

Time-Dependent Response of Thin-Film Piezoelectric Polymer Polyvinylidene Fluoride

Aleksandra M. Vinogradov*
Montana State University, Bozeman, Montana 59717

and
Shane C. Schumacher†
University of Wyoming, Laramie, Wyoming 82071

A summary of recent research results regarding the time-dependent response of a thin-film piezoelectric polymer polyvinylidene fluoride is presented. At present, polyvinylidene fluoride and its copolymers comprise the principal commercially available group of polymers that exhibit strong piezoelectric properties. In this paper, the mechanical response of polyvinylidene fluoride has been studied on the basis of a comprehensive experimental program. It is shown that, within certain limits, the material can be treated as linearly viscoelastic. However, under long-term conditions involving superimposed static and oscillatory loads, the polymer tends to exhibit nonlinear creep behavior that depends on the magnitude of mean stresses, stress amplitudes, and frequencies. The findings reported are of immediate practical significance given that polyvinylidene fluoride thin films are typically employed as sensors or actuators designed to function in vibratory environments.

Nomenclature

| | | |
|-----------------|---|---|
| C_n | = | creep compliance, GPa^{-1} |
| E_n | = | relaxation function, GPa |
| n | = | direction of material properties ($n = 1, 2$) |
| T | = | temperature, $^{\circ}\text{C}$ |
| t | = | time, s |
| Γ | = | gamma function |
| ε | = | strain, mm/mm |
| ε_m | = | static creep strain, mm/mm |
| ε_v | = | vibrocreep strain, mm/mm |
| σ | = | stress, MPa |
| σ_a | = | stress amplitude, MPa |
| σ_m | = | mean stress, MPa |
| σ_Y | = | yield stress, MPa |
| ω | = | frequency, Hz |

Introduction

IN the past few decades, a new generation of synthetic piezoelectric polymers has emerged that possess the ability to react actively to changing stimuli as a result of energy conversion from mechanical to electrical and vice versa. Piezoelectric polymer systems have been increasingly integrated in structural design as active elements capable of sensing and responding intelligently to external stimuli. A broad range of applications utilizing such functions include active vibration damping, acoustic suppression, damage detection, shape and position control of compliant structures, and self-inspection of structural integrity.^{1,2}

In general, the diverse group of piezoelectric materials includes a variety of synthetic polymers such as polypropylene, polystyrene, and poly(methyl methacrylate); semicrystalline polyamides such as nylon-11; and amorphous polymers such as vinyl acetate. However, piezoelectric effects in these materials are relatively weak, often unstable, and, therefore, are of limited practical significance. Strong piezoelectricity has been observed only in a synthetic polymer polyvinylidene fluoride (PVDF or PVF_2) and PVDF copolymers.

Currently, polyvinylidene fluoride (PVDF) is the principal commercially available polymer that exhibits strong piezoelectric properties. Typically, PVDF is produced in the form of thin films of thickness ranging from 102×10^{-4} to 762×10^{-3} mm. A thin layer of nickel, copper, or aluminum is deposited on both surfaces of the material to provide electrical conductivity when an electrical field is applied, or to allow measurements of the charge induced by mechanical deformations.

Since the discovery of piezoelectric effects in PVDF by Kawai,³ the properties of this material have been studied by many investigators. However, research efforts in this subject area have focused mainly on the piezoelectric response of the polymer, whereas the mechanical properties of PVDF have attracted limited attention.^{4–6}

The main objective of this paper is to provide a summary review of recent research findings regarding the mechanical behavior of PVDF thin films. Particular attention is given to the time-dependent response of the material under static and cyclic loading conditions.

Physical Properties of PVDF

Polyvinylidene fluoride is a semicrystalline polymer with typical crystallinity of, approximately, 50%. The amorphous phase of the polymer has the properties of a supercooled liquid with the glass transition temperature of about -50°C .

The molecular structure of polyvinylidene fluoride consists of the repeated monomer unit $-\text{CF}_2-\text{CH}_2-$. The atoms are covalently bonded together, forming long molecular chains. Because the hydrogen atoms are positively charged and the fluoride atoms are negatively charged with respect to the carbon atoms, PVDF is inherently polar. However, the net polar moment of the material in its original state is zero due to the random orientation of the individual crystallites.⁵

Piezoelectric properties of PVDF are obtained by subjecting the polymer to an elevated, typically, 130°C temperature and an electric field of up to 100 kV/mm. Stretching and polling of extruded thin sheets of the polymer causes an alignment of its molecular chains in the stretch direction. The material is then cooled down while the poling field is maintained. The result is that the alignment of the dipoles is permanently fixed.

