Change in Crystallinity of Poly(vinylidene fluoride) Due to Thermal Evaporation

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ABSTRACT: Dielectric properties are reported for thin transparent poly(vinylidene fluoride)(PVDF) films, with thickness less than 1 μm, obtained by the thermal evaporation technique. This technique had to be used with the utmost care and control over the temperature of the evaporation source to obtain transparent, undegraded films of PVDF. Capacitance and loss tangent measurements were carried out on these films in the frequency range of 20 Hz to 1 MHz and the temperature range of 25–160°C. It was found that the maximum in $\varepsilon''-t$ plots at 1 kHz and tan $\delta-t$ plots at 100 Hz for these films appeared at 50 and 35°C, respectively, which are lower temperatures than those reported for solution cast PVDF films. This is attributed to the lowering of crystallinity in the thermally evaporated films. X-ray diffraction studies and IR studies also confirmed these observations. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 225–230, 1997

Key words: dielectric; polymer; PVDF; crystallinity; vacuum evaporation

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a widely studied polymer for various applications due to its high mechanical strength, low accoustic impedance, large piezoelectric coefficient, and good resistance to most corrosive chemicals. PVDF is a semicrystalline polymer. The material consists of about 50% lameller crystals on the order of 10^{-6} cm thick and up to 10^{-5} cm long.[1] The crystals are embedded in an amorphous phase that has supercooled liquid properties. Presently, at least four crystalline forms of PVDF are known that are referred to as forms I, II, III, and II$_p$ (or IV), or β, α, γ, and δ, respectively.[1–3] The α form is known to be nonpolar whereas the other three forms are polar. Form I (β form) gives rise to the highest piezoelectric activity, but form II (α form) also has a large piezoelectric effect.[4–6]

Most applications are realized using solution cast PVDF films with thickness on the order of a few tens of microns. However, for the applications in the electronic industry thin films on silicon or similar substrates must be grown. It is also necessary to study the dielectric properties of these films before making the choice for their applications. Therefore, we report some of the dielectric properties of PVDF films fabricated on glass substrates using the thermal evaporation technique.

EXPERIMENTAL

The PVDF powder used for evaporation was supplied by Aldrich Chemicals. The average molecular weight of the powder was more than 500,000 amu.

The PVDF films were fabricated on glass substrates in the form of metal–polymer–metal (MPM) devices (cf. Fig. 1) by sequential evaporation of Al, PVDF, and Al using appropriate masks. The pressure in the evaporation chamber during the deposition was less than 10^{-5} torr and was obtained using an Edwards, (U.K.) vacuum coater
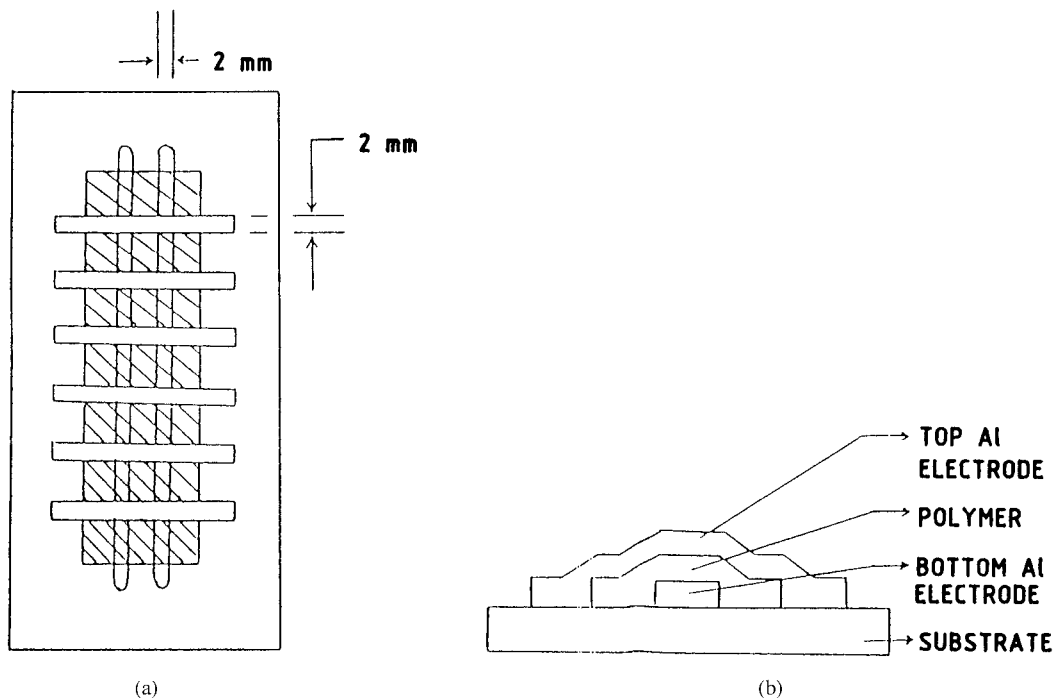
Figure 1   *MPM* devices: (a) Planar structure and (b) cross section.

