Irradiation Effects on Electrical Properties of Cellulose Nitrate

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SYNOPSIS

Cellulose nitrate (CA-80-15) films were exposed to UV and neutron irradiations. An increase of the electrical conductivity was observed. The values of the activation energy diminish with irradiation from 0.42 to 0.15 eV for UV and to 0.31 eV for neutron irradiation. A sharp increase in the current was observed after exposing CA-80-15 samples to fission neutron fluences of $1*10^7$ n/cm^2. The electrical conduction in cellulose nitrate is governed by the Shottky mechanism. The value of the electron affinity of the polymer used is 4.46 eV. This value is increased after both types of irradiation. The dielectric permittivity (ε') of the above samples together with the dielectric loss factor (ε'') were measured over a range of temperatures (293–403 K) at fixed frequencies ($1*10^3$, $1*10^4$, and $1*10^5$ Hz). Three neutron exposures (ϕ = $1*10^5$, $1*10^6$, and $1*10^7$ n/cm^2) were used. The obtained results made it possible to determine a complete set of conduction parameters including dielectric susceptibility χ, ac conductivity σ_{ac}, and temperature coefficient of permittivity TC_ε'. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Cellulose nitrates are frequently used as track detectors for charged particles.[1] Bonetti et al.[2] studied the effect of α particle beams on LR-115 cellulose nitrate that is used widely as solid-state nuclear track detector (SSNTD), with detection system efficiency of 100% for α particles lying in the response region of LR-115. The electrical and other properties of cellulose nitrates are acquiring increased interest. The effect of different ionizing radiations is therefore the criterion that determines their applications. Amin et al.[3] studied the effect of γ irradiation on the electrical properties of cellulose nitrate. Two types of cellulose nitrate were studied: the red cellulose LR-115 and the light pink CA-80-15 samples. Conductivity and dielectric constant measurements were carried out. The destruction of cellulose nitrate by γ irradiation produces mainly NO_2 radicals at 77 K, and polymeric matrix radicals stable up to 373 K. The enhancement of alkaline etching of γ-irradiated detectors results from both the direct radiation induced destruction of polymeric chains and from the destruction of the matrix initiated by the active centers.[4]

The aim of the present work is to pursue a systematic study of the conduction mechanism and dielectric behavior of cellulose nitrate films of the CA-80-15 type exposed to UV and neutron irradiation.

EXPERIMENTAL

Cellulose nitrate is a carbohydrate polymer composed of anhydroglucose units. The samples used in this study were CA-80-15 films with thickness of 100 μm, and were obtained from Kodak (France). The samples were coated with a thin film of gold using gold ion sputtering (Jeol JFC-1100 E), and were then fixed between two gold electrodes. The conduction current was measured using a dc nanoammeter Continu-EVA (France). The minimum current (I) measured by this instrument is as low as 10^{-9} A, with an accuracy of ±4%.

The samples were irradiated by UV (PMQ photometer system, Zeiss, Germany) at λ = 250 nm at room temperature.

The capacitance C and the dielectric loss tangent were measured directly by a Stanford Research System

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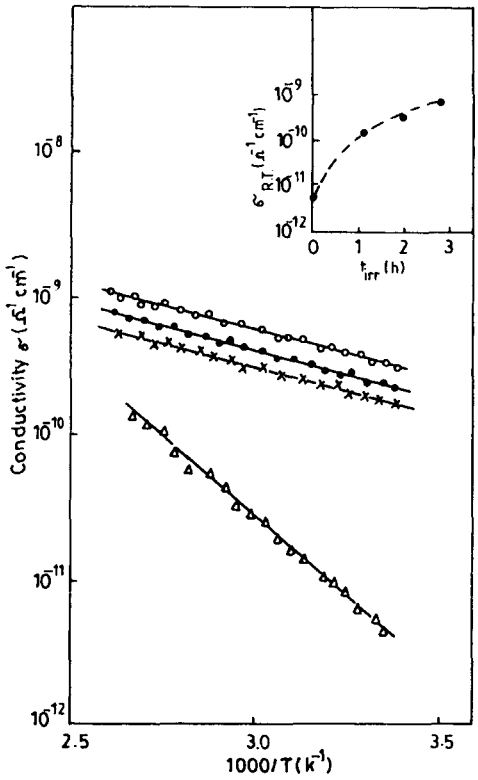

Figure 1 Temperature dependence of dc conductivity for cellulose nitrate films at constant applied voltage of 80 V, before and after UV irradiation (λ = 250 nm). (Δ) 0 h, ($\times$) 1 h, ($\bullet$) 2 h, (O) 3 h. The inset figure shows σ at RT against t_{irr}.

