

Volume Strain Changes of Plasticized Poly(vinylidene fluoride) during Tensile and Creep Tests

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ABSTRACT: The volume strain changes of plasticized poly(vinylidene fluoride) during tensile and creep tests were characterized. A negative volume strain was observed. This phenomenon was ascribed to compaction taking place during mechanical testing, which further delayed the onset of plastic instability and, therefore, the cavitation process. It was suggested that this compaction was caused by the ori-

entation of amorphous chain segments leading to material densification. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1784–1791, 2004

Key words: plasticized poly(vinylidene fluoride); tensile tests; creep; volume strain

INTRODUCTION

Materials used to design pipes for offshore structures need to be flexible and to withstand a corrosive environment at relatively high temperatures. Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer suitable for this kind of application because it exhibits intrinsic chemical resistance and good mechanical properties. However, in service, cavitation effects can occur at a microscopic level in PVDF. Consequently, polymer cavitation has to be analyzed in detail, and this can be achieved by the measurement of the volume strain (ϵ_v).

The results of ϵ_v modifications that take place during tensile and creep tests for neat PVDF have been the subject of various articles.^{1–3} Nonetheless, this polymer is generally plasticized to enhance its flexibility. Inevitably, this treatment has an impact on the mechanisms of plastic deformation.

The objective of this article is to highlight ϵ_v changes during tensile and creep tests for plasticized PVDF and to interpret them in terms of microstructural mechanisms.

EXPERIMENTAL

Materials

Plasticized PVDF (Kynar 50 HD CP 900, Atofina) was provided by the Institut Français du Pétrole in the

form of dumbbell specimens (6 mm thick, 10 mm wide, 60 mm in gauge length) machined from extruded plates. The index of crystallinity, obtained by differential scanning calorimetry, was about 50 wt %.

As mentioned in previous publications, PVDF is characterized by two glass transitions.^{2,3} The main glass transition (T_α) is well defined and is located at -40°C , and the secondary one ($T_{\alpha'}$) is between 40 and 60°C . The existence of these two glass transitions has been ascribed to the presence of two amorphous phases: free and constrained.^{4,5} Between T_α and $T_{\alpha'}$, the free amorphous phase is rubbery, and the constrained phase is glassy. Both amorphous phases are rubbery above $T_{\alpha'}$, whereas both are glassy below T_α .

The addition of a plasticizer to neat PVDF induced a reduction in the interchain interactions due to the increase in the space between chains. Consequently, the chain mobility increased, and both T_α and the material stiffness were reduced. In addition, a broadening of the main glass-transition peak was observed. Surprisingly, the position of $T_{\alpha'}$ seemed to be unaffected by the presence of a plasticizer (Fig. 1).

Sample preparation and method

The intrinsic behavior of plasticized PVDF was characterized under tension, under both a constant true strain rate and creep at a constant true stress. The tensile tests were performed with the VidéoTraction system⁶ in a new configuration described in detail elsewhere.^{2,3} This latter method is based on the real-time analysis of relative displacements of four dots initially printed on one of the main faces of a sample (Fig. 2). Thus, the true axial strain (ϵ) and true transversal

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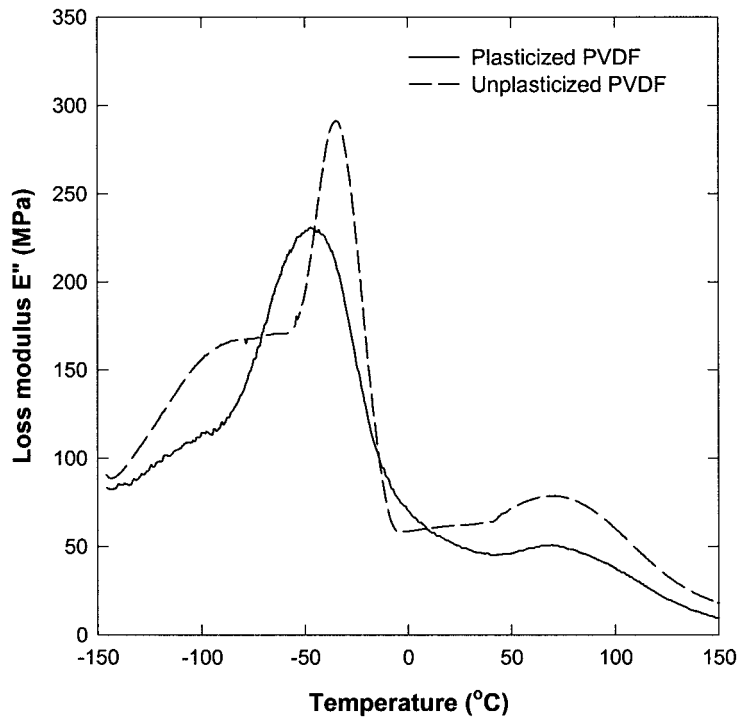