(model E-306). The evaporation chamber consisted of a four source turrette and a mask changer assembly that helped to position the required source and the mask before evaporation. A Maxtek (U.S.A.) film deposition controller (model FDC 440) was used to monitor the thickness of the films. The film thickness was also checked using the Tolansky interferometry technique.

Initially Al was evaporated through an appropriate mask onto a thoroughly cleaned glass microscope slide to form two 60×2 mm parallel strips separated by 5 mm. The PVDF evaporation was carried out using a high purity alumina crucible. The vapors of PVDF were allowed to deposit on the aluminum strips using a suitable mask that left the ends of the strip uncoated for use as electrical contacts. Finally, aluminum was deposited through a suitable mask to form six cross strips, each 20×2 mm. Thus, 12 MPM devices were formed on a single glass substrate that helped to carry out all the measurements on the fabricated devices essentially under identical conditions. The entire deposition was carried out without breaking the vacuum at any stage.

The electrical measurements on these devices were carried out after transfering the substrate with devices to a cryostat that could be evacuated to a pressure of about 10^{-2} torr. The temperature of the devices inside the cryostat could be varied between 100 and 450 K and was monitored using a chromel–alumel thermocouple mounted close to the device under study. The lower air pressure inside the cryostat helped to avoid loss of heat due to conduction, thus providing better control over the temperature. The dielectric measurements were carried out using a Hewlett–Packard LCR meter (model HP 4284A) in the frequency range of 20 Hz to 1 MHz.

A few PVDF films were also solution cast, using the powder from the same batch used for evaporation. These were used to obtain IR and X-ray diffraction (XRD) plots to compare with respective IR and XRD plots of thermally evaporated films. For this purpose, 100 mg of PVDF powder was dissolved in 10 mL dimethylformamide (DMF). The solution was heated to 60°C and was kept at that temperature for 1 h with constant stirring, using a Teflon needle driven by a magnetic field. The homogenized solution was poured on a carefully leveled glass plate maintained at 60°C and was allowed to cool slowly to room temperature. This film was not subjected to annealing or stretching treatments but was used as fabricated for IR and XRD studies. The thickness of the films was measured using a thickness monitor gauge and was found to be 10 μm.

To keep the experimental conditions identical for the evaporated PVDF films for which IR and
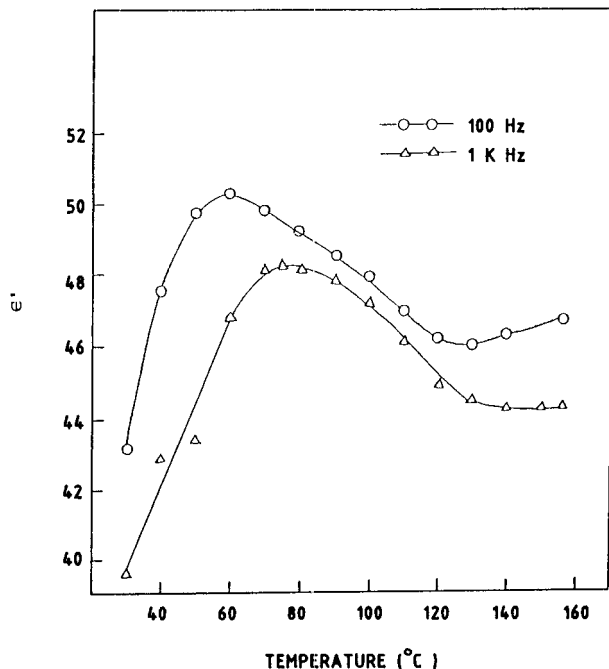
Figure 2 Dielectric constant versus temperature curves for PVDF film of thickness 1200 Å.

