

# Asian Resonance

## Dielectric Loss Factor of Polyvinylidene Fluoride Thin Foils by Transient Current

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### Abstract

The dielectric loss factor of polyvinylidene fluoride (PVDF) thin foils (20 $\mu$ m) by using transient currents studies in charging and discharging mode. The variation of transient currents studies in charging and discharging with electric field at different temperature 40-80 °C at polarizing field 100 kV/cm for Al-Al system in charging mode and Al-Al system in discharging mode. The two distinct mechanisms shall be responsible for the current decay. One mechanism is operative in the range of short time giving rise to a straight line on log I vs log t plot with a particular value of decay constant,  $n_1$ , and the other mechanism is operative in the range of long times giving rise to another straight line in log I vs log t plot with a decay constant,  $n_2$ , of higher value. The value of  $n_1$  in short time region is 1.76 and value of  $n_2$  in long time region is 2.62 for Al-Al electrode system in charging and discharging (Table1). The Activation energy can be found by isochronal curve (Table2). The dielectric loss factor of polyvinylidene fluoride (PVDF) thin foils (20 $\mu$ m) by using transient currents studies in charging and discharging mode with the help of applied step voltage  $f$  is Hamons frequency (0.1/t). The space charge polarization and Richardson mechanism is contributed in this paper.

**Keywords:** Polyvinylidene fluoride (PVDF), transient current, space charge region

### Introduction

Polyvinylidene fluoride (PVDF) is a ferroelectric polymer that contains polar crystals in which the direction of polarisation can be reversed by applying an appropriate electric field. The elucidation of the charge injection and carrier migration processes will become essential for the future use of these materials so far; only little work has been reported on transient current in polyvinylidene fluoride (PVDF) foils<sup>[1-4]</sup>. The isothermal condition as well as desorption currents decay approximately in most of the cases as  $t^{-n}$ , where  $t$  is the time elapsed after the application of the step voltage and ' $n$ ' is an exponent whose value may be greater or less than 1, depending upon the properties of the material chosen and the experimental conditions<sup>[4-9]</sup>. It also provides useful information about the molecular motion of dielectric loss behavior is important because of the possible technical application of polymers of insulation, isolation and passivation in microelectronics. At room temperature, charge decay measurements are rather time consuming, because at such temperatures, the dipoles and charge remain virtually immobile. However, when an electrets is heated, the dipoles and charges quickly regain their freedom of motion.

The dielectric loss factor of pure polyvinylidene fluoride (PVDF) foils can be calculated by help of transient current in charging and discharging mode along with  $c$  is the geometrical capacitance of the electric assembly without the sample is the applied step voltage and  $f$  is Hamon's frequency ( $=0.1/t$ ).

In this paper, an experimental study of dielectric loss of transient currents in charging and discharging mode in polyvinylidene fluoride (PVDF) is reported. The aim behind the present study is to determine the dielectric loss of transient currents studies in charging and discharging mode behavior of polyvinylidene fluoride (PVDF) foils (20 $\mu$ m) sandwiched between metal electrodes combinations. We have used the isothermal immersion technique to pure polyvinyl polyvinylidene fluoride (PVDF) foils (20 $\mu$ m) foils because it provides foils, which are uniform, structurally reproducible and show no significant ageing effects.

### Theory of Transient Current in Dielectric behavior

When an electric field is applied to a dielectric specimen kept

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between two plane metal electrodes, absorption current flows in the external circuit. This current is composed of two components namely the polarization current component and the conduction current on assuming that the polarization is due to dipoles of a single relaxation frequency  $\alpha$  (T), the polarization current can be written as

$$dP_s(t)/dt + \alpha(T)P_s(t) = \epsilon_0[\epsilon_s - \epsilon_0]\alpha(T)E \dots\dots\dots(i)$$

where T is the absolute temperature, t is the time  $\epsilon_0$  is the permittivity of free space and  $\epsilon_s$  are the static and high frequency dielectric constants respectively. The density of current generated by in polarization is given by

$$i_p(t) = dP(t)/dt = -\alpha(T)P_s(t) + \epsilon_0(\epsilon_s - \epsilon_0)\alpha(T)E \dots\dots\dots(ii)$$

