Mechanical and Dielectric Relaxations in Poly (vinylidene fluoride) PVDF films

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ABSTRACT

Dielectric and Dynamic Mechanical Spectroscopy, as well as Differential Scanning Calorimetry measurements associated with X-ray diffraction (XRD), were conducted on PVDF films. Several mechanical and dielectric relaxations were observed at approximately -48°C, 84°C and -42°C, 13°C respectively, at a frequency of 1 Hz in unstretched PVDF film. The main objective of this study was to compare the β and α mechanical relaxations and enhance the understanding of the structural changes that occur in the crystalline phase during stretching at various temperatures. Reorientation of the chains and an increase in the degree of crystallinity were observed with stretching at different temperatures.

Mots-clés :
Polymère - PVDF - Relaxation - DSC - DRX.

RÉSUMÉ :

La spectroscopie diélectrique et mécanique dynamique, ainsi que les mesures de calorimétrie différentielle à balayage (DSC) associées à la diffraction des rayons X (DRX), ont été réalisées sur des films de PVDF. Plusieurs relaxations mécaniques et diélectriques ont été observées à environ -48°C, 84°C et -42°C, 13°C respectivement, à une fréquence de 1 Hz dans le film de PVDF non étiré. L'objectif principal de cette étude était de comparer les relaxations mécaniques β et α et d'améliorer la compréhension des changements structuraux qui se produisent dans la phase cristalline lors de l'étirement à différentes températures. Une réorientation des chaînes et une augmentation du degré de cristallinité ont été observées lors de l'étirement à différentes températures.

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1. INTRODUCTION

Poly (vinylidene fluoride) (PVDF) is a semi-crystalline, tough, chemically inert thermoplastic material with a low dielectric constant. Since the discovery of piezoelectricity by Kawai in 1969 [1]. PVDF is commonly used in fields such as power generators, battery separators [2], sensors, flexible electromechanical devices [3], water treatment [4], and biomedical applications [5,6]. It is also used as an ultrasonic wave transducer [7,8]. This material has been intensively studied because of its interesting properties, including low acoustic impedance and excellent acoustic performance across a wide band. These characteristics make it well-suited for various transducer applications [9,8]. Numerous research efforts have been devoted to its technological significance [10-12] as well as the exploration of its fundamental origins [13,14].

PVDF theoretically has nine crystalline phases [15], and five of these crystalline phases have been observed experimentally with different conformations called (α or (II), β or (I), γ or III, δ or IV, ε or V [16,17]. Various strategies have been developed to obtain high content Phase I-PVDF, including fast cooling from melt [18] stretching [19], poled electric fields [20], magnetic fields [21] and pressing and folding [22]. In order to produce a piezo, pyro, and ferroelectric material [23].

In this work the relaxation phenomenon of PVDF II is studied by mechanical and dielectrical spectrometry. Deformation processes are not intimately associated with film production and use. Oriented films are often subject to additional stress during service and morphological change may occur primarily in the direction perpendicular to the preferred warp orientation, where mechanical properties are weaker. In our study, a set of experiments are carried out on PVDF II in order to improve our knowledge of the structure and the dipole change that will take place in this material following the deformation processes as a function of temperature.

2. MATERIAL AND EXPERIMENTAL

Samples of extruded PVDF 1008 films, 0.2 mm in thickness, were provided by Solvay Belgium. The samples were stretched four times their initial lengths using a traction machine. The thicknesses of the samples after stretching are collated in Table 1.

Table 1. Thicknesses of samples after stretching at a speed of 0.0167 mm/s.

T (°C)	65	75	95	115
e (mm)	0.06	0.08	0.08	0.09

The X–ray diffraction, measurement was carried out with INEL X–ray diffractometer using Co Kα radiation with a wavelength of λ_{Co}= 0, 17902 nm. The degree of crystallinity χ_c and the average size of the crystallites perpendicular to the (110), according to the following relationships (1) and (2):

$$\chi_c(\%) = \frac{Ac}{Ac+Aa} \times 100 \qquad (1)$$

$$D_{hkl} = \frac{0.9\lambda}{\delta(2\theta).\cos\theta} \qquad (2)$$

such that:

A_c : the area corresponding to the crystalline phase;
A_a : the area corresponding to the amorphous phase;
D_{hkl} : apparent dimension of crystallites perpendicular to the planes (hkl);
θ : The Bragg angle corresponding to the reflection on the planes (hkl);
δ(2θ): the width at mid-height of the peak;
λ : The wavelength.

