

The Variation of the Dielectric Constant and Loss Index with Temperature and Draw Ratio in α -PVDF

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ABSTRACT: In this study, the effect of measurement temperature and uniaxial drawing on the real (dielectric constant, ϵ') and imaginary (loss index, ϵ'') parts of the complex dielectric constant of α -crystalline phase poly(vinylidene fluoride) (PVDF) was investigated. The samples having different draw ratios (λ) were obtained by drawing the PVDF film at constant speed and temperature. The dielectric measurements were performed in the frequency range of 100 Hz–1 MHz and in the temperature range of 80–400 K. Although ϵ' and ϵ'' were not affected by the orientation pro-

cess during the β -relaxation transition, it was observed that there were systematical variations for the α -relaxation transition. ϵ' and ϵ'' showed different behaviors depending on the draw ratio at different temperatures. Especially, ϵ'' was more affected by the orientation process at 380 K. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2482–2485, 2009

Key words: uniaxially drawn poly(vinylidene fluoride) films; polymer capacitors; dielectric constant; dielectric relaxation

INTRODUCTION

Electrical energy storage has long been an interesting subject both scientifically and technologically. The systems storing the electrical energy are used extensively in many applications such as telecommunication devices, stand-by power systems, and medical devices. The most important ones are capacitors.^{1–5} The capacitors with different properties used in electronic circuits can be produced according to necessity. Recently, polymers are used as dielectric materials to produce capacitors having high-energy density. In this way, great advances have been achieved in capacitor technology. In addition, the other reasons for preference of polymers in capacitors are flexibility and durability under stress and lower production cost.^{1–3,5–8}

Because of its high dielectric constant (10–14), low dissipation factor, and high dielectric strength, the poly(vinylidene fluoride) is one of the suitable polymers for the dielectric capacitors. PVDF is a semi-crystalline polymer with a carbon backbone in which each monomer $[-CH_2-CF_2-]$ unit has two dipole moments, one associated with CF_2 and the other with CH_2 . Because hydrogen and fluorine atoms dispose symmetrically along the polymer chain, PVDF

has a very high dielectric constant among polymer materials.^{1,6,9–12} PVDF has four crystalline modifications, having different physical properties, called as α , β , γ , and δ . The α - and β -phases are most common of these modifications. α -phase can be obtained by melt crystallization below 150–160°C at atmospheric pressure. It is known that the β crystalline phase with the highest piezoelectricity can be obtained by mechanical drawing of the α -PVDF films at optimal conditions. Because it shows piezoelectric properties, PVDF has become an important material for the production of transducers as well.^{13–21}

The molecular chains, which are entangled, are rearranged along the draw axes, and hence, the polymer shows anisotropic physical properties. The morphological changing because of the orientation affects the mechanical and electrical properties. For instance, the physical quantities such as elastic stiffness constant and dielectric constant along the draw axes are higher compared with unoriented polymers.^{22,23}

In our previous article, the changing of morphological structure and dielectric relaxation transitions with uniaxially orientation process were investigated in details.²⁴ In this study, the variation of the real and imaginary parts of the complex dielectric constant of α -crystalline phase PVDF with both temperature and draw ratio has been investigated. There are many studies that investigate the variation of the dielectric properties depending on the orientation. However, in our studies, the drawing process was performed under the conditions, where the $\alpha \rightarrow \beta$ phase transition did not occur.

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EXPERIMENTAL

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 films were drawn uniaxially at constant speed and temperature. The details of the drawing process were given in the previous article.²⁴ The real (dielectric constant, ϵ') and imaginary (loss index, ϵ'') parts of the complex dielectric constant of the three PVDF samples having different draw ratios ($\lambda = 1.46$, $\lambda = 1.93$, and $\lambda = 2.5$) were measured. The measurements were performed between 100 Hz and 1 MHz as a function of temperature by LCR meter (Agilent 4284A). The temperatures, ranging between 80 and 400 K, were controlled using a liquid nitrogen cryostat (Oxford-ITC 502).

