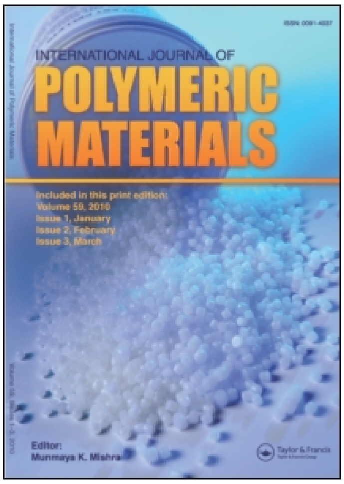

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DIELECTRIC BEHAVIOR OF ANNEALED POLY(VINYLIDENE FLUORIDE)

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This study deals with the effect of annealing temperature of Polyvinylidene Fluoride quenched from melt into ice-water on the dielectric behavior. Measurements were carried out in the temperature range 25° C to 130° C and in the frequency range 1 kHz to 10 MHz. It was found that the dielectric permittivity and dielectric strength decreases with increasing annealing temperature. This is a result of morphological changes including defects creation, recrystallization and additional crystallization at expense of the amorphous phases.

Keywords: dielectric, annealing, dielectric strength, ac conductivity

1. INTRODUCTION

A study of dielectric behavior of semi-crystalline polymers gives a good indication of the various polarization mechanisms. Such studies also help in detecting structural transitions [1]. However, the electrical properties of semi-crystalline polymers can be modified by careful control of structure or composition during fabrication process [2]. The interest in the electrical properties of Polyvinylidene Fluroide (PVF_2) from a technological point view is due to its good piezoelectric and

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pyroelectric properties [3]. Kepler et al. [4] found that the changes in the amount of order in PVF_2 play an important role in the pyroelectric effect. Furthermore, some attention has been paid to the influence of gamma radiation on the physical properties of PVF_2 [5]. It was found that the crystallinity increases with radiation dose due to crosslinking [6]. The Differential Scanning Caloromitry (DSC) results reveal double melting peaks attributed to the melting recrystallization process [7]. It was found that the morphology of PVF_2 depends on the conditions of crystallization when crystallized from melt or from amorphous solid [8–9]. The main aims of this work were to investigate the effect of crystallization temperature on the dielectric behavior of PVF_2 quenched from melt into ice-water. However, the crystallization temperature of PVF_2 is 140°C, therefore, annealing at temperature just below the crystallization temperature causes a melting of original crystals of the isothermally crystallized samples. To study the effect of crystallization temperature on the dielectric behavior of PVF_2, the samples were annealed at different temperatures: 120, 130 and 140°C for one hour and then cooled slowly to room temperature.

2. EXPERIMENTAL

2.1 Samples Preparation

Material used in this study is a Polyvinylidene Fluoride (PVF_2) commercially supplied in the form of pellets by Aldrich Chemical Company (Germany), Catalogue No. 34,707–8, the molecular weight average (M_W) is 5×10^5, the glass transition temperature (T_g) is $(-38°C)$, melting point (T_m) is (167°C), and the chemical structure is $(-CH_2CF_2-)_n$.

For dielectric measurements, discs having a diameter 1 cm and 1 mm thickness were produced by squeezing PVF_2 pellets on a hot plate between a glass slide and a cover slip. The pellets were heated to 200°C and then quenched quickly to ice water. For isothermal annealing the discs were heated to the required temperature for one hour and then cooled slowly to room temperature.

2.2 Dielectric Measurements

The ac measurements were carried out in the temperature range 25 to 130°C and in the frequency range 1 kHz to 10 MHz using an hp impedance analyzer bridge 4294A. The films were covered with a thin gold coating by sputtering and placed in an insulating chamber. Two thin copper wires were fixed to both faces of each disc by conducting silver paint to form ohmic contacts, where ac impedance and phase angle were measured. The dielectric constants and ac conductivity were determined from these measurements. The temperature was controlled using a small oven with a temperature control unit (Leybold) using Ni-Cr thermocouples.

3. RESULTS AND DISCUSSION

At any particular frequency, the complex ac impedance Z* and the complex dielectric constant ε^* may be expressed in terms of their real and imaginary components as follows:

$$Z^* = Z' - iZ''$$

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

where Z' and ε' are the real components of ac impedance and dielectric constants respectively and Z'' and ε'' are the imaginary components of the ac impedance and dielectric constant respectively. The relationship between Z and ε [7] are given by

$$\varepsilon' = Z''/2\pi f\ C_0 Z^2$$

and

$$\varepsilon'' = Z'/2\pi f\ C_0 Z^2 = \varepsilon' \tan\delta$$

where f is the frequency and C_0 is the capacitance of the electrodes ($C_0 = 0.701\,pF$ for the films used in this study), $Z' = Z\cos\theta$. And $Z'' = Z\sin\theta$, where θ is the phase angle.

