

The Effect of Uniaxial Orientation on the Dielectric Relaxation Behavior of α -PVDF

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ABSTRACT: α -crystalline phase poly(vinylidene fluoride) (PVDF) film was oriented uniaxially at different draw ratios. Morphological effects of orientation were investigated by X-ray diffraction and differential scanning calorimetry (DSC) measurements on the oriented samples. The dielectric loss factor was measured from 100 Hz to 1 MHz range between 80 and 400 K as a function of frequency and temperature. While the activation energy of the α -relaxation transition was not affected by the orientation, it

was observed that there is a linear increase in the activation energy of the β -relaxation transition with draw ratio. The relaxation time of the β -relaxation transition was more affected by the orientation process at lower temperatures. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3878–3886, 2008

Key words: poly(vinylidene fluoride); orientation; dielectric loss factor; dielectric relaxation; activation energy

INTRODUCTION

PVDF, a semicrystalline and thermoplastic polymer, is used in many technological applications such as capacitor dielectrics and transducer materials. Piezoelectric polymers offer some advantages over ceramic piezoelectric materials. Since the piezoelectric polymers have low acoustic and mechanical impedance, they are widely used in medical and underwater systems. PVDF is a very important material, due to its piezoelectric and pyroelectric characteristics when appropriately oriented.^{1–10} PVDF has four different crystalline modifications (α , β , γ , and δ).^{7–15} The most common and most studied of these crystalline modifications are the α - and β -phases. The α -phase is obtained by melt crystallization at temperatures below 160°C.^{2,7,8,11,13,14} The β -phase can be obtained through mechanical drawing α phase films.^{2,7–11,13–15} The γ -phase may be produced by crystallization from the melt at high pressure or by crystallization from certain solutions such as dimethylacetamide and dimethylsulfoxide.^{7,8,11,13,15} The δ -phase can be obtained by poling the α -phase at high electric fields.^{7–9,11,13,15} The β -phase, which has a planar zig-zag structure, has a much higher dipole moment compared to α -phase. Hence, the β -phase shows piezoelectric characteristics. Since PVDF involves fluorine atoms with high electronegativity,

it has high electric dipole. Therefore, motion of the molecules, which have been excited by electric field and heat, can be analyzed through dielectric measurements.^{4,10}

The molecular chains, which are entangled, are rearranged along the draw axes and hence, the polymer shows anisotropic physical behavior.^{16–18} In some polymers the orientation occurs during the polymerization process. However, in general the polymers are oriented by using various deformation methods. The most common of these are, uniaxial or biaxial drawing and rolling.^{17–20}

The alignment of molecular dipoles in the field direction cannot take place instantaneously when an electric field is applied. This situation is similar to the strain, which takes time to develop after the application of a stress. The dielectric properties and the dielectric relaxation behavior of polymers are directly affected by their molecular structure and morphology. Thus, research related to dielectric properties are frequently used in the study of molecular dynamics of polymers. Another reason for the use of this technique in studying dipolar polymers is that the dielectric measurement allows the analysis over wider range of frequency (10^{-4} Hz to 10^{14} Hz) than mechanical measurements.^{17,19,21}

The dielectric relaxation behavior of PVDF has been studied by many researchers using different techniques. Thermostimulated depolarization current measurements (TSD), thermostimulated current spectroscopy measurements (TSC), and dielectric measurements (DEA) can be given as examples.^{3,10,12,22–25}

Similar to other semicrystalline polymers, when the results of the relaxation studies of PVDF are

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analyzed, a number of relaxation processes (α , β , and γ) have been observed. The α -relaxation transition is related to thermal movement processes near the crystalline melting point. The β -relaxation transition is due to micro-Brownian motions of the linear chain segments close to the glass transition temperature. The γ -relaxation transition results from thermally-activated local molecular oscillations in the amorphous phase.^{10,12,21,22,26–29}

In this study, changing of morphological and dielectric properties with the draw ratio in α -crystalline phase PVDF was investigated. The drawing process was performed under the conditions, where no β -crystalline phase development existed. Hence, the oriented samples, which are in α -crystalline phase, were obtained. Morphological effects of the drawing process were investigated by X-ray and DSC measurements, and its effect on the dielectric relaxation behavior was investigated by the dielectric measurements as a function of temperature and frequency. There are many studies about dielectric properties of PVDF. On the contrary, for the oriented PVDF samples which only α -crystalline phase is dominant, studies that investigate the change of dielectric properties depending on draw ratio are very limited.

EXPERIMENTAL

Materials

Unoriented PVDF (FV 301460) films with dimensions of $300 \times 300 \times 0.8 \text{ mm}^3$ and a density of 1.76 g/cm^3 supplied by Goodfellow (Cambridgeshire, England), were used. The unoriented film in the α -crystalline phase is shown by DSC and X-ray diffraction measurements in a previous paper.²⁹ Drawing samples with the size of $200 \times 20 \times 0.8 \text{ mm}^3$ were cut from the main sample. The drawing process was performed in a specially designed cell heated by hot air and then, was repeated many times to determine the optimum drawing temperature. This temperature was determined as 155°C , at which the drawing process can be performed without yielding, and the β -crystalline phase did not develop. The temperature accuracy was $\pm 1^\circ\text{C}$. The drawing process was performed at a constant speed of 0.005 mm/s for 70 min.

