

PROCESSING AND CHARACTERIZATION OF A NOVEL NONPOROUS POLY(VINYLDENE FLUORIDE) FILMS IN THE β -PHASE

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Abstract

Poly(vinylidene fluoride) (PVDF) has remarkable properties leading to electro-optics, electro-mechanical and biomedical applications. In particular its piezo- and pyroelectric properties provide possibilities for many technological applications. The semicrystalline nature of PVDF, combined with the occurrence of at least four crystalline phases implies a complicated physical microstructure. The most frequently described and important phase is the β . The piezo and pyroelectric properties mainly depend on this phase, so increasing the β phase content has always been a great concern. It is possible to obtain films in the β phase by solution but this material presents a high porosity leading to an opaque appearance and a decrease of the mechanical and electrical properties. In this work, porous films in the β phase were obtained directly from the solution at 60°C. After applying pressure perpendicular to the surface of the film at elevated temperature, the pores in the original sample are eliminated. The changes on the morphology and crystallinity associated to the pressure applied to the samples were also studied.

Keywords: piezoelectric polymers, ferroelectrics, PVDF, processing

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1. Introduction

Poly(vinylidene fluoride), PVDF, is a polymer with interesting piezoelectric properties, which allows important electro-optical, electromechanical and biomedical applications. This polymer shows at least four crystalline phases called α , β , γ e δ [1, 2, 3]. The one with the best piezo- and pyroelectric properties, after poling, is the β phase [3]. Until recently, this phase was exclusively obtained by mechanical stretching of films originally in the non-polar α phase [1, 2, 4], which is the most stable one from a thermodynamic point of view and directly obtained from the melt. This process results in films mostly in the β phase, but with a small percentage of α phase material [5, 6, 7, 8]. Unoriented films exclusively in the β phase were obtained from the crystallization of PVDF from solution with N,N-Dimethyl Formamide or Dimethyl Acetamide at temperatures below 70°C[9]. These films showed a high degree of porosity, which makes them opaque (milky) and fragile [10]. Further, these pores cause a degradation of the electrical properties of the material (lower dielectric constant) and do not allow the poling of the films, which is essential for the applications involving the piezo-, pyro- and ferroelectric effects [3, 11, 12]. Further, the mechanical properties are also affected by the high porosity and the films can not be oriented by stretching due to the big fragility. In this work, films exclusively in the β phase and without porosity were obtained by pressing at high temperature films obtained from solutions with N,N-Dimethyl Formamide. Far Infrared Spectroscopy, Scanning Electron Microscopy and Differential Scanning Calorimetry experiments show that the high temperature pressing does not change the type of the crystalline phase present in the material, eliminates the porosity and slightly increases the degree of crystallinity.

2. Experimental procedures

Films with thickness of ~ 30 μm were obtained by spreading a solution of PVDF (FORAFLON F4000-Atochem) in N,N-Dimethyl Formamide (DMF) on a glass slide. The initial weight concentration of the solution was 20% of PVDF. The total evaporation of the solvent was performed at 60 °C for 120 minutes in order to ensure the removal of the solvent by evaporation and the isothermal crystallization of PVDF. The film was then removed from the glass substrate and a pressure larger than 7.5 MPa at a temperature that can range from 140 to 160 °C for and a time from 5 to 15 minutes was applied in a hydraulic press. The crystalline phase or phases present in the samples was confirmed by Fourier Transformed Infrared Spectroscopy (FTIR) (*Perkin-Elmer*

Spectrum 1000 apparatus). The values of the enthalpy (ΔH), proportional to the degree of crystallinity of the samples was determined by differential scanning calorimetry (DSC) (*Perkin-Elmer DSC-7 series*), using a heating rate of 10°C/min. Electronic micrographs were obtained by Scanning Electron Microscopy (SEM) by a Phillips X230 FEG apparatus.

3. Results and discussion

Figure 1 shows an image of the film obtained by crystallization from solution at 60°C. Under these conditions the film crystallizes exclusively in the β phase [9] but a high porosity is present. The porosity induces opacity and fragility to the film. The milky aspect (Figure 1) is caused by the cavities between spherulites (Figure 2 and 3), which produce interfaces solid/air that reflect and refract visible and even infrared radiation in the 900 to 4000 cm^{-1} range, what produces an inclination in the base line of the spectra [13]. When a pressure of 15 MPa is applied for 10 minutes at 140 °C, the film becomes transparent (circular region in Figure 1) and gains an excellent flexibility. These films allow deformations larger than 500% with induce the transformation to a microfibrillar structure and the orientation of the polymeric chains [14]. On the other hand, the maximal deformations allowed by the porous films is the ~50%. Higher pressures also induce the decrease in the pore dimensions and quantity, but in an incomplete way. Higher pressures allow a reduction in the application time. On the other hand, higher temperatures also allow the pore reduction but β to α transformation can be induced.