The conduction current  $i_c$  at affixed temperature T and field E is defined as

$$i_c = \sigma(T)E \dots\dots\dots(iii)$$

where  $\sigma(T)$  is the conductivity of the material at a fixed temperature T. Thus, the total absorption current will be the sum of both the components, i.e.

$$i_{ab} = i_c + i_p(t) = [\epsilon_0(\epsilon_s - \epsilon_0)\alpha(T) + \sigma(T)]E - \alpha_s P_s(T) \dots\dots\dots(iv)$$

The desorption current is obtained when the sample is short-circuited and the field is made zero. Thus, from Eq. (ii) we have

$$dP_s(t)/dt + P(t)\alpha(T) = 0 \dots\dots\dots(v)$$

where  $\alpha$  (T) is a time dependent parameter. The above equation is a differential equation with constant coefficient. Its isothermal solution can be written as

$$P_s(t) = P_0 \exp[-\int \alpha(T) dt] \dots\dots\dots(vi)$$

The current generated during deorientation of dipoles is only due to polarization. There is no conduction current since the external field is zero. The desorption current is then given by

$$i_d(t) = -dP_s(t)/dt = \epsilon_0 E f(t) = [\alpha(T)P_0 \exp\{-\alpha(t)t_0\}] \dots\dots\dots(vii)$$

where E is the steady charging field, f (t) is the dielectric response function,  $P_0$  is the initial polarization and  $\alpha$  (T) is the dielectric response loss peak in frequency domain.

Alternatively, this can also be expressed in terms of the frequency response of the complex dielectric constant,  $\epsilon(w)$

$$\epsilon(w) = \epsilon'(w) - i\epsilon''(w)/(1+iw) \dots\dots\dots(viii)$$

where  $\epsilon'(w)$  and  $\epsilon''(w)$  are the real and imaginary part of the dielectric constant and w are the angular frequency.

Thus, isothermal depolarization current measurements offer an alternative technique for dielectric constant and dielectric loss measurement as a function of temperature and frequency.

Thus, the dielectric loss factor can also be obtained using Hamon's approximation<sup>10</sup> i.e.,

$$\epsilon''(t) = i(t)/2\pi f c v \dots\dots\dots(ix)$$

where I (t) am the magnitude of the transient current at time (t), c is the geometrical capacitance of the electric assembly without the sample is the applied step voltage and f is Hamon's frequency ( $=0.1/t$ ). This approximate method gives good accuracy in calculation of dielectric loss provided these are a broad distribution of relaxation times. Charging and discharging transients in a dielectric may be used to obtain information on the low

frequency behavior of the dielectric and also the temperature dependence of its loss factor  $\epsilon''$ . In this particular case, the Hamon's approximation has been used for this purpose.

According to this approximation the conversion is as follows

$$\epsilon'' = I(t)d/2\pi f \epsilon_0 A \dots\dots\dots(x)$$

where I (t) is the transient current is the foils thickness, as is foils area,  $\epsilon_0$  is permittivity of free space is applied charge voltage is the time at which current I (t) is measured and  $f = 0.1/t$  (in sec) is the Hamon's frequency.

