The Effect of Frequency and Temperature on Dielectric Properties of Pure Poly Vinylidene Fluoride (PVDF) Thin Films

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***Abstract*— In this work we have evaluated the dielectric properties of poly vinylidene fluoride (PVDF) thin films of thickness (≈ 20µm) as a function of temperature from 40-70^{0}C and frequency varying from 500 Hz to 100 kHz respectively for Al-Al and Cu-Cu electrode configuration. The dielectric constant values increases with the increase in temperature. A broad peak is found at around (70±5)0C. The maximum value of dielectric constant and dielectric losses were attributed to the phase transition of the polymer. The variation in dielectric constant and loss tangent suggest the net effect of some internal field within the polymer along with the external A.C. field.**

***Index Terms*— Poly Vinylidene Fluoride (PVDF), Space Charge Polarization, Dipole Orientation.**

I. INTRODUCTION

The dielectric constant and dissipation factor are the crucial quantities in the design of a device. These quantities are invaluable to engineers in their design of microelectronic equipments. The physicists, on other hand, are more interested in the microscopic processes responsible for the dielectric relaxation. Moreover, the study of dielectric constant and dielectric loss factor, as a function of temperature and frequencies is one of the most convenient and sensitive methods of studying the polymer structure [1]. The dielectric properties (dielectric constant and dielectric loss) of a number of polymers have been investigated in the last two decades [2-7], but the molecular orientation behavior and associated relaxation mechanism are not fully understood. The dielectric properties of poly vinylidene fluoride (PVDF) polymer films are strongly dependent on the fabrication process. This is due to the fact that PVDF exists in several crystalline phases and the predominance of the individual phases can be controlled by the film fabrication process. The relaxation behavior of PVDF is strongly dependent on its crystalline morphology. The dielectric loss of thin films is very important behavior because their possible technical application for insulation and isolation in microelectronic circuits. Tanaka [8] investigated dielectric relaxation in polymers.
This work reports the results of dielectric properties (dielectric constant and dielectric losses) of poly vinylidene fluoride as a function of temperature and frequency with Al-Al and Cu-Cu electrode combination. This might assist in understanding the relaxation processes in PVDF more clearly.

II. THEORY OF DIELECTRIC BEHAVIOR

Debye [9] gave the classical picture of relaxation of polarization with a single relaxation time. In his work he considered a set of non-interacting dipoles free to rotate in opposition to some viscous resistance in a fluid like medium. The equation for complex permittivity is

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau}$$

Where ε_0 = Dielectric constant at low frequency

ε_∞ = Dielectric constant at high frequency

ω = Angular frequency

τ = Relaxation time

According to Frohlich, the real and imaginary part of the dielectric constant are given by

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2} \quad and \quad \varepsilon'' = \left(\frac{\varepsilon_0-\varepsilon_\infty}{1+i\omega\tau}\right)\omega\tau$$

The maximum value of ε' and ε'' is,

$$\varepsilon' = \frac{\varepsilon_0+\varepsilon_\infty}{2} \quad \text{and} \quad \varepsilon'' = \frac{\varepsilon_0-\varepsilon_\infty}{2}$$

$$\varepsilon_0 - \varepsilon_\infty = \left(\frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty}\right)\left(\frac{\varepsilon_0 + 2}{3}\right)\frac{4\pi n g \mu^2}{3kT}$$

Where n = Dipole Moment

g = Parameter related to dipole interaction

T = Temperature

The polymers rarely follow the Debye theory and they show much broader dispersion and low loss as compared to single relaxation process. Cole [10] pointed out this anomaly arises due to the fact that the chain molecular compounds do

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Manuscript received,December 17, 2009.

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not have a single relaxation time. On the δ contrary their relaxation times are distributed within certain minimum and maximum limits. Every molecular dip[ole in a given chain is coupled to neighboring dipole of the same chain by primary valence bands so the motion of any dipole affects the motion of neighbors and they in turn influence its response to a torque. Further, in various configurations, which in chain molecule can assume, we can find another segment of chain acting effectively as a co-operative electrical unit and these segments will of course vary in length between the improbable extremes of a single nonnumeric unit and the whole extended chain. Such a state leads to distribution of relaxation time.

On eliminating the parameter ωτ between the two equations and rearranging the two parameters (ε' and ε") we get,

$$\left[\varepsilon' - \frac{\varepsilon_0 - \varepsilon_\infty}{2}\right]^2 + \varepsilon"^2 = \left[\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right]^2$$

The above equation is of a circle of radius $\frac{\varepsilon_0 - \varepsilon_\infty}{2}$. Only the semicircle over which ε" is positive has physical significance. Materials with single relaxation time yield a semicircle in ε' and ε" plane. Polymers do not yield such a semicircle and the ε'-ε" plane falls within the Debye semicircle. Cole [10] modified the Debye equation by empirical equation for the complex permittivity.