XRD plots were to be taken, a glass slide and a KBr pellet were mounted as substrates in the evaporation chamber of the Edwards vacuum coater at the same distance from the source. The PVDF was evaporated at 10^{-5} torr to deposit simultaneously on both glass and KBr substrates. Thus the films of the same thickness were obtained on both substrates. The film fabricated on the KBr pellet was used to obtain the IR spectrum over a range of $400-4000$ cm^{-1}; XRD over a range of 2θ from $15°$ to $40°$ was obtained for the film fabricated on the glass slide.

RESULTS

Figure 2 gives the dielectric constant, ε', versus temperature, t, curves at frequencies of 100 Hz and 1 kHz for a typical film sample of 1200 Å thickness. The ε' increased as the temperature of the device increased, attained a maximum, and then decreased as the temperature was further increased. The maximum in ε' shifted to a higher temperature as the test signal frequency increased. For a signal frequency of 100 Hz the maximum appeared at 60°C, which shifted to 75°C when the frequency was increased to 1 kHz.

The dielectric losses ε'' versus temperature t

curves are shown in Figure 3 for the sample with film thickness of 1200 Å. The nature of the curves is similar to that for the $\varepsilon'-t$ curves for both frequencies, 100 Hz and 1 kHz. However, the maximum in dielectric loss appears at 40 and 50°C for frequencies of 100 Hz and 1 kHz, respectively.

Figure 4 gives the dissipation factor, tan δ, versus temperature, t, curves for the same sample for the 100 Hz and 1 kHz frequencies. The nature of the curves is essentially the same as that of the $\varepsilon''-t$ curves with maximum in tan δ appearing at 35 and 70°C for 100 Hz and 1 kHz frequencies, respectively.

The solution cast films prepared by the method described in the experimental section showed a peak in the $\varepsilon''-t$ curves at 80°C for 1 kHz. Similarly, a plot of tan δ versus t showed a maximum at 60°C for 100 Hz.

The IR spectrum of solution cast film and thermally evaporated film are shown in Figure 5. The thermally evaporated film mainly contains form II (α form) PVDF peaks. The absorbance peak at 761 cm^{-1} for the thermally evaporated film shows a fall in absorbance to thickness ratio compared to the absorbance to thickness ratio for the solution cast film.

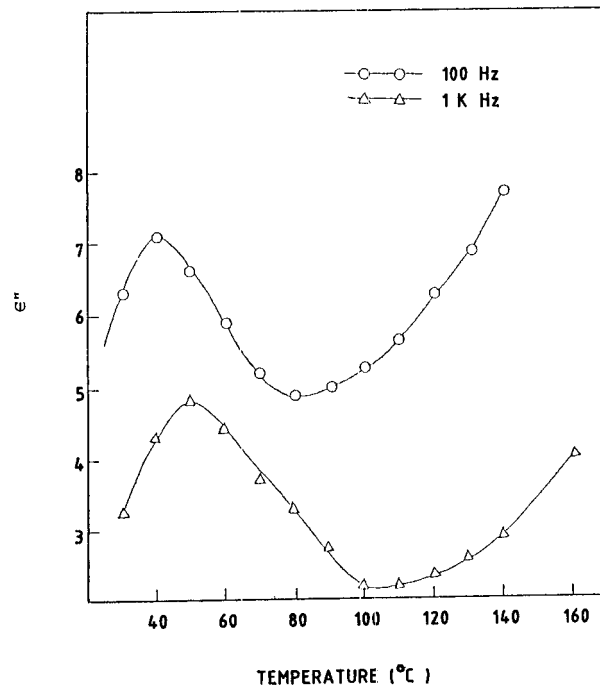Figure 6 gives XRD plots of thermally evaporated PVDF film [Fig. 6(a)] and solution cast film

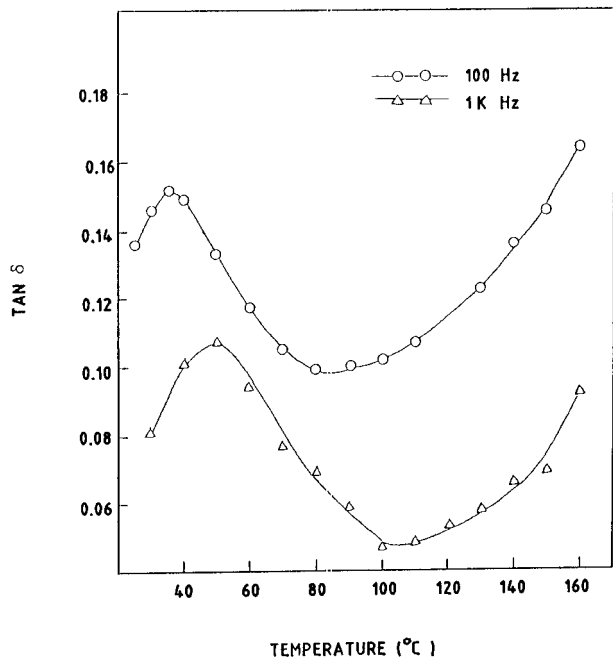**Figure 3** Dielectric loss versus temperature curves for PVDF film of thickness 1200 Å.

