Relaxation Behavior in Polarized PVDF Films under the Influence of Mechanical and Thermal Multistresses above Glass-Transition Temperature

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ABSTRACT: The discharging currents in cast-prepared PVDF films are measured under the influence of mechanical and thermal multistresses. Analysis of the experimental data in the framework of the Kohlrausch-Williams-Watt's function is carried out. A linear relationship between the logarithm of the relaaxation time and the applied stress is verified, which is displayed as the mechanical offset stress increases. With the aid of the rate theory and the concept of the free volume, the activation volume, v^*, has been determined and is consistent with the reported value. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 859–864, 1998

Key words: relaxation behavior; polarized PVDF films; mechanical and thermal multistress; glass transition temperatures

INTRODUCTION

Much research has been aimed at investigation of polarization and depolarization processes in dielectrics. Many polymers are dielectric and, in an electric field, accumulate electric charges and form electrets, i.e., dielectrics with quasipermanent charge or polarization.[1] The process of depolarization of the sample is accompanied by a current flow due to reorientation of dipoles and movement of free excess charges, and it is determined by reheating the polarized or charged dielectric in short circuit and measuring the ensuing discharge current. Measurements of depolarization charges in the thermally stimulated depolarization current (TSDC) spectra under different experimental conditions is employed for analysis of dipole structure and carrier trapping.[2,3]

The concept of the free volume structure of solids, and subsequently the correlation between free volume and the physical properties of solids and its interpretation, is a very useful and popular idea in the physics of disordered systems, especially polymers.[4,5] The role of the free volume in relaxation processes is well predicted by a molecular model[6] for the relaxation of internal energy and volume in polymer glasses. In general, electrets exhibit piezoelectric and pyroelectric properties. That is, they respond electrically to mechanical and thermal stresses. The term relaxation process is used to describe processes in which a system that is initially out of equilibrium relaxes into a steady state. It, thus, includes a wide variety of phenomena, including structural relaxation, volume relaxation, dipole relaxation, and the movement of free charges.

The present contribution is concerned with the time-dependent depolarization current, which is a direct consequence of the relaxation process in electrets. Above all, current decays, which are displayed as the mechanical offset stress increases, will be discussed. A physical model,

based partially on the rate theory, to describe the relaxation process of electrets under combined thermal and mechanical multistresses and partially on the free volume concept, is proposed, and its applicability is analyzed and discussed.

Theoretical Considerations

It is considered that polarization/depolarization of the material during a thermally stimulated experiment is a rate process,[7] then rotation of the dipole is equivalent to passage over an energy barrier.[8] Because there is equilibrium between the initial reacting species and the transition state, the probability of forming the activated complex is determined by the Boltzmann factor $\downarrow$ e$^-\Delta G/RT$, where $\Delta G = \Delta H - T\Delta S$. G, ΔH, and ΔS are activation parameters, T is the absolute temperature, and R is the gas constant. With no stress acting, a dynamic equilibrium exists, chain segments moving with frequency over the potential barrier in each direction given by:

$$\nu = \nu_o \exp(-\Delta H/RT) \quad (1)$$

where $\nu_o = (KT/h)$ e$^{\Delta S/R}$ includes the entropy factor, K is the Boltzmann constant, and h is Planck's constant.

It is assumed that deformation of the polymer involves the motion of chain molecules or parts of the chain molecule over a potential energy barrier. The basic molecular process could be either intermolecular (e.g., chain sliding) or intramolecular (e.g., a change in the conformation of the chain). Hence, the application of a stress, σ, produces linear shifts, $v^* \sigma$, of the energy barriers in a symmetrical fashion,[9] where v^* is the activated volume. The temperature shifts could be interpreted in terms of an activated process, where the activation energy fell in a linear fashion with increasing stress. For the net flow of the material, eq. (1) becomes

$$\nu = \nu_o \exp(-\Delta H/RT) \sinh(v^* \sigma/RT) \quad (2)$$

So as a first-order approximation, where $\sinh(x) = 1/2 \exp(x)$, eq. (2) becomes:

$$\nu = (\nu_o/2) \exp[(\Delta H - v^* \sigma)/RT] \quad (3)$$

The relaxation time, τ, i.e., the time required to go over the energy barrier is given by:

$$\tau = 1/\nu = 2(\nu_o)^{-1} \exp[(\Delta H - v^* \sigma)/RT] \quad (4)$$

With this equation, the value of v^* can be obtained from the plot of ln (τ) vs. σ.