Figure 1 Loss modulus versus the temperature for plasticized and nonplasticized PVDF (see ref. 1 for the characteristics of nonplasticized PVDF).

strain (ϵ_t), defined as logarithmic strains (Hencky true strains), are described by the following relationships:

$$\epsilon = \epsilon_{33} = \ln\left(\frac{CD}{C_0D_0}\right) \quad (1)$$

$$\epsilon_t = \epsilon_{22} = \ln\left(\frac{AB}{A_0B_0}\right) \quad (2)$$

where $A_0, B_0, C_0,$ and D_0 are the initial positions of the center of gravity of the dots and $A, B, C,$ and D are the

new positions after stretching at a given time. If the deformation is transversally isotropic, ϵ_v can be written as follows:

$$\epsilon_v = \epsilon + 2\epsilon_t = \ln\left(\frac{V}{V_0}\right) \quad (3)$$

As for the true axial stress, it is defined as the Cauchy stress (σ):

$$\sigma = \frac{F}{S_0} \exp(-2\epsilon_t) \quad (4)$$

where F and S_0 represent the load and the initial cross section, respectively.

During the tensile tests, the strain rate was held constant through the control of the variation of ϵ with time. As for the creep experiments, they were performed at a constant stress by the adjustment, in real time, of the force level.

With this method, the strain and ϵ_v measurements made sense only in the homogeneous plastic deformation region, that is, before the onset of plastic instability. Therefore, all experiments presented in this article were carefully limited to the deformation range before the occurrence of necking.

The accuracies of the strain and ϵ_v values were 1.5×10^{-3} and 5×10^{-3} respectively, and the reproduc-

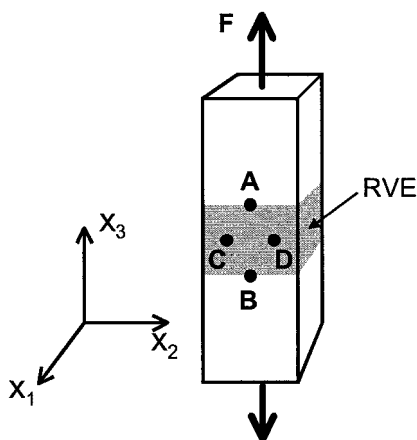


Figure 2 Disposition of the markers on the specimen delimitating the representative volume element in which the strains are assessed.