The properties of PVDF thin films are commonly defined by the constitutive equations of linear piezoelectricity, which describe the interaction between the mechanical and electrical responses of the material in terms of stress, strain, electric flux density, electric field, and dielectric tensors.⁷ The functional relations between these characteristics are linear, implying, in particular, direct proportionality between mechanical loads and deflections and no energy

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*Professor, Department of Mechanical and Industrial Engineering, 220 Roberts Hall. Member AIAA.

†Graduate Student, Department of Mechanical Engineering.

dissipation when the material is subjected to loading–unloading cycles. However, experiments indicate that these assumptions have certain limitations. In particular, it is shown that PVDF is a polymer characterized by a stress-dependent nonlinear piezoelectric response.⁸ The polymer has also demonstrated creep and relaxation behavior,^{9–11} as well as measurable energy losses under cyclic conditions.^{12–16}

Stress–Strain Behavior of PVDF

Static stress–strain tests have been performed using PVDF thin film samples of 28- μm thickness. The material has been tested in two material directions, that is, the directions parallel (direction 1) and perpendicular (direction 2) to the aligned molecular chains of the polymer. The results have demonstrated that PVDF is an orthotropic material.^{10,17}

The stress–strain diagrams shown in Figs. 1 and 2 illustrate the mechanical response of PVDF in two in-plane material directions. According to Fig. 1, progressive loading of the material tested along its aligned molecular chains causes a steady increase of stresses, culminating in sudden failure. This response of PVDF is similar to the typical rubbery behavior of polymers. In contrast, the stress–strain diagram in direction 2 is characterized by an increase of stresses, reaching a certain maximum value, at which point deformation becomes localized, forming a neck. This behavior is similar to that of polymeric materials in their glassy state. The mechanical characteristics of PVDF thin films in both in-plane material directions are summarized in Table 1.^{5,6,10}

Creep and Relaxation Properties of PVDF

Creep and relaxation characteristics of PVDF thin films have been determined from a series of experiments involving thin-film PVDF

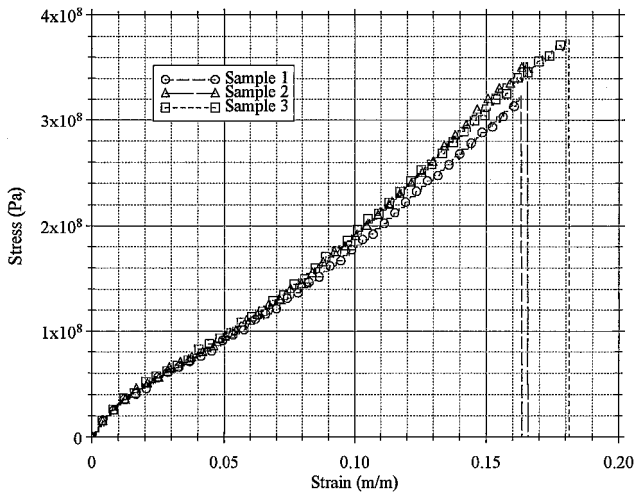


Fig. 1 Stress–strain diagram of PVDF (direction 1).

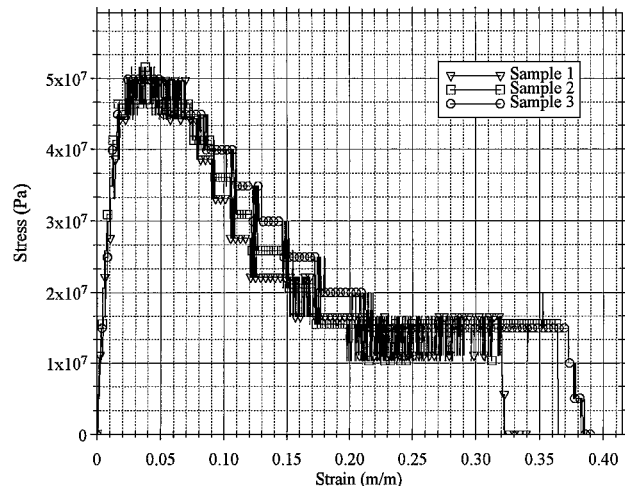


Fig. 2 Stress–strain diagram of PVDF (direction 2).