Model SR 720-RLC Meter. Cellulose nitrate samples were irradiated with fission neutrons from a 50 μgm $^{252}C_f$ source manufactured by Radio-Chemical Center (Amersham, England). The dielectric measurements were carried out directly after irradiation.

RESULTS AND DISCUSSION

Temperature Dependence of Electrical Conductivity $\sigma(T)$

Effect of UV Irradiation

The effect of UV irradiation on the electrical conductivity is mainly caused by ionic migration. The behavior is shown in Figure 1 for cellulose nitrate films before and after UV irradiation. The samples were irradiated with UV at λ = 250 nm for 1, 2, and 3 h. The inset in Figure 1 shows that the electrical conductivity (σ_{RT}) increases with exposure time of UV.

After turning off the light source it is observed that the color of the samples is slightly changed, probably due to the formation of conjugate double bonds and the rapid free radicals.[5] The activation energy (ΔE) for cellulose nitrate is decreased after UV irradiation. Its value is found to be 0.15 eV. The electrical conductivity has increased because of the liberation of nitrogen gas and the formation of nitroxide-type radicals and hydroxyl groups.[6,7] There are similarities between the UV, the argon plasma, and the X-ray induced degradations of cellulose nitrate. Short et al.[8] studied the changes in surface chemistry of cellulose nitrate by a glow discharge argon plasma that causes the loss of some nitrate esters leaving a hydrocarbon residue; others were converted to more highly oxidized functionalities. Similarly, some of these changes took place for cellulose nitrate exposed to oxygen glow-discharge plasmas.[9]

From the above discussion we can conclude that UV irradiation changes the chemical structure of cellulose nitrate and hence its electrical conductivity.

Effect of Neutron Irradiation

The cellulose nitrate samples (CA-80-15) were irradiated with fission neutrons from a 50 μgm $^{252}C_F$ source in the range 10^5–10^7 n/cm^2. Straight lines

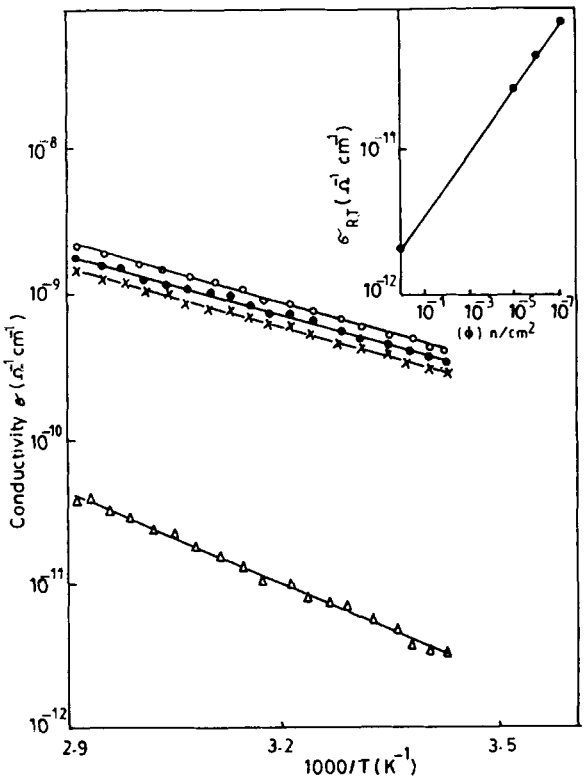

Figure 2 Temperature dependence of dc conductivity for cellulose nitrate films at constant applied voltage of 80 V, before and after neutron irradiation fluences. (Δ) Before irradiation, ($\times$) at ϕ = 1*10^5 n/cm^2, ($\bullet$) at ϕ = 1*10^6, (O) at ϕ = 1*10^7 n/cm^2. The inset figure shows σ at RT against doses ϕ.