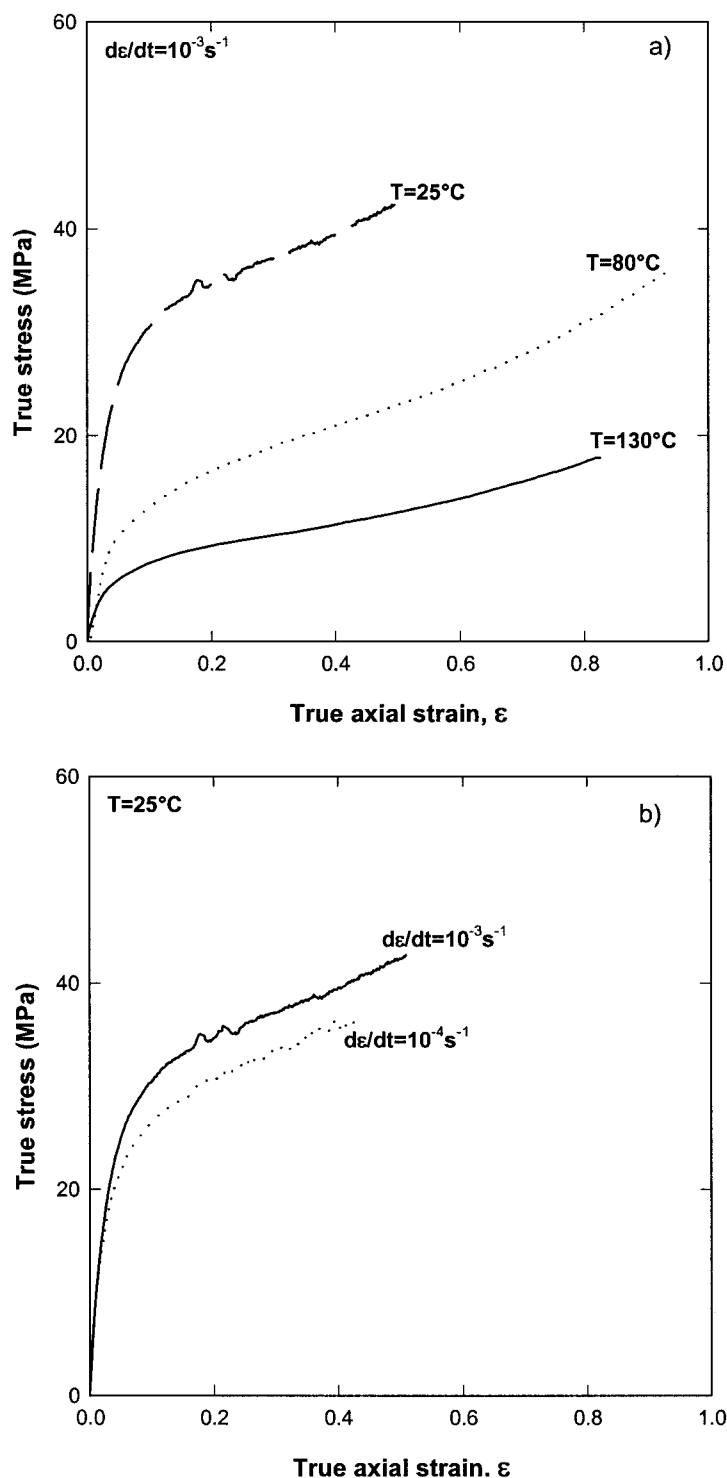


Figure 3 True stress versus ϵ (a) at 10^{-3} s^{-1} and three temperatures and (b) at 25°C and two strain rates.

ibility was ensured by the superpositioning of at least three experiments for a given experimental condition.

RESULTS AND DISCUSSION

Effects of the temperatures and strain rates

The graphs in Figure 3(a) show the mechanical behav-

ior upon tensile testing at 10^{-3} s^{-1} for three temperatures (25, 80, and 130°C). In Figure 3(b), the tensile curves refer to tensile tests at 25°C for two strain rates (10^{-3} and 10^{-4} s^{-1}). All the curves display the same trend: up to $\epsilon = 0.1$, that is, yield point, the polymer exhibited a typical viscoelastic behavior, and beyond this point, homogeneous plastic deformation

TABLE I
 $d\sigma/d\epsilon$ at Two Strain Rates and Three Temperatures

Temperature (°C)	$d\sigma/d\epsilon$ (MPa)	
	10^{-3} s^{-1}	10^{-4} s^{-1}
25	23.8 ₄	26.4 ₈
80	21.8 ₇	22.7 ₈
130	9.7 ₉	11.0 ₃

took place, characterized by strain hardening. Increasing the temperature reduced Young's modulus [Fig. 3(a)], whereas it remained almost unaffected by the strain rate [Fig. 3(b)]. Also, the yield stress showed a marked decrease while the temperature increased or the strain rate decreased.

Strain hardening analysis

Table I depicts the strain hardening ($d\sigma/d\epsilon$), which is defined as the slope of the stress-strain curve measured in the linear region of plastic deformation, that is, within $\epsilon = 0.1$ and $\epsilon = 0.5$. $d\sigma/d\epsilon$ changed with both the temperature and strain rate. As such, increasing the temperature reduced $d\sigma/d\epsilon$ at a given strain rate. This phenomenon was due to the increase in the molecular mobility, which facilitated both crystal and amorphous chain orientation. Conversely, reducing the strain rate induced a strain-hardening increase at a given temperature. This effect may be attributed to the increase in the number of both amorphous chain segments and crystals involved in the orientation process.