The values of the melting enthalpy ΔH, related to the crystallinity of the film, were measured by differential scanning calorimeter (DSC131 Evo) at a heating rate of 10°C/min. The degree of crystallinity χ_c can be calculated from the melting enthalpy ΔH based on the following equation:

$$\chi_c = \Delta H/\Delta H_m \qquad (4)$$

where ΔH: is the area under the melting peak (J/g) and ΔH_m: is the enthalpy of fusion of the crystalline phase (J/g) (at PVDF ΔH_m=25 cal/g) [25,26].

The lamellae thickness l_c, was calculated from the Gibbs Thomson equation:

$$T_{fx} = T_f^0\left(\frac{1-2\sigma_e}{\Delta H_f^0 L_c}\right) \qquad (5a)$$

$$\Rightarrow l_c = \frac{2\sigma_e T_f^0}{\Delta H\left(T_f^0 - T\right)} \qquad (5b)$$

Where T^0_f = 186 °C is the equilibrium melting point of an infinite perfect crystal, ΔH_m= 2,06108 J/m^3 is the melting enthalpy per unit volume of crystal of type II and σ_e = 0,07×10^{-2} J/m^2 is the surface free energy of basal plane. [25-35]. Dielectric measurements were performed with a TA Instruments DEA 2970 Dielectric Analyzer with parallel plane electrodes. The real (ε') and imaginary (ε'') parts of the permittivity were measured in the frequency range 3×10^{-2}Hz to 10KHz at a temperature rate 1°C.min^{-1} from -170°C to 300°C. Dynamic mechanical analysis (DMA) measurements were carried out using the tensile mode of a thermo-mechanical Analyzer under isothermal conditions between -150 and 500°C.

3. RESULTATS AND DISCUSSION

3-1. XRD analysis:

The diffractograms of the PVDF films are shown in Figure 1. The spectrum (a) is that of an unstretched film, corresponding to phase II. The characteristic lines of this phase are respectively located at 2θ = 20.64°, 21.25°, and 23.14°, relating to diffractions of planes (100), (020), and (110). Spectra (b), (c), (d), and (e) correspond to those of films stretched at 115°C, 95°C, 75°C, and 65°C respectively. While the I-phase of the PVDF film stretching (e) just presented a peak at 2θ = 23.75°, 23.80°, corresponding to the overlapping diffraction of (110+200) planes, the transition from phase II to phase I was evident, with no apparent reflection peaks of planes (100), (020), and (110) in the diffractogram curves of the PVDF film stretching (d) and biaxial stretching (e).

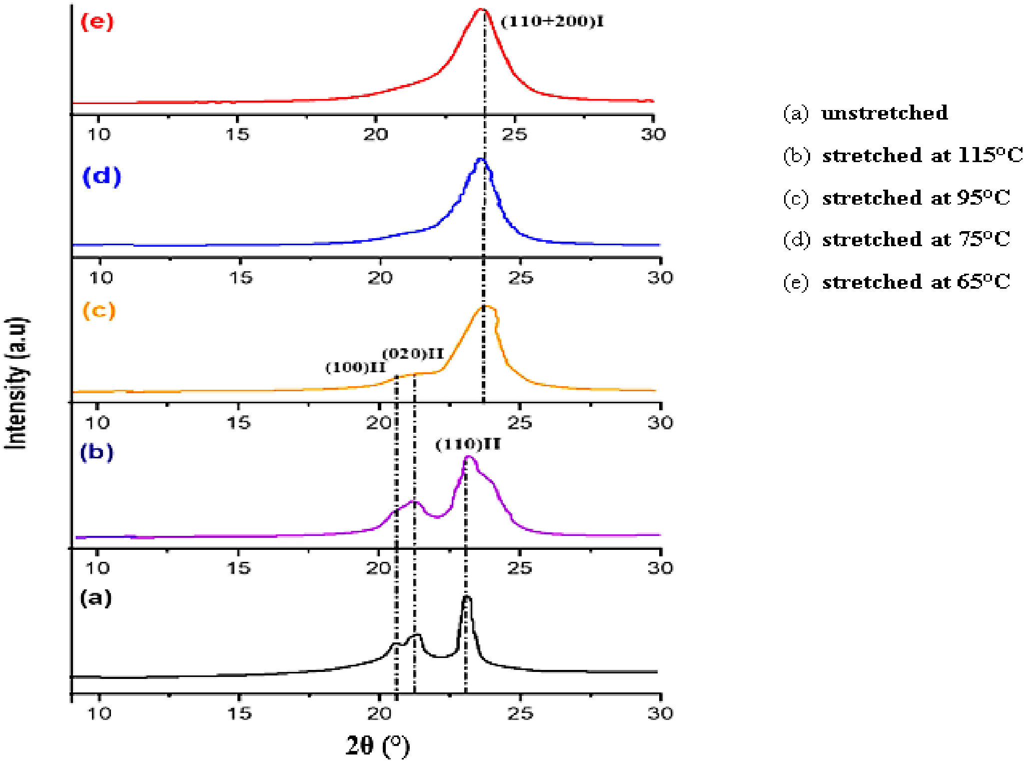

Figure 1: XRD patterns and peak as segments of II and I and phases of the PVDF films: unstretched (a), stretched at 115°C (b), stretched at 95°C (c), stretched at 75°C (d), stretched at 65°C (e),