MATERIALS AND METHODS

Material and Film Preparation

Commercially available Poly(vinylidine fluoride), PVDF, was obtained from Polysci. Inc. USA. Polymer films were prepared by the cast technique. It is a semicrystalline polymer, of which the crystallinites vary in a typical range of 40–60% ,which is confirmed by our X- ray data. The material was dissolved in dimethylformamide (DMF), and the solution was poured into a shallow glass Petri dish. The solvent was evaporated at 397 K. Films, having thickness ranging from 25–35 μm, as measured by the traveling microscope, were obtained. Conducting circular surface of a radius of 5 mm were made on the film surface from graphite.

Measuring Methods

Details of the experimental arrangements, measuring techniques, and poling procedure have been described in other articles.[10,11] Thermoelectrets were prepared by placing the PVDF film in the dielectric cell, raising the sample temperature to $T_p = 373$ K, applying a polarizing electric field $E_p = 10^7$ V/m for $t_p = 30$ min. The sample is cooled from T_p to room temperature while the field is on. The electret is kept in the dielectric cell, in shorted position for about 5 min to remove stray charges. The sample is subsequently heated to a predetermined measuring temperature T_m, and is then subjected to a certain compressive force (stress σ). This produces a gradual discharge and depolarization current flows. All measurements were performed using the two-terminal method with guarding in order to avoid undesirable surface currents. Discharging currents were recorded using a Keithly Picometer model 485. The measurements are accurate to within +5% .

RESULTS AND DISCUSSIONS

Figures 1(A) and (B) show the depolarization current $J(t)$ in the PVDF film under constant applied stress $\sigma = 50.56 \times 10^4$ N/m^2 and for various constant measuring temperatures, T_m. An anom-
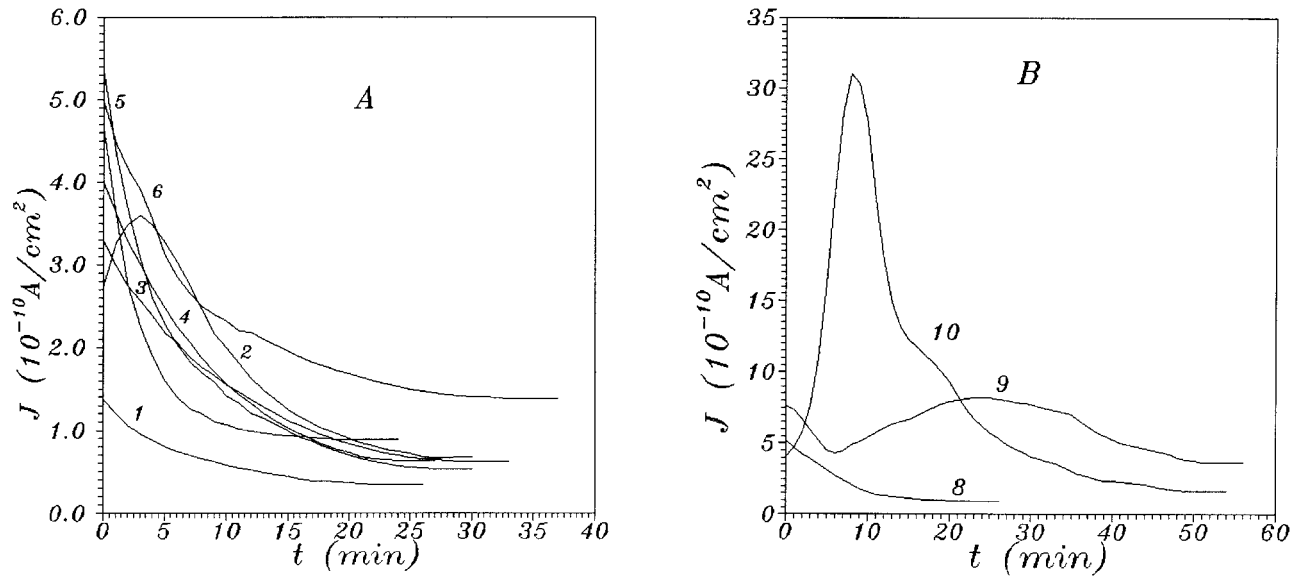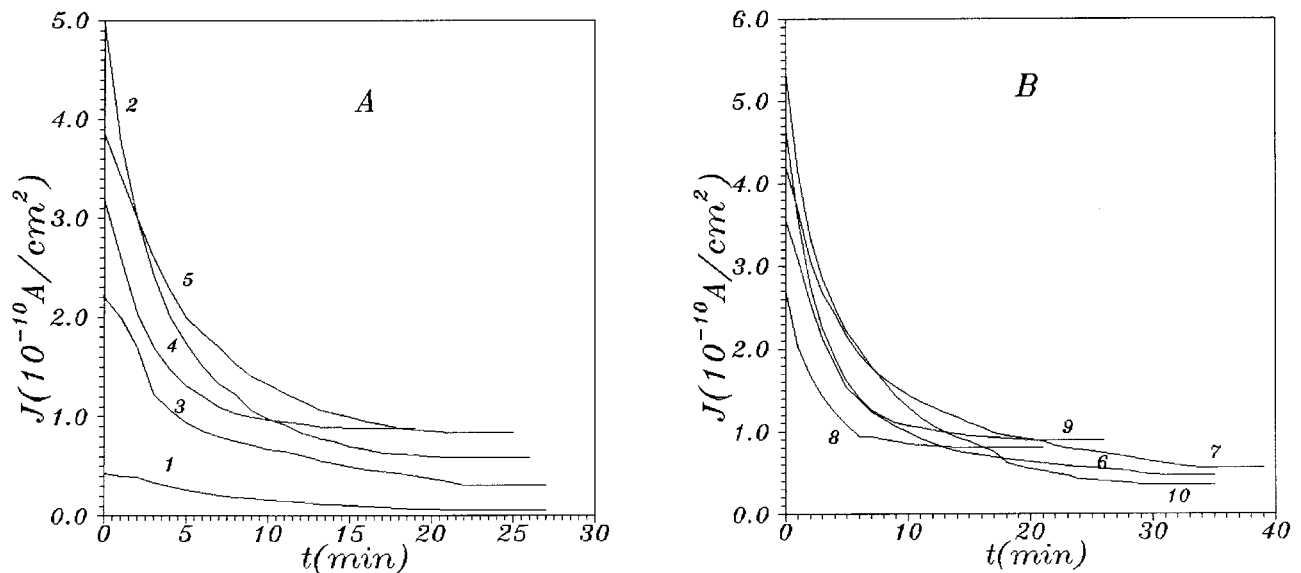
Figure 1. (A, B). Discharging currents in PVDF (25 μm) under applied stress, σ = 50.56 × 10⁴ N/m² and for various measuring temperatures: 1–303k, 2–323k, 3–333k, 4–343k, 5–353k, 6–363k, 7–373k, 8–383k, 9–393k, 10–403k.