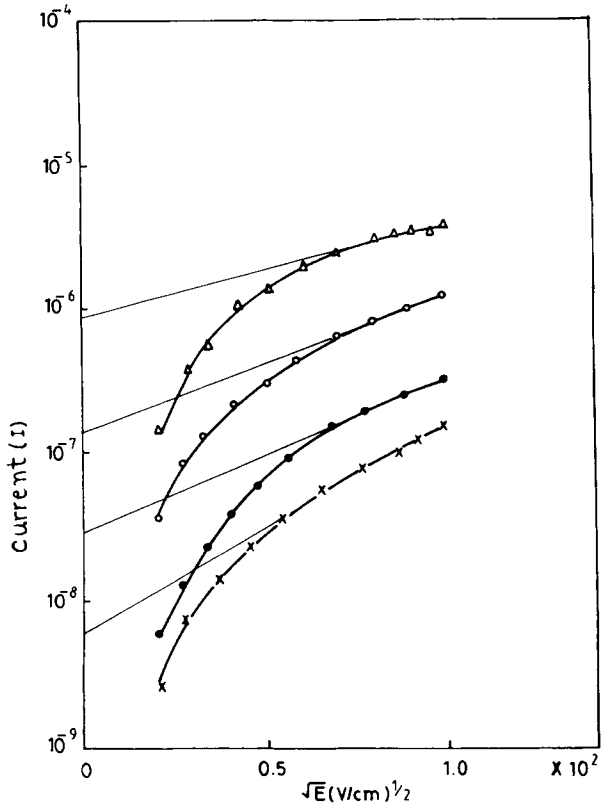

Figure 3 Schottky conduction plot for cellulose nitrate films at different temperatures. (×) 293 K, (●) 333 K, (○) 353 K, (△) 373 K.

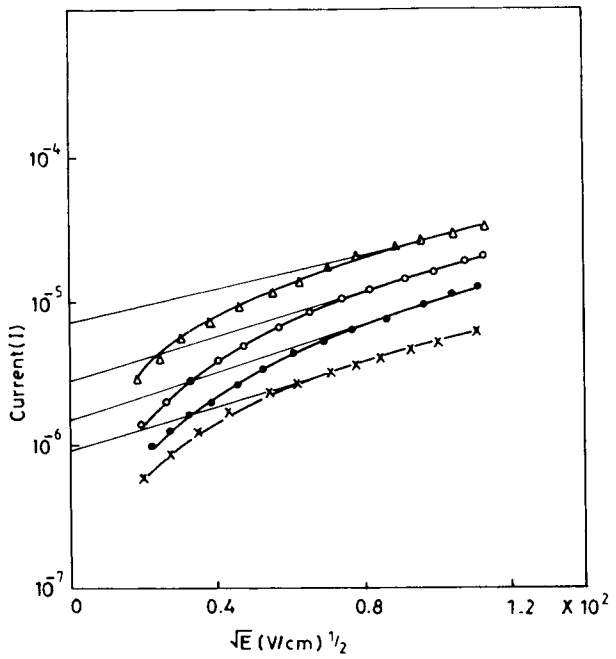

Figure 4 Schottky conduction plot for cellulose nitrate films at different temperatures after UV irradiation, λ = 250 nm for 3 h. (×) 293 K, (●) 323 K, (○) 343 K, (△) 373 K.

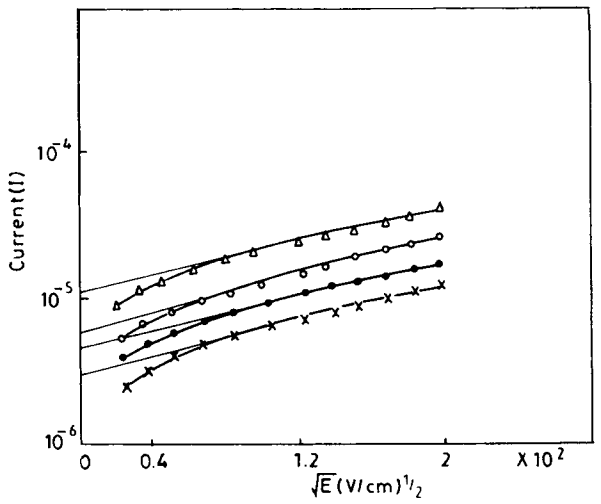

Figure 5 Schottky conduction plot for cellulose nitrate films at different temperatures after neutron irradiation, $\phi = 1*10^7$ n/cm^2. (×) 293 K, (●) 313 K, (○) 333 K, (△) 353 K.

of (σ) vs. ($1/T$) were obtained after the neutron irradiation (Fig. 2). The apparent activation energy (ΔE) was found to be 0.31 eV for the exposed samples. The inset in Figure 2 shows the dependence of the electrical conductivity at room temperature (σ_{RT}) on the neutron irradiation fluence (ϕ). The decrease in the activation energy of the cellulose nitrate samples after the neutron irradiation indicates that free charge carriers are formed.