RESULTS AND DISCUSSION

It is known that the polymers exhibit different behaviors depending on frequency and temperature.^{25–27} In Figure 1, variation of the real and imaginary parts of the complex dielectric constant with temperature at different frequencies for $\lambda = 1$ (unoriented PVDF film) and $\lambda = 2.5$ are compared.

The maximum ϵ'' 's, which shifted toward high temperatures because of the increase in the frequency, are the characteristic α - and β -relaxation

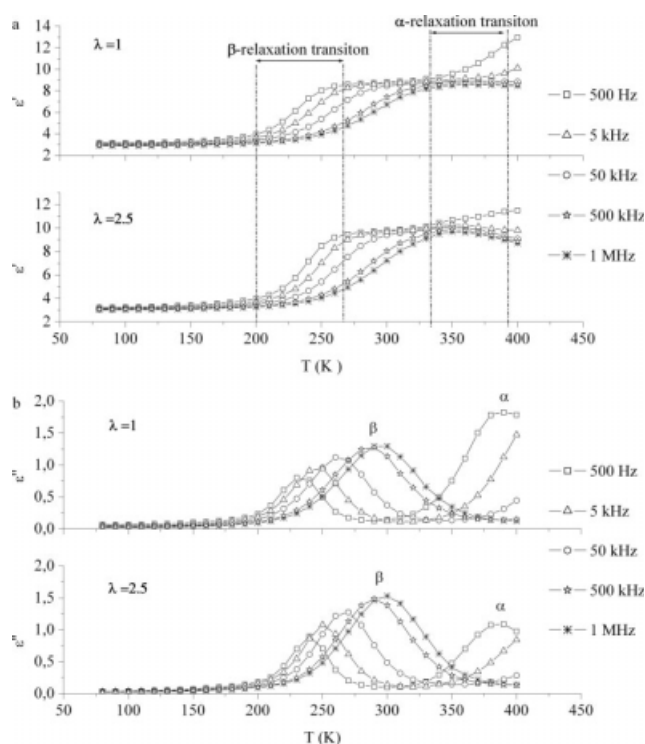


Figure 1 Temperature dependent variations of (a) real (b) imaginary parts at different frequencies for samples $\lambda = 1$ and $\lambda = 2.5$.

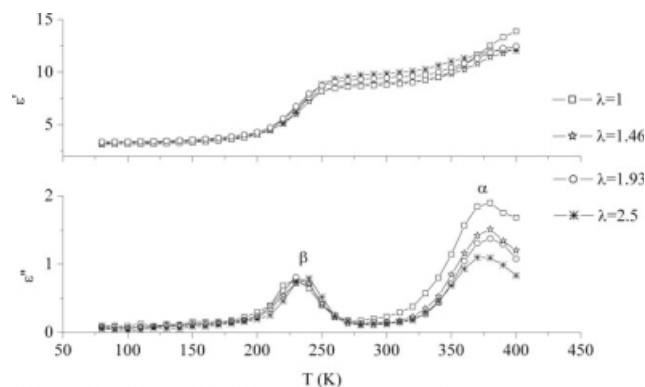


Figure 2 Temperature dependent variations of real and imaginary parts at 200 Hz constant frequency for samples having different draw ratios.

transitions of PVDF. β -relaxation transition is associated with the glass transition, and it is due to rotational and translational motions of the segments of polymer chains in the amorphous regions. The peak, observed at high temperatures, belongs to the α -relaxation transition, associated with rotational and translational motions of the dipole groups in the crystalline regions.^{9,11,24,28–30}

In Figure 2, variation of the real and imaginary parts of the complex dielectric constant with temperature for the PVDF samples having different draw ratios at 200 Hz is shown. This frequency value was selected from small set of frequencies at which both relaxation transitions can be seen in this temperature range.