We observe that at T_s<75°C, the disappearance of the peaks (100) and (020) of phase II and the appearance of the peaks (110+200) corresponding to phase I occur. At T_s = 95°C, there is a mixture of phase I and II. At T_s = 115°C, only oriented phase II is present. From the XRD diffractograms, we calculated the degree of crystallinity (χ_c), the average dimension of the crystallites perpendicular to the (110) plane, the interplanar distance, and the lattice parameter 'a' using relationships (1) and (2).

The degree of crystallinity (χ_c (%)), the dimension of the crystallites (D_{110}(nm)) and strips (l_c (nm)) of different films: unstretched, stretched at 115°C, 95°C, 75°C, and 65°C are summarized in the Table 1. The characteristic lines of these phases are respectively located at 2θ = 20.64°, 21.25°, 23.14°, 23.75°, and 23.80°, relating to diffractions of planes (100), (020), (110), and (110+200). From these results, we can underline that:

- The degree of crystallinity calculated from XRD analysis is comparable to that calculated from DSC analysis.
- The degree of crystallinity and the dimension of the apparent crystallites perpendicular to the planes (110) are highest for the stretched films compared to the non-stretched one. However, the thicknesses of the lamellae remain practically constant, except for the stretching temperatures at 115°C and 95°C, where they decrease. This shows that stretching causes the transition from phase II to phase I. Moreover, for films stretched at 115°C and 95°C, the morphology was modified while maintaining phase II orientation.

3-2. Thermal analysis:

PVDF1008	D_{110} (nm) (DRX)	χ_c (%) (DRX)	T_{f2} (°C)	T_{f1} (°C)	ΔH (J/g)	χ_c (%) (DSC)	l_c(nm), (DSC)	
							T_{f1} (°C)	T_{f2} (°C)
unstretched	23.67	48	173	166	50	48	9.86	6.41
Stretched at 115°C	7.35	54	172	165	58	56	9.15	6.11
Stretched at 95°C	7.36	53	171	167	53	51	8.55	6.75
Stretched at 75°C	7.35	52	173	-	53	51	9.86	-
Stretched at 65°C	7.38	53	173	-	54	52	9.86	-

Table 1 summarizes some results related to dimension of the crystallites D_{110} (nm), degree of crystallinity χ_c (%), melting temperature T_f (°C), melting enthalpy ΔH (J/g) and lamellae thickness l_c(nm) of different films (unstretched, stretched at 115°C, 95°C, 75°C and 65°C).

Table 1: Dimension of the crystallites D_{110}, degree of crystallinity χ_c, melting T_f , melting enthalpy and l_c.

The melting points and the melting enthalpy were measured by DSC (DSC131 Evo). The results for the PVDF films: unstretched, stretched at 115°C, 95°C, 75°C, and 65°C, are reported in Figure 2. From the DSC thermograms (Figure 2), we calculated the degree of crystallinity χ_c (%) and the thickness of the lamellae of the samples, l_c (nm), and compiled them in Table 1.

We note that:

- There is a splitting of the peak located between 166°C and 173°C, which evolves according to the stretching temperature, without changing its position. At low stretching temperatures, there is one melting peak showing the existence of the crystalline phase I. However, at 95°C and 115°C, the two melting peaks correspond respectively to a mixture of phases (II + I) and to phase II, based on the results of the X-rays.
- Phase I increases to the detriment of phase II when the stretching temperature decreases.
- The first peak melting temperature of the unstretched and stretched films at 95°C and 115°C, as well as the thickness of the crystalline lamellae, are the lowest compared to the other films stretched at 75°C and 65°C.
- The disappearance of small crystals during drawing at low temperatures leads to a reorganization of the crystals, which causes changes in the dimensions of the lamellae.

From these results, it can be seen that, for all samples, the degree of crystallinity in stretched films is slightly higher than in unstretched films. The increase in the degree of crystallinity can be explained by stretching, although there is uncertainty introduced because the ΔH value used for the calculation corresponds to the type II crystalline phase. This shows that during drawing at low temperatures, all small crystals and defects of the amorphous phase disappear. Recrystallization during drawing induces slight modifications in the thickness of the crystalline lamellae. It is evident that the degree of crystallinity in stretched PVDF film is higher than in non-stretched film, highlighting the significance of mechanical deformation. This indicates that stretching causes significant changes in the microstructure.