Figure 4   Dissipation factor versus temperature for PVDF film of thickness 1200 Å.

[Fig. 6(b)]. Some of the α peaks present in the solution cast films do not appear in the thermally evaporated film. Further, the peak intensities are higher in the solution cast film compared to the film obtained by thermal evaporation.

DISCUSSION

PVDF exhibits three types of relaxations (α, β, and γ) in the order of decreasing temperatures of their appearances.[7,8] The α relaxation is due to molecular motion in the crystalline regions. The solution cast PVDF films of form II have two types of α relaxations,[9,10] namely, crystalline relaxation, α_c, and amorphous relaxation, α_a. The temperature, T_m, at which the maximum appears in the $\varepsilon''-t$ curve corresponding to α_c is reported to be 90°C and that for α_a is −20°C at 1 kHz frequency.[9,10] From the results obtained for the thermally evaporated film (Fig. 3) the T_m in ε'' at 1 kHz frequency is 50°C, which is lower than that reported in the solution cast films. Similarly the T_m in tan δ at 100 Hz is reported to be around −23°C for α_a and around 77°C for α_c in solution cast films,[11] whereas T_m obtained for thermally evaporated films in tan δ at 100 Hz is 35°C.

The T_m is found to depend on the density and lamellar thickness of the film and also on the degree of crystallinity of the sample.[9,10,12] It is well
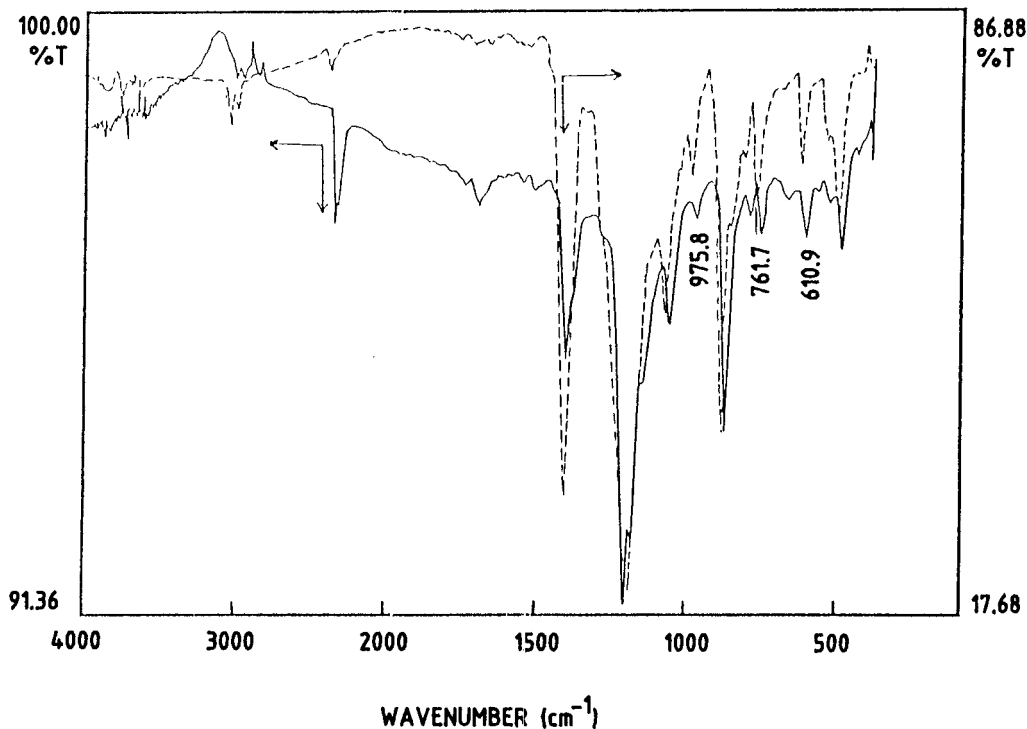

