techniques for investigating the electrical properties and is found to be in agreement with the α -relaxation mechanism observed in PVDF.

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