Table 1 Elastic characteristics of PVDF

| Symbol | Value | Unit |
|------------------------|-------------------|------|
| <i>Young's modulus</i> | | |
| E_1 | 2.7×10^9 | Pa |
| E_2 | 2.5×10^9 | Pa |
| <i>Yield stress</i> | | |
| σ_{Y1} | 4.5×10^7 | Pa |
| σ_{Y2} | 3.9×10^7 | Pa |
| <i>Yield strain</i> | | |
| ε_{Y1} | 1.8 | % |
| ε_{Y2} | 1.4 | % |
| <i>Ultimate stress</i> | | |
| σ_{U1} | 3.5×10^8 | Pa |
| σ_{U2} | 5.0×10^7 | Pa |
| <i>Ultimate strain</i> | | |
| ε_{U1} | 16.9 | % |
| ε_{U2} | 2.5 | % |
| <i>Poisson's ratio</i> | | |
| ν_1 | 0.326 | — |
| ν_2 | 0.348 | — |

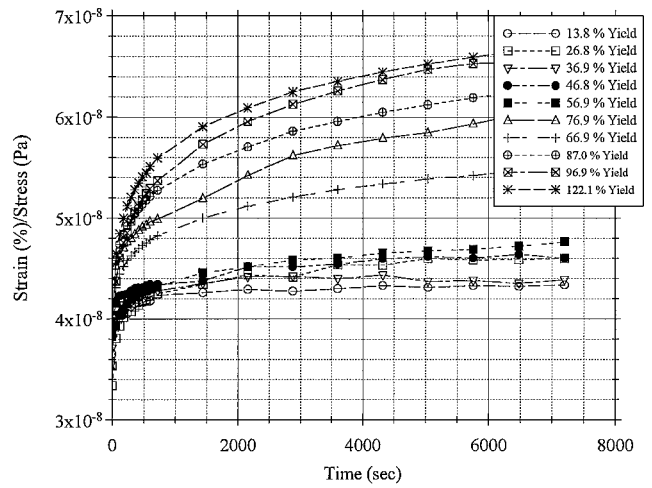


Fig. 3 Creep of PVDF (direction 1).

samples tested in both in-plane material directions at 10 different stress levels.^{10,11,17} Tests have been performed under sustained loading conditions at room temperature. Strain measurements have been taken using LVDT with an automated data acquisition system.

Based on these experiments, it has been observed that, at stress levels below 57% of σ_{Y1} and 76% of σ_{Y2} in the material directions 1 and 2, respectively, the time-dependent response of PVDF thin films can be treated as stress independent. Hence, within these limits, the creep properties of PVDF can be characterised as linearly viscoelastic.^{18,19} The results of the creep tests for both in-plane material directions are illustrated in Figs. 3 and 4.

Because the thickness of PVDF thin films is negligible in relation to their in-plane material dimensions, their creep properties in the linear viscoelastic range are defined in terms of the following material characteristics: creep compliances $C_n(t)$ and relaxation functions $E_n(t)$ in the material direction n ($n = 1, 2$). Accordingly, the viscoelastic behavior of the material is represented by the constitutive equation in the form¹⁹

$$\varepsilon(t) = \sigma(0)C_n(t) + \int_0^t C_n(t - \tau) \frac{d\sigma}{d\tau} d\tau, \quad n = 1, 2 \quad (1)$$

Based on the obtained experimental data,^{10,11,17} the functions $C_n(t)$, ($n = 1, 2$) have been represented analytically in the form of a power law:

$$C_n(t) = a_n + b_n t^{\lambda_n}, \quad n = 1, 2 \quad (2)$$

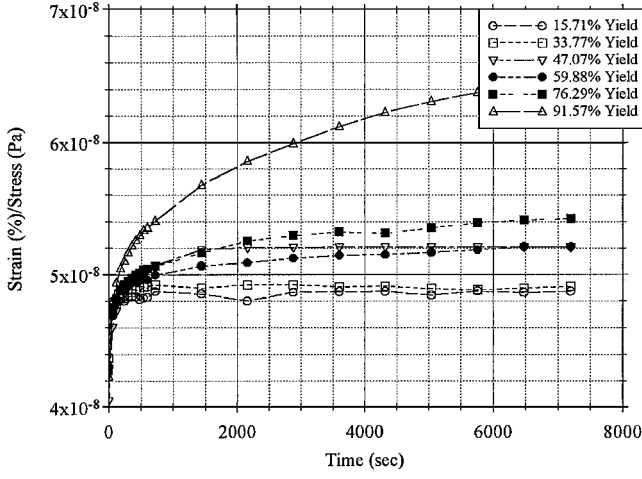


Fig. 4 Creep of PVDF (direction 2).