To measure the draw ratios, prior to the orientation process a grid patterned serigraphic print with 1-mm interval was printed on the sample. From this oriented sample, three samples of 6-mm diameter with different draw ratios ($\lambda = 1.46$, $\lambda = 1.93$, and $\lambda = 2.5$) were taken. Then, the samples were mechanically smoothed with emery paper. Nonparallelism along the diameters between the surfaces of these samples was about $\pm 0.003 \text{ mm}$.

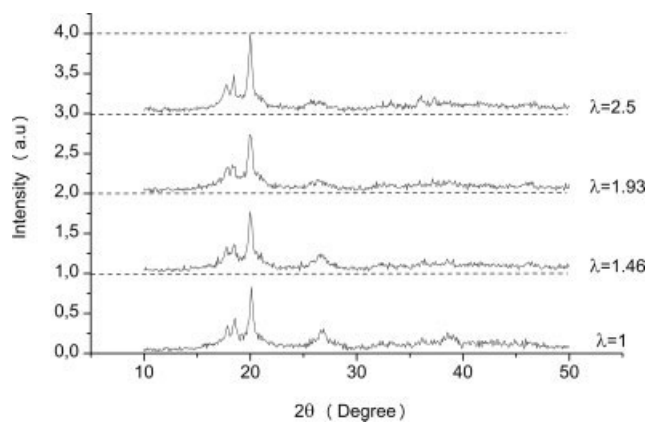


Figure 1 X-ray diffraction patterns of PVDF samples for different draw ratios.

Measurements

X-ray diffraction measurements were performed using RIGAKU D-max 2200 Diffractometer with $\text{Cu K}\alpha$ radiation on the oriented and unoriented PVDF samples.

Differential scanning calorimetry measurements (DSC6-Perkin-Elmer) were carried out between 220 and 400 K at a heating rate of 10 K/min. The surfaces of the samples were covered with silver paste to form electrodes. The dielectric measurements were performed between 100 Hz and 1 MHz frequency range at different temperatures by using a LCR meter (Agilent 4284A). The temperatures, ranging between 80 and 400 K, were controlled by using a liquid nitrogen cryostat (Oxford-ITC 502).

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction peaks for PVDF samples having different draw ratios.

To compare the positions of the diffraction peaks, the diffraction intensities of each sample were normalized to one. Therefore, all of the diffraction intensities were divided by the greatest of these intensities and the diffraction peaks for each oriented sample shifted by 1 U on the axis. As can be seen in Figure 1, it was observed that the peak intensities were changed depending on the draw ratio. For example, at high draw ratios, peak intensities of the crystal planes (100), (020), (110), and (200) increase, while at low draw ratios peak intensities of the crystal planes (120), (021), and (111) decrease (Fig. 2). The increase in the degree of crystallinity with orientation will affect the number of crystal planes. Hence, the peak intensities will change with draw ratio.

It is known that some crystalline polymers transform from one phase to another under stress and deformation.^{2,4,7–11,14,15} When the α -PVDF film is

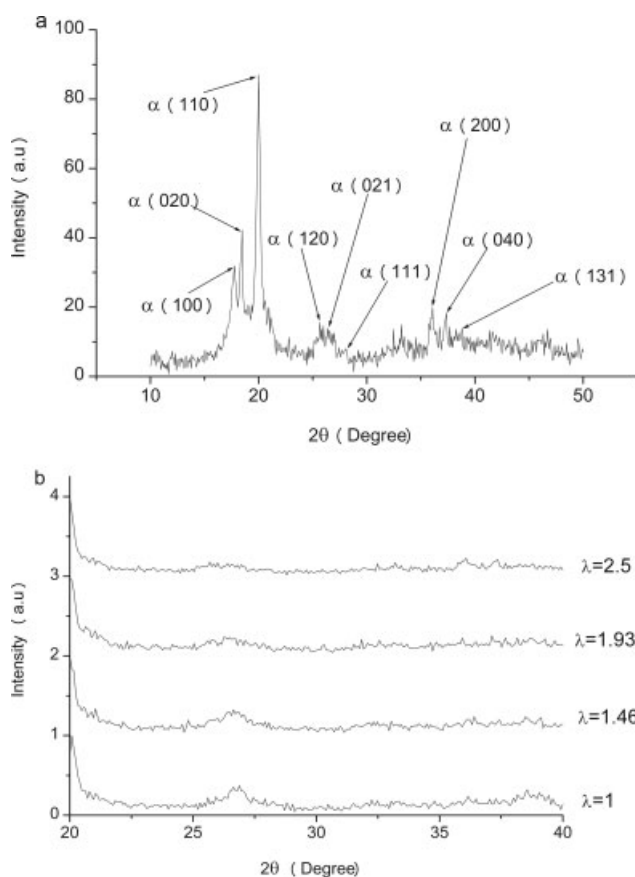


Figure 2 (a) X-ray diffraction patterns of unoriented PVDF sample, (b) X-ray diffraction patterns of PVDF samples having different draw ratios for the 2θ range between 20° and 40° .

drawn at temperatures lower than 100°C , transformation from α -phase into the β -phase occurs for draw ratios 3 or 4.^{8,14} At higher drawing temperatures (above 120°C), conversion of the α in to the β -phase more decreases.^{2,4,8,14,15} However, at high temperatures, the β -phase appears for draw ratios higher than 5.^{2,14}

For the unoriented PVDF, the diffraction peaks were observed at degrees 2θ 17.84, 18.41, 20.08, 25.76, 26.64, 27.92, 36.16, 37.28, 38.56 [Fig. 2(a)].^{6,30–32} These peaks belong to orthorhombic α -PVDF which has lattice constants of $a = 4.96 \text{ \AA}$, $b = 9.64 \text{ \AA}$, $c = 4.62 \text{ \AA}$.^{5,13,33}

If the β -crystalline phase had appeared by drawing processes, new diffraction peaks would have been observed at degrees 2θ between 20 and 21 and between 36 and 37.^{30–32} As seen in Figure 2(b), these peaks which belong to β -crystalline phase were not observed for the oriented samples. Therefore, it can be said that the samples oriented at 155°C are still in the α -crystalline phase.

