

Thermally Stimulated Current and Effect of Annealing on the Electrical Properties of Cellulose Nitrate

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SYNOPSIS

The investigated samples were of cellulose nitrate CA-80-15. The dc conductivity (σ) and the dielectric permittivity decreased with increasing time of annealing. The activation energy is 0.46 eV in a temperature range from 298 to 385 K. The thermally stimulated current (TSC), J_D , was measured. The maximum value of the TSC (J_m) increases with increasing the rate of heating and shifts slightly toward higher values of temperature. The activation energy (0.25 eV) is independent of the variation of the rate of heating. In addition, the peak positions for the constant rate of heating were unaffected by increasing the polarization time, but the maximum value of the current increases and the activation energy decreases. The dipolar relaxation time was calculated theoretically and studied as a function of temperature. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermally stimulated current (TSC) and annealing effects in cellulose nitrate (CN-85) have been previously investigated.¹ Also, the effect of γ -irradiation on the electrical conductivity of two types of cellulose nitrate, LR-115 and CA-80-15, was studied.² It was established that the electric conduction in such polymers can be considerably enhanced by irradiation.³ The increase in the conductivity of irradiated polymer could be attributed to the formation of free charge carriers and radicals.^{4,5}

The physical and mechanical properties of γ -irradiated poly(methyl methacrylate)-cellulose nitrate copolymers have been studied.⁶ It was found that hardness and abrasion were improved by increasing the cellulose nitrate content and, also, that both the first and the second transition points were shifted to higher values. The effect of the type and energy of radiation on the chemical etching of irradiated cellulose nitrate has been investigated.⁷ Hon and Gui⁸ studied the photodegradation of cellulose nitrate films that were photolytically degraded

in air and in vacuum. The strain-time response under tensile loading and the stress-strain response under a constant tensile stress rate have been evaluated at different temperatures for cellulose nitrate.⁹

The aim of this work was to study the effect of annealing on the electrical properties of CA-80-15 and also to study the thermally stimulated current of this material.

EXPERIMENTAL

Cellulose nitrate CA-80-15 films used in this study were obtained from Kodak, France. The films had an average thickness of 100 μm . An electric oven was used to control the ambient temperature in the range 293–398 K. The conduction current was measured using a dc nanoammeter Continu EVA made in France. To ensure good contact, the sample was coated with a thin film of gold using gold ion sputter (JEOL JFC-1100 E), then fixed between two gold electrodes.

The thermoelectrets were prepared at a polarizing temperature $T_p = 393$ K for different polarizing times (1, 2, and 3 h) using a polarizing field strength of $E_p = 2 \times 10^2$ kV/cm, which is a moderate value, since the electric strength of cellulose nitrate ranges

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between 3 and 5×10^2 kV/cm. The samples were cooled, with the poling field on, down to room temperature. After removing the field, the samples were shorted immediately and then heated at a constant rate of 10 K/min. The effect of variation of the rate of heating (7, 8, 10, and 18 K/min) on the thermally stimulated current (TSC), J_D , was studied.

The dielectric permittivity was measured using a Precision Capacitance bridge (Tesla, BM 400G) working at 800 Hz and with a least count of 10^{-4} pF.

RESULTS AND DISCUSSION

Figure 1 shows the I-V characteristics of cellulose nitrate at different temperatures. It is clear that the increase of current with voltage is strongly dependent on the ambient temperature. The I-V plots are linear in the voltage range (5–100 V) where ohmic behavior predominates and corresponds to the conduction of CA-80-15 films. The leveling off of the I-V characteristics at 373 K and above 75 V would imply some sort of saturation, which could be confirmed at still higher values of V in the future.