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}$$

Where α is an empirical parameter. It lies between 0 and 1 and it denotes the angle of tilt of circular arc from real axis.

The modified expression measures the small deviation from the ideal Debye behavior, but some material deviates very much the Debye behavior. Havirilik and Negami [11] gave an expression which is of the form,

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^{1-\beta}}$$

The dielectric constant and losses were calculated using the equation valid for parallel plate capacitor,

$$\varepsilon' = \frac{C_x d}{\varepsilon_0 A} \text{ And } \varepsilon" = \varepsilon' \tan\ \delta$$

Where C_x is the sample capacitance in Farad, A is area of the sample, d is the thickness of the sample and ε_0 is a constant representing permittivity of free space.

The variation of dielectric constant and loss tangent, suggest the net effect of some internal field within the polymer along with the external A C 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 dielectric constant on frequency can be determined from the equation,

$$C = C_g + \frac{S\tau}{1 + \tau^2\omega^2}$$

where C_g is the geometrical capacitance, S the conductance corresponding to the absorption current, τ the dipole relaxation time and ω the angular frequency. Above equation show that C should diminish with increasing frequency. The increase in losses at low frequency could be associated with the polarization of the trapped charge carriers. With increase in frequency, polarization decreases and becomes vanishing small at high frequencies. The expression for dielectric loss is given by the equation [18, 19],

$$\tan\delta = \frac{\omega^2\tau^2(G_{in} + S) + G_m}{\omega\{S\tau + C_g(\omega^2\tau^2 + 1)\}}$$

where G_{in} is the conductance for the residual current. Obviously, form equation,

$$Lim_{\omega\to 0} tan\delta = \infty$$

Differentiating equation with respect to ω and equating the derivative to zero, it is possible to obtain the value of ω of the frequency corresponding to maximum loss.

III. EXPERIMENTAL

The sample of Poly Vinylidene Fluoride (PVDF) used is obtained from Glaxo Laboratories, Mumbai. The polymer was dissolved in the DMA (Di-methyl Acetate) at 50^0C. Films were prepared by casting this solution on glass substrates. The films were detached after the evaporation of the solvent. For measurements aluminum electrodes were deposited on both sides of the films. Dielectric studies were carried out on the all entire sample to study dielectric constant and dielectric loss. The instrument used was HP4192A impendence analyzer, with frequency range 500 Hz to 1000 KHz and temperature range 40^0C to 70^0C.

IV. RESULTS AND DISCUSSIONS

The dielectric constant and losses of poly vinyledene fluoride samples are observed in the temperature of range 40^0C to 70^0C with frequency range 500 Hz to 1000 KHz. The results are interpreted in terms of existing theories.

A. *Dielectric Constant*

1. *Effect of Temperature*

To observe an effect of temperature on dielectric constant, its variation as a function of temperature is plotted at different frequencies (i.e. 500 Hz, 2,10, 100, 500 and 1000KHz) are shown in the figures 1 and 2 for Al-Al and Cu-Cu combinations. It is clear from these figures that the value of dielectric constant decreases with increasing frequencies. For higher frequencies the value of dielectric constant increases attaining maxima at 70^0C and then decreasing. This nature is not observed for other frequencies.

