

α - to - β Transformation on PVDF Films Obtained by Uniaxial Stretch *

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*Dedicated to the memory of Manuel Vítor Moreira

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Abstract. The α to β phase transformation of PVDF through the stretching process at different temperatures was investigated. The optimum stretching conditions were studied and characterised by infrared spectroscopy and differential scanning calorimetry. The maximum β -phase content was achieved at 80°C and a stretch ratio of 5. Accompanying the phase transformation, a orientation of the polymer chains and a packing of the crystalline structure is observed. The stretch ratio does not significantly affect the degree of crystallinity.

Introduction

Poly(vinylidene fluoride) (PVDF) is being widely investigated due to its outstanding pyro- and piezoelectric properties [1-7]. These properties generated various applications, especially in the field of sensor and actuator devices and technologies [1,2]. The existence and the optimization of these properties are intimately related with the crystallinity level, structure and orientation of the crystalline part of the polymer, which in turn heavily depend on the processing conditions [1]. PVDF is a semi-crystalline polymer which shows polymorphism and is commonly crystallized in non-polar crystalline α -phase. The piezo- and pyroelectric properties mainly depend on the β -phase content and its characteristics. Thus, the increment of the β -phase content has always attracted great interest [1,2,6,7].

The β -phase can be induced by several techniques, the most common being the mechanical stretching of the α -phase films at a suitable temperature. The α -phase is developed directly from the melt. The conversion of α into β -phase takes place when stretching at temperatures below 100°C, using a stretch ratio between 3 and 5.

In this work the formation of the β -phase through the stretching process at different temperatures was studied. The optimum stretching conditions were studied and characterised by infrared spectroscopy. Due to its effects on pyro- and piezoelectric properties of films, the changes in crystallinity are also reported.

Experimental

Films with thickness around 30 μm were obtained by spreading a solution of PVDF (FORAFILON F4000-Atochem) in DMF on a glass slide. The initial concentration of the solution was 20% of PVDF. The system was kept inside of an oven at a controlled temperature of 120°C for 60 min. This

time was sufficient to ensure the removal of the solvent by evaporation and the isothermal crystallization of PVDF. After removing the solvent, the sample was melted at 220°C for 10 minutes. Then, the samples was removed from the oven and cooled down to room temperature. The polymer obtained by this procedure is predominantly α -PVDF.

These films were then uniaxially drawn at the temperatures of 80°C, 90°C and 100°C with draw ratios ($R = L_{\text{final}}/L_{\text{initial}}$) of 1 to 5, resulting in different percentages of β -phase content with different degrees of orientation

The crystalline phase (or phases) present in each sample was confirmed by infrared (IR) spectroscopy (*Perkin-Elmer* apparatus). The values of the enthalpy (ΔH), proportional to the degree of crystallinity of each sample were determined by differential scanning calorimetry (DSC) (*Perkin-Elmer DSC-7 series*), using a heating rate of 10°C/min. Electronic micrographs were obtained by a Phillips X230 FEG equipment.

Results and Discussion

In order to determine the fraction of the content of β -phase present in each sample, IR absorption bands at 766 and 840 cm^{-1} , characteristics of the α and β -phases, respectively and a procedure similar to that of Gregorio et al and Salimi et al were used [4-7].

Assuming that the IR absorption follows the Lambert-Beer law, the A_{α} and A_{β} absorbancies at 766 and 840 cm^{-1} , respectively, are given by:

$$A_{\alpha} = \text{Log}\left(\frac{I_{\alpha}^0}{I_{\alpha}}\right) = C.K_{\alpha}.X_{\alpha}.L \quad (1)$$

and

$$A_{\beta} = \text{Log}\left(\frac{I_{\beta}^0}{I_{\beta}}\right) = C.K_{\beta}.X_{\beta}.L \quad (2)$$

for a sample of thickness L and with an average monomer concentration C . The α and β subscripts refer to the crystalline phases, I_0 and I are the incident and transmitted intensities of the radiation, respectively; K is the absorption coefficient at the respective wave number, and X the degree of crystallinity of each phase [7].

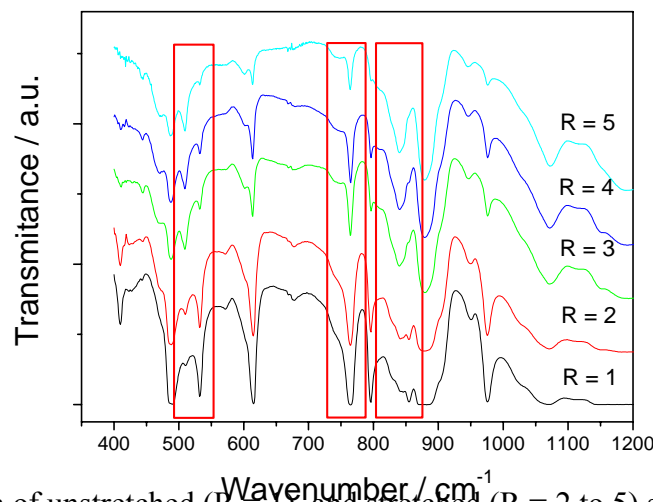


Fig. 1: Infrared spectra of unstretched ($R = 1$), and stretched ($R = 2$ to 5) samples at 80°C.