Figure 1 shows the variation of the real part of the dilectric constant (ε') versus frequency measured at 25°C for different annealing temperature. The overall behavior exhibits a decrease in (ε') with increasing crystallization temperature, whereas (ε') increases with decreasing frequency. The increase of (ε') with decreasing frequency is similar to that observed for many polymers [10–13]. It is due to contribution of ionic conduction which possibly results from some impurities in the samples. Davies [14] reviewed low-frequency dielectric phenomena in condensed phases, showing that they can be caused by Maxwell-Wagner (interfacial) absorption and/or electrode polarization resulting from electrical conductance. The results indicate that the effect of impurities on the dielectric behavior at low frequencies is lessened by heat treatment at high temperature. However, the decrease in (ε') with increasing annealing temperature indicates that some morphological changes took place as a result of annealing. Low

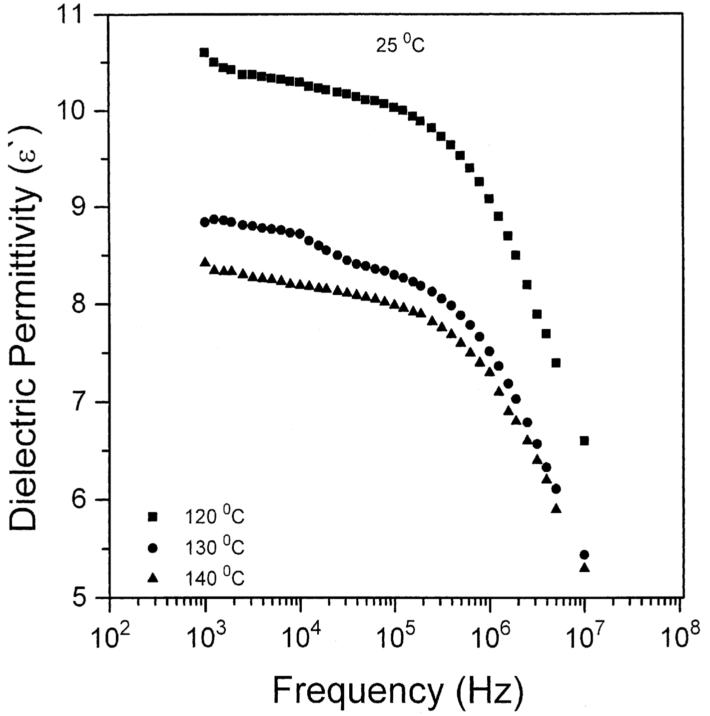

FIGURE 1 Dielectric permittivity (ε') versus frequency at different annealing temperatures for PVF_2 samples at 25°C.

annealing temperature produces an imperfect crystal structure, whereas annealing close to the crystallization temperature produces reorganization and additional crystallization at the expense of the amorphous phase. Figure 2 represents the variation of dielectric permittivity versus temperature at 100 kHz at different annealing temperatures. An overall decrease in ε' was observed with increase annealing temperature, ε' decreases form 11 to $\sim$8. This decrease confirms that annealing produces recrystallization in addition to a decrease in the concentration of defects in the bulk material. Therefore, the observed decrease in (ε') with increased annealing temperature is due to an increase in the degree of crystallinity and defects concentration, which reduce the effect of space charge polarization. The variation of dielectric loss as a function of frequency for samples annealed at different temperature is shown in Figure 3. A shap increase in ε'' with decreasing frequency was observed in the low frequency range. The plot of log tan δ (dissipation factor) versus log f in the low frequency region yields a nearly perfect straight line with a