Nonplasticized PVDF revealed strain hardening only for temperatures beyond the secondary glass transition, that is, 60°C.² This difference in terms of the strain hardening between the plasticized and nonplasticized PVDF at room temperature could be explained by a difference in the prevailing plastic deformation mechanism. Indeed, the plastic deformation of semicrystalline polymers is governed by the competition between a crystal slip mechanism and lamellar fragmentation.⁷⁻⁹ The former generates strain hardening due to crystal shearing, whereas the latter involves no or little strain hardening because of the chain-unfolding process occurring over the course of crystal fragmentation. Thus, the increase in chain mobility due to the presence of a plasticizer eases crystal orientation and consequently favors the predominance of crystal slip mechanisms at lower temperatures than those of virgin PVDF.

Strain rate sensitivity

In Table II, we report the results of the assessment of the coefficient of the strain rate sensitivity, $m = [\partial \ln \sigma / \partial \ln \dot{\epsilon}]_{T, \epsilon}$, where $\dot{\epsilon}$ represents the strain rate. In this study, m was estimated at the yield point,

that is, $\epsilon = 0.1$. A steady increase in m with the temperature was observed. This result is consistent with a more macroscopic homogeneous plastic deformation. Indeed, as mentioned previously, plastic deformation mechanisms of semicrystalline polymers can be regarded as a competition between two processes⁷⁻⁹ characterized by their own intrinsic m value: crystal slip, giving rise to homogeneous macroscopic deformation, and crystal fragmentation, a precursor of plastic instability. The former is thermally activated, whereas the latter is less sensitive to both the temperature and strain rate. Therefore, a crystal slip mechanism must have a higher intrinsic m value than a lamellar fragmentation mechanism. Thus, the measured m value could be considered, at first approximation, as a mean value of both intrinsic m values. At last, because increasing the temperature facilitates crystal orientation, the crystal slip mechanism becomes preponderant and takes place at the expense of lamellar fragmentation, thereby inducing an increase in m .

The m values of plasticized PVDF were systematically higher than those of nonplasticized PVDF over the entire range of studied temperatures.² For instance, at 80°C, m was 0.03 for nonplasticized PVDF and 0.07 for plasticized PVDF. This suggested that plasticized PVDF had a higher propensity to develop homogeneous plastic deformation; this was still in line with the increase in the molecular mobility introduced by the presence of a plasticizer.

Effects of the deformation, temperature, and strain rate on ϵ_v

Graphs in Figure 4(a) depict ϵ_v versus ϵ at 10^{-3} s^{-1} for three temperatures. At 25°C, ϵ_v was almost negligible or, if significant, was limited to -0.02 . It can thus be stated that, at room temperature and for $\epsilon < 0.4$, the slow tensile deformation of plasticized PVDF was nearly isochoric. In contrast, at 80 and 130°C, ϵ_v showed complex variations. First, in the viscoelastic range, ϵ_v remained nearly zero or possibly showed a very small positive value. Subsequently, for $\epsilon > 0.1$ at 80°C and for $\epsilon > 0.19$ at 130°C, the material underwent effective compaction because markedly negative values of ϵ_v were recorded under increasing tensile strain, reaching -0.08 at 80°C and -0.105 at 130°C.