Crystalline regions inside the polymer are irreversibly transformed into amorphous ones[10] upon exposure to different ionizing radiations. This behavior implies destruction of the structural regularity of main chains of the polymeric molecules upon irradiation. Therefore the dc conductivity may increase because of the generation of a large number of free electrons, ions, and holes formed as a result of the primary act of interaction of radiation with matter.[11]

Table I Dependence of Experimental Schottky Coefficient β_{RS} (10^{-23} C cm$^{1/2}$ V$^{1/2}$) on the Temperature for Cellulose Nitrate Films

T [K]	Pure	UV-Irrad.	Neutron
293	13.51	5.41	2.71
313	—	—	2.79
323	—	8.07	—
333	11.63	—	3.43
343	—	7.88	—
353	10.09	—	3.46
373	7.67	6.81	—

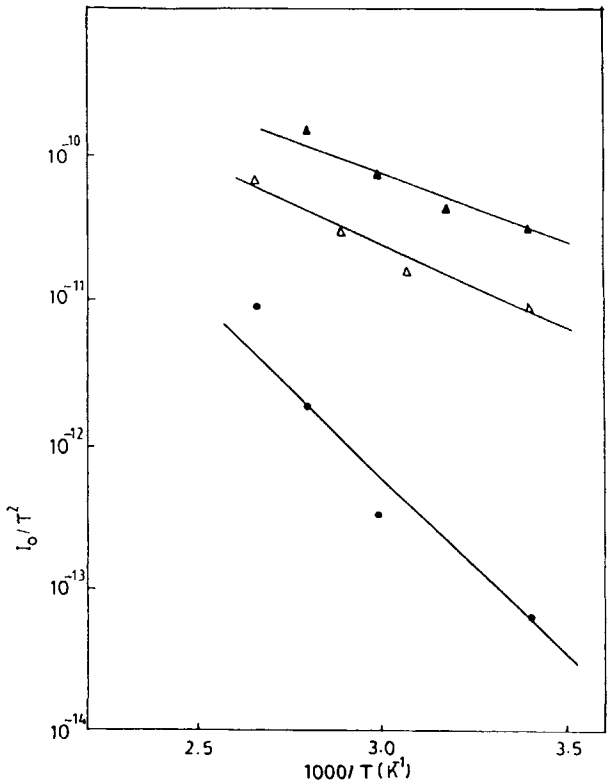

Figure 6 $\text{Log}(I_0/T^2)$ vs. $(1/T)$ for cellulose nitrate films. (●) pure sample, (△) after UV irradiation, (▲) after neutron irradiation.

Conduction Mechanism of Cellulose Nitrate

The [I–V] characteristics for cellulose nitrate before and after UV irradiation and neutron irradiation are presented in the form $\log(I)$ against $(E^{1/2})$ at different temperatures. The obtained graphs would suggest that the conduction in cellulose nitrate samples is governed by the Schottky conduction mechanism (see Figs. 3–5).

The Schottky coefficient was calculated and found to be: β_{RS} (theoretically) $= 2.36*10^{-23}$ C cm$^{1/2}$ V$^{1/2}$, taking the dielectric permittivity of cellulose nitrate to be $\varepsilon' = 6.6$ at 300 K and $1*10^6$ Hz.[12] The experimental values of β_{RS} have been calculated at different temperatures for all samples from the gradients of the plots $\log(I)$ against $(E^{1/2})$, and listed in Table I.

The Schottky barrier potential (ϕ_s) was obtained from the slopes of the plots $\log(I_0/T^2)$ against $(1/T)$, for cellulose nitrate before and after irradiation (see Fig. 6) where I_0 is the extrapolated value of I at $E = 0$. The values of ϕ_s are evaluated and listed in Table II. The potential barrier at the metal–polymer interface (ϕ_s) is given by[13]:

$$\phi_s = W - E_a$$

where W is the work function of the metal and E_a is the electron affinity of the polymer used. Taking $W = 5.1$ eV for gold[12] and the obtained values of ϕ_s, then E_a of cellulose nitrate are determined and listed in Table II.