Furthermore, it is observed that the thickness of the lamellae (l_c) is practically the same for all samples, except for films stretched at high temperatures where the lamellae size decreases.

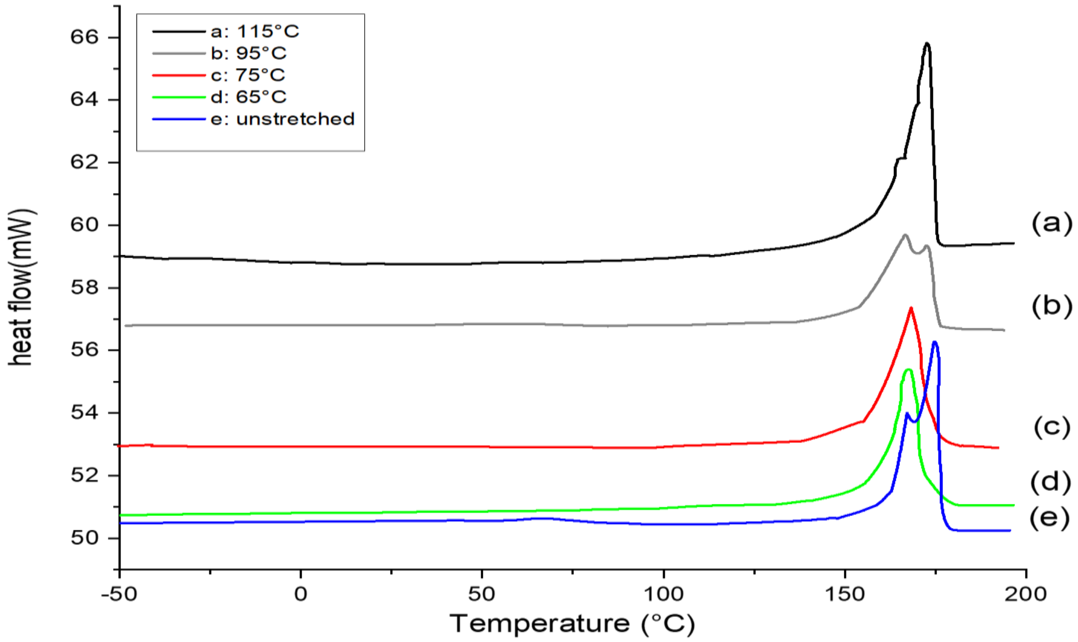

Figure 2: DSC thermograms of to the PVDF films: unstretched, stretched at 115°C, 95°C, 75°C and 65°C.

3-3. Dynamic analysis by dielectric spectrometry:

Figure 3 shows the permittivity (ε') and tan(δ) spectra obtained by dielectric spectrometry of the unstretched PVDF 1008 film. Compared to the non-stretched PVDF film, taken as a reference, we observe that at a frequency of 1 Hz, the variation of the loss peak located around -42°C is associated with a sudden increase in permittivity over several decades in magnitude, which corresponds to the glass transition of the amorphous part. This is attributed to the β relaxation.

The appearance of β relaxation occurs near -42°C, with β′ relaxation located around 13°C. We also observe the absence of α relaxation, which is attributed to the conduction phenomenon at high temperatures. This suggests the presence of impurities in the film.

The activation energy (E_{VTF} = 0.099 eV) and T_g = -42°C obtained by dielectric spectrometry are higher than those obtained by mechanical spectrometry (E_{VTF} = 0.082 eV) and T_g= -48°C. The dynamic glass transition was analyzed using the Vogel-Tamann-Fulcher relaxation formalism:

$$\tau = \tau_0 e^{\left(E_{VTF}/K(T-T_0)\right)} \tag{6}$$

The frequency dependence analysis yields the apparent activation energy E_{VTF} = 0.09885 eV and pre-exponential factor $\tau_0 = 5.99\times10^{-12}$ s. Comparing the results obtained for the same relaxation in phase II-PVDF ($\tau_0 = 1.2\times10^{-11}$ s and E_{VTF} = 0.088 eV), the critical temperature at which molecular motions in the material become infinitely slow is T_0 = 187.5 K. We observe an increase in the E_{VTF} energy and a decrease in the pre-exponential factor [28].

A relaxation near 80°C is associated with the α relaxation, which can be attributed to molecular motions within the crystalline phase. [27].