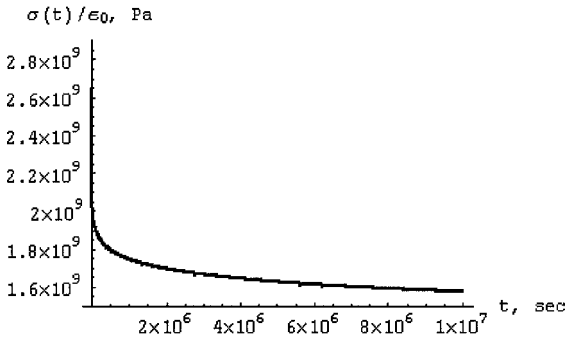


Fig. 5 Relaxation function of PVDF (direction 1).

such that, in the material direction 1,

$$a_1 = 3.206 \times 10^{-10}, \quad b_1 = 5.018 \times 10^{-11}, \quad \lambda_1 = 0.107 \quad (3)$$

and, in the material direction 2,

$$a_2 = 3.514 \times 10^{-10}, \quad b_2 = 0.111 \times 10^{-11}, \quad \lambda_2 = 0.085 \quad (4)$$

The relaxation functions of PVDF in each in-plane material direction have been obtained by solving Eq. (1) in terms of $\sigma(t)$. By the substitution of Eq. (2) into Eq. (1), the latter assumes the form of an inhomogeneous Abel integral equation (see Ref. 20)

$$\varepsilon(t) = a_n \sigma(t) + b_n \lambda_n \int_0^t \left[\frac{\sigma(\tau)}{(t-\tau)^{1-\lambda_n}} \right] d\tau \quad (5)$$

The latter has been solved in terms of $\sigma(t)$ using the Laplace transformation method. The respective solution has been obtained in the form

$$\sigma(t) = \frac{\varepsilon(t)}{a_n} - \frac{1}{a_n} \int_0^t \sum_{k=1}^{\infty} \frac{[(b_n \lambda_n / a_n) \Gamma(\lambda_n) (t-\tau)^{\lambda_n}]^k}{(t-\tau) \Gamma(k \lambda_n)} \varepsilon(\tau) d\tau \quad (6)$$

where $n = 1, 2$, and $\Gamma(\lambda_n)$ and $\Gamma(k \lambda_n)$ denote gamma functions.

At a constant strain $\varepsilon(t) = \varepsilon_0$, Eq. (6) describes stress relaxation of PVDF. By the specification in Eq. (6) of the coefficients a_n , b_n , and λ_n , ($n = 1, 2$) from either Eq. (3) or Eq. (4), the relaxation modulus $E_n(t)$ ($n = 1, 2$) in the respective material direction has been obtained using the software package MATHEMATICA. A graphical representation of the relaxation functions of PVDF for both in-plane material directions of the polymer is given in Figs. 5 and 6, respectively.

Table 2 Cyclic test conditions for PVDF thin films

| Mean stress $\sigma_m = k_1 \sigma_{Y1}, k_1$ | Amplitude $\sigma_a = k_2 \sigma_{Y1}, k_2$ | | | |
|--|--|-----|------|-----|
| 0.30 | 0.1 | 0.2 | — | — |
| 0.45 | 0.1 | 0.2 | 0.35 | 0.4 |
| 0.60 | 0.1 | 0.2 | 0.40 | 0.5 |

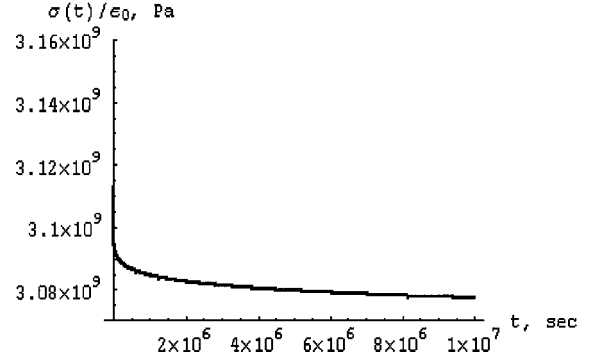


Fig. 6 Relaxation function of PVDF (direction 2).

Equations (5) and (6) provide complete characterization of the creep and relaxation properties of PVDF. Note that, based on the experimental data, it is clear that time-dependent effects in the mechanical response of PVDF are of greater significance in the principal material direction 1.