As the β -crystalline phase is negligible, the definition "relative crystallinity" was used instead of "apparent crystallinity" for the level of crystallinity.

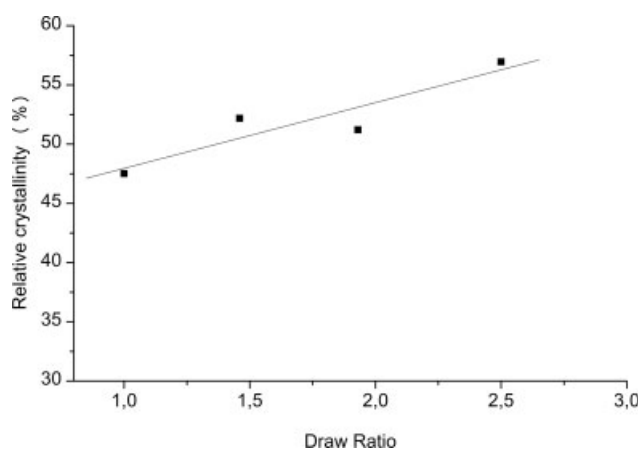


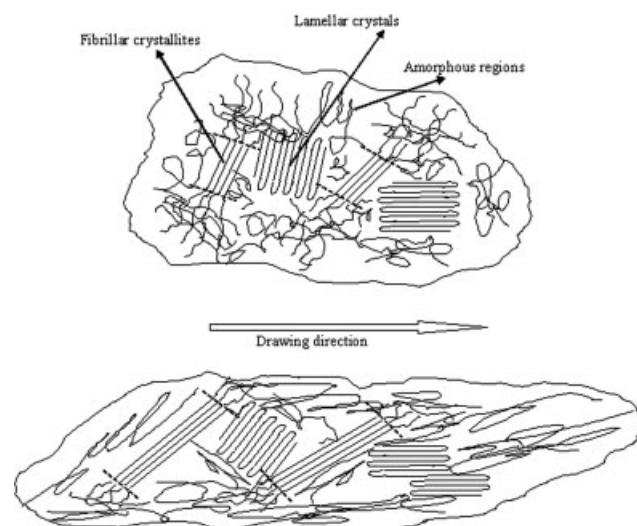
Figure 3 Relative crystallinity versus draw ratio.

In this manner, the degree of crystallinity was calculated by dividing the area formed by crystalline peaks by the total area. This method is often used to quantitatively compare the degrees of crystallinity.^{19,34} Figure 3 shows variation of the relative crystallinity with the draw ratio.

As can be seen in Figure 3, the degree of crystallinity increases linearly with the draw ratio. Some of the tie molecule chains which has overflowed from fibrillar crystallites between fibrillar crystalline and amorphous phases became a part of the crystalline regions by drawing process and hence, the degree of crystallinity increased.

The proposed morphological change in the samples with the drawing process is shown in Scheme 1.

Figure 4 shows DSC thermograms for the oriented and unoriented samples. Note that, the heat flow is given per unit mass.



Scheme 1 A schematic presentation for the effect of drawing on the morphology.

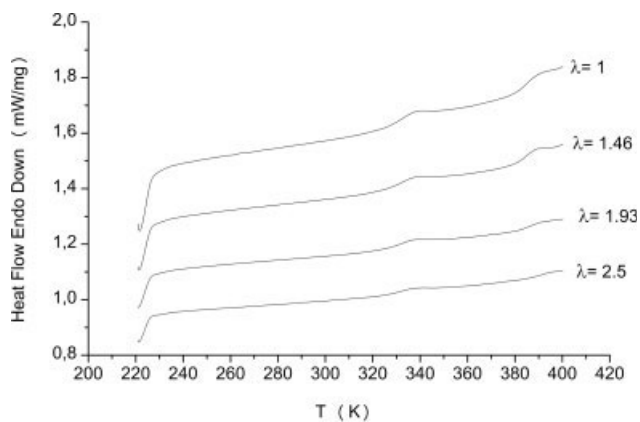


Figure 4 DSC thermograms of PVDF at different draw ratios (heating rate 10 K/min).

DSC thermograms show that the magnitude of c_p step, observed approximately at 340 K, decreases with the draw ratio. This step is due to the secondary glass transition, which is observed in some semi-crystalline polymers, and is defined as the upper glass transition $T_g(U)$. This transition is attributed to the rotational and translational motions of the tie molecules in the crystalline–amorphous interphase.^{1,3,23,29} The decrease in the magnitude of the c_p step with the draw ratio indicates that the number of mobilizable tie molecules in the crystalline–amorphous interphase decreased with drawing. This observation also confirms the morphological change given in Scheme 1.