## Experimental Details

The isothermal immersion technique was applied for preparing foils of polyvinylidene fluoride (PVDF). The solution was prepared in a glass beaker by first dissolving 2.4 gram polyvinylidene fluoride (PVDF) in 30ml chemically pure chloroform at room temperature and continuously stirred for 60 min by means of a Teflon-coated magnetic stirrer. Thereafter, it was stirred and heated to 40°C to yield a homogeneous solution. The solution was then immersed in a constant temperature oil bath. Ultrasonically cleaned vacuum metallized microscopic glass slides were immersed vertically into the solution for a period of about 10 min. after the deposition of the foils the glass slide was taken out and dried in an oven at 40°C for 24h. The metallic electrode area 1.22 cm<sup>2</sup> are vacuum deposited on infeasible layers i.e. the area of foils. This was followed by room temperature outgassing at 10<sup>-5</sup> torr for a function period 24h. The upper of electrode was also vacuum deposited on the upper surface of the foils to obtain a sandwich configuration. The voltage was applied from a high voltage unit EC-4800D and current was recorded with an electrometer (Keithley 600B), which was carefully shielded and grounded to avoid loops or extraneous electrical noise. A linear heating rate of 3°C/min was used. The thickness of the sample where determined by measuring its capacitances of 10MHz using a dielectric constant  $\epsilon = 3$ . The assembly was held in a thermostat and the temperature was measured with a precalibrated thermocouple. The capacitances and losses were measured with a systronics LCR bridge type 921 using Philips AFGeneratrter model GM2308/90.

## Results

The general characteristics of the observed results on transient currents in charge in and discharging mode are:

### Time dependence

The time dependence of the charging and discharging currents in polyvinylidene fluoride (PVDF) foils has been investigated over a period of time 01-100 minutes. Figs. 1 shows log I vs log t plots for charging mode, charged at temperature from 40 to 90 °C at polarizing fields ( $E_p$ ) 100 kV/cm for Al-Al system. Figs.2 shows discharging mode is in under the same temperature, fields, and configuration conditions. In both the case, PVDF foils of 20µm thickness is used. These graphs show that the current decays at a faster rate for the first few minutes and then the decay rate slow down to reach the steady value. The transients

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are observed to obey the CurieVon Schweilder relationship.

$$I(t) = A(T) t^{-n}$$

where  $t$  is the time after the application or removal of the field,  $A(T)$  is temperature dependence faster and  $n$  is the decay constant.

## Temperature dependence

The charging and discharging transient observed for samples charged with fields of 40-90°C at 100 kV/cm for charging and discharging mode. The curves exhibit  $t^{-n}$  dependence. The temperature dependence of the observed transients can be expressed more conveniently by plotting currents observed at various constant times (isochronal) against temperature for Al-Al Figs.3 Such isochronal have been constructed for various constant fields for fixed times 02,05,10,20 and 40 min. from these plots it is evident that the current shows thermal dependence. The isochronal are characterized by a peak located at 70 °C for discharging mode. A careful observation reveals that the isochronal profile tends to shift towards high temperature, which suggests the presence of a thermal activated process.

## Electrode materials dependence:

Two sets of electrode material system are considered, i.e. Al-Al system. It has been observed that, in general, the current values are higher by one order of magnitude in similar electrode system over that of dissimilar electrode combinations

## General characteristics of the curves:

- (i) The transient current polarity is found to be positive in both the cases of charging and discharging modes and observed current approaches stable value in relatively short period under high fields.
- (ii) Curves illustrating the time dependence of charging as well as discharging transients are characterized by two regions, which are designated as short time and long time regions, respectively.
- (iii) Curves illustrating the temperature dependence of charging and discharging transients at various constant times (isochronals) are characteristics by a peak at 70 °C for discharging mode
- (iv) Isochronal currents at various constant times show a non-linear field dependence characterized with a maximum at a certain field value for a particular temperature for charging mode.
- (v) The activation energy, in general, shows an increase with increasing field also with the time of observation. By comparing the value of activation energy for different configuration, it is evident that the value of activation energy is, in general, much higher in the case of dissimilar electrode combination than for similar configuration.
- (vi) The variation of dielectric loss as a function of Hamon's frequency at various temperatures for laminates charged with varies field. The curved shows a decrease in dielectric loss with decreasing Hamons frequency and in certain

cases show an increase with still further lower value of Hamons frequency shown in figure no.4.