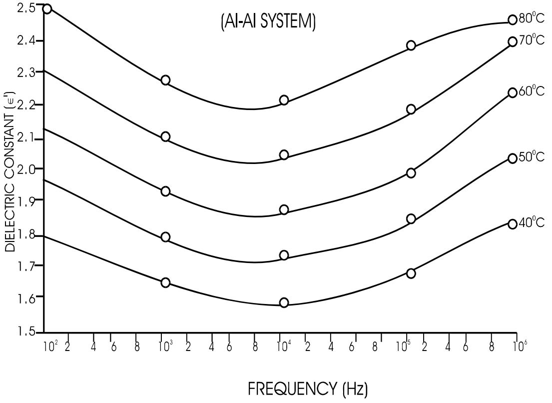

Fig. 1 Dielectric Constant Vs Frequency for Al-Al system

ISBN: 978-988-18210-5-8
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

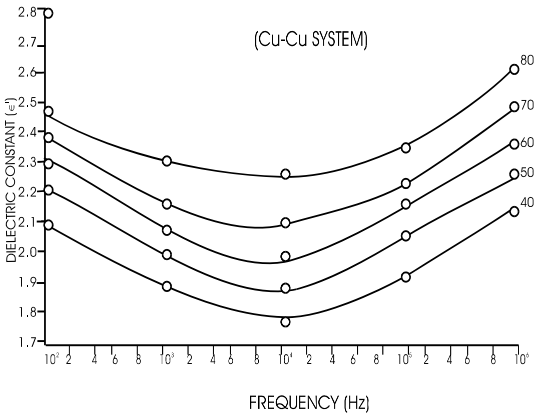

Fig. 2 Dielectric Constant Vs Frequency for Cu-Cu system

2. Effect of Frequency

The frequency dependence of dielectric constant of the sample at different temperatures (i.e. 40, 50, 60, 70^{0}C) is shown in figures 3 and 4 for Al-Al and Cu-Cu electrodes system. It is found that with increasing temperature dielectric constant increases. It is clear that the value of dielectric constant decreases up to 10^4 Hz and beyond this it increases.

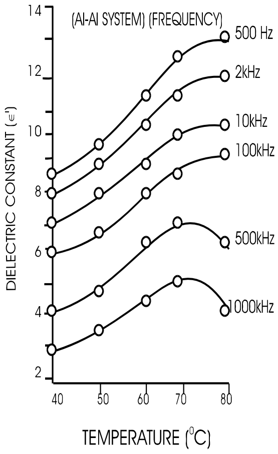

Fig. 3 Dielectric Constant Vs Temp. for Al-Al system

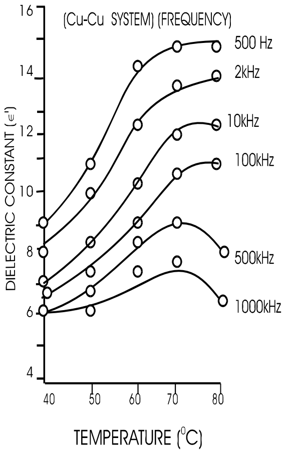

Fig. 4 Dielectric Constant Vs Temp. for Cu-Cu system

B. Dielectric Losses

1. Effect of Temperature

The effect of temperature on dielectric losses as a function of frequency is shown in Figures 5 and 6. The dielectric loss values sharply decays attaining minima and again it sharply increases. It is interesting that,

(i) the value of dielectric losses is lower for higher temperature in the first half and after attaining a minimum value the value of dielectric losses is more and (ii) the position of minima shifts towards lower frequency range. The nature of all the curves is similar.

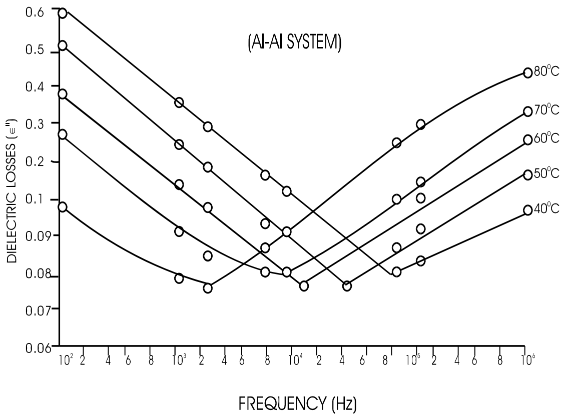

Fig. 5 Dielectric losses Vs Frequency for Al-Al system

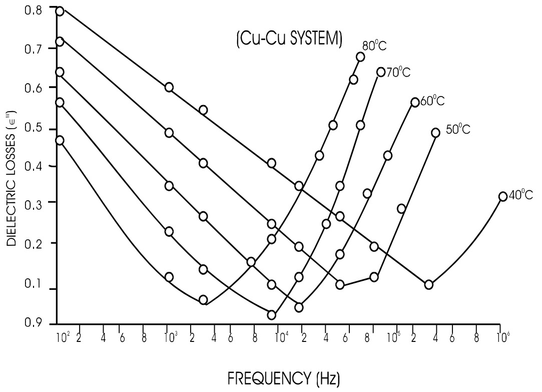

Fig. 6 Dielectric losess Vs Frequency for Cu-Cu system

2. Effect of Frequency

The dielectric losses versus temperature curves are shown in the figures 7 and 8 at the constant frequencies (i.e. 500 Hz, 2, 10, 100, 500 and 1000 KHz) for Al-Al and Cu-Cu combinations. The nature of the curves is approximately similar. Generally, a dielectric loss decreases with increasing frequency.