Figure 5   IR spectra of (—) thermally evaporated and (---) solution cast PVDF.
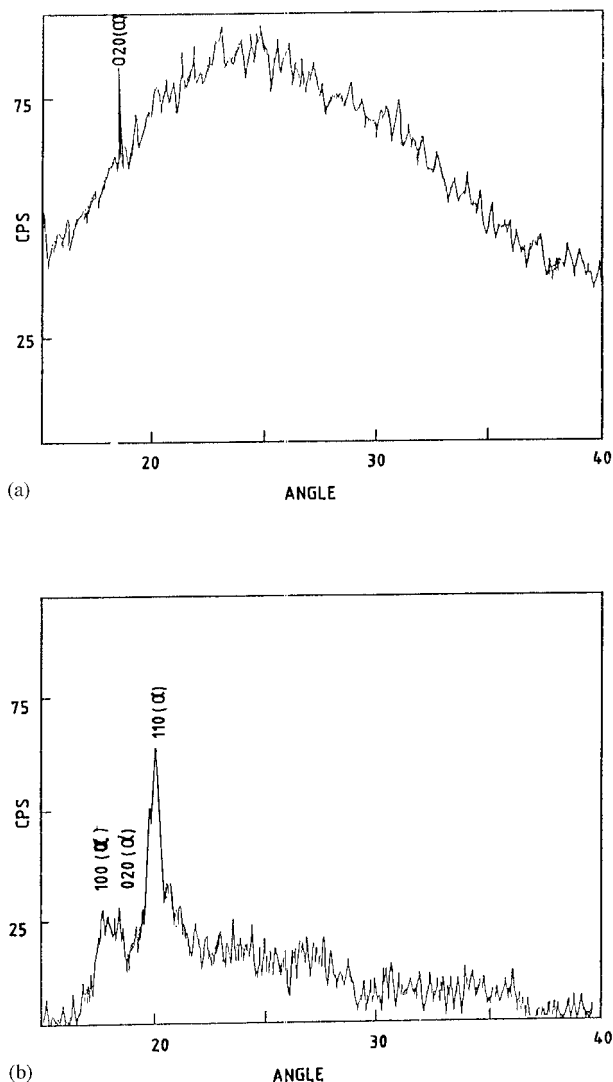
Figure 6 X-ray diffractometer scans of (a) thermally evaporated and (b) solution cast PVDF.

known that thin films obtained by thermal evaporation are at best polycrystalline in nature, and unless special precaution is taken they tend to be amorphous. The PVDF molecule has a helix form with the zigzag disposition of the links. Its degree of crystallinity can be affected by thermal history, that is, quenching or annealing from the melt. It is highly susceptible to ordering and concomitant enhancement of crystallinity by orientation, either by drawing while still in a semimolten state or by cold orientation. The substrate used in our case for casting the films was glass, which is amorphous in nature; it was also not kept at higher temperature to promote crystallization. The solution cast films, prepared by the method as described in the Experimental section, were neither

stretched nor annealed after preparation, which would have increased crystallinity. Hence, we obtained a peak in the $\varepsilon''-t$ curve for solution cast film at 80°C compared to the reported value of 90°C for an oriented film. Such change in T_m with respect to crystallinity was also reported by other workers[13] for PVDF. Thus, the decrease in T_m in thermally evaporated films could be attributed to the decrease in the degree of crystallinity.

If the absorption of IR spectra obtained are assumed to follow the Lambert–Beer law and to not interfere with each other, then the ratio of absorbance to the thickness of the films will be directly proportional to the degree of crystallinity.[14] In the α form of PVDF the absorption peaks at 610, 769, and 1073 cm^{-1} are sensitive to the changes in sample crystallinity.[15] Thus, the decrease in the ratio of absorbance to thickness (D/L) in Figure 5 at 761 cm^{-1} shows the decrease in crystallinity of thermally evaporated PVDF.

The XRD analysis (Fig. 6) shows that the thermally evaporated films of PVDF are more amorphous compared to the solution cast films. The results reported by other workers[16] for solution cast PVDF films were for the films annealed after casting. This might have resulted in a further increase in their crystallinity.

CONCLUSION

It is concluded that the PVDF films formed on a cold glass substrate by thermal evaporation are of the α form and have a lower degree of crystallinity as compared to the solution cast films.

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