

# Dynamic mechanical analysis and creep behaviour of $\beta$ -PVDF films

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## Abstract

In this work, tensile dynamic mechanical analysis (DMA) was used to characterise the solid-state rheological properties of a commercial  $\beta$ -polyvinylidene fluoride (PVDF) film in the two main directions (longitudinal and transversal to the stretch direction). The  $\beta$ -relaxation, assigned to the segmental motions within the amorphous phase, is observed at  $\sim -25^\circ\text{C}$ . The  $\alpha_c$ -relaxation is observed above room temperature. This relaxation is the main responsible for the anelastic properties of the material and to the short-term creep behaviour. Longer-term creep tests along the longitudinal direction were also performed and the Eyring model was applied, in order to characterize the flow-process within the polymeric structure. The results suggest that long-term creep is mostly controlled by the deformation of amorphous tie-chains that connect adjacent crystalline lamellae.

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## 1. Introduction

Progress in the electronic industry demands for the development of pyro-piezoelectric materials. Polyvinylidene fluoride (PVDF) in its  $\beta$ -phase is known for its interesting piezo- and pyroelectric properties [1,2]. Piezoelectric properties of PVDF are obtained through a technological process involving stretching and poling of extruded thin sheets of the material. In the past decades PVDF and PVDF co-polymers have been increasingly used in devices as sensors, transducers and actuators for different applications, including acoustics, ultrasound, medicine, robotics, etc. In its non-polar crystalline phase,  $\alpha$ -PVDF has also been used in different structural applications (offshore, chemical industry, sutures for medical applications ...). Note, in this context, that other classifications are found for  $\beta$ - and  $\alpha$ -PVDF, such as I- and II-PVDF, respectively [3].

In many of its applications the materials are often subjected to mechanical loads (some of them cyclic). Therefore there is a need for characterizing the mechanical performance and the damping capabilities of the materials. In

this study, the mechanical properties of  $\beta$ -PVDF will be analysed by both dynamic mechanical analysis (DMA) and creep experiments in order to provide further phenomenological informations about the viscoelastic properties of such materials. Although mechanical and dielectric spectroscopy methods have been used in PVDF-based materials [4–10], to our knowledge, the anisotropy of piezoelectric  $\beta$ -PVDF films has not been explored. Further, creep studies on such kind of materials have been scarcely reported [11]. The approach used in this work will also add further informations about the general creep behaviour in semi-crystalline polymers, that may be compared with data obtained in other polymers (especially polyolefins), in order to discuss the influence of the chemical structure on the mechanical deformation.

## 2. Experimental

The analysed material was a  $28\text{ }\mu\text{m}$  thick commercial  $\beta$ -PVDF film from Measurements Specialties Inc. (Fairfield, NJ, USA). Rectangular samples ( $\sim 3\text{ mm}$  wide and  $20\text{ mm}$  long) were cut from the original sheet both perpendicular and parallel to the stretch direction. Longitudinal samples will label the specimens in which the mechanical tests were

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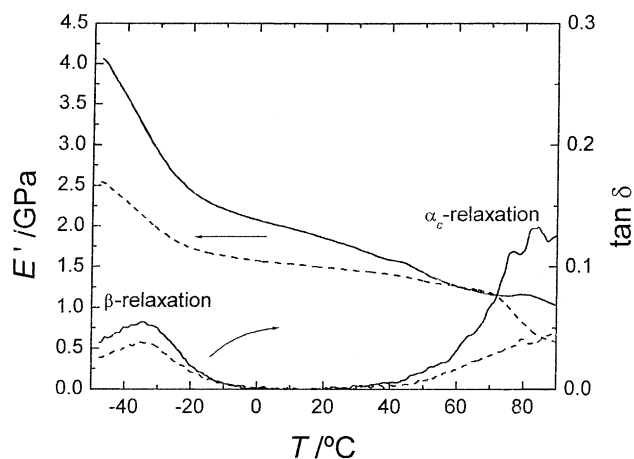


Fig. 1. DMA results in longitudinal samples (solid lines) and transverse samples (dashed lines) obtained at a frequency of 1 Hz.

performed along the stretch direction, whereas transverse samples are for experiments perpendicular to the stretch direction. The stretch direction was indicated by the supplier and complementary mechanical tests confirm the more brittle and stiffer properties of the film in the longitudinal direction [12].