TABLE II
 m at Three Temperatures

Temperature (°C)	m
25	0.05 ₉
80	0.07 ₀
130	0.09 ₄

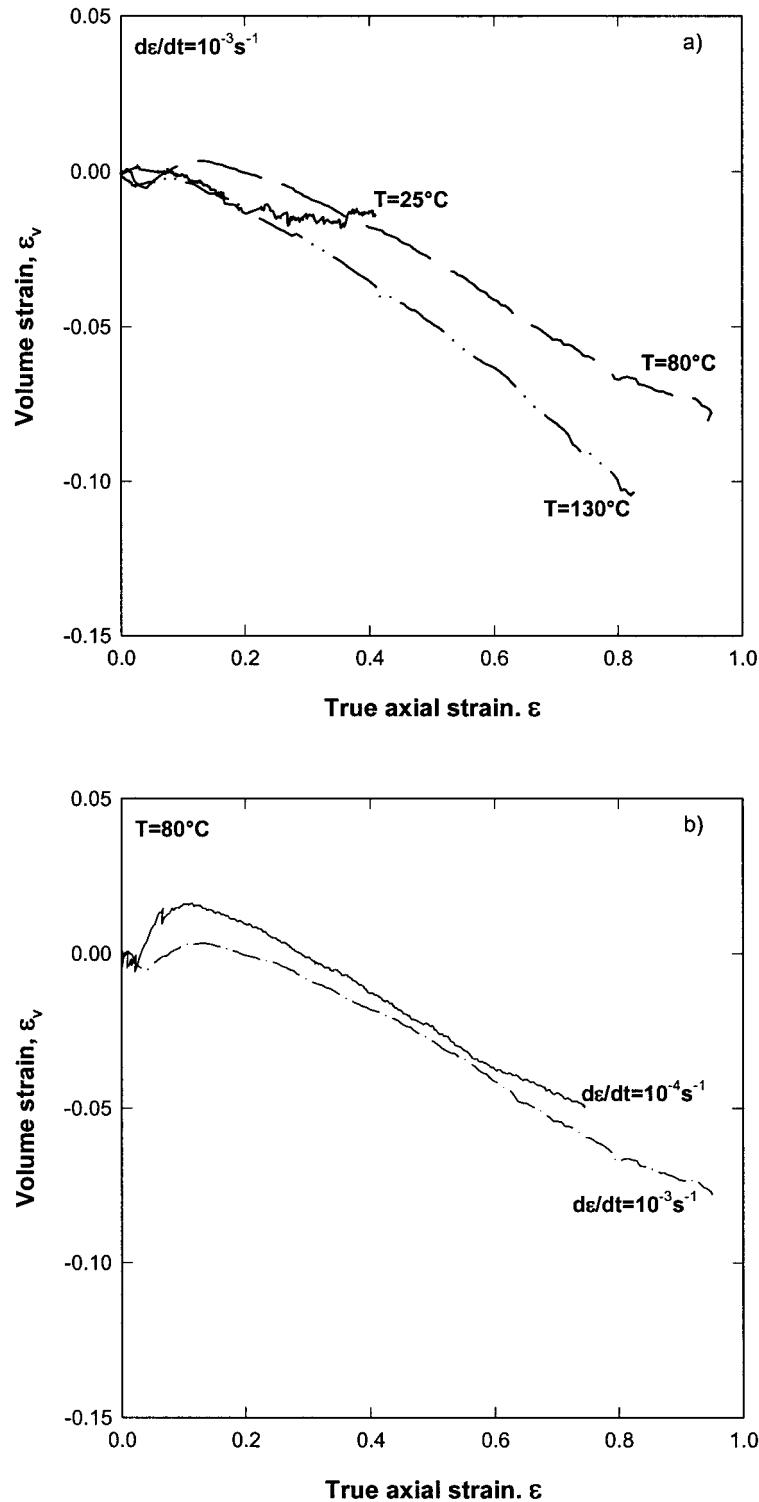


Figure 4 ϵ_v versus ϵ (a) at 10^{-3} s^{-1} and three temperatures and (b) at 80°C and two strain rates.

Figure 4(b), which displays the influence of the strain rate on ϵ_v at 80°C , shows (1) that for the experiment carried out at the lowest strain rate ($\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$), ϵ_v increased up to 0.01 until the yield point was reached (at $\epsilon = 0.1$) before becoming negative and (2) that the compaction kinetics in the plastic range

seemed to be mostly insensitive to the strain rate because $d\epsilon_v/d\epsilon$ was approximately -0.11 for both strain rates.

For comparison, it is worth mentioning that non-plasticized PVDF did not exhibit any negative values of ϵ_v when it was subjected to tensile tests at a constant