When the variations of both ϵ' and ϵ'' with temperature were investigated, it was observed that the behaviors of oriented and unoriented samples were similar up to 300 K. ϵ' and ϵ'' were not affected by the orientation process during the β -relaxation transition. As the β -relaxation transition belongs to glass transition in the amorphous fraction, it can be said that the orientation, which occurred in the amorphous region, can not be enough to affect the motions of the dipole groups.

Above 300 K, ϵ'' decreases systematically with draw ratio during the α -relaxation transition. This is due to the decrease with drawing process in the total number of the dipole groups that can move in the external field. However, it was shown in the previous article that these dipole groups were not wholly belonging to chain segments in the crystalline region, and the crystalline regions were not affected directly by the drawing process.²⁴

The fact that there is no important variation in ϵ'' for the β -relaxation transition indicates that the drawing process more affects the region located between crystalline and amorphous fraction. Consequently, the dipole groups affected by the orientation are located on the chain segments in the fringes

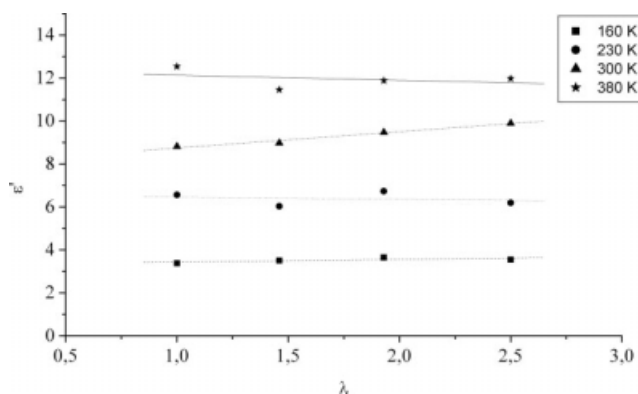


Figure 3 Variation of real part depending on the draw ratio for 200 Hz constant frequency value.

of fibrillar crystallites and on parts of the crystal lamellae adjoining the amorphous region.

To see the effects of the drawing process and temperature on the real and imaginary parts of the complex dielectric constant, the variations given in Figures 3 and 4 are important.

At 200 Hz, 160 and 300 K, the temperature values are located outside the relaxations transition, and at 230 and 380 K are the temperatures belonging to β - and α -relaxation transitions, respectively.

Although there is a negligible increase in ϵ' below the glass transition (160 K), for 230 K value, which the β -relaxation transition was observed, there was no clear variation in ϵ' . At these temperatures (160 and 230 K), the thermal mobility is quite limited. In addition, the motion capability of the chain segments was more reduced due to decreasing in the specific volume with the orientation. Hence, ϵ' was almost invariable with draw ratio at these temperatures.

It was observed that there was a more obvious increase in ϵ' for 300 K value, which refers to the region between two relaxation transitions. This case was due to the increase in the average dipole

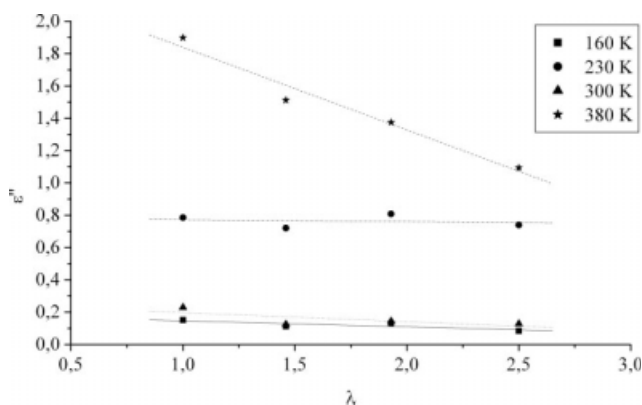


Figure 4 Variation of imaginary part depending on the draw ratio for 200 Hz constant frequency value.