The cavities between the spherulites, which are at the origin of the high porosity, can be observed in through a SEM image (Figure 2) of the surface of the film before the pressure was applied. Figures 3 and 4 show a fracture region of the sample before and after the pressing, respectively. These images evidence a strong reduction of the porosity of the sample. The fracture was performed after the film was immersed in liquid nitrogen.

Far Infrared Spectroscopy is one of the most used experimental techniques in order to identify the phase or phases present in the films as well as the orientation of the polymeric chains [8, 14, 15]. In this context, the presence of the β phase is identified by the characteristic absorption bands at 442, 468, 510 and 840 cm^{-1} . The presence of the α phase is identified by the 410, 531, 615, 765, 795, 855 and 976 cm^{-1} absorption bands [9, 16, 17]. Figure 5 shows the FTIR spectra of the sample before (a) and after (b) the pressing process. In both cases the presence of exclusively β phase can be observed, through the presence of the 510 and 840 cm^{-1} absorption bands. No considerable absorption bands related to the presence of the α phase were detected before and after

the pressing process. This demonstrates that the pressing does not change the crystalline phase present in the sample. Just a decrease in thickness occurs.

Figure 6 shows the DSC thermographs for the sample before (a) and after (b) the pressing. A slight increase in the value of the melting enthalpy after the pressing process can be observed: 50.3 Jg⁻¹ for the porous and 52.3 Jg⁻¹ for the nonporous sample. From the DSC curves the degree of crystallinity $\Delta X_c(\%)$ can be calculated (Equation 1) from the enthalpy of the melting peak ΔH_f , taken into consideration the enthalpy for a fully crystallized PVDF ($\Delta H_{100} = 103.40 \text{ Jg}^{-1}$ for β -PVDF) [1, 5]:

$$\Delta X_c = \frac{\Delta H_f}{\Delta H_{100}} * 100 \quad \text{Equation 1}$$

The calculations indicate a slight increase in the degree of crystallinity of the sample from 48.6% from 50.6% with the pressing of the material. The crystallinity of the films is superior to the ones of the β -phase films obtained by stretching from α phase films as the stretching process needed for the phase transformation decreases the degree of crystallinity of the material.

4. Conclusions

As a conclusion, films of PVDF exclusively in the β phase and without pores were obtained by crystallization from solution at $T < 70^\circ\text{C}$ and subsequent pressing at high temperatures. With respect to the porous films obtained by crystallization from solution, the films show better mechanical properties, are transparent and excellent flexibility. Further, they allow poling and orientation of the polymeric chains by stretching. With respect to the β phase films obtained by stretching from α phase films, these films show a higher β phase content and a higher degree of crystallinity.

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Figure Captions

Figure 1: Picture of the film obtained from solution. The transparent circular region is the one in which the pressure was applied.

Figure 2: SEM image of the surface of the film obtained from solution with DMF at 60⁰C.

Figure 3: SEM image of the fracture of the film before pressing.

Figure 4: SEM image of the fracture of the film after pressing.

Figure 5: FTIR spectra of the film before (a) and after pressing (b).

Figure 6: DSC curves of the film before (a) and after pressing (b). The dotted boxes mark the areas where appear the characteristic absorption bands of the β -phase (840 and 510 cm^{-1}).