Cyclic Creep of PVDF

In a separate study, the time-dependent behavior of PVDF has been investigated under the conditions of combined static and cyclic loads. The investigation has been motivated by the empirical evidence that, in general, polymers tend to exhibit measurable changes in their creep response due to the presence of cyclic loads. This phenomenon, known as vibrocreep, is typically observed in terms of accelerated creep rates as compared with the creep rates at the respective static loads.^{21–25}

The understanding of vibrocreep effects in PVDF is of particular importance, first, because the polymer is typically employed in sensing and actuation devices designed to functions in vibratory environments and, second, because, in practice, PVDF thin films perform only in the tension–tension mode, always requiring static pretension.

In this study, thin film 7.62×76.2 mm PVDF samples of $28\text{-}\mu\text{m}$ thickness with two $10\text{-}\mu\text{m}$ silver layers deposited on both surfaces of the film were tested under the conditions of superimposed static and cyclic loads such that

$$\sigma(t) = \sigma_m + \sigma_a \sin \omega t \quad (7)$$

where ω denotes cyclic frequency.

To implement the experimental program, a special apparatus was designed, involving a load pretension device, electrodynamic vibration exciter, power amplifier, and signal generator. Displacements were measured by LVDT. Test data were processed using a software supported data acquisition system.

Because PVDF thin films have demonstrated greater creep rates in the direction of the aligned molecular chains, vibrocreep experiments have been performed in the principal material direction 1. Tests have been conducted at the temperature $T = 23^\circ\text{C}$, at three different frequencies, $\omega = 5, 10$, and 20 Hz, over a range of mean stresses σ_m and stress amplitudes σ_a , defined in proportion to the yield stress σ_{Y1} of the material as shown in Table 2.

Throughout the entire program, PVDF samples were prepared in compliance with American Society for Testing and Materials D882–95a standards. At least three–five identical experiments have been performed to ensure reproducible results.

In the program, vibrocreep effects have been characterized in terms of the measured vibrocreep strain $\varepsilon_v(t)$, or normalized vibrocreep creep strain $\varepsilon_v(t)/\sigma_m$. The obtained experimental results have

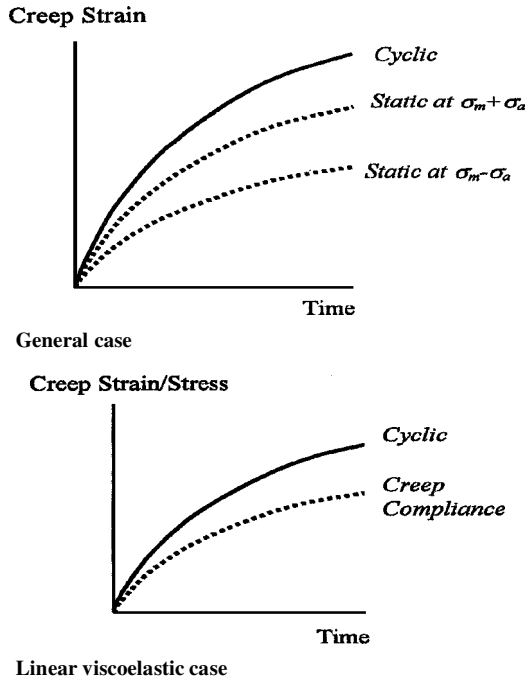
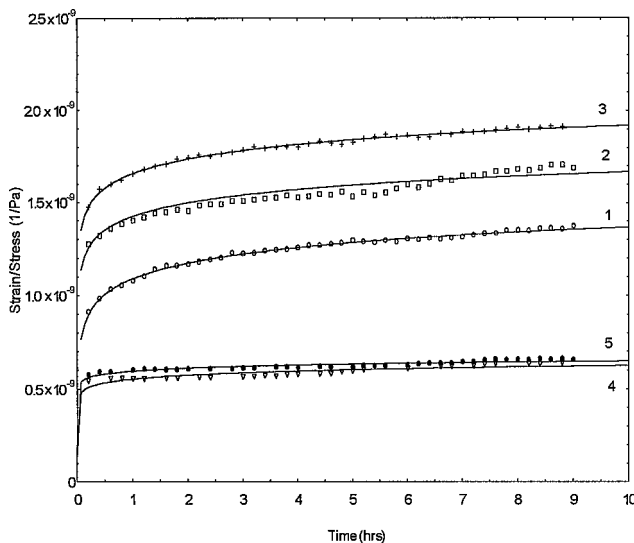


Fig. 7 Vibrocreep criteria.