Temperature Dependence of Permittivity ε' (T)

The dielectric permittivity of cellulose nitrate (CA-80-15) is measured at fixed frequencies ($1*10^3$, $1*10^4$, and $1*10^5$ Hz). Figure 7 shows the temperature dependence of the dielectric permittivity ε' for cellulose nitrate before and after neutron exposures ($\phi = 1*10^5$, $1*10^6$ and $1*10^7$ n/cm^2). There is almost no change of ε' for the unirradiated sample over the whole temperature range; the value of $\varepsilon' \simeq 3.9$. The dielectric permittivity is also nearly frequency independent in the studied range before and after irradiation.

The neutron fluence ($\phi = 1*10^5$ n/cm^2) induces a hump in the ($\varepsilon' - T$) relationship, followed by a gradual drop. The dielectric permittivity tends to increase after neutron irradiation due to the presence of several polarizable elements created by irradiation.[10]

Temperature Dependence of Dielectric Relaxation

Typical results on dielectric loss factor ε'' as a function of temperature at three fixed frequencies ($1*10^3$, $1*10^4$, and $1*10^5$ Hz) for unirradiated cellulose nitrate films are shown in Figure 8. Only one dielectric loss peak was found at ≃338 K, which is close to the glass transition temperature of cellulose nitrate (T_g = 326–339 K).[14] In fact, the α process in polymers occurs around and above T_g, where the segmental motion is possible even in alternating fields of high frequency. It is caused by the micro-Brownian motion of segments in polymeric chains. Dielectric losses of this kind are called dipole-segmental losses; dielectric relaxation caused by the localized movement of molecules are known as dipole-group relaxation.[15,16] It is also observed in Figure 8 that the position of the peak shifts toward higher temperatures as the frequency increases.

Table II Values of Potential Barrier (ϕ_s) and Electron Affinity of Cellulose Nitrate Films

Sample	ϕ_s (eV)	E_a (eV)
Pure	0.64	4.46
Annealed	0.58	4.52
UV irrad.	0.29	4.81
Neutron	0.23	4.87