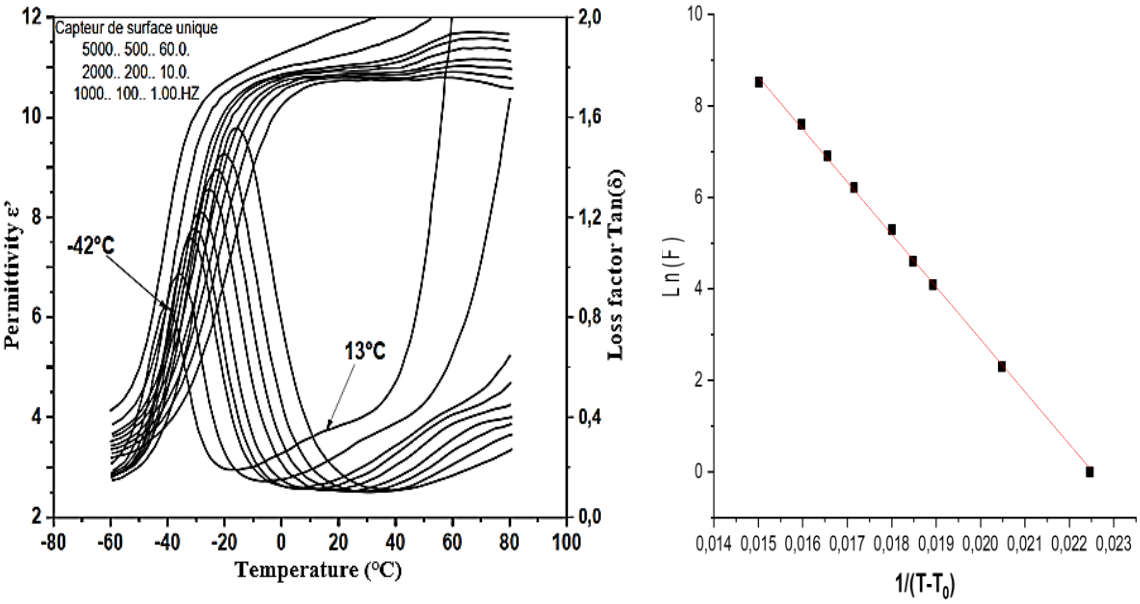

Figure 3: Dielectric permittivity measured for the phase II- PVDF between – 60°C and 80°C at several frequencies (left) and Vogel-Tammann-Fulcher fit of the β relaxation of PVDF phase II (right).

3-4. Dynamic shear modulus:

Multichronal (frequencies = 0.3 Hz, 1 Hz, and 10 Hz) curves displayed in Figures 4, 5, 6, 7, and 8 were obtained for each sample of the PVDF films: unstretched (a), stretched at 65°C (b), stretched at 75°C (c), stretched at 95°C (d), and stretched at 115°C (e).

A relaxation around -48°C is associated with a drastic drop in modulus over several decades in magnitude, corresponding to the glass transition of the amorphous phase; this is the β-relaxation. The frequency dependence analysis yields an apparent activation energy of 0.082 eV and a pre-exponential factor of 1.58×10^{-11} s. A similar relaxation process was observed. The α-relaxation observed near 84°C, is associated to molecular motions within the crystalline fraction.

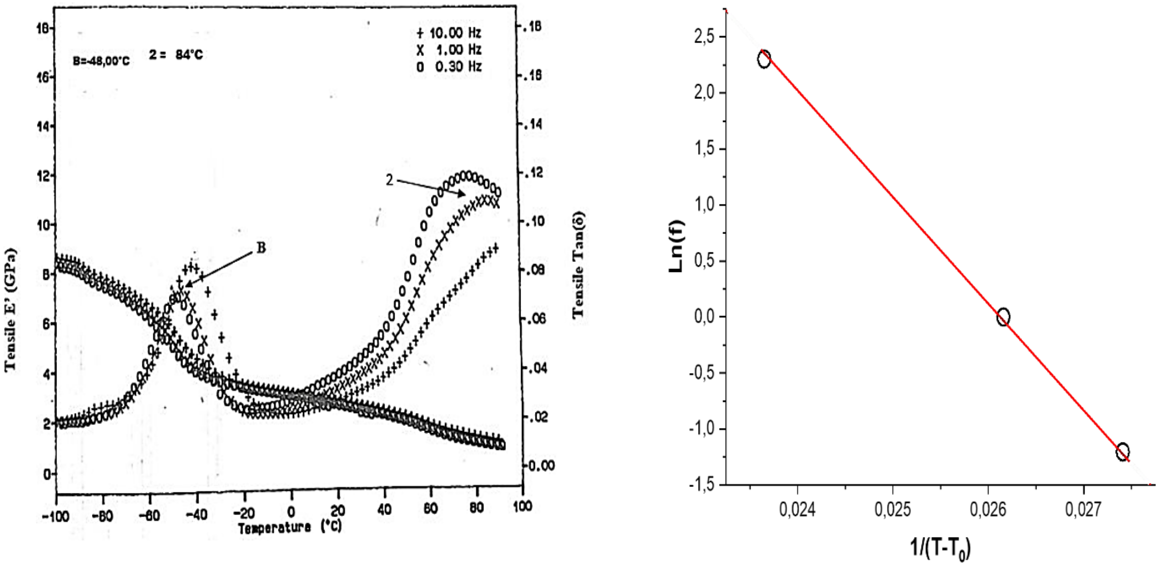

Figure 4: Dynamic shear modulus for the unstretched film between -100°C and 100°C at several frequencies (left) and Vogel-Tammann-Fulcher fit of the β relaxation of PVDF phase II (right).