## Discussion

From the above characteristics, it is evident that at least two distinct mechanisms shall be responsible for the current decay. One mechanism is operative in the range of short time giving rise to a straight line on log  $I$  versus log  $t$  plot with a particular value of decay constant,  $n_1$ , and the other mechanism is operative in the range of long times giving rise to another straight line in log  $I$  versus log  $t$  plot with a decay constant,  $n_2$ , of higher value. The main mechanisms that have been put forward in order to interpret the transient current decay flowing through a dielectric are already discussed. We now try to analysis the observed results in the light of the existing models, i.e., dipolar relaxation; tunneling to empty traps, charge injection leading to space charge effects and electrode polarization considering the variation of such currents with time, temperature, and field and electrode materials [10].

In the case of tunneling to empty traps, it is well established that the tunneling current should be independent of temperature and proportional to the field at moderate fields. However, in the present case, charging and discharging transients at fixed times show thermal dependence and exhibit a complex dependence on the electric field. Thus, it seems that tunneling to empty traps can be ruled out as a possible mechanism for the observed transients

In the case of electrode polarization, the transient current are reported to be proportional to  $t^{-n}$  with the value of decay constant  $n = 0$  at short times, and  $n > 1$  at longer times. However, in the present case, at short times the value of  $n$  is found to vary from 0.43 to 0.62 for Cu-Cu and Sn-Sn electrode system. These observations show that the process of electrode polarization is unlikely to be dominant in the present case [11].

Analyzing the experimental results further, we know that dipolar relaxation [12,13] can also account for  $t^{-n}$  type of time dependence. However, it has to be borne in mind that, as a general rule, dipolar processes involved in polymer are characterized by a distribution in relaxation times and that overlapping of several processes are likely to be present. This also implies that the curie law can only be considered more or less a rough approximation of the real time dependence and can only depict the transient phenomena over short periods of time. Keeping this in mind, the following points may be considered in favour of this model.

In the present case transient current at fixed times show an isothermal peak localized at 70°C. Further, the charging and discharging currents are mirror images of each other over most of the temperature range. Thus, it seems likely that the dipolar relaxation process in PVDF could be responsible for the transient component of charging and discharging current. It may be noted her a that linear dependence on field as expected of a dipolar process has been observed in polymers only when

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current are measured at temperature sufficiently lower than the glass transition temperature [14]. It seems that at shorter times only dipoles with short relaxation times are oriented/reoriented resulting in a smaller value of decay constant,  $n_1$ . However, at longer time dipoles with longer values of relaxation time also start orienting / reorienting resulting in a current that decays/ charges at a faster rate resulting in a higher value of  $n_2$ .

It has been observed that current shows complex field dependence. Further, the activation energy has been found to increase with the time of observation. Thus, it can be concluded that the observed current may have contribution from charge carriers hopping amount-localized states. The presence of amorphous regions in PVDF entails existence of localized states in the band gap.

In fact, systems dominated by hopping of ionic and electronics charge carriers, generally, show a transient decay divided into two successive domains [15]. With the aid of two site models, has derived an expression for transient behavior, which allows only value of  $n_1$  i.e. there is no restriction on the value of  $n$ . The model assumes that the localized states which are distributed in energy and charge carriers undergo limited trisections to adjacent sites. The observed increase in the value of activation energy at longer times may be explained by the hopping mechanism, which requires the existence of such localized states distributed in energy. Thus, it seems that hopping of charge carriers may also be a possible mechanism for the observed transient.

The increases in the value of activation energy at longer times may adequately be explained in the light of transients controlled by space charge formation in the bulk of the sample. The following observed characteristics are in support of the space charge mechanism.

The complex dependence of the isochronal transients on the field strength, supports the consternation that the field at the electrode (cathode or anode) is modified by the space charge, and

Isochronal current peak shifts towards higher fields at shorter times, thus suggesting the presence of space charges.