alous current peak appeared at T_m = 323 K. This anomalous current peak can be ascribed to neutralized ionic species near the electrode.[12] On the other hand, a reversal in the discharge current behavior occurred at T_m = 393 K. The behavior of the discharging current at T_m > 383 K, as shown in Figure 1(B), cannot be explained by any relax-

ation process. It may be ascribed to detrapped charge carriers that are supposed to be located in the crystalline–amorphous interface region and from interfacial polarization.[13]

Figures 2(A) and (B) represent the discharging current in PVDF electrets maintained at T_m = 373 K and under various constant applied

Figure 2. (A, B). Discharging currents in PVDF at T_m = 373 K and for various applied stresses: (1—zero, 2—6.24, 3—12.48, 4—18.73, 5—24.97, 6—31.21, 7—37.45, 8—50.56, 9—62.24) × 10⁴ N/m².

stresses. Measurements showed that the discharging currents reach the maximum value J_o, after the application of the applied stress σ, within the time range of 1–10 s, so the first point plotted in Figures 1 and 2 is after time elapse of about 10 s. The general features of the discharge current are shown in Figures 1 and 2. It may be observed that a quasisteady-state discharging current is reached within a limited time range, t_s. This time range is both temperature, T_m, and applied stress, σ, dependent.

If the sample was polarized at a temperature T, the polarization would have a value $P(o)$ after an infinite time; thus, decay of the polarization after removal of the field is given by

$$P(t) = P(o) \exp[- t/\tau(T)] \qquad (5)$$

The corresponding depolarization current, $J(t)$, which is the quantity usually measured, is given by $J(t) = -dP(t)/dt$ so that $J(t) = P(t)/(T)$, where P is the polarization at any time t, and τ is a relaxation time.