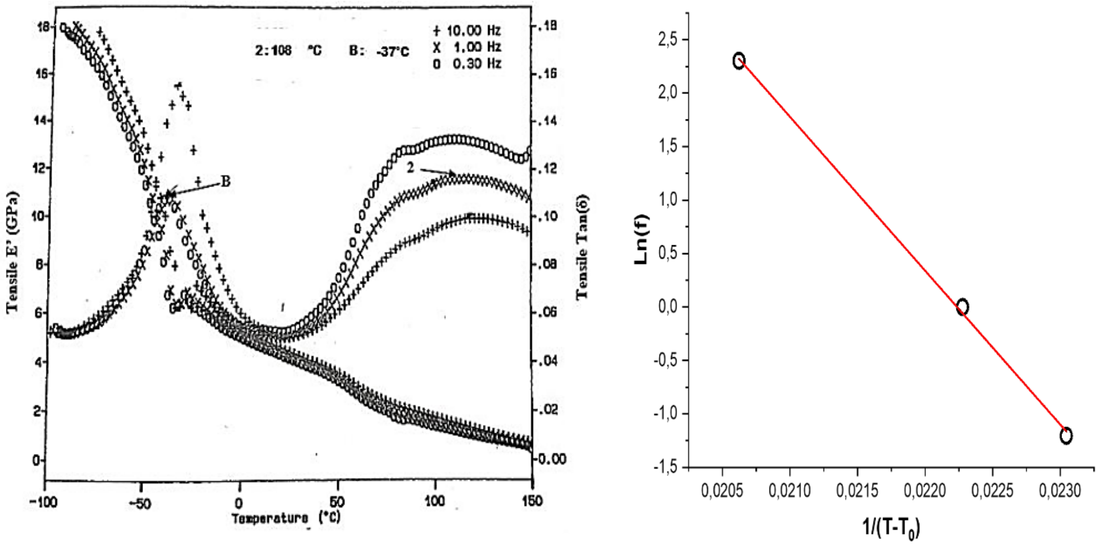

Figure 5: Dynamic shear modulus for the stretched film at 65°C between -100°C and 150°C at several frequencies (left) and Vogel-Tammann-Fulcher fit of the β relaxation of PVDF phase II (right).