The c_p step that occurred approximately at 390 K, is a consequence of rotational and translational motions of segments of polymer chains in the crystalline regions. Several researchers consider these motions as the beginning of the melting process. That is why this step is sometimes called a premelting crystalline transition.^{1,12,35} As seen in Figure 4, the magnitude of this step decreases with the draw ratio. It is difficult to explain this decrease with the rotational and translational motions of segments of polymer chains in the crystalline regions, because the specific volume did not change in the crystalline region after orientation. If there had been any change in volume, a new crystalline phase should have appeared. Therefore, only a specific volume change can be considered between amorphous fraction and crystalline–amorphous interface with orientation. Thus, the decrease in this step can be attributed to the restriction of the movements of the molecule chains in the surface of crystal lamellae next to amorphous phase.

In Figure 5, variation of the absorbed heat energy from the samples, given per unit mass, with draw ratio for two different temperatures (293 and 373 K) is shown. These temperatures were especially

selected in the two different regions where there is no transition in the DSC thermograms. Note that the heat energy absorbed from the system decreases with draw ratio.

As a result of the orientation of the molecular chains in the amorphous phase the local free volume decreases and hence, the specific volume decreases. A decrease in the specific volume restricts the capability of the thermal mobility of the molecule chains. For this reason, the absorbed energy is lower.

In Figure 6, variation of the dielectric loss factor ($\tan \delta$) with temperature for PVDF samples having $\lambda = 1$ and $\lambda = 2.5$ draw ratios at different frequencies is presented.

Two relaxation transitions (α and β), which shifted toward high temperatures due to the increase in the frequency, were observed as expected.³⁶ It is known that, the α -relaxation transition is the result of rotational and translational motions of the molecules in the crystalline regions, whereas the β -relaxation transition belongs to the glass transition of the amorphous fraction.^{3,10,12,22,23,27,29}

While the dielectric loss factor in the β -relaxation transition is not affected by orientation, the dielectric loss factor in the α -relaxation transition decreases systematically with orientation (Fig. 7).

The decrease seen during the α -relaxation transition is due to more decrease with the drawing process in the total number of the dipole groups which can move easily in the external field. Because, mobility of the dipole groups which are located on the chain segments in the fringes of fibrillar crystallites and on parts of the crystal lamellae near the amorphous regions decreased.

In Figure 8, variation of the dielectric loss factor with frequency for the PVDF samples having different draw ratios at two different temperatures is presented. The maximums observed at 400 and 240 K belong to α - and β -relaxation transitions, respec-

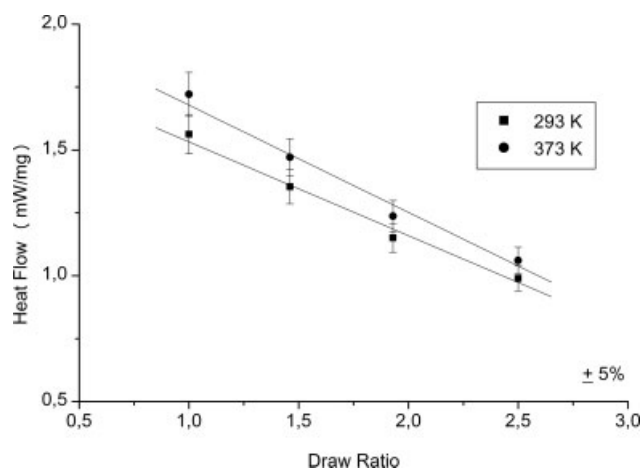


Figure 5 Heat flow versus draw ratio.

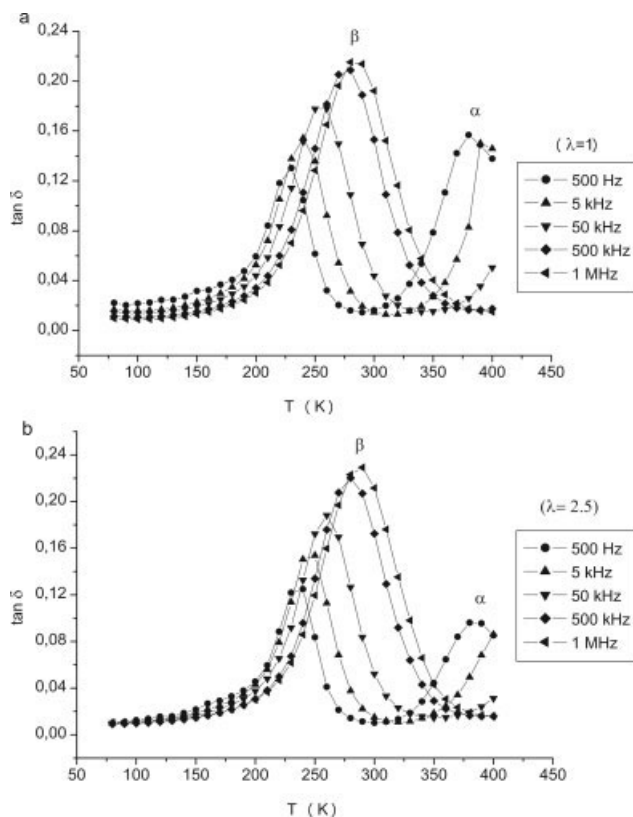


Figure 6 Dielectric loss factor for PVDF versus temperature at different frequencies: (a) $\lambda = 1$ and, (b) $\lambda = 2.5$.

tively. As seen in Figure 8, the dielectric loss factor of the α -relaxation transition is more affected by the drawing process compared to β -relaxation transition.