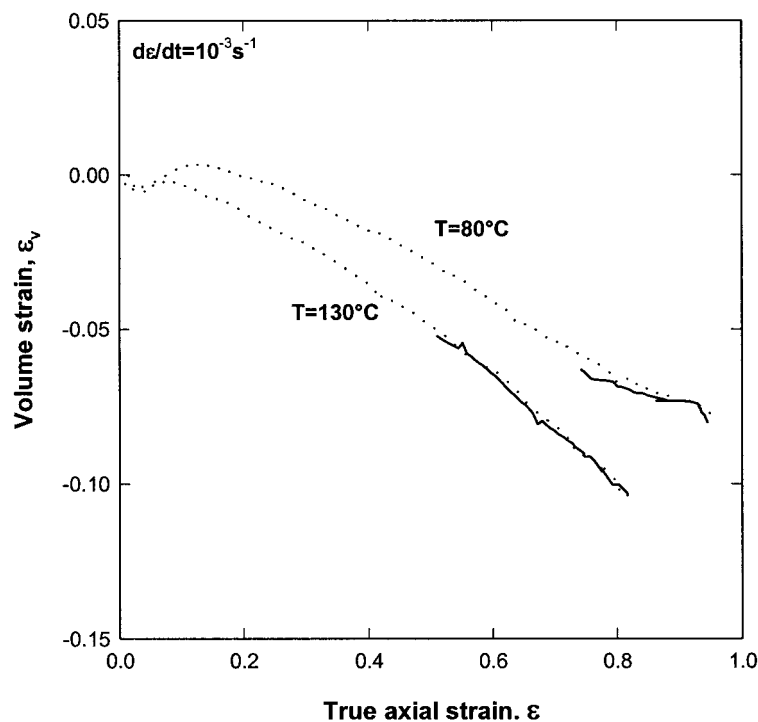


Figure 5 Reversibility of ϵ_v (continuous lines) upon unloading at 10^{-3} s^{-1} and two temperatures.

strain rate.² However, for creep at temperatures beyond 80°C , that is, above the glass-transition temperature of the constrained amorphous phase, we reported in a previous article³ that nonplasticized PVDF did show significant compaction (while ϵ_v remained positive at 25°C). For the latter material, we suggested that at 80°C , when the overall amorphous phase was rubbery, the chain orientation process (which induced material densification) overrode the cavitation processes (which favored dilatation). Now, in the case of plasticized PVDF, the increase in chain mobility favored the orientation mechanisms in the strain range under investigation. The partial recovery of ϵ_v on unloading favored this argument (continuous lines in Fig. 5).

At last, it is obvious that the dilatational phenomenon observed for the experiment carried out at 80°C and 10^{-4} s^{-1} can be assigned to elastic deformation because it occurred up to the yield point and attained $\epsilon_v \approx 0.01$ at $\epsilon \approx 0.1$, the ϵ_v value predicted with a Poisson's ratio of $\nu \approx 0.37$. Unexpectedly, this positive ϵ_v value was not observed for any other experimental conditions presented in this article. One explanation could be that the order of magnitude of the compaction induced by the orientation of amorphous chain segments, at the early stage of the deformation, may have been comparable to the dilatation caused by elastic deformation. As a result, both phenomena overlapped, and no ϵ_v value was measured up to $\epsilon = 0.1$. However, the presence of a positive ϵ_v value at 80°C and 10^{-4} s^{-1} remains unclear.

Creep behavior

Figure 6 depicts the creep behavior of plasticized PVDF at 80°C and 15 MPa. The curve of the true axial stress versus the elapsed time displays three domains: (1) instantaneous elastic deformation up to $\epsilon = 0.1$, (2) primary creep from $\epsilon = 0.1$ to $\epsilon = 0.27$ characterized by a steady decrease in the strain rate ($d\epsilon/dt$) due to an increase in the defect density hindering molecular mobility, and (3) secondary creep beyond $\epsilon = 0.27$ characterized by a constant value of $d\epsilon/dt$ ($2.6 \cdot 10^{-6} \text{ s}^{-1}$) due to chain relaxation and molecular rearrangements keeping the defect density constant. Finally, the corresponding ϵ_v value decreased regularly with time.

Figure 7 shows ϵ_v plotted as a function of ϵ . Two domains can be seen: (1) up to $\epsilon = 0.1$, that is, in the region of instantaneous elastic deformation, ϵ_v increases for $\epsilon_v \approx 0.01$, and (2) beyond $\epsilon = 0.1$, ϵ_v decrease linearly with a slope of $d\epsilon_v/d\epsilon = -0.11$. For a tensile test, the former domain was ascribed to the dilatational effect induced by the elastic deformation, and the latter was attributed to chain orientation taking place during the deformation.

At this point, two remarks should be made: (1) the same $d\epsilon_v/d\epsilon$ value found in the tensile test was still obtained, and this suggested that the orientation phenomenon was only temperature-dependent, and (2) once again, the dilatational effect associated with elastic deformation was observed for the creep test performed at 80°C .