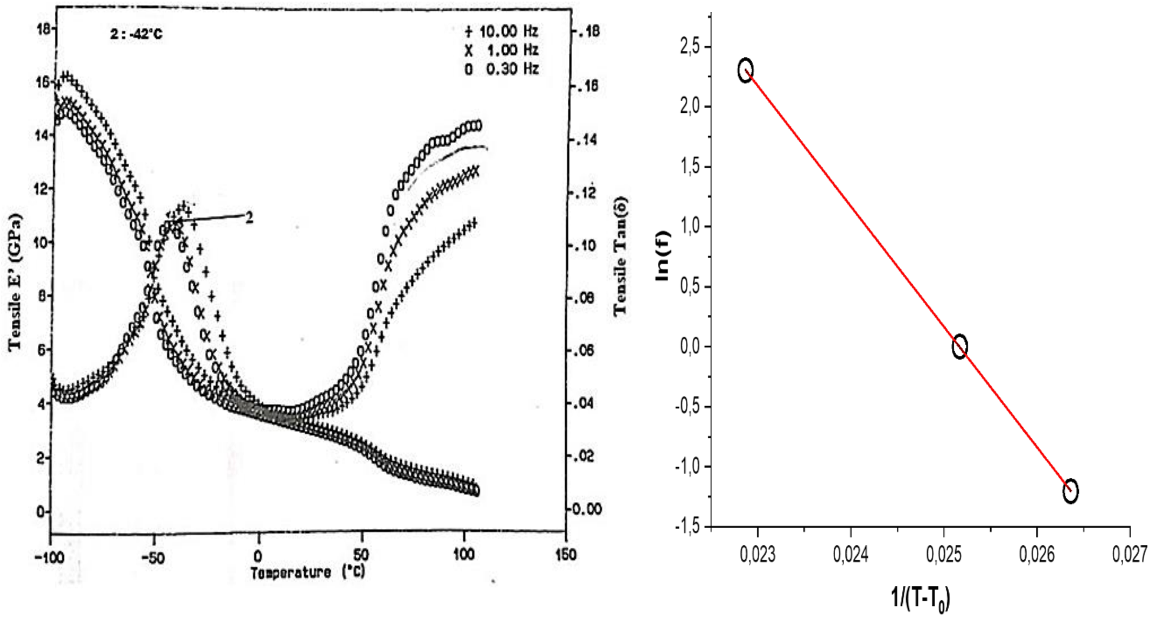

Figure 6: Dynamic shear modulus for the film stretched at 75°C between -100°C and 150°C at several frequencies (left) and Vogel-Tammann-Fulcher fit of the β relaxation of PVDF phase II (right).

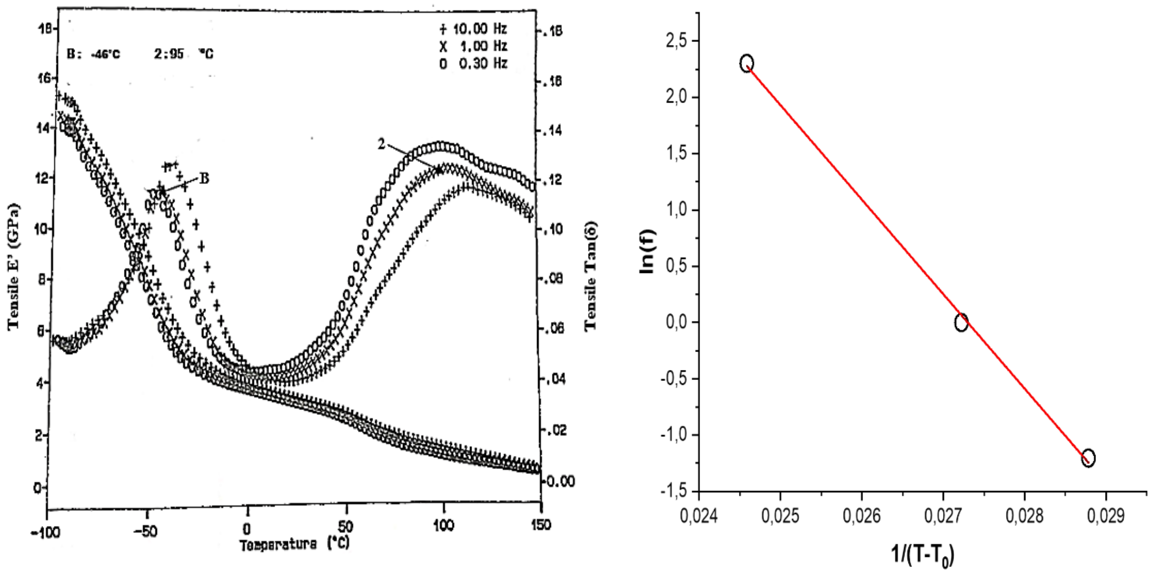

Figure 7: Dynamic shear modulus for the film stretched at 95°C between -100°C and 150°C at several frequencies (left) and Vogel-Tammann-Fulcher fit of the β relaxation of PVDF phase II (right).

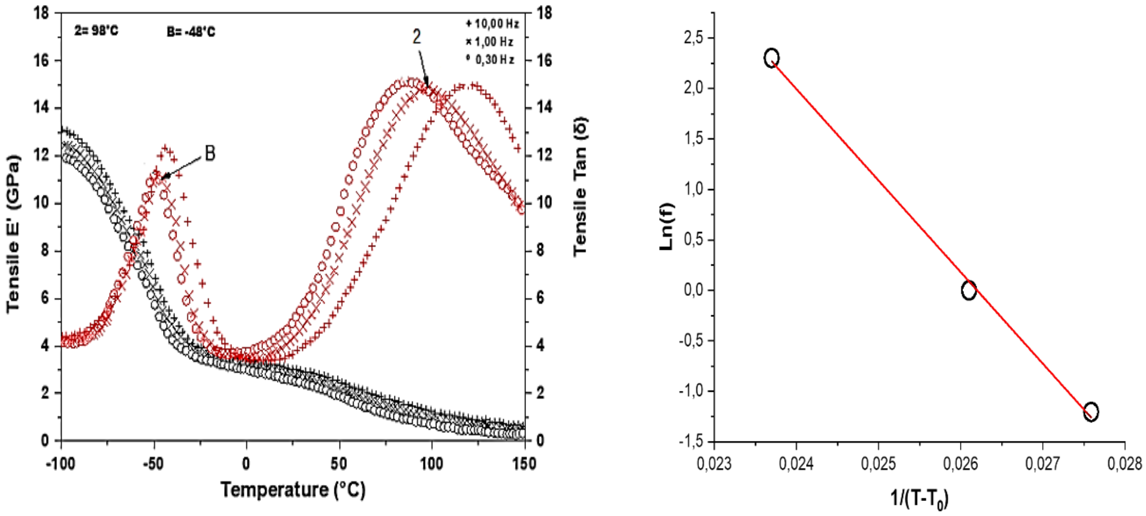

Figure 8: Dynamic shear modulus for the stretched at 115°C between -100°C and 150°C at several frequencies (left) and Vogel-Tammann-Fulcher fit of the β relaxation of PVDF phase II (right).