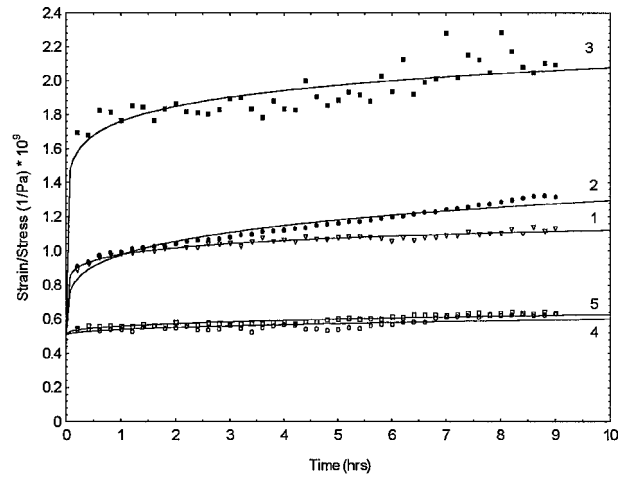
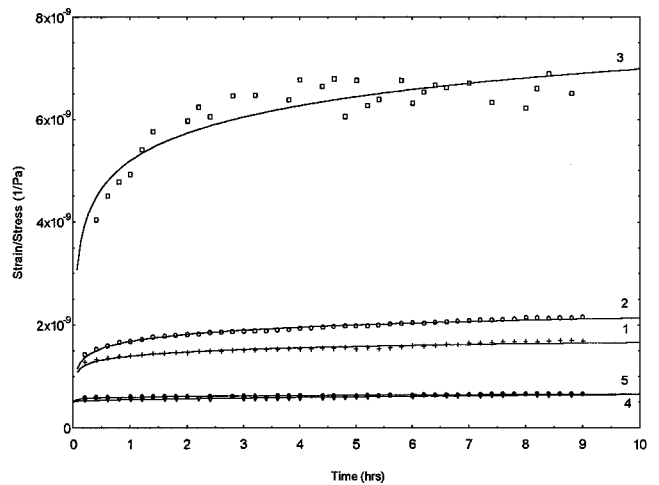
Fig. 8 Vibrocreep of PVDF, frequency effect: cyclic ($\sigma_m = 0.45\sigma_{Y1}$ and $\sigma_a = 0.1\sigma_{Y1}$): 1, $\omega = 5$; 2, $\omega = 10$; and 3, $\omega = 20$ Hz; static: 4, $0.45\sigma_{Y1}$ and 5, $0.6\sigma_{Y1}$.

been assessed in relation to static creep defined in terms of $\varepsilon_m(t)$ or $\varepsilon_m(t)/\sigma_m$, where $\varepsilon_m(t)$ denotes time-dependent strain under constant stress σ_m .

It has been considered that the polymer exhibited measurable vibrocreep effects if the cyclic creep curve $\varepsilon_v(t)$ was observed outside the envelope formed by the creep curves $\varepsilon_{m+a}(t)$ and $\varepsilon_{m-a}(t)$, corresponding to static stresses $(\sigma_m + \sigma_a)$, and $(\sigma_m - \sigma_a)$, respectively. In the linear viscoelastic range, vibrocreep effects have been assessed through a comparison of normalized vibrocreep strains $\varepsilon_v(t)/\sigma_m$ and the respective creep compliances $\varepsilon_m(t)/\sigma_m$. These vibrocreep criteria are illustrated schematically in Fig. 7.

Some representative results demonstrating vibrocreep effects on the time-dependent response of PVDF in the material direction 1, depending on the frequency, mean stress, and stress amplitude, are shown in Figs. 8–13. A more complete account of the results obtained from this investigation is given in Ref. 25.

The diagrams in Figs. 8 and 9 provide a comparison between the creep response of PVDF under combined static and cyclic loading conditions (curves 1, 2, and 3) and the respective creep behavior of the polymer subjected to static loads (curves 4 and 5). Both Figs. 8

Fig. 9 Vibrocreep of PVDF, frequency effect: cyclic ($\sigma_m = 0.3\sigma_{Y1}$ and $\sigma_a = 0.1\sigma_{Y1}$): 1, $\omega = 5$; 2, $\omega = 10$; and 3, $\omega = 20$ Hz; static: 4, $0.3\sigma_{Y1}$ and 5, $0.45\sigma_{Y1}$.Fig. 10 Vibrocreep of PVDF, amplitude effect: cyclic ($\sigma_m = 0.45\sigma_{Y1}$ and $\omega = 10$ Hz): 1, $\sigma_a = 0.1\sigma_{Y1}$; 2, $\sigma_a = 0.2\sigma_{Y1}$; and 3, $\sigma_a = 0.4\sigma_{Y1}$; static: 4, $0.45\sigma_{Y1}$ and 5, $0.6\sigma_{Y1}$.

and 9 demonstrate that PVDF samples undergo considerable acceleration of creep rates due to cyclic loading effects. Consistently, cyclic creep rates tend to increase as the frequency increases from 5 to 10 Hz and, further, to 20 Hz.