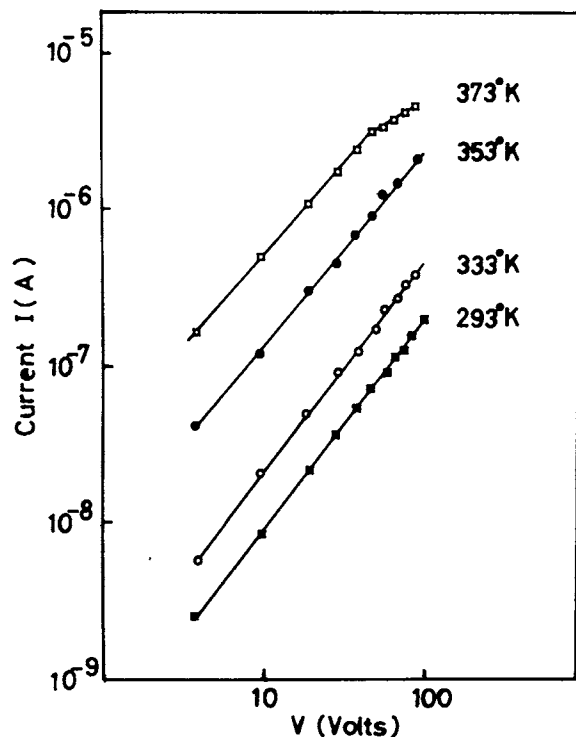


Figure 1 I-V characteristics at different temperatures for CA-80-15 samples.

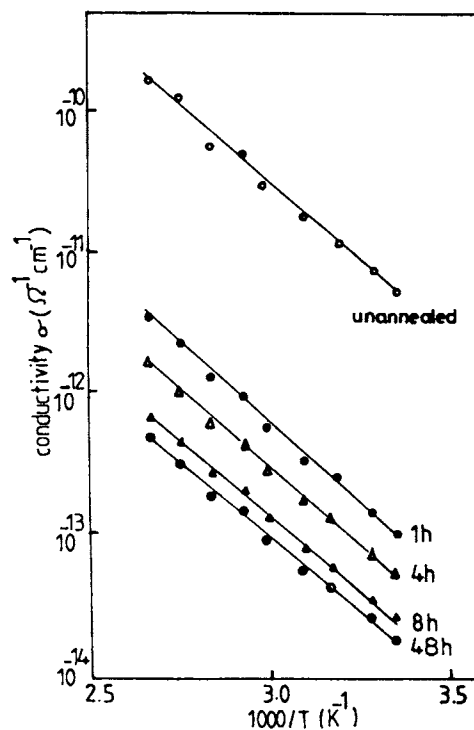


Figure 2 σ vs. $1/T$ for CA-80-15 samples with different thermal annealing times at temperature 368 K.

The electrical conductivity of annealed and unannealed samples of cellulose nitrate is shown in Figure 2. It is clear that the electrical conductivity increases with temperature, i.e., $d\sigma/dT$ is positive, whereas it decreases with increasing annealing times. The activation energies were calculated for the annealed and unannealed samples. These values are 0.42 and 0.46 eV, respectively. It is natural that the activation energy for conduction should depend on the annealing process. Actually, the conductivity diminishes with annealing time due to freeing the material from some structural imperfections. The conduction current in the present material is composed of contributions from accidental impurities as well as those from intrinsic sources. In other words, annealing would naturally lead to a diminishing the role of the impurities. This also is in accordance with the growth of TSC with annealing.

Figure 3 shows the TSC current [$J_D(T)$] for cellulose nitrate CA-80-15. The temperature dependence of TSC at a constant rate of heating, 10 K/min, revealed one peak at T_m of about 325 K. The position of T_m is independent of polarizing time. The inset in Figure 3 shows the dependence of the maximum current (J_m) on the polarizing time (t_p).

Figure 4 shows the variation of $\ln J_D$ as a function

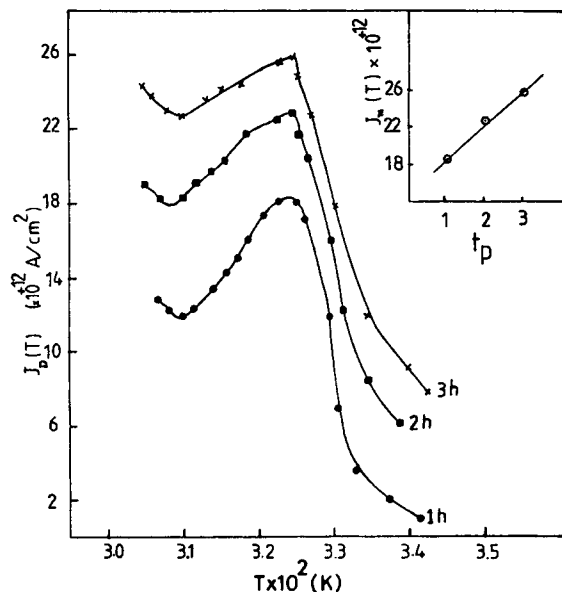


Figure 3 TSC as a function of temperature at different polarizing times (t_p) and constant rate of heating 10 K/min. Polarizing temperature $T_p = 393$ K; polarizing field strength 2×10^2 kV/cm. Inset: Dependence of J_{max} on t_p .

of $1/T$ for different polarizing times (t_p). The activation energies for this process decrease ($\Delta E' = 0.25, 0.16,$ and 0.086 eV) with increasing polarizing time (t_p ; 1, 2, and 3 h), respectively.