Figure 1 shows the IR spectra of unstretched and stretched samples at different drawn ratios at a temperature of 80°C. The value of K_α is 6.1×10^4 and K_β is 7.7×10^4 cm²/mol [4,6,7]. For a system containing α and β -phases, the relatively fraction of the β -phase, $F(\beta)$, can be calculated using Eq. 3:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta / K_\alpha)A_\alpha + A_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (3)$$

According to previous studies [1-5], the uniaxial stretching of PVDF films results in the development of the β -phase. A transformation mechanism is reported to occur at certain conditions. For FORAFOLON F4000 films, the variation of the β -phase content, $F(\beta)$, with the stretch ratio and stretching temperature are represented in figure 2.

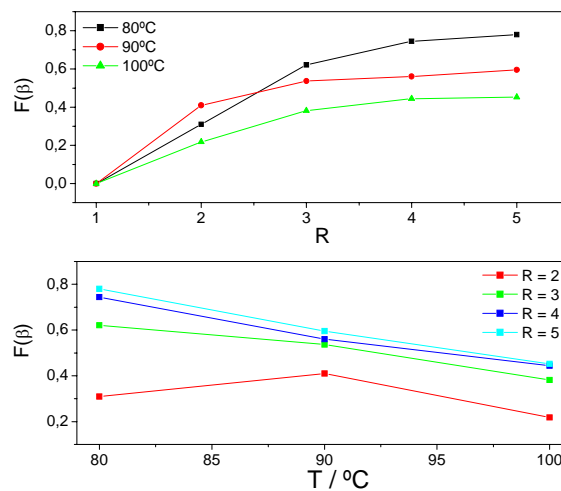


Fig. 2: Variation of β -phase content as a function of stretch ratio (above) and stretching temperature (below).

During stretching, film whitening occurs. Necking and a reduction of the thickness occurred at the film and propagates along the unstretched regions on both sides of the stretched region. The α to β transformation was reported to begin with the necking [6]. Necking marks the transformation from a spherulitic to a micro fibrillar structure. Small blocks of lamella are torn away from the original lamellae to form a fibrillar structure of crystallites. This mechanism induces all-trans planar zigzag conformation into the crystals [5,6]. In the Figure 2 (above) the variation of the β -phase content with stretch ratio at several temperatures is depicted. The β -phase content increases markedly upon increasing the stretch ratio. The maximum value of the β -phase content occurs at 80°C for a stretch ratio of 5.

Upon increasing the temperature, the α to β -phase transformation is attenuated. For temperatures above 120°C, the consequent increase in chain mobility mainly results in crystal orientation along the stretching direction without considerable conformational changes into the crystals. The resulting material consists predominantly of oriented α -phase [4,6]. Thus, rising the stretching temperature to much reduces the α to β -transformation efficiency.

It is evident that $F(\beta)$ is more affected by the stretch ratio than by the stretching temperature and that the maximum value of $F(\beta)$ is achieved at 80°C with a stretch ratio of 5. A maximum $F(\beta)$ of 80% was calculated.

Figure 3 shows the chain orientation as a function of the stretch ratio. The fibrillar structure of the three samples can be observed. As the deformation increases, the fibrils of the polymer start to get closer and the sample gets oriented.

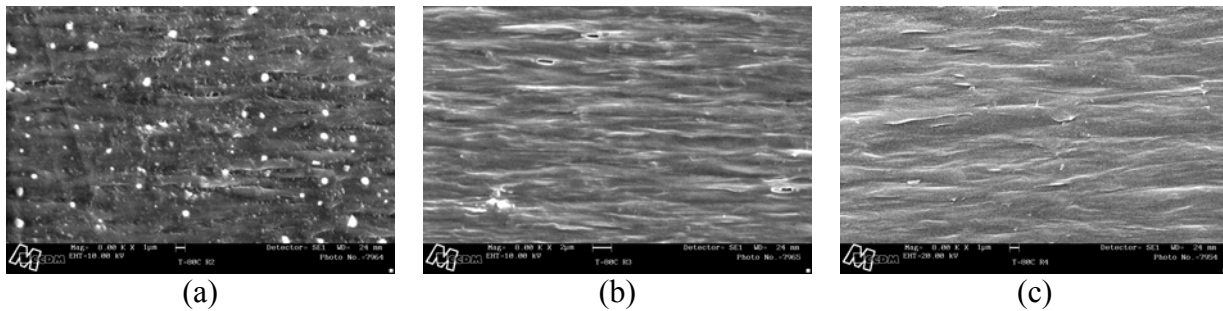


Fig. 3: SEM Micrographs obtained from samples stretched at 80°C: (a) R=0, (b) R=3 and (c) R=5.

Table 1 shows the melting enthalpy (ΔH) for samples stretched at 80°C with different drawn ratios. The value of ΔH decreases almost linearly with increasing temperature.

ϵ	ΔH [J/g]
R = 3	42.5
R = 4	41.3
R = 5	40.6

Table 1: DSC results for samples obtained by stretching at 80°C with different stretch ratios.

Conclusions

The processing conditions deeply influence the morphology and the phase content of PVDF. Stretching the film results in the α to β -phase transformation. In this transformation, the polymer chains are realigned in the crystals, so that all trans-planar zigzag (TTT) conformation was induced. This allows the dipoles on the polymer chains to align normal to the direction of the applied stress. The maximum value of the β -phase content was obtained at 80°C with a stretch ratio of 5. The stretch ratio affects the α to β -phase transformation more than the stretching temperature. Fourier Transform Infra Red spectroscopy (FTIR) was used for detecting relative fractions of the variations of α and β phases.

As expected, for higher draw ratios the polymer chains get more oriented and the crystal structure more packed. DSC results shows that the ΔH is not strongly affected by the stretch ratio.

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