The diagrams in Figs. 10 and 11 demonstrate that, similarly to frequency effects, PVDF samples exhibit acceleration of creep rates as the cyclic amplitudes tend to increase. Note that curve 3 in Fig. 10 illustrates considerable creep acceleration caused by a combination of cyclic loading effects and the stress-induced viscoelastic non-linearity. This observation is based on the fact that, in the latter experiments, the maximum stress $\sigma_m + \sigma_a = 0.85\sigma_{Y1}$ exceeds the viscoelastic linearity limit of $0.57\sigma_{Y1}$ for PVDF films in the stretch direction.

The diagrams in Figs. 12 and 13 demonstrate the effects of mean stress magnitudes on the cyclic creep response of PVDF. Based on these results, one can observe that increases of mean stresses lead to accelerated creep rates of PVDF samples (curves 1–3) in comparison with static creep represented by curves 4–6. However, this effect appears to diminish as the magnitude of the mean stress approaches the viscoelastic linearity limit.

It is of interest to evaluate the observed vibrocreep response of PVDF in light of other related research findings reported in the literature. Clearly, PVDF samples subjected to combined static and cyclic loads have consistently shown creep acceleration as compared with the respective creep behavior of the polymer under static loading conditions. Similar results have been reported for other polymers.^{23–28}

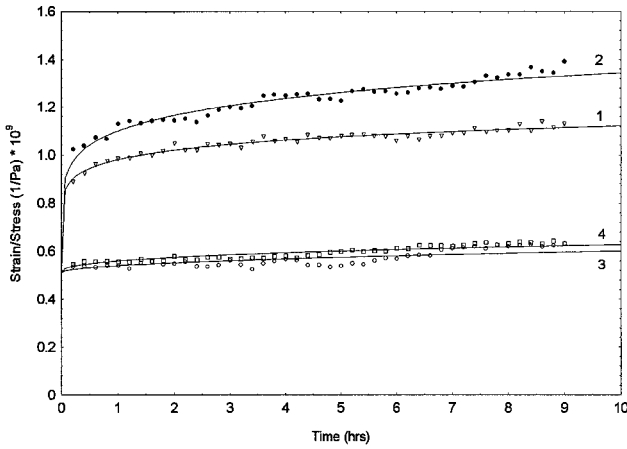


Fig. 11 Vibrocreep of PVDF, amplitude effect: cyclic ($\sigma_m = 0.3\sigma_{Y1}$ and $\omega = 5$ Hz): 1, $\sigma_a = 0.1\sigma_{Y1}$ and 2, $\sigma_a = 0.2\sigma_{Y1}$; static: 3, $0.3\sigma_{Y1}$ and 4, $0.6\sigma_{Y1}$.

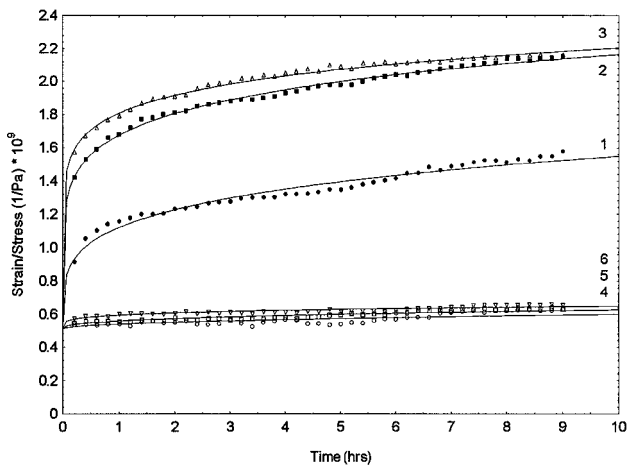


Fig. 12 Vibrocreep of PVDF, mean stress effect: cyclic ($\sigma_a = 0.2\sigma_{Y1}$ and $\omega = 10$ Hz): 1, $\sigma_m = 0.3\sigma_{Y1}$; 2, $\sigma_m = 0.45\sigma_{Y1}$; and 3, $\sigma_m = 0.6\sigma_{Y1}$; static: 4, $0.3\sigma_{Y1}$; 5, $0.45\sigma_{Y1}$; and 6, $0.6\sigma_{Y1}$.