Figure 9(a) and (b) show the variation of the maximum value of the dielectric loss factor with the draw ratio at selected frequencies for the β - and α -relaxation transitions, respectively.

It is known that the dielectric loss factor is maximum during the transition.^{21,36,37} However, it is important whether the variations of this maximum

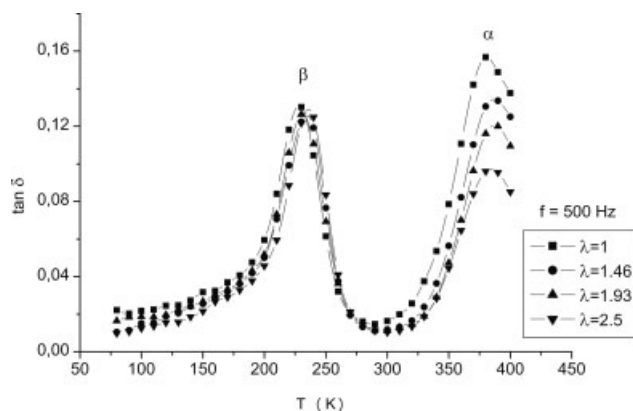


Figure 7 Dielectric loss factor for PVDF having different draw ratios versus temperature for 500 Hz.

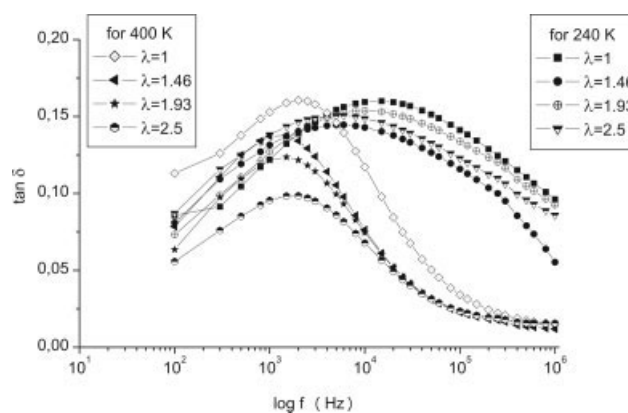


Figure 8 Dielectric loss factor for PVDF having different draw ratios versus frequency at different temperatures.

value according to draw ratio are random or not. As can be seen in Figure 9(a), the peak intensity of the loss factor with the draw ratio is almost invariable for the β -relaxation transition. In other words, the energy that is lost during the β -relaxation transition

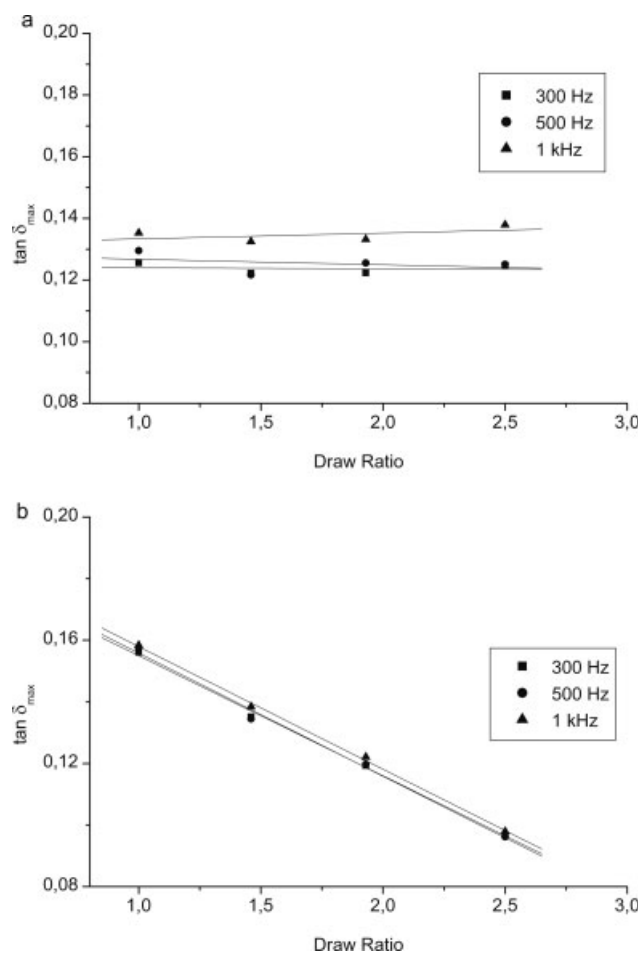


Figure 9 Maximum values of dielectric loss factor versus draw ratio: (a) for β -relaxation transition and, (b) for α -relaxation transition.