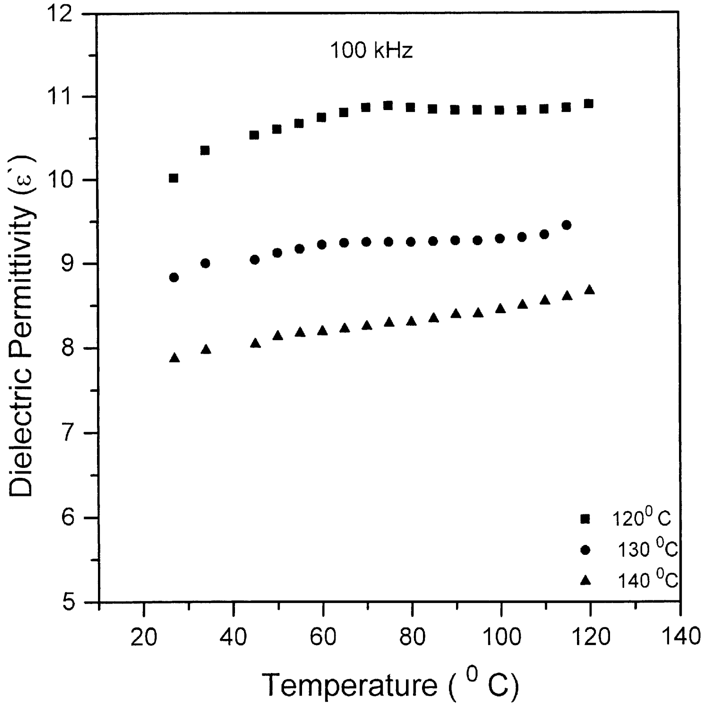

FIGURE 2 Dielectric permittivity (ε') versus temperature at different annealing temperatures for PVF_2 samples at 100 kHz.

slope approximately 0.5 as shown in Figure 4. If we assumed that the main contribution to the dielectric constant at low frequencies is due to the impurities in the samples then the dissipation factor $\tan\delta$ can be written as [10]:

$$\tan\delta = \varepsilon''/\varepsilon' = \mathrm{l}(\pi \mathrm{f}/\mathrm{D})^{1/2}$$

where l is the distance between the electrodes, f is the frequency, D is the diffusion coefficient.

According to this equation, a plot of log $\tan\delta$ versus (log f) yields a straight line with a slope of ½ at low frequencies, indicating that in this range of frequencies the electrode polarization effects presumably dominate. The slope of log $\tan\delta$ curves as shown in Figure 4 are about ½, which may confirm that the sharp increase in dielectric loss in the low frequency range is mainly due to the contribution of impurities on the dielectric behavior. On the other hand, well defined relaxation peaks were observed at frequency 5×10^6 Hz. It is

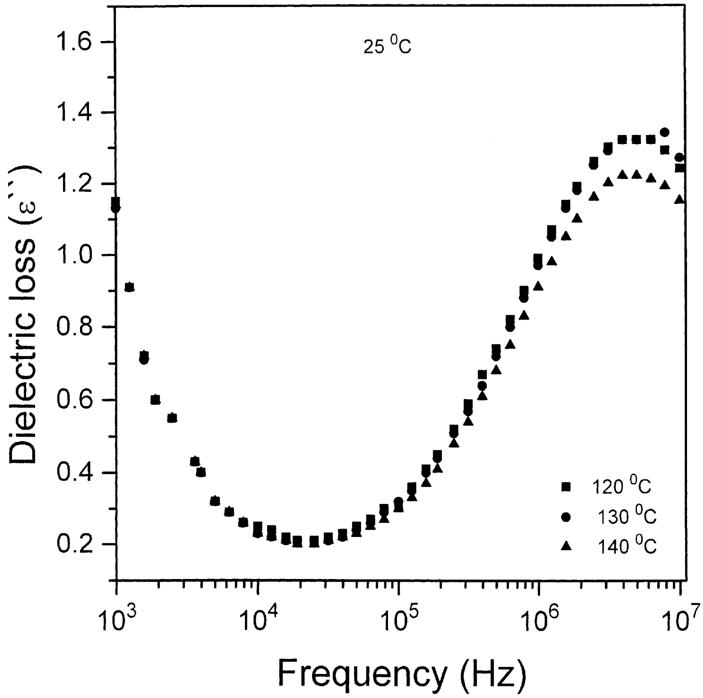

FIGURE 3 Dielectric loss factor (ε'') versus frequency at different annealing temperatures for PVF_2 samples at 25°C.

believed that this relaxation is an α-relaxation, which is associated with the glass transition in the amorphous region. Therefore, the observed decrease in the intensity of the relaxation peak at annealing temperature of 140°C confirms that a recrystallization process took place at the expense of the amorphous phase. In addition, annealing at 140°C decreases the volume concentration of the dipolar species and some static orientation constraints were imposed due to a recrystallization process.

The Cole-Cole plots for annealed PVF_2 samples yield nearly perfect semi-circles for all annealed samples at different temperature as shown in Figure 5. The dielectric strength $\Delta\varepsilon = \varepsilon_r - \varepsilon_u$, where ε_r is the relaxed dielectric constant and ε_u is the unrelaxed dielectric constant, which are representing the limiting values at low and high frequency, define the relaxation strength which depends on the volume concentration of the dipole species and their orientation constraints. $\Delta\varepsilon$ differ significantly as given in Table 1 between the sample annealed