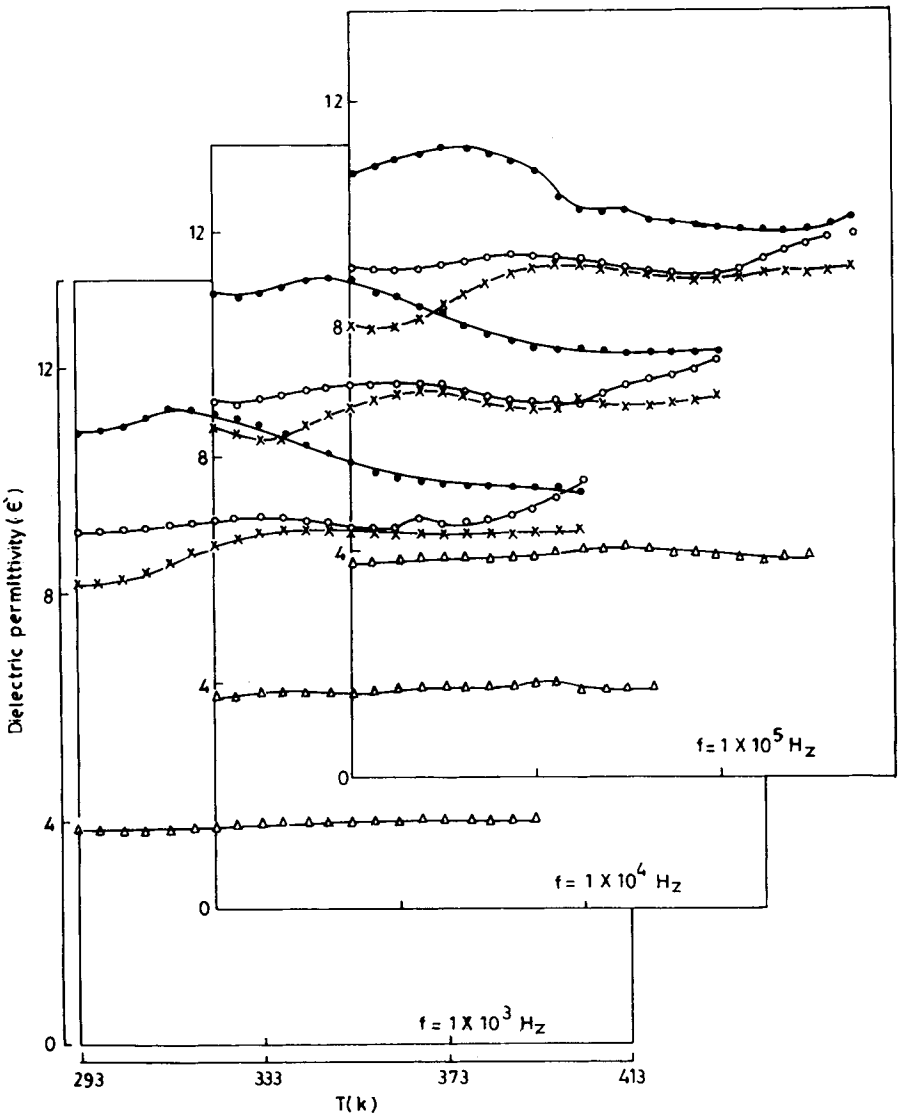

Figure 7 Variation of dielectric permittivity with temperature at different frequencies [f] for cellulose nitrate films before and after neutron irradiation. (△) unirradiated, (●) $\phi = 1*10^5$, (○) $\phi = 1*10^6$, (×) $\phi = 1*10^7$ n/cm^2.

When the samples were irradiated with a neutron fluence of $1*10^5$ n/cm^2 as in Figure 9, the magnitude of the dielectric loss factor ε'' increased. The position of the peaks shifts toward higher temperatures as the frequency increases. The shift increase in the dielectric loss of the peaks indicates the formation of electric dipoles and deformation losses in the samples after irradiation.[17] The neutrons have probably enhanced the relaxation processes.

The values of (tan δ) for good electrically insulating materials employed in high-frequency and high-voltage technology are on the order of 10^{-3}–10^{-4}. In the case of materials with a lower quality used in less critical cases, tan δ [tan $\delta = Q^{-1}$] may reach 10^{-2}.[18] The dielectric loss is due to the perturbation of the phonon system by an electric field; the energy transferred to the phonons is dissipated in the form of heat.[19] Moreover, the arbitrary chain arrangements in the amorphous region of the polymer may result in alterations of the Van der Waals forces from place to place. In the crystalline regions, however, because of the presence of hindering structural units (due to greater density of these regions), the polymeric chains move with greater difficulty than in the amorphous regions.[20] This hindrance can be assumed to possess a certain potential energy.

When the polymer is heated the movement of the large segments of the main chain sets in, becoming a maximum at T_g, at which the loss tangent attains

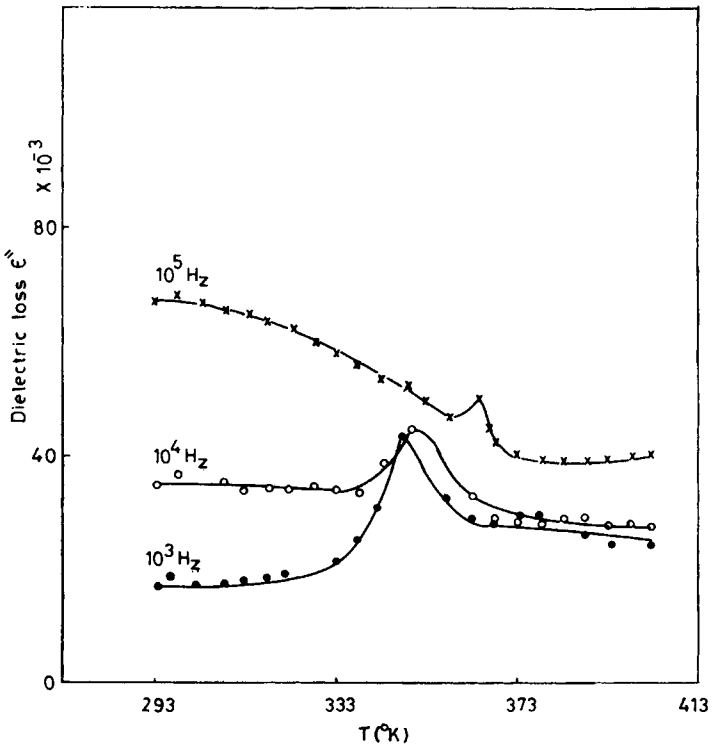

Figure 8 Variation of dielectric loss with temperature at different frequencies [*f*] for cellulose nitrate films.