Figure 5 shows the strong dependence of the position of T_m on the rate of heating (q). The inset reveals that the peak current (J_m) is sharply increasing with q . When the heating rate increases, the initial polarization has to be released in a shorter time. Thus, the peak increases and shifts to a higher temperature.¹⁰

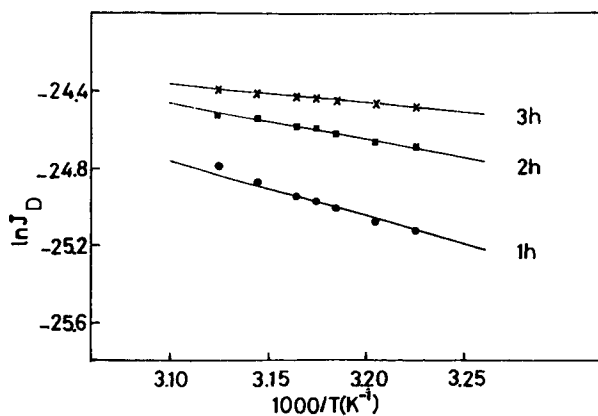


Figure 4 Plot of $\ln J_p$ vs. $1/T$ at different polarizing times (t_p).

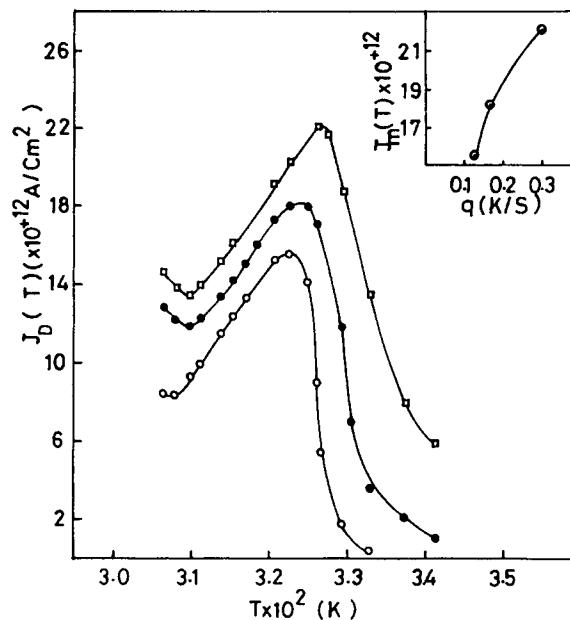


Figure 5 TSC as a function of temperature T at different rates of heating q : (\circ) 0.130 K/s; (\bullet) 0.167 K/s; (\square) 0.300 K/s. The inset shows the variation of J_m as a function of the rate of heating.

The activation energy of nondistributed relaxation processes can be easily calculated from a single TSC experiment¹⁰ by means of some characteristic elements of the peak such as half-width, inflection point, or initial part of the current rise.¹¹ Using the Arrhenius shift equation,

$$\ln J(T) = \text{const} - \Delta E'/KT \quad (1)$$

where K is the Boltzmann constant; T , the absolute temperature; J , the thermally stimulated current; and $\Delta E'$, the activation energy.

The variation of $\ln J$ as a function of $1/T$ for different rates of heating is shown in Figure 6. The activation energy is 0.25 eV, which is independent of q .¹²

The relaxation times for polarized and depolarized samples of cellulose nitrate CA-80-15 may be considered identical. The decay of polarization after the removal of the field is given by

$$P(t) = P_e \exp(-t/\tau) \quad (2)$$

where P_e is the steady state polarization, and τ , the dipolar relaxation time.