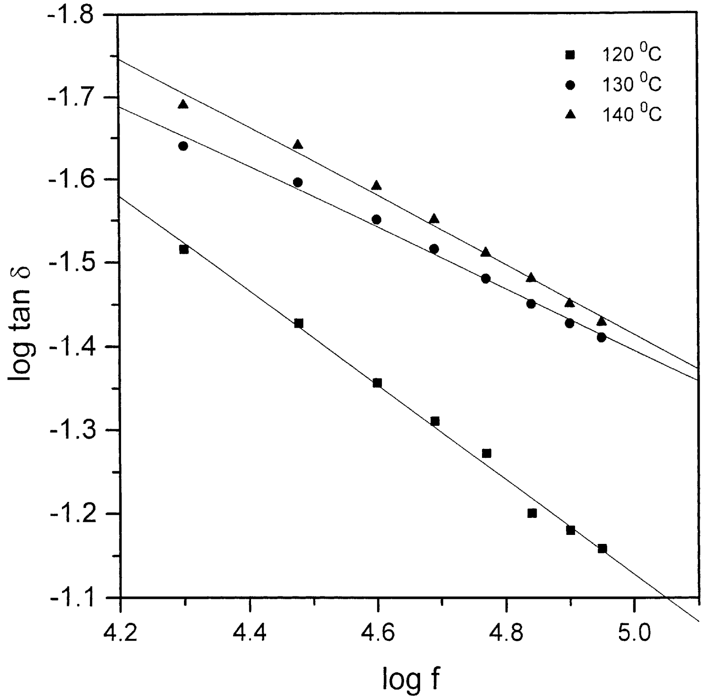

FIGURE 4 Log dissipation factor (tan δ) versus log *f* at low frequencies region for annealed PVF_2 samples.

at 120°C and that annealed at 140°C, indicating that the material in the amorphous phase has been drastically reduced by annealing at 140°C and recrystallization and additional crystallization took place with more perfect crystal structure. Tashiro et al. [15] show that during the annealing process the crystallites grow mainly in the direction of the polymer chains, the chain links that are built in a crystallite during annealing show a preferential dipolar orientation in the direction of its polarization, consequently the dielectric strength was reduced as a result of annealing at high temperature.

The ac conductivity (σ) of the material can be determined from the relation $\sigma = 2\pi f \varepsilon'' C_0$ where f is the frequency, ε'' is the loss factor and C_0 is the capacitance of electrodes. Table 2 gives the values of σ and the dielectric permittivity calculated at the same frequency. A decrease in ac conductivity was observed with increased annealing temperature, attaining a value of 3.67×10^{-8} $(\Omega.\text{m})^{-1}$ at annealing temperature (140°C), which is approximately comparable to that reported for Silicon as a semi-conductor material. The decrease in ac conductivity

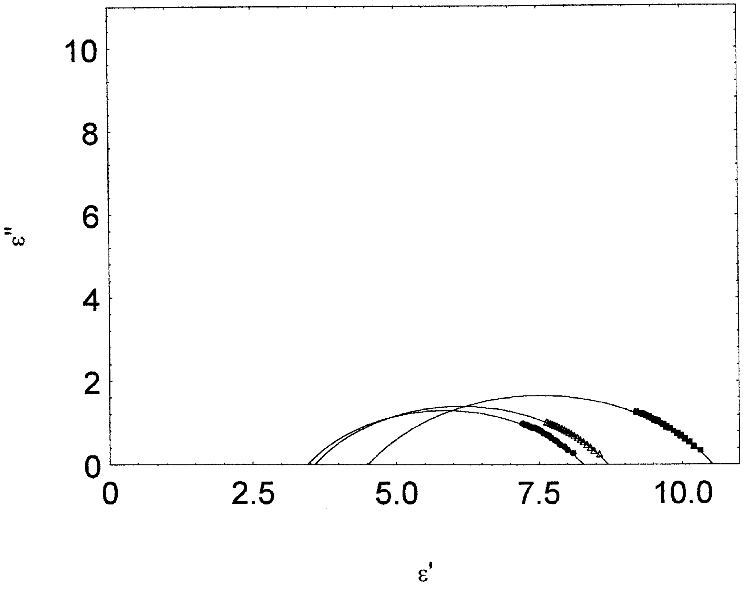

FIGURE 5 Cole-Cole plot for PVF_2 samples annealed at different temperatures.

TABLE 1 Dielectric strength $\Delta\varepsilon$ for annealed PVF_2

Crystallization temperature °C	$\Delta\varepsilon$
120	8.05
130	6.80
140	6.44

TABLE 2 AC conductivity and dielectric constant at 100 kHz for PVF_2 annealed samples

Annealing temperature °C	$\sigma(\Omega.\text{m})^{-1}$	ε
120	7.73×10^{-8}	10.3
130	3.86×10^{-8}	8.6
140	3.67×10^{-8}	8.1

when the sample annealed at temperature higher than 120°C confirms that annealing produces morphological changes in the bulk where recrystallization took palce.

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