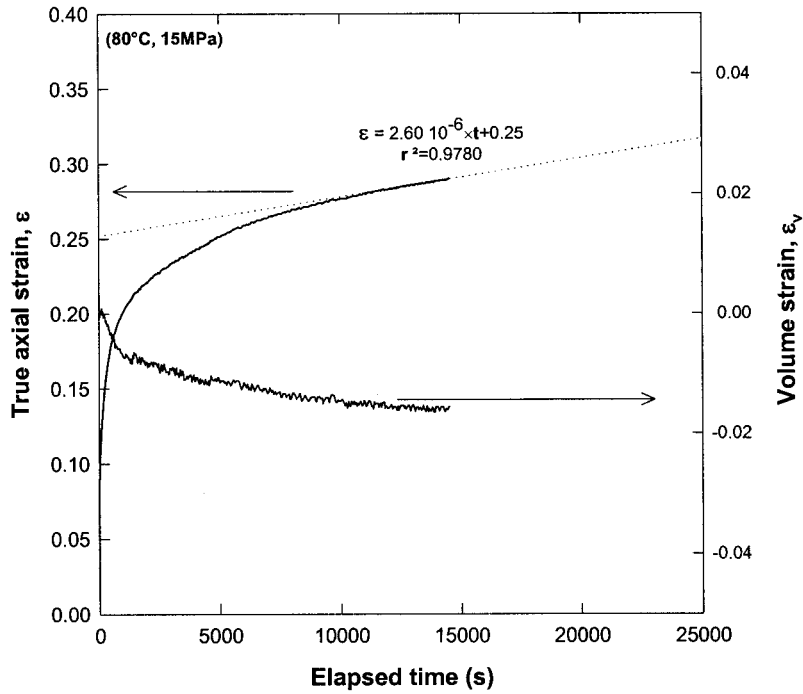


Figure 6 ϵ and ϵ_v versus the elapsed time for plasticized PVDF under creep testing at 80°C and 15 MPa.

CONCLUSIONS

This study has revealed that the first stage of plastic deformation of plasticized PVDF occurs via a compaction phenomenon. This compaction arises during the early stage of the deformation, that is, as early as the

yield point, and over the entire range of investigated temperatures and strain rates. This process is more pronounced as the temperature increases and seems to be independent of the strain rate. The partial recovery of the deformation suggests that amorphous chain

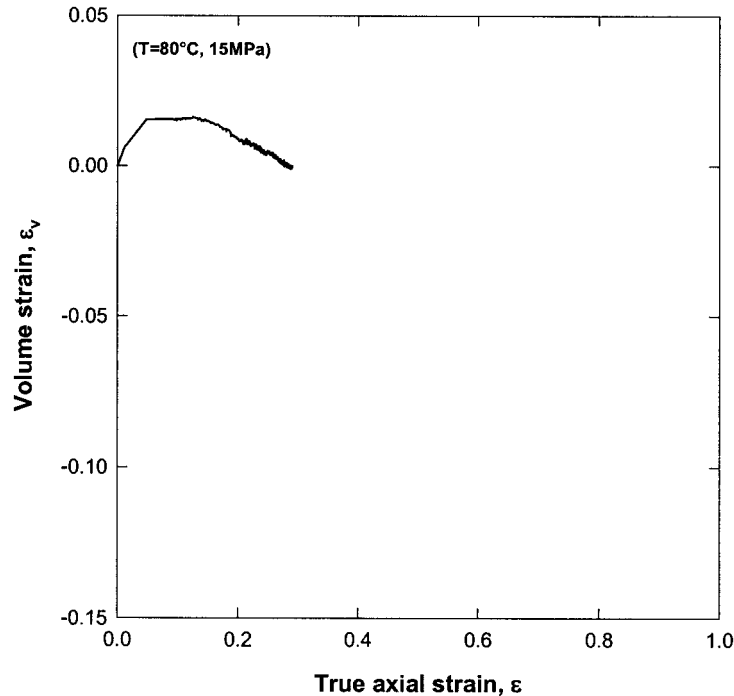


Figure 7 ϵ_v versus ϵ for plasticized PVDF during creep testing at 80°C and 15 MPa.

orientation is the micromechanism responsible for this behavior. This negative variation of ϵ_v with strain is an asset to plasticized PVDF. Indeed, this mechanism delays, further in deformation, the onset of plastic instability and its accompanying cavitation process. Thus, damage resistance is greatly improved.

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