A consequence of the values of the adjustment parameters of the VTF relaxation plot is the calculation of the brittleness parameter [24]:

$$m = \frac{E_{VTF}/_{KT_g}}{(ln\,10)(1-{}^{T_0}/_{T_g})^2} \tag{7}$$

where “m” is an indication of the slope of variation of the properties of the material (viscosity, relaxation time....) when the T_g is reached.

A high m value defines a brittle material while a strong one will be characterized by small m values. The values of several glassy amorphous polymers range from 46 (polyisobutylene) to 191 (polyvinyl chloride), the m(T_g) value with VTF parameters for PVDF II is 92 determined at the glass transition temperature where the relaxation time is equal to 100s. The value for PVDF II is 87 [29].

The fragility parameters of PVDF II and I are very similar. This demonstrates that only the amorphous part of the material is involved in the relaxation process. The brittleness parameter indicates that PVDF is not a very brittle material compared to the polymers analyzed. The low brittleness may be associated with the semi-crystalline nature of this polymer [30].

According to Table 2, we observe that:

- The relaxation times (τ) decrease as the activation energy (E_{VTF}) increases.
- The activation energy (E_{VTF}) increases for films stretched at 65°C compared to the unstretched film, and decreases for films stretched at 95°C and 115°C. For phase II, the The values of $E_{VTF} = 0.088$ eV and $\tau = 1.12\times10^{-11}$ s [29] are comparable to our results for unstretched PVDF 1008. On the other hand, for phase I, the value of $E_{VTF} = 0.061$ eV decreases and the relaxation time $\tau = 0.58\times10^{-11}$ s increases [31] compared to PVDF stretched at 65°C. This indicates that the microstructure of the amorphous phase has changed due to plastic deformation.
- The glass transition temperature (T_g) of the stretched films is higher than that of the unstretched films, except for the film stretched at 115°C, because the latter crystallizes in phase II.
- The values of the fragility parameters (m) calculated at T_g according to relationship (2) vary between 65 and 79. According to S. Lanceros-Mendez et al. [31], the values of m(T_g) for PVDF I and PVDF II are 92 and 87, respectively, which are slightly higher than our results for PVDF 1008 stretched at 65°C and unstretched (m(T_g) = 79). This shows that β relaxation occurs in the amorphous phase. Subsequent stretching of the plastic induces a complete reorientation of the crystal lamellae.
- Morphological changes in semi-crystalline polymers during the application of stress have been studied by Flory [34] and Takahashi et al. [32], who proposed that plastic deformation occurs through melting and recrystallization of the crystalline phase present in the semi-crystalline polymer. This model has been used to explain a local 90° reorientation of polymer segments in the crystal structure of PVDF [33], as observed by creep and stress-strain experiments.

Table 2: The relaxation times (τ), the activation energy (E_{VTF}), The glass transition temperature (Tg), and the fragility parameter~~s~~ of different films: unstretched, stretched at 115°C, 95°C, 75°C and 65°C.

PVDF	**τ (s)**	**E_{VTF} (eV)**	**Tg (°C)** (at 1Hz)	**m**
Unstretched *(Dielectric spectroscopy)*	5.99×10^{-12}	0.099	-42	73
Unstretched *(Mechanical spectroscopy)*	1.58×10^{-11}	0.082	-48	79
stretched at 65°C	1.26×10^{-14}	0.124	-37	79
stretched at 75°C	1.08×10^{-11}	0.086	-42	65
stretched at 95°C	1.11×10^{-10}	0.074	-46	66
stretched at 115°C	1.31×10^{-10}	0.078	-48	75

4. CONCLUSION

Films of semi-crystalline poly (vinylidene fluoride) (PVDF) in phases II and I have been studied using Dielectric, Dynamic Mechanical Spectroscopy, and Differential Scanning Calorimetry measurements, in conjunction with X-ray diffraction (XRD). Notably, modifications occurring during the deformation process have been observed. Differential Scanning Calorimetry measurements reveal the structural changes that take place in the crystalline phase during stretching at various temperatures. The reorientation of chains and an increase in the degree of crystallinity were observed with stretching at different temperatures.

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