The time dependence of any property (enthalpy, structure factor, dielectric behavior, stress response) may be given by the Williams-Watt or Kohlrausch function. The relaxation in complex, slowly relaxing, strongly interacting materials often follows the stretched exponential form.[14,15]

$$J(t)/J_o = \exp - (t/\tau_s)^\beta \qquad (6)$$

where $0 < \beta < 1$ and τ_s is the characteristic time for stretched law. This "anomolous" relaxation appears to be for more common than the above "conventional" Debye exponential form ($\beta = 1$). If there is no physical aging and the structure is stationary throughout the time period of measurement and assuming that the transition rate, i.e., the rate of decrease of that property at any time, is the same,[16] then it can be verified that the relaxation rate is

$$- d\log J(t)/d\log(t) = \beta(t/\tau_s)^\beta \qquad (7)$$

A plot of $\log[-d\log J(t)/d\log(t)]$ vs. $\log(t)$ will be a straight line, as shown in Figures 3(A) and (B) with slope β. Values of the parameters β and τ_s are compiled in Tables I and II. β is almost less than unity, especially for data obtained at a fixed temperature and under the influence of various applied stresses.

Figure 4 represents $\ln (\tau_s)$ vs. σ: a straight line can pass through most of the experimental τ_s points, according to eq. (4), with a slope equal to $v*/KT$. For $T_m = 373$ K, $v* = 8.5$ nm^3 , this value is very close to the flow volumes derived from the Eyring theory.[17] This result indicates that there exists a distribution of free volume in the amorphous region of the PVDF polymer.[18] Consequently, the distribution of the relaxation times observed in PVDF is due to the distribution of the activation free volume.

The experimental results shown in Figure 4 confirm that interaction between the applied stress and the polymer segment takes place. However, it seems that there is a critical applied stress value ($\sigma = 3 \times 10^5$ N/m^2), above which eq. (4) is confirmed. This is reasonable because in the low applied stress region ($0–30 \times 10^5$ N/m^2) the response of the PVDF molecule to relax, i.e., to undergo reorientation, is to some extent weak. Generally speaking, in the polar PVDF polymer, the segmental dipoles react to a sudden imposition of the applied stress, σ, by reorienting from the original orientation in the direction of the field to the state of randomization. The reorientation cannot take place at once, however, because the rate at which the molecules can reorient is limited by its ability to undergo configurational changes. However, in the application of the stretched function to describe the relaxation process, it is essential to take account of the fundamental difference between dielectric and mechanical relaxation on the one hand and the process such as the structural relaxation on the other hand. Because PVDF is partially crystalline, mechanical relaxation can be produced only by molecular motions of the molecular chains in the amorphous chains. Hence, the relaxations are ascribed to molecular and segmental movements of amorphous chains, where a distribution of the free volume should exist as a result of inhomogeneity due to the distributions of crystalline parts and the molecular chains in the amorphous parts. That is, the molecular chains alternate between region of order (the crystallites) and disorder (the amorphous regions). Therefore, the distribution of the relaxation times observed in the semicrystalline PVDF is due to the distribution of the activation free volume.