Charges can be injected directly from the electrodes leading to space charge formation inside the dielectric. These charges may get trapped at various trap levels. The faster decay of current corresponding to a higher value of constant  $n_2$  in the long time region for different sample indicates the existence of energetically distributed localized traps levels. It seems that at shorter times, only shallow trap levels get filled/emptied contributing to a charge / discharging current that charges at a slower rate. However, at longer times deeper traps capture/release the charges due to which current decays at the observed faster rate than the observed activation energy value is greater [16-18].

It has been observed in the present investigation that the magnitude of the transient current is generally higher in case of similar electrode system. This can be understood in the light of interfacial polarization. It

seems that due to the higher conductivity of PVDF, more interfacial charge is localized on PVDF during charging using Al-Al electrode configuration, giving a higher value of charging transients. Similarly, during discharging a higher conduction current will flow in PVDF resulting in a higher value of the discharging current.

The complex nature of field dependence may be explained in the manner that the internal field created by the interfacial polarization decreases the external applied field. The effect of the internal field would be to decrease the apparent charge carrier mobility. The interfacial charge is thus expected to exhibit a maximum at a certain field value. However, the internal field due to interfacial polarization becomes nearly constant at higher polarizing field. The effect of the internal field may then decrease relative to the applied external field so that the apparent mobility of charge carriers again increases. The interfacial space charge shall, therefore, again increase for higher polarizing fields. It has show that solid like polymers are not in thermodynamic equilibrium at temperatures below their glass transition [19]. For such materials, free- volume enthalpy and entropy value are greater than they would be in equilibrium state. The gradual approach to equilibrium affects many properties, e.g., the free-volume of the polymer may decrease. The decrease in free volume lowers the mobility of chain segments and also charges carriers. The decrease in mobility may be expected to reduce conductivity. At higher electric fields, a change in mobility may take place faster than at lower fields and also recombination of charge carriers may be more. This may be responsible to make the observed current in the present case to approach a stable value in relatively shorter periods under high fields. The field dominant behavior, more so at lower is polarizing temperatures at the initial current being controlled by the bulk phenomena such as polarization effects and/or ionic currents. The dipolar relaxation seems to be the major contributor to the transient current, particularly at lower polarizing temperature. The PVDF is polar polymer. Its loss values depend strongly on temperature [20]. The first loss maxima are observed it is called dipole-segmental is associated with orientation/rotation of the polar units of the macromolecular under condition where segmental movement is possible, i.e. in the rubber-like state ( $>T_g$ ) of the polymer [21-24].

The dielectric loss peak is also located in the same temperature range, further the charging and discharging current are mirror images of each other over most of the temperature range, thus it seems likely that the dipolar relaxation process in PVDF could be responsible for the transient component of charging and discharging current. It may be noted here that linear dependence on field as expected of a dipolar process has been observed in polymer only when current are measured at temperature sufficiently lower than the glass transition temperature. It seem that at shorter times only dipoles with short relaxation times are oriented/reoriented resulting in a smaller value of decay constant  $n_1$ . However, at longer times

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dipoles with larger value of relaxation time also start orienting/reorienting resulting in a current that decays/charges at a faster rate resulting in a higher value of n. Charging and discharging transients in a dielectric may be used to obtain information on the low frequency behavior of the dielectric and also the temperature dependence of its loss factor  $\epsilon''$ . In this particular case, the Hamon approximation has been used for this purpose.

### Conclusions

The results obtained in the present investigation have been discussed in detail in the light of the available literature at appropriate sections. The results have indicated that dipole relaxation; interfacial polarization and space charge effects are jointly operative in the present case of PVDF. The space charges may be injected homo space charge and hetero space charges. The charge is mainly injected into the bulk of the specimen.

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**Table 1**  
Value of n for different field, temperature and polarity conditions

E (kV)	V o	Charging current (Al-Al system)					Discharging current (Al-Al system)				
		4	5	6	7	8	4	5	6	7	8
		1	n	1.	1.	2.	0.	2.	1.	1.	1.
	n	1.	1.	3.	3.	1.	1.	1.	2.	3.	3.
2	n	2.	2.	2.	1.	2.	2.	2.	2.	1.	1.
	n	3.	3.	1.	1.	1.	3.	4.	1.	1.	1.
5	n	0.	0.	1.	2.	0.	0.	1.	2.	1.	1.
	n	2.	1.	1.	1.	1.	2.	2.	1.	3.	2.