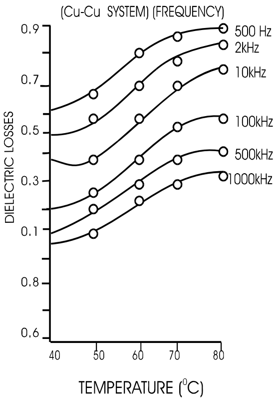

Fig. 7 Dielectric losses Vs for Cu-Cu system

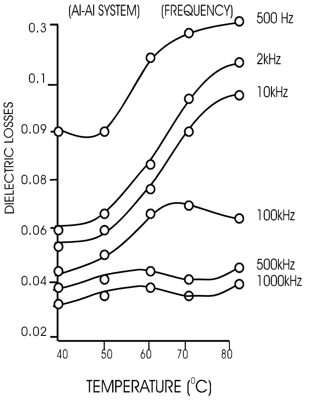

Fig. 8 Dielectric losses Vs temp. for Al-Al System

The dielectric properties of a polymer are determined by the charge distribution and also by statistical thermal motion of its polar group. The polarization of a dielectric is contributed by ionic, electronic and dipole polarization. The electronic polarization occurs during a very short interval of time of order of 10^{-10}sec, but longer then for electronic polarization i.e. 10^{-3}-10^{-2}sec required for the process of ionic polarization. To set in dipole polarization it requires longer time. In case of polar polymers, the dielectric constant begins to drop at a certain frequency. The dipole molecules cannot orient themselves in the lower temperature region. However, owing to thermal expansion, the ration of the number of molecules to effective length of dielectric decreases when the temperature increases. As the temperature increases, the orientation of dipoles is facilitated and this increases the dielectric constant. This behavior is apparent from the upward trend of the slopes of the dielectric constant curves in neighboring of glass transition temperature (T_g). on further increase in temperature, the chaotic thermal oscillation intensifies and therefore degree of order of orientation is diminishing.

The dielectric dispersion appearing at high temperature is generally admitted to be the ordinary motion of the molecules from one quesi-stable position to another around the skeletal bond involving large scale conformational rearrangement of the main chain, and is known as primary dispersion region or the α-relaxation. 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 known as the secondary dispersion region or β-relaxation.

Thin polymers are known to be mixture of amorphous and crystalline regions. The amorphous regions are the area in which chains are irregular and entangled, whereas, ion crystalline regions in which the chains are regularly folded or orderly arranged. In the crystalline areas, because of presence of hindering structural units (due to greater density of regions) the polymeric chains move with a greater difficulty than in amorphous regions. The hindrance can be assumed to possess a certain potential energy. When the polymer is heated the movements of the main chain sets in, becoming maximum at T_g, at which losses occur corresponding to α-relaxation. This relaxation corresponding to T_g, may also be understood by free volume theory [12] according to which the molecular mobility (and consequently the relaxation time) near T_g depends mainly on free volume. In the glassy state below T_g, the free volume will be frozen in and remain fixed. As the temperature increases, the glassy state will expand due to normal expansion of all the molecules, which results from the changing irrational amplitude of bound distances [13]. T_g is reached, in addition to the normal expansion process. There will be an expansion of free volume itself, which results in a larger expansion of the rubber like polymer. This yields room for rotational or translational motion of molecules to occur at T_g, according for the maximum dielectric loss at T_g[14].

The presence of dipole molecules may also contribute in the process. The dipoles associated with the backbone of a segment of polymer chain will orient with a certain frequency governed by the elastic restoring force which binds the dipole to their equilibrium positions and rotational frictional forces exerted by neighboring dipoles [15]. In the crystalline or ordered polymers, the forces which hold the structural unit together are of a homo-polar chemical binding nature and are much stronger than Vander Walls forces between the molecules in the amorphous phase which vary from region to region. Moreover, the dipolar molecules in the crystalline phase will make discontinuous jump from one equilibrium position to another equilibrium position and hence contribute to the absorption at the same temperature or frequency, whereas, in the amorphous phase dipolar molecules should be able to orient from one equilibrium to another equilibrium position relatively more easily and will contribute to the absorption over a wide frequency or temperature range since each dipole in the later case would have slightly different environments and hence would have different intermolecular interaction.

V. CONCLUSION

The analysis of various results (i.e. Dielectric constant and dielectric losses) indicates that the phenomena responsible in this case are due to the dipolar reorientation and space due to molecular motions associated with the side chains and charge effects resulting from trapping of injected charge carrier in energetically distributed traps. Charge carriers trapped at the crystalline – amorphous interfaces make a large contribution to the dielectric parameters at lower frequencies.

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