Both DMA and creep experiments were carried out in a Perkin-Elmer DMA7e apparatus using the tensile mode. The DMA experiments were performed at isochronal conditions (frequency 1 Hz), from  $-50$  to  $120^{\circ}\text{C}$  at a heating rate  $2^{\circ}\text{C min}^{-1}$ . The amplitude of the dynamic stress was 0.1 MPa, which was small enough to ensure a linear viscoelastic response from the samples. Creep experiments were carried out at different temperatures (from  $55$  to  $95^{\circ}\text{C}$ ) and stresses (from 5 to 17 MPa). In those cases a small pre-tensile load (less than 5% of the creep load) was applied to make sure that the sample was taut. Short-term creep experiments (30 min) were carried out at  $\sigma_0 = 15$  MPa on both longitudinal and transverse samples, at different temperatures. The long-term (up to 15 h) creep experiments were performed only on longitudinal samples.

### 3. Results and discussion

#### 3.1. Dynamic mechanical analysis and short-time creep experiments

In Fig. 1, the storage modulus ( $E'$ ) and the loss factor ( $\tan \delta = E''/E'$ ) for a fixed frequency  $f = 1$  Hz are shown against temperature for both longitudinal and transverse  $\beta$ -PVDF samples. As expected,  $E'$  is higher for the longitudinal sample, as the molecular alignment is higher along the direction of the mechanical tests. This mechanical anisotropy was already probed by conventional quasi-static experiments [12], where longitudinal films were found to be stiffer, brittle and with a higher ultimate strain and lower strain at break than the transversal ones.

A relaxation process with a maximum in  $\tan \delta$  is detected at  $T \approx -35^{\circ}\text{C}$ . This process, also detected by dielectric methods, has been labelled  $\beta$  or  $\alpha_a$ . It has been assigned to the cooperative segmental motions within the main chains of the amorphous regions [5–10]. Dielectric relaxation spectroscopy studies on the same film indicated that the central relaxation time of this process depends upon temperature according to the Vogel–Tammann–Fulcher (or the equivalent WLF) model [13], as it is observed in the relaxation assigned to the dynamic glass transition in amorphous and other semi-crystalline polymers. The damping associated with the  $\beta$  process seems to be higher for the longitudinal sample. A similar behaviour was observed, for example, for the same process in polyethylene, PE [14], indicating that the viscoelastic properties in anisotropic specimens depend strongly on the direction of the test [15,16].

Above  $30^{\circ}\text{C}$  a new relaxation process emerges (Fig. 1), being more pronounced in terms of  $\tan$  for the longitudinal sample. This process, labelled  $\alpha$  or  $\alpha_c$ , is associated with motions within the crystalline fraction [6–9]. This higher- $T_g$  relaxation is also found in a variety of flexible semi-crystalline polymer, including PE, poly(methylene oxide), poly(ethylene oxide) and isotactic polypropylene [17,18] and its origin should be similar to the one observed in PVDF. It should be noticed that this relaxation is not clearly observed as a peak in the  $\tan \delta$  plot. This may be a result of the morphology of the crystalline fraction in the films, that is highly oriented. As for polyethylene, this process should involve  $180^{\circ}$  flip motions of the chain stems in the crystalline lamellae [17,18]. This screw motion process involves both rotational and translation mobility within the chains [19]. A significant cooperative character was found for polyethylene, indicating that diffusion processes involving chains in the amorphous region should accompany the  $\alpha_c$ -relaxation [20]. A similar degree of cooperativity was also found for the  $\alpha_c$ -relaxation of PVDF [21], strengthening the attribution of the  $\alpha_c$ -relaxation in PVDF and in PE to the same origin at the molecular level.

The  $\alpha_c$ -relaxation influences the solid-state rheological features of PVDF above room temperature. To better analyse this effect, short-term creep experiments were performed at different temperatures for the longitudinal and transverse samples. The master curves were successfully built at  $T = 76^{\circ}\text{C}$  for the two main directions, from simple shifting of the creep curves obtained at different temperatures along the  $\log t$ -axis (Fig. 2). As a consequence of the existence of the  $\alpha_c$ -relaxation, a clear delayed deformation response is detected. The higher compliance of the transverse sample is also distinguished, which is compatible with the dynamic results that show lower stiffness in this direction. The shift factors associated with the construction of the master curves are also shown in the relaxation map of Fig. 2, suggesting a thermally activated behaviour for the underlying relaxation process, as observed in the  $\alpha_c$ -relaxation studied by dynamic methods. The activation energies, calculated from the linear fitting of  $\log a_T$  versus  $1/T$ , are 279 and  $264 \text{ kJ mol}^{-1}$  for