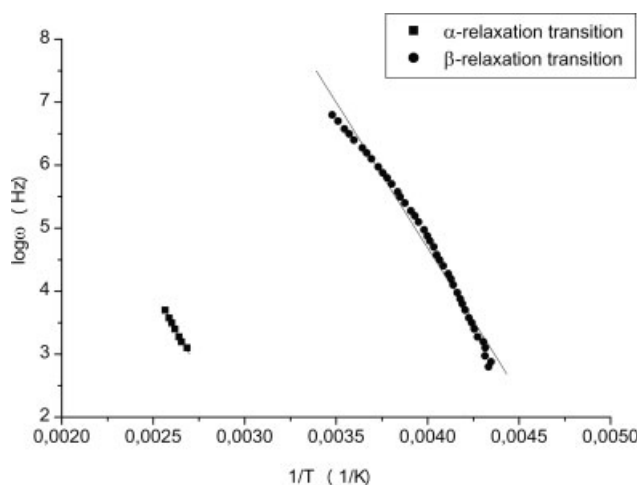


Figure 10 Arrhenius plots of the logarithm of the angular frequency ω versus $1/T$ for PVDF having $\lambda = 2.5$ draw ratio.

is not affected by the orientation at all for all PVDF samples. This relaxation transition is effectively caused by the glass transition in the amorphous fraction. The fact that the dielectric loss observed during this transition is not affected by the drawing process shows that the number of the dipole groups which can rotate under external field in the amorphous region does not change significantly. As the tie molecules in the crystalline–amorphous interphase became a part of the crystalline regions, the degree of crystallinity increased. When the tie molecules are in the amorphous phase (unoriented situation), their contribution to β -relaxation transition is negligible. The decrease in the dielectric loss is then also negligible when these molecules enter the crystalline phase. In the α -relaxation transition, however, the loss factor decreased linearly with the draw ratio, as discussed before [Fig. 9(b)].

Figure 10 shows the plot of the logarithm of the angular frequency ω versus $1/T$ for α - and β -relaxation transitions of PVDF having $\lambda = 2.5$ draw ratio according to the Arrhenius equation.

Although the α -relaxation process shows a linear variation, the β -relaxation transition process does not. The fact that α -relaxation transition can only be observed in a very small temperature range may cause doubts about the linear change. The dielectric measurements could not be performed at higher temperatures since at higher temperatures the samples return to their unoriented stage. Both the linearity of the obtainable results and the linear Arrhenius plot of this transition, known from past studies, remove this doubt.^{10,12,19}

The relaxation time for the α -relaxation transition is given in the Arrhenius equation as follows,

$$\tau = \tau_0 e^{\Delta U/kT} \quad (1)$$

where τ_0 is a constant, ΔU is activation energy, and k is Boltzmann's constant ($k = 86.1321 \mu\text{eV K}^{-1}$).

The reason why the β -relaxation transition does not obey the Arrhenius relationship is because, the micro-Brownian translational and rotational motions of many of the chain segments, which leads to a distribution of relaxation times; hence, the existence of different relaxation temperatures. For this relaxation, the Vogel-Fulcher-Tamman-Hesse (VFTH) equation was used;

$$\tau = \tau_0 e^{\frac{C}{T-T_0}} \quad (2)$$

where C and τ_0 are constants. T_0 , named as standard temperature, is given by $T_0 \approx T_g - 50$ K relationship.^{10,19,21,38–40} Thus, T_0 was found ~ 170 K.

When the constant C in eq. (2) is multiplied by the Boltzmann's constant, the result has dimension of energy; it is defined as the activation energy of the β -relaxation. In this case, the VFTH equation can be given as in eq. (3), in the form of eq. (1).

$$\tau = \tau_0 e^{\frac{kC}{T-T_0}} \quad (3)$$

Figure 11 shows the plot of the logarithm of the angular frequency ω versus $1/(T-170)$ based on eq. (3) for the sample oriented at 2.5 draw ratio. The variation now is quite linear.

For all the samples, activation energy values of the α - and β -relaxation transitions are given in Table I.

The change in the activation energies of the α - and β -relaxation transitions with the draw ratio are presented in Figures 12 and 13, respectively.

The activation energy of the α -relaxation transition is almost invariable with draw ratio (Fig. 12). Hence, it can be said that the crystalline regions were not

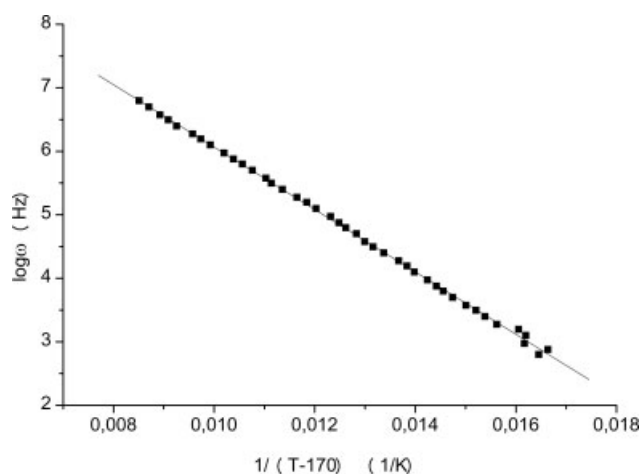


Figure 11 VFTH plots of the logarithm of the angular frequency ω versus $1/(T - T_0)$ for β -relaxation transition of PVDF having $\lambda = 2.5$ draw ratio.

TABLE I
Activation Energies for α - and β -Relaxation Transitions, Respectively

λ	Activation energy of β -relaxation (eV)		Activation energy of α -relaxation (eV)	
	This work	Literature	This work	Literature
1	0.075	0.096 (Ref. 10)	1.026	0.928 (Ref. 18)
1.46	0.090	–	1.063	–
1.93	0.082	–	1.002	–
2.5	0.097	–	1.027	–

affected by the drawing processes. However, the crystalline regions oriented along the drawing direction and the distance between the lamellae decreased with the drawing process. The number of rotatable dipole groups, which are located above the lamellar surfaces and chain segments of the fibrillar crystallites near the amorphous region decreased because of the amorphous orientation (Scheme 1). Because of this decrease, $\tan \delta_{\max}$ also decreased linearly with the draw ratio for the α -relaxation transition [Fig. 9(b)].