The corresponding depolarization current density is given by

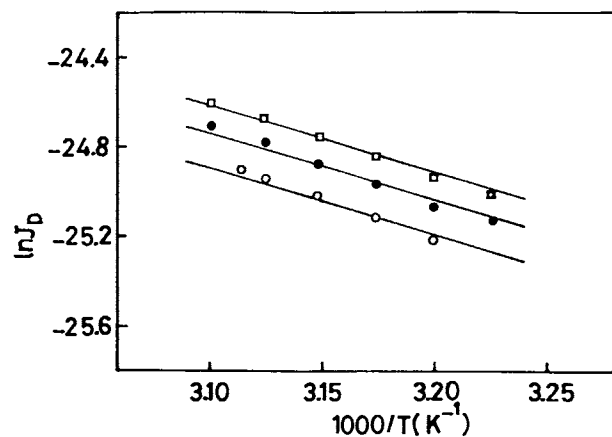


Figure 6 $\ln J_D$ vs. $1/T$ at different rates of heating: (○) 0.130 K/s; (●) 0.167 K/s; (□) 0.300 K/s.

$$J(t) = -dP(t)/dt = P/\tau \quad (3)$$

The temperature variation of relaxation time τ is conventionally given by

$$\tau(T) = \tau_0 \exp(\Delta E'/KT) \quad (4)$$

where τ is the time at finite temperature; τ_0^{-1} , the characteristic frequency factor of the material; and $\Delta E'$, the activation energy of dipolar orientation and disorientation.

From eqs. (2)–(4), the entire range of temperature covered by the TSC peak¹³ can be written as

$$\ln \tau(T) = \ln \left[\int_{t(T)}^{\infty} J(t') dt' \right] - \ln J_D(T) \quad (5)$$

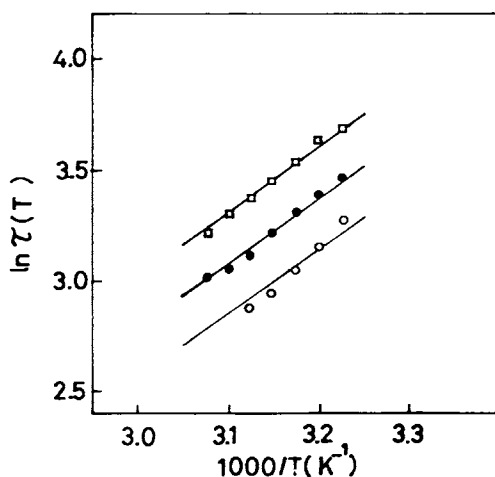


Figure 7 $\ln \tau(T)$ vs. $1/T$ at different rates of heating: (○) 0.130 K/s; (●) 0.167 K/s; (□) 0.300 K/s.

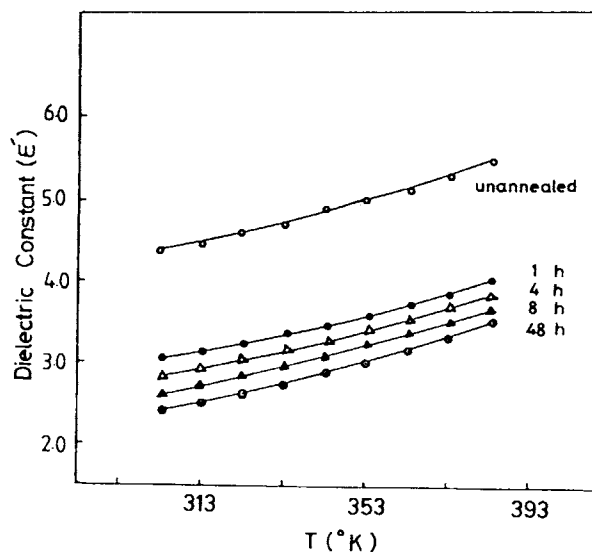


Figure 8 The dielectric constant as a function of temperature for CA-80-15 samples with different annealing times.

or

$$\tau(T) = \int_{t(T)}^{\infty} J(t) dt / J_D(T) \quad (6)$$

The integral is determined from the area under the TSC curve and $\tau(T)$ is inversely proportional to $J_D(T)$, which is determined point by point from Figure 5. By plotting $\ln \tau$ as a function of $1/T$ at different rates of heating [Figure 7], a straight line is obtained with a slope equal to $\Delta E'/K$ according to eq. (4). The activation energy is found to be constant and equal to 0.25 eV.

The effect of thermal annealing on the dielectric permittivity of CA-80-15 at constant frequency (800 Hz) is shown in Figure 8. The dielectric permittivity of unannealed and annealed samples at 368 K (for different annealing times) increases with temperature, probably due to the ease with which existing dipoles respond to the applied field.

We notice from Figure 8 that the dielectric permittivity decreases with increasing the time of annealing. This decrease may be attributed to the disappearance of the effect of impurities that may favor the formation of artificial polarization.

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