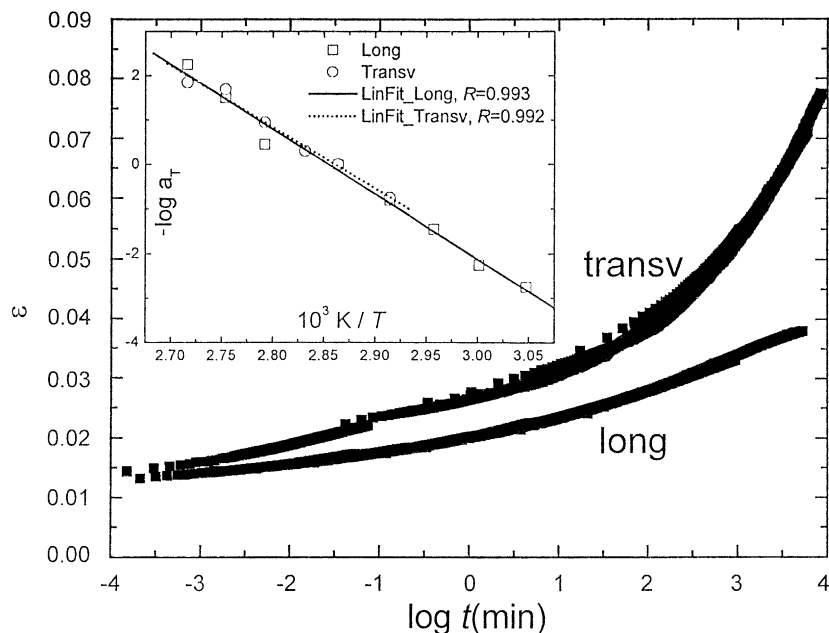


Fig. 2. Master-curves of short-time creep experiment both on longitudinal and transversal samples reduced at  $T = 76^\circ\text{C}$ ; the stress used in all experiments was 15 MPa. Inset: Arrhenius graphics with the shift factors obtained during the construction of the master curves (squares—longitudinal sample; circles—transverse samples) and the corresponding linear fittings.

the longitudinal and transverse samples, respectively. Note that these values are higher than the activation energy reported for the crystalline  $\alpha_c$ -relaxation of PVDF obtained from dielectric studies, that is of the order of  $92 \text{ kJ mol}^{-1}$  [9]. However, the activation energies may depend on both the micro-structure of the sample used and the technique that probes in a different way the molecular mobility.

### 3.2. Creep tests along the drawn direction

Creep experiments are a simple way to obtain information concerning the viscoelastic properties of materials, which may be correlated with structural features. From a more practical point of view, creep is also a common phenomenon for engineering applications where products are subjected to loads. The creep behaviour of  $\beta$ -PVDF samples along the longitudinal direction was investigated. This direction has better mechanical properties and thus more interesting for practical purposes. Results obtained at distinct combinations of temperature and stress are shown in Fig. 3.

The total mechanical response of a specimen includes perfect elasticity (related with the “instantaneous” strain in Fig. 3), a coupling of elastic and viscous components, called anelasticity, and a total irreversible flow. The simplest model, where the anelastic component is characterised by a single characteristic time that describes this entire response, is the four-elements model (a Maxwell and a Voigt elements in series). However, such models are too simplistic and usually a distribution of characteristic times must be assumed, even when studies are performed in the linear viscoelastic regime. The instantaneous elastic response and the viscoelastic properties can be studied using quasi-static tests or DMA. Creep

is a suitable technique to address the long-term permanent flow.

The Eyring’s model of the flow of solids [22] has been used to describe the motions of polymer chains (or groups of segments of chains) slipping over one another from one (metastable) position to another when stress is applied (plastic deformation). The model presupposes that this type of motions take place by individual jumps over an energy barrier with a frequency proportional to  $\exp(-\Delta H/kT)$ , where  $\Delta H$  is the enthalpy required to take a segment across the potential well. Eyring assumed that the development of shear stresses within the material change the barrier height, so that it decreases by a factor of  $\sigma_s V^*$  in the direction of the stress and the reverse motions must cross a potential barrier of  $\Delta H + \sigma_s V^*$ .  $V^*$  is the activation volume and represents