a maximum value that nearly corresponds to the α-relaxation peak of the TSC.[21]

Frequency Dependence of a.c. Conductivity

In ac fields, the energy loss per unit volume per unit time may be expressed as,[16,22]

$$W = E_0^2 \varepsilon_0 \varepsilon' \omega \tan \delta / 8\pi \quad (1)$$

where E_0 is the peak value of the sinusoidal ac field; ε_0 is the permittivity of free space, $8.85 * 10^{-12}$ F/m; ω is the angular frequency; tan δ is the dissipation factor or dielectric loss tangent; and ε' is the dielectric permittivity of cellulose nitrate.

Table III Conductivity of Cellulose Nitrate at RT and at Different Frequencies, Before and After All Neutron Doses ϕ

Sample	f [Hz]	$\chi = \frac{\varepsilon' - 1}{4\pi}$	$TC_{\varepsilon'}$ (K^{-1})	W (watts)	σ_{ac} (Ω^{-1} cm^{-1})
Unirrad.	$1*10^3$	$7.56*10^{-2}$	$-2.31*10^{-4}$	$2.15*10^{-6}$	$5.43*10^{-10}$
	$1*10^4$	7.33	−2.25	$3.98*10^{-5}$	$1.00*10^{-8}$
	$1*10^5$	7.22	−2.23	$7.83*10^{-4}$	$1.91*10^{-7}$
$\phi = 1*10^5$ n/cm^2	$1*10^3$	$35.77*10^{-2}$	$-7.32*10^{-4}$	$6.25*10^{-6}$	$1.57*10^{-9}$
	$1*10^4$	35.96	−7.26	$1.04*10^{-4}$	$2.61*10^{-8}$
	$1*10^5$	34.61	−7.17	$2.16*10^{-3}$	$5.42*10^{-7}$
$\phi = 1*10^6$ n/cm^2	$1*10^3$	$28.52*10^{-2}$	$-6.17*10^{-4}$	$4.33*10^{-6}$	$1.09*10^{-9}$
	$1*10^4$	28.25	−6.13	$8.59*10^{-5}$	$2.15*10^{-8}$
	$1*10^5$	28.77	−6.05	$1.80*10^{-3}$	$4.54*10^{-7}$
$\phi = 1*10^7$ n/cm^2	$1*10^3$	$24.06*10^{-2}$	$-5.66*10^{-4}$	$3.91*10^{-6}$	$9.85*10^{-10}$
	$1*10^4$	24.90	−5.61	$7.34*10^{-5}$	$1.85*10^{-8}$
	$1*10^5$	24.35	−5.56	$1.45*10^{-3}$	$3.66*10^{-7}$

Dielectric susceptibility χ, temperature coefficient of permittivity $TC_{\varepsilon'}$, energy loss W, and σ_{ac}.