As can be seen in Figure 13, as a result of smaller local free volume revising in the region among chain segments in the amorphous phase due to orientation, the activation energy of the β -relaxation transition tends to increase with the draw ratio.

If the orientation process had been performed at lower temperatures with higher draw ratios, a clear variation in the energy values of the α -relaxation transition would have been observed due to development of the β -crystalline phase. Since the aim of this study was to investigate the relaxation behavior of α -PVDF, the temperatures were selected so that the β -crystalline phase did not occur.

In Figure 14, the circle diagram (Cole-Cole plot) for 250 K is shown. This temperature (250 K) was

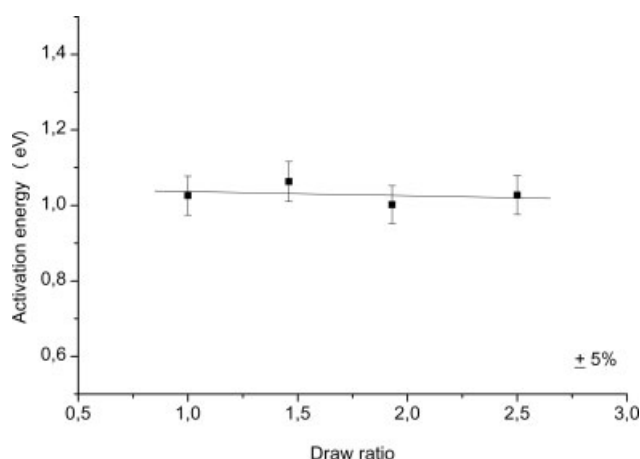


Figure 12 Activation energy versus draw ratio for α -relaxation transition.

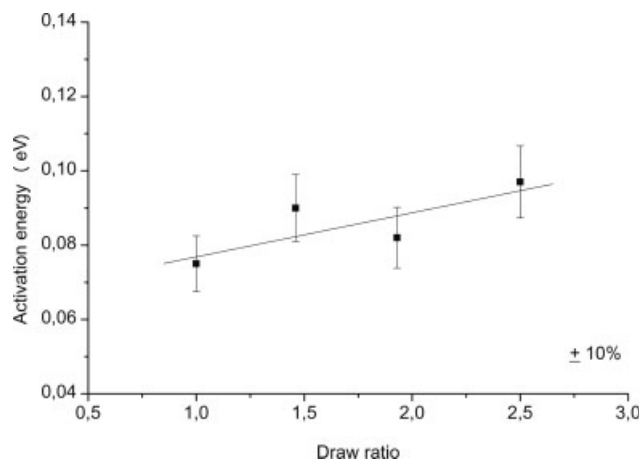


Figure 13 Activation energy versus draw ratio for β -relaxation transition.

selected from a small set of temperatures at which a semicircle can be seen.

To obtain the relaxation time τ , the static dielectric constants ϵ_0 for all PVDF samples were determined at different temperatures, as illustrated in Figure 14. The values of ϵ_0 for different temperatures are given in Table II.

In this manner, the relaxation time can be calculated by using the equation below [eq. (4)];

$$\left| \frac{\epsilon' - \epsilon_0}{\epsilon''} \right| = \omega\tau \quad (4)$$

where ϵ' and ϵ'' are the real and imaginary parts of complex dielectric constant at the definite ω frequency, respectively.^{19,37,41}

Figure 15 shows variation of the relaxation times, calculated from eq. (4) for 500 Hz, with temperature

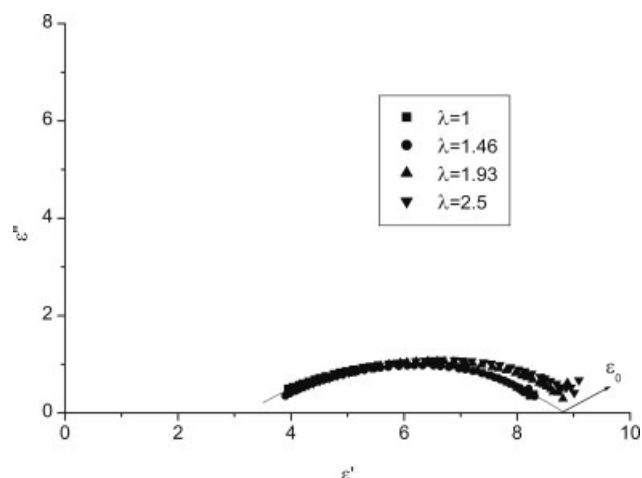


Figure 14 Argand complex plane plots of $\epsilon'' - \epsilon'$ for PVDF samples at different draw ratios during the β -relaxation transition at 250 K. The fit is for the Cole-Cole function.

TABLE II
 ϵ_0 Values for Different Temperatures

λ	T(K)								
	200	210	220	230	240	250	260	270	280
1	8.89	8.87	8.85	8.82	8.98	8.58	8.68	8.74	8.78
1.46	9.21	9.17	9.11	9.08	9.27	8.77	8.75	8.90	8.96
1.93	9.48	9.46	9.44	9.40	9.59	9.15	9.27	9.33	9.39
2.5	9.97	9.93	9.89	9.85	9.98	9.69	9.60	9.70	9.80

of the β -relaxation transition for different draw ratios.