TABLE I
 ϵ' Values for the Samples at Various Temperatures at 200 Hz

λ	ϵ' values			
	1	1.46	1.93	2.5
160 K	3.38	3.50	3.64	3.55
230 K	6.56	6.03	6.73	6.19
300 K	8.81	8.97	9.47	9.89
380 K	12.54	11.45	11.88	11.97

moments with orientation of the C-F dipoles located on the main chain segment by drawing process.

For the 380 K value, which the α -relaxation transition was observed, ϵ' is almost invariable with the draw ratio. The increase in the free volume at this temperature causes the easy orientation of the dipole components, and hence, ϵ' reached about 12. The increase in the free volume at this temperature provided the easiness of the orientation. However, this easiness dominated the orientation effect of the dipoles occurred by drawing. That is why ϵ' has almost the same value for all draw ratios.

According to all of the variations given in Figure 3, it was observed that ϵ' values of the oriented and unoriented PVDF samples increased depending on the increase in the temperature (Table I). The specific volume and the thermal mobility of the molecule chains increased due to the increase in the temperature, and hence, the average dipole moments of the dipole segments increased.

In Figure 4, the variations of ϵ'' with draw ratio for the same temperature values are presented.

For the 230 K value, which the β -relaxation transition was observed, ϵ'' is almost invariable with draw ratio. As mentioned earlier, this situation was caused by the fact that the orientation that occurred in the amorphous region did not quite affect the motion of the dipole segments. Because, when this temperature is over, the specific volume increases instantly and the restrictive effects, caused by the orientation, are trivial at all draw ratios.

The orientation effects are more obvious at the other temperatures (160, 300, and 380 K). ϵ'' decreased depending on the increase in the draw ratio for these temperatures. This can be explained by more regular morphology due to the orientation. In this regular morphology, as the dipole segments are oriented more easily by the external electric field, they can store most of their energies as dipolar energy.

CONCLUSIONS

α -crystalline phase PVDF film was oriented uniaxially at different draw ratios at constant speed and temperature. The effect of the drawing process on the real and imaginary parts of the complex

dielectric constant was investigated depending on frequency and temperature. When the variation of the real and imaginary parts of the complex dielectric constant with temperature was investigated, it was observed that the oriented and unoriented samples exhibited very similar behaviors until 300 K, but above this temperature, the ϵ'' value decreases with draw ratio.

The fact that both ϵ' and ϵ'' were not affected by the drawing process during the β -relaxation transition (230 K) indicated that the orientation, occurred in the amorphous region, did not quite affect the motion of the dipole segments.

In the α -relaxation transition (380 K), ϵ'' decreased obviously with draw ratio. The decrease as mentioned above was about 42% for the sample with the highest draw ratio compared with the unoriented sample, due to the decrease with orientation in the total number of the dipole groups that can move easily in the external field.

Before the β -relaxation transition (160 K), due to the restriction of thermal mobility and the mobility of the chain segments with orientation, the increase in ϵ' was quite limited. This increase was about 5% for the sample with the highest draw ratio compared with the unoriented sample. ϵ'' decreased with the draw ratio in this temperature range. This decrease was about 38% for the sample with the highest draw ratio compared with the unoriented sample.

For the 300 K, which refers to the region between two relaxation transitions, the average dipole moment increased due to the orientation of the dipole segments, and hence, ϵ' increased with the draw ratio. This decrease was about 13% for the sample with the highest draw ratio compared with the unoriented sample. ϵ'' decreased depending on the increase in the draw ratio for this temperature range. This decrease was about 43% for the sample with the highest draw ratio compared with the unoriented sample.

It was observed that the real and imaginary parts of the complex dielectric constant exhibited different behaviors depending on the temperature. Considering the low loss and the high dielectric constant for the dielectric capacitors, the results that were obtained between two relaxation transitions are interesting. It was determined that the decrease in the loss and increase in the dielectric constant depending on the draw ratio was the greatest between two relaxation transitions.

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