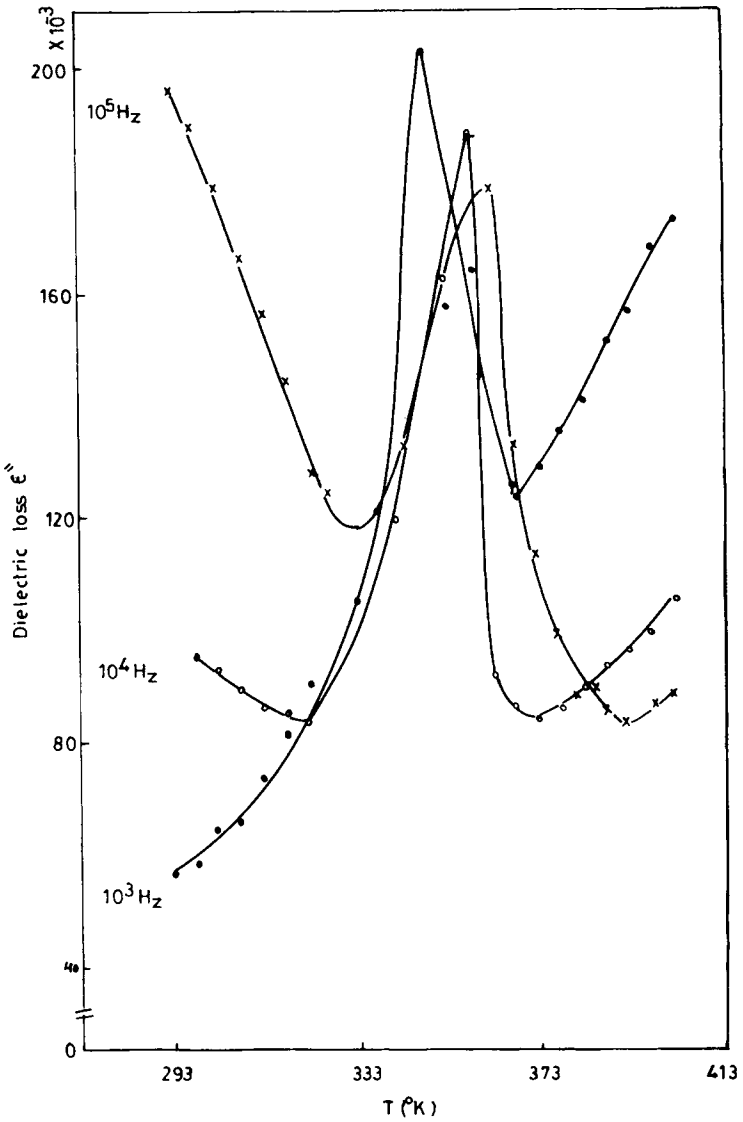

Figure 9 Variation of dielectric loss with temperature at different frequencies [f] for cellulose nitrate films after neutron irradiation. $\phi = 1*10^5$ n/cm^2.

The energy loss (watt) is proportional to tan δ, as long as the other factors like voltage, frequency, and capacitance are constant. Equation (1) may be rewritten as[23]:

$$W = (\omega E^2 \varepsilon_0 / 8\pi)\varepsilon''. \quad (2)$$

The values of the energy loss were calculated for cellulose nitrate before and after neutron irradiation and are listed in Table III. On the other hand, in a dielectric in which losses are only due to electrical conduction, the losses should be expressed by formula (2), i.e., W should not depend on frequency. In this case[18]:

$$\sigma_{ac} = [f/(1.8 \times 10^{10})]\varepsilon''. \quad (3)$$

The values of σ_{ac} for unirradiated and irradiated samples are listed in Table III.

The temperature coefficient of permittivity ($TC_{\varepsilon'}$) for cellulose nitrate was found to be 10^{-4} K^{-1} at RT and at different frequencies before and after neutron irradiation. These values are calculated from the equation[18]

$$TC_{\varepsilon'} = -[(\varepsilon' - 1)(\varepsilon' + 2)/\varepsilon']\alpha_L \quad (4)$$

taking the linear expansion coefficient of cellulose nitrate to be[24] $\alpha_L = 12*10^{-5}$ K^{-1}. The dielectric sus-

ceptibility χ of the cellulose nitrate was also established. Data are listed in Table III.

CONCLUSION

The electrical conductivity was increased after exposure to both UV and neutron irradiations due to the formation of free charge carriers. The activation energy was decreased after UV irradiation (0.15 eV), and reached 0.31 eV for samples exposed to neutron fluence.

A sharp increase in the current was observed after exposing cellulose nitrate films to fission neutron fluences of $\phi = 1*10^7$ n/cm^2. The electrical conduction in cellulose nitrate is governed by the Schottky mechanism. The value of the electron affinity of cellulose nitrate is 4.46 eV. This value is increased after UV and neutron irradiation.

A hump appears in the $(\varepsilon' - T)$ plot at the neutron fluence $\phi = 1*10^5$ n/cm^2, followed by a gradual drop. Only one dielectric loss peak was found at $\simeq$ 338 K, which is close to the T_g of cellulose nitrate. The temperature coefficient of permittivity, $TC_{\varepsilon'}$, of cellulose nitrate was found to be $\sim 10^{-4}$ K^{-1}.

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