7	n	2.	0.	2.	1.	1.	2.	0.	0.	3.	3.
	n	2.	2.	3.	1.	2.	1.	2.	1.	2.	2.
1	n	2.	2.	1.	2.	1.	2.	0.	2.	2.	3.
	n	1.	1.	2.	2.	2.	1.	1.	2.	2.	2.

**Table 2**  
Activation energy of PVDF sample in charging and discharging mode

Temperature (°C)	Activation energy (Ea) in Charging current	Activation Energy (Ea) in Discharging current
40	0.69	0.74
50	0.59	0.69
60	0.93	0.79
70	0.85	0.82
80	0.87	0.97

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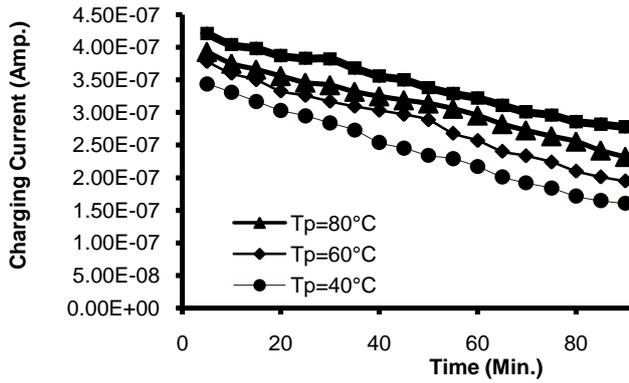


Fig. No. 1. Transient current vs time in charging mode with polarizing field 100kV/cm with different Al-Al system.

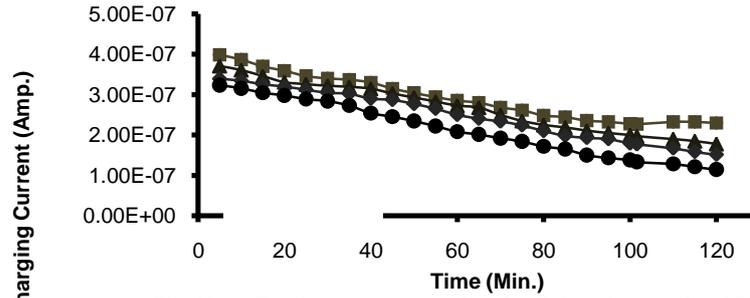


Fig. No. 2. Transient current vs time in discharging mode of PVDF poled with polarizing field 100kV/cm with different polarization temperatures for Al-Al system.

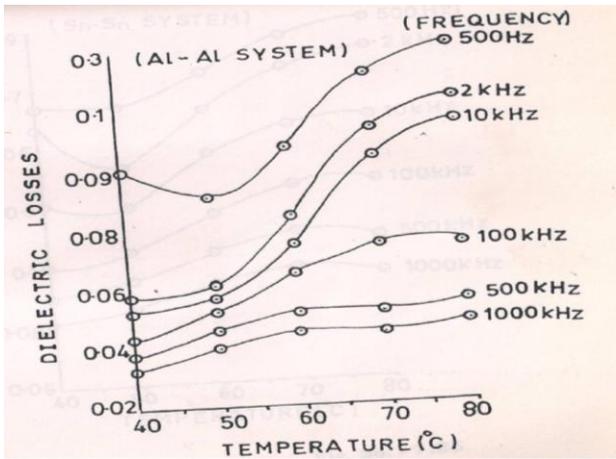


Figure No. 3  
 Dielectric Losses vs temperature at constant frequency (500Hz, 2, 10, 100, 500 and 1000 kHz) for Al-Al system of PVDF sample

Figure No. 4  
 Dielectric loss vs Hamon's frequency for PVDF sample (20µm) in charging mode