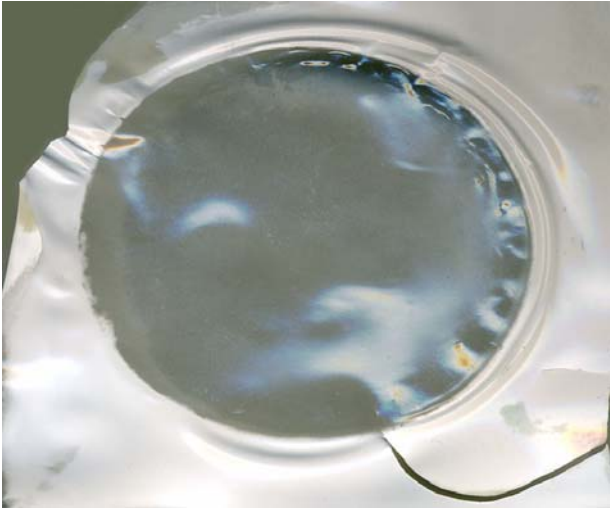


Figure 1

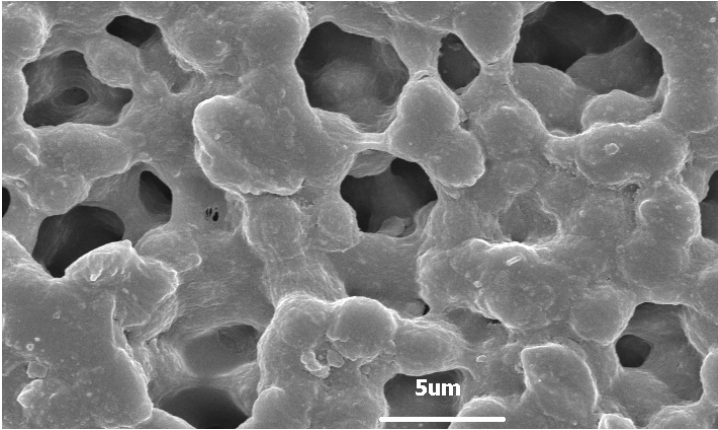


Figure 2

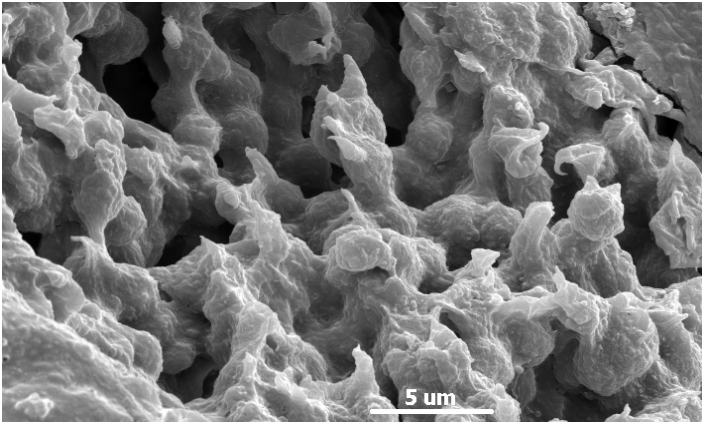


Figure 3

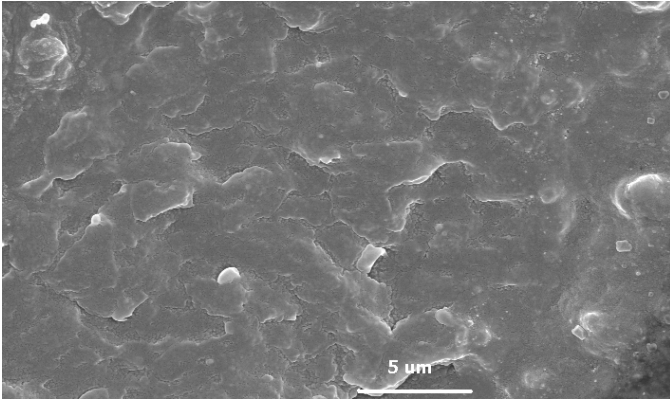


Figure 4

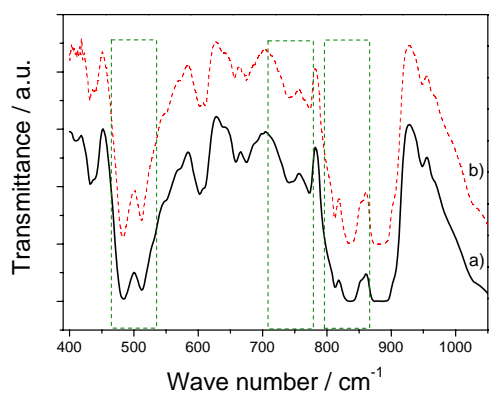


Figure 5

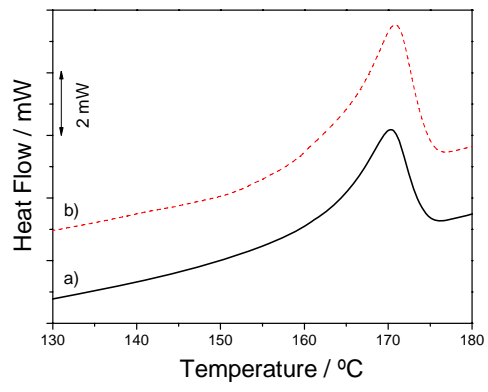


Figure 6