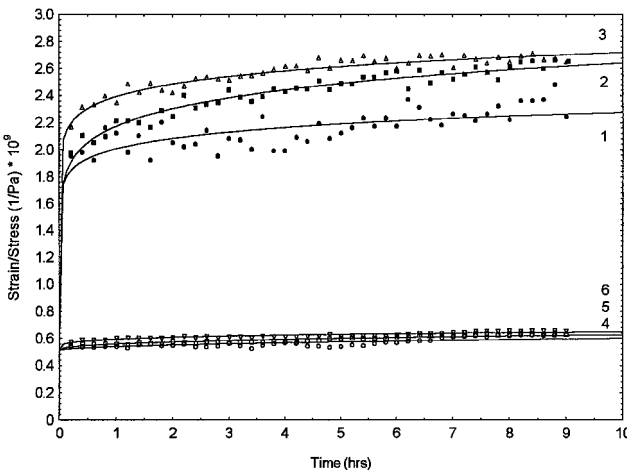


Fig. 13 Vibrocreep of PVDF, mean stress effect: cyclic ($\sigma_a = 0.2\sigma_{Y1}$ and $\omega = 20$ Hz): 1, $\sigma_m = 0.3\sigma_{Y1}$; 2, $\sigma_m = 0.45\sigma_{Y1}$; and 3, $\sigma_m = 0.6\sigma_{Y1}$; static: 4, $0.3\sigma_{Y1}$; 5, $0.45\sigma_{Y1}$; and 6, $0.6\sigma_{Y1}$.

In general, cyclic loading effects on the time-dependent response of polymer systems have been treated in terms of creep-fatigue interaction.^{21,22,26,29} It has been observed that these effects are produced by couplings between several mechanisms including intrinsic creep, damage evolution, and hysteretic heating. The significance of each mechanism depends on the loading and temperature conditions, as well as the type of the polymer under consideration. For example, it is shown that fatigue failure of polymers is dominated by

hysteretic heating at higher stress levels and frequencies, whereas damage accumulation processes become critical at lower stresses and frequencies.²²

Essentially, the process of cyclic damage development in polymers tends to evolve through several progressive stages such as crazing, crack nucleation, and crack propagation.^{21,30,31} Even before the appearance of crazes, polymers undergo measurable changes of their properties due to cyclic loading regimes.²⁸ In this regard, experiments indicate that, at the initial stages of damage development, polymers are sensitive to cyclic frequency effects, such that damage evolution in terms of nucleation and propagation of crazes tends to accelerate in response to increased cyclic frequencies.²⁶ The latter observations may well explain the frequency-dependent vibrocreep effects in PVDF, as shown in this study. Note, however, that the effects of mean stresses and cyclic amplitudes on the time-dependent response of PVDF, among other polymers, are not clearly understood and require further investigation.

Conclusions

The paper provides a summary review of the mechanical properties of the piezoelectric polymer PVDF. Experiments indicate that PVDF thin films are orthotropic, time-dependent materials. Static tests demonstrate that there are significant differences between the responses of the material in two in-plane material directions, those coinciding with, and perpendicular to, the aligned molecular chains of the polymer. Although the elastic moduli in both material directions are practically identical, other mechanical characteristics of PVDF differ considerably.

Creep tests of PVDF thin films under sustained loading conditions at ambient temperature demonstrate that the linear viscoelastic theory based on the Boltzmann's superposition principle accurately represents the time-dependent response of PVDF, provided that the applied stresses remain below certain limits, that is, 57% of σ_{Y1} and 76% of σ_{Y2} in the in-plane material directions 1 and 2, respectively. For higher stresses, creep properties of PVDF must be characterized by a nonlinear viscoelastic constitutive model.

In the linear viscoelastic deformation range, the creep compliances of PVDF in both in-plane material directions have been represented in the form of a power law. The respective relaxation properties of the material have been defined in terms of gamma functions.

The results of the study concerning the cyclic creep response of PVDF demonstrate that the polymer tends to exhibit accelerated creep rates under the conditions of superimposed static and cyclic loads. Creep acceleration due to cyclic loading effects has been observed even in the range of stresses well below the viscoelastic linearity limit. It is clear that the long-term cyclic response of PVDF is essentially nonlinear because it does not represent a simple superposition of the responses to static and fully reversed cyclic loads applied separately.

Acknowledgment

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J. Lassiter
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