The temperature range was selected between 200 and 300 K because the error in determination of ϵ_0 is minimum in this temperature region. As can be seen in Figure 15, the exponential decrease in the relaxation time with temperature for all oriented samples is an expected result according to eq. (3).^{36,37}

An increase in the temperature affects the relaxation time in two ways. The first is an increase in the thermal motion and the second is an increase in the free volume. The increases in thermal mobility and specific volume reduce the time needed for the relaxation of dipoles. The observed variation for a certain draw ratio, shown in Figure 15, is the combined result of these two effects. However, the samples having different draw ratios show different temperature dependence. These different dependencies prove that the orientation affects the relaxation time.

When the external electric field is turned off, the relaxation of the dipoles becomes much more difficult, and the time needed for the relaxation of dipoles increases, since the orientation reduces the specific volume.²¹ This case is clearly shown in Figure 16. Also in Figure 16, the dependence of the relaxation time on the draw ratio is greater at low temperatures. This can be explained by the fact that the free volume decreases more rapidly with the increase in draw ratio at low temperatures.

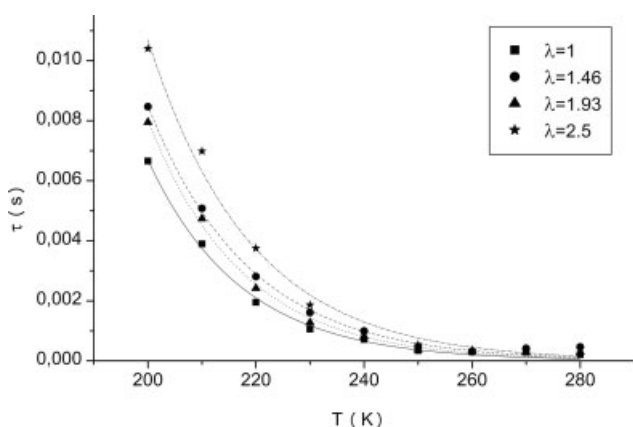


Figure 15 β -relaxation times versus temperature for PVDF samples having different draw ratios for 500 Hz.

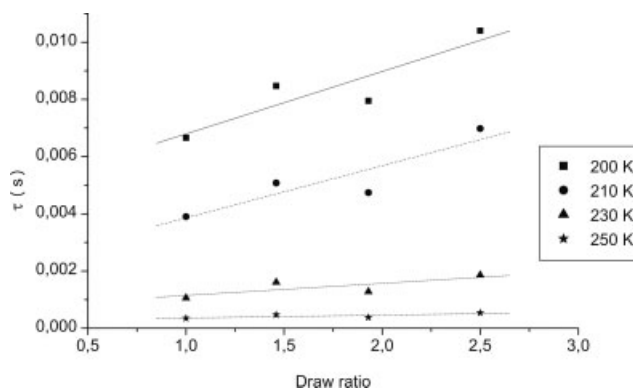


Figure 16 Relaxation time versus draw ratio for β -relaxation transition at different temperatures.

CONCLUSIONS

α -crystalline phase poly(vinylidene fluoride) (PVDF) film was oriented uniaxially at different draw ratios. Morphological effects of orientation and its effect on the dielectric relaxation behavior were investigated by X-ray diffraction and differential scanning calorimetry (DSC) measurements on the oriented samples.

Both the X-ray diffraction intensities and the changes of DSC thermograms with draw ratio show that the β -crystalline phase did not develop as a result of our drawing process at 155°C. The degree of crystallinity of the samples increased with the draw ratio as expected. This increase was about 17% for the sample with the highest draw ratio compared with the unoriented sample. The heat energy absorbed by the samples decreased linearly with the draw ratio in DSC experiments. This behavior was attributed to the fact that orientation reduces the specific volume in the amorphous phase.

The dielectric loss factor was measured from 100 Hz to 1 MHz, between 80 and 400 K, as a function of frequency and temperature. During the measurements two relaxation processes of PVDF were observed. The loss factor was not affected by the drawing process during the β -relaxation corresponding to the glass transition. The dielectric loss maxima, corresponding to the α -relaxation transition, due to motion of the dipole groups in the crystalline regions, decreased linearly with the draw ratio. This decrease was about 39% for the sample with the highest draw ratio compared with the unoriented sample. This can be attributed to the fact that the orientation capability of the dipole groups located on the fringes of the fibrillar crystallites and at the boundaries of the crystal lamellae decreases by the external field.

The activation energy of the β -relaxation transition increased with the draw ratio. This increase was 23% for the sample with the highest draw ratio

compared with the unoriented sample. It was determined that the drawing process does not change the activation energy for the α -relaxation transition. It was not possible to increase the temperature to the levels at which the relaxation time for the α -relaxation transition can be calculated more accurately since the oriented samples at these levels of the temperatures return to their unoriented stage. For this reason, it was not possible to investigate the change for this relaxation transition with the draw ratio.

It was observed that the relaxation time of the β -relaxation transition was affected by temperature while it was more affected by the orientation process at low temperatures. The relaxation time for the β -relaxation transition increased linearly with the draw ratio, about 67 and 42%, for the highest drawing ratio, compared with the unoriented samples at 200 and 250 K, respectively.

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