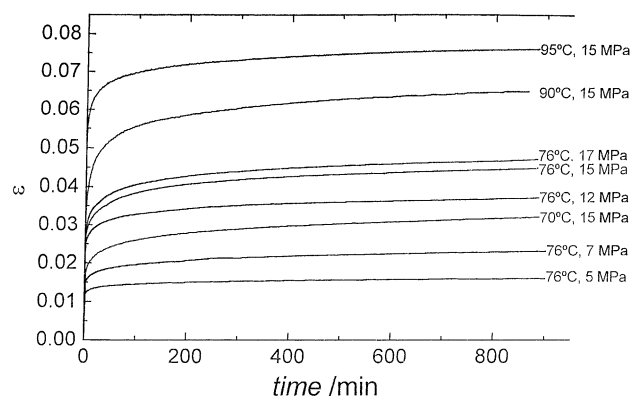


Fig. 3. Creep results up to 15 h in longitudinal samples at different temperatures and stresses (indicated for each curve).

the volume of the polymer segment that has to move as a whole in order to occur plastic deformation for each molecular event. Therefore, the forward jump is facilitated under the influence of shear stress,  $\sigma_s$ , becoming the rate of segment jumping in the direction of the stress fast enough to arise a measurable strain change. Note that no entropic effects are included in this model. Neglecting also the reverse jump rate in comparison with the forward rate, the strain rate,  $\dot{\epsilon}_p$ , is given by

$$\dot{\epsilon}_p = \dot{\epsilon}_0 \exp\left(-\frac{\Delta H}{kT}\right) \exp\left(\frac{\sigma V^*}{2kT}\right). \quad (1)$$

In the previous equation  $\sigma = 2\sigma_s$  is the tensile stress and  $\dot{\epsilon}_0$  is a pre-exponential factor, commonly known as the “availability of event sites”, and is related to the fundamental jumping frequency for the flow units [23]. Permanent flow processes may be then characterised by three parameters:  $V^*$ ,  $\Delta H$  and  $\dot{\epsilon}_0$ . Eyring-rate approaches have been used in several systems, but especially in polyethylenes [24–27]. Ward and co-workers suggested that the plastic flow could be described by two sets of a spring and Eyring dashpot arranged in parallel [24,25]. A less rigid arm should be related with the flow occurring within the amorphous network. The higher stress process would be dominated by the crystalline deformation. As the stresses applied in this work are not very high, only the low stress regime will be considered. Note, for example, that a critical stress level of  $\sim 0.5$  GPa (much higher than the stresses exploit in this work) dividing the two stress levels was found in PE [25].

The next step in this analysis will be the description of the dynamics of this plastic flow creep process using the Eyring-rate equation (Eq. (1)).

The three parameters were obtained by fitting the long-term strain rates,  $\dot{\epsilon}_p$ , obtained at different temperatures and stresses (Fig. 3) to Eq. (1). The activation volume ( $V^*$ ) was obtained by fitting the strain rate at different stresses and at  $T = 76^\circ\text{C}$  (circles in Fig. 4). A value  $V^* = 0.491 \text{ nm}^3$  was obtained. Considering that  $\beta$ -PVDF has an orthorhombic unit cell composed by two repeat units  $-(\text{CH}_2-\text{CF}_2)-$  and that each unit cell has a volume of  $\sim 0.108 \text{ nm}^3$  [28],  $V^*$  is equivalent to approximately 18 carbon atoms [23]. For PE, the  $V^*$  values reported in the literature may differ strongly, being less than  $0.1 \text{ nm}^3$  [25] in some ultra-high modulus linear PEs or higher than  $4 \text{ nm}^3$  in some oriented linear PEs [29].

The activation enthalpy,  $\Delta H$ , was obtained by fitting the creep rate (in logarithmic scale) against reciprocal temperature, for a fixed stress (15 MPa). According to Eq. (1),  $\Delta H$  may be calculated from the slope of the fitting (squares in Fig. 4), that for a single Eyring process is  $-\Delta H/\ln(10)k + V^*/[2\ln(10)k]$ . The best fit for  $\Delta H$  (in energy units per mole) yields  $47.7 \text{ kJ mol}^{-1}$ , which is slightly higher than the activation enthalpy obtained from high-density PE extruded films, that ranged between 22 and  $28 \text{ kJ mol}^{-1}$  [27]. This may be explained by hindering of the molecular mobility by the bulky fluoride atoms along the PVDF chains. However, the activation energies also depend on the general morphology of the specimen or on the molecular weight [24,26]. This fact complicates any discussion that includes the comparison between results from different materials.