CONCLUSION

We have applied the two parameters function to analyze the relaxation data of PVDF electrets.
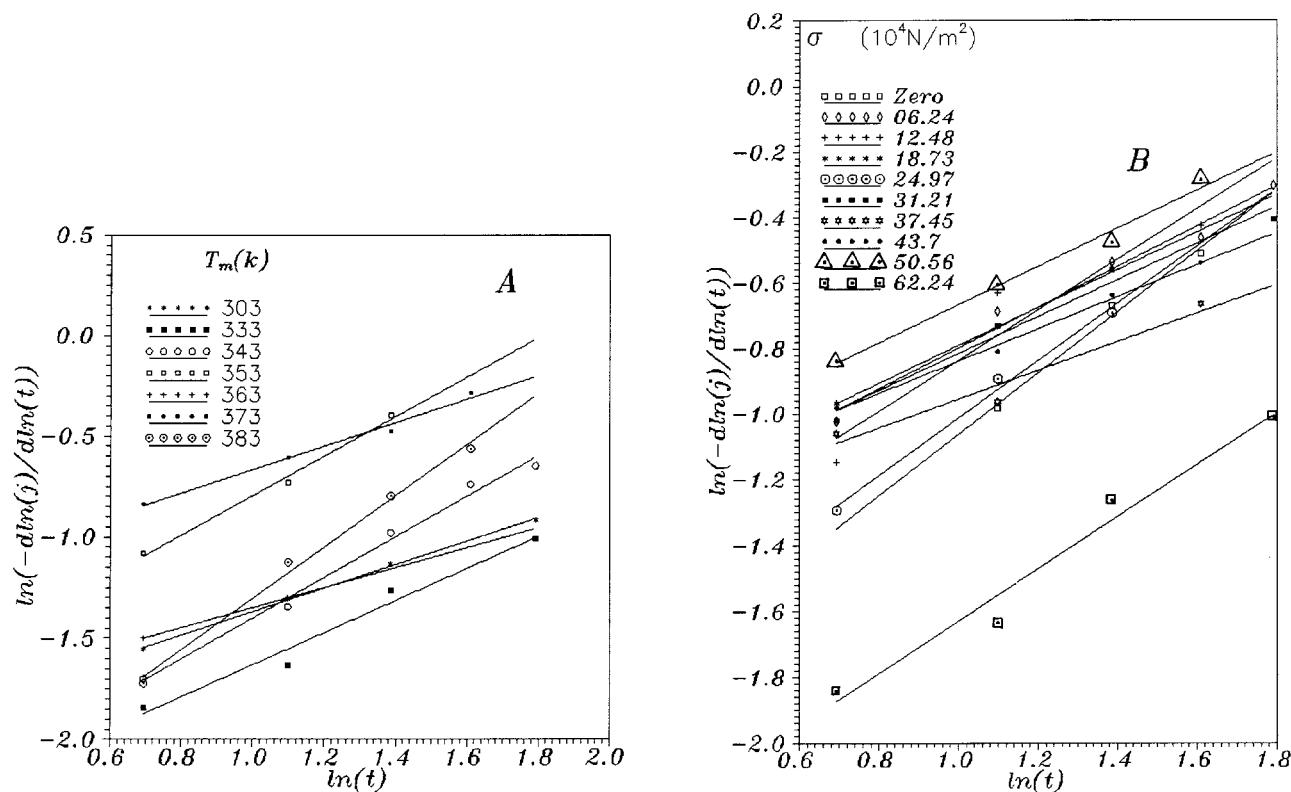
Figure 3. (A) Time-dependent depolarization relaxation rate of PVDF at various temperatures: (1—303, 2—333, 3—343, 4—353, 5—363k, 6—373, 7—383 K). Applied stress σ $= 50.56 \times 10^4$ N/m^2. (B) Time-dependent depolarization relaxation rate of PVDF at various applied stresses: (1—zero, 2—6.24, 3—12.48, 4—18.73, 5—24.97, 6—31.21, 7—37.45, 8—50.56, 9—62.24) $\times 10^4$ N/m^2. Measuring temperature $T_m = 373$ K.

The relaxation behavior of PVDF above T_g can be described by the extended exponential function of the Kohlrausch-Williams-Watts form. The relaxations are ascribed to molecular and segmental movements of the amorphous chains, that is, the molecular chains alternate between regions of order and disorder. On appling the rate theory and the concept of the free volume, originally pro-

posed for amorphous polymers, the value of the activated volume could be evaluated and the results showed a reasonable agreement between that reported and our data, regardless the percent crystallinity.

Table I   The Parameters, τ_S and β [Eq. (7)] of Polarized PVDF for Various Measuring Temperatures

T (K)	β	τ_S (min)
303	0.581	11.26
333	0.792	11.856
343	1	11
353	0.98	5.99
363	0.493	9.99
373	0.582	3.37
383	1.27	9.13

Table II   The Parameters τ_S and β [Eq. (7)] of Polarized PVDF for Various Applied Stresses

σ (10^4 N/m^2)	β	τ_S (min)
0.0	0.934	7.88
6.24	0.621	4.55
12.48	0.773	5.755
18.73	0.576	4.123
24.97	0.875	7.42
31.21	0.562	4.15
37.45	0.44	3.64
43.7	0.491	3.515
50.56	0.582	3.37
56.18	0.667	5.611
62.24	0.52	2.7
68.6	0.797	6.863
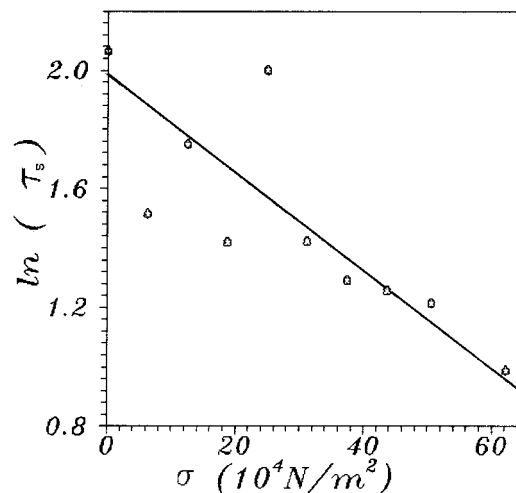
Figure 4. Dependent of the relaxation time τ_s on the applied stress in PVDF relaxation processes.

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