Finally, the availability of creep sites was obtained from the fitting of logarithm of creep rate versus  $-\Delta H/\ln(10)kT + V^*/[2\ln(10)kT]$  (triangles in Fig. 4), yielding  $\dot{\epsilon}_0 = 8.44 \text{ min}^{-1}$  from the intercept (note that a slope of  $\sim 1$  was

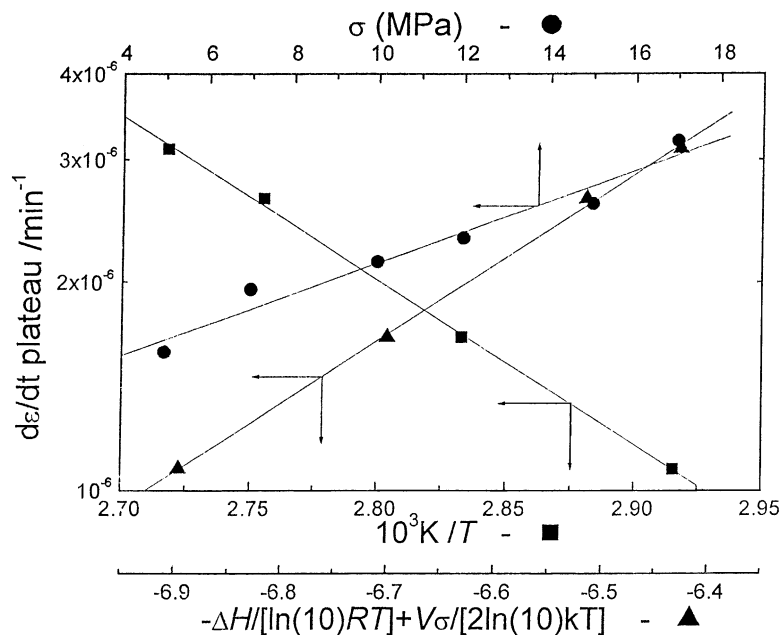


Fig. 4. Fittings of the creep data of Fig. 3 with Eq. (1) to obtain the activation volume (circles), activation energy (squares) and pre-exponential factor (triangles).

obtained, as expected from Eq. (1)). Such values are also of the same magnitude of those obtained in PE [27]. Zhou and Wilkes showed, in anisotropic PE films, that whereas  $\dot{\epsilon}_0$  depends strongly on the direction of the tests [27], both activation volume and enthalpy are similar. The explanation given for the difference in  $\dot{\epsilon}_0$  was based on the more or less facility for the separation of crystalline lamellae during deformation: if the separation is higher, more creep sites (non-taut tie-chains) are activated and  $\dot{\epsilon}_0$  increases.

It would be then important to understand which kind of molecular motions within the amorphous structure would be involved in the plastic deformation of the  $\beta$ -PVDF. The discussion may be very similar to the same processes occurring in other flexible semi-crystalline polymers such as in PE [27]. The chains in the amorphous bulk state could be hardly associated to this process as their relaxation times are very small at the creep temperatures. In fact, the mobility of such segments is associated to the  $\beta$ -relaxation that occurs at much lower temperatures (Fig. 1). Only the presence of trapped entanglements among such segments could contribute as load transfer for permanent deformation. There are also amorphous segments suspended from the chain-folding surfaces of the crystalline lamellae that could not be involved in the plastic flow creep, either. The third amorphous region is related to the tie-chains that directly link adjacent crystalline lamellae. It was suggested for the case of PE that this process would dominate the long-term creep behaviour in the pre-yielding region [27]. In the case of the studied oriented  $\beta$ -PVDF film, we expect that the tie-chains are highly taut and highly constrained and will also dominate the creep behaviour in the plateau regime of the creep rate. Note that this is a completely distinct mechanism from that occurring during the short-term creep, which is governed by the anelastic process of molecular mobility within the crystalline fraction ( $\alpha_c$ -relaxation). The activation of such tie-chain may change the orientation of the crystalline lamellae as it was observed recently in FTIR studies [12]: a reorientation of the chains from perpendicular to parallel to the stress direction was observed to occur in the plastic region, right after yielding.

As a future work, the previous analysis should be extended to PVDF films with different orientation levels (including isotropic films) in order to better understand the influence of the morphology on the Eyring parameters. Other models should be tested in the description of the results. One should refer in this context the defect diffusion model, proposed by Reneker [30,31].

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