Effect of Fast Neutrons and γ Radiation on Cobalt-Gelatin Film

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ABSTRACT: The real and imaginary parts of the dielectric constant (ε' and ε'') were measured as a function of temperature at 10 kHz for a cobalt-gelatin film before and after exposure to different values of fast neutron fluences and γ doses. The values of the ac conductivity were found to be affected to some extent by the type of irradiation in comparison with that of the unirradiated ones. However, the behavior of ε', ε'', and ac conductivity seemed to be the same at higher and lower doses of both types of radiation. This behavior was also observed by comparing the calculated values of the activation energies for co-gelatin films before and after irradiation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1749–1755, 2001

Key words: dielectric constant; fast neutrons; γ radiation; co-gelatin film

INTRODUCTION

In the past few years, many physicists and chemists focused their efforts on studying the physical properties of gelatin.[1–4] In our daily life, gelatin is widely used in different applications such as foods, films, light filters for mercury lamps, and recently for many laser applications and contact lenses.[5,6]

Gelatin is not found in nature, but its products can be obtained by the partial hydrolysis of collagen. In contrast to collagen, gelatin contains free α-amino groups and C-terminal amino acids.[6,7] Its glass to rubber transition temperature (T_g) strongly depends on its water content, even a small amount. A shift in the T_g value can amount to 5–7° through a 1% change of the water content. Moreover, the bound water is an intrinsic element of structural order and acts as a natural plasticizer that lowers the T_g value, while free water in gelatin forms a rigid ice matrix that inhibits the T_g.[8] In addition, one may expect that interaction of fast neutrons or γ radiations with gelatin as a biomaterial results in the rupture of chemical bonds, which yields electrons and free radicals from the broken bonds and displacement of electrons and atoms.[9]

Consequently, the energetic free radicals produced may react to change the chemical structure and alter the physical properties of such materials, as well as causing a direct changes of amino acid residues at the active sites of proteins.[10,11] These changes include the primary, secondary, and tertiary structure of the gelatin.[12] In addition, these charge carriers move toward the appropriate electrodes when applying an electric field, causing an amount of current to flow. Thus, a change in conductivity is established.

In the present work, a study of the electrical properties of a thin aggregated film of a cobalt-gelatin as a function of temperature at a frequency of 10 kHz was carried out before and after

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irradiation with different values of both neutron fluences and γ doses.

EXPERIMENTAL

All chemicals used in this work were in Analar grade form (BDH). The gelatin powder was dissolved in triply distilled water at ~50°C in a water bath. The inorganic additive $COCl_2 \cdot 6H_2O$ was dissolved with 5 wt % concentration in triply distilled water and added in a soluble form to the gelatin aqueous solution. Later the mixture was cast in a Petri dish placed on a level plate in a furnace at the same temperature of preparation (~50°C) for 24 h to remove any residual solvent. Complete drying was checked by weighing the Petri dish with the sample before and after preparation. The obtained sample of 0.09-mm thickness was kept inside a vacuum desiccator to get rid of any humidity.

Fission neutron energy from 50 μg ^{252}CF (Biophysics Department, Cairo University) was used for irradiating the Co-gelatin samples. The source was manufactured by the Radiochemical Center, Amersham, U.K. The yield of the source was 4 $\times 10^6$ n/s. The samples were exposed to different fast neutron fluences ranging from 7.6×10^5 to 0.5×10^9 n/cm^2. These neutron fluence values were found by varying the exposure time according to the relation

$$\phi = at/R\pi x^2$$

where ϕ is the neutron fluence, a is the neutron yield at the exposure date, x is the sample to source distance (cm), and t is the exposure time (s).

Another group of Co-gelatin samples were exposed to γ doses of 0.25–1 Gy. The γ tube (Philips SL 75-5) at the National Institute for Cancer, Cairo University, was used.

All irradiation processes were performed in a normal atmosphere at a room temperature (29°C). The relative permittivity measurements, as well as the ac conductivity, were carried out before and after irradiation as a function of temperature at a fixed frequency (10 kHz) using an RLC bridge (model SR 720). At this frequency value, the dipoles of the main chain or segmental parts have the ability to follow the field variation, leading to an increase of the real (ε') and imaginary (ε'') dielectric constants and sharp peaks. This ability is lessened at higher frequency values (>10 kHz). These facts were reported in our preceding study of the effect of the field frequency on the dielectric properties for different gelatin samples.[9] The temperature of the sample in the present work was measured using a copper–constantan thermocouple with a junction in contact with the sample.

RESULTS AND DISCUSSION

Figure 1 correlates the real part of the dielectric constant ε' as a function of the absolute temperature (270–430 K) for a gelatin film containing 5 wt % Co^{2+} ions at a frequency of 10 kHz before and after irradiation with different fast neutron fluences. From this figure it is clear that ε' values of the unirradiated sample exhibit a strong dispersion (ε' peak) at about 300 K and then decrease to reach a minimum at 370 K. This peak can be attributed to the evaporation of bound water.[13] In other words, a loss of the multiple hydrogen bound water molecules, as well as a single hydrogen, can occur.[14] Above 370 K the decrease in the ε' of the 5% Co-gelatin film returns to its transition from the ordered to disordered state.[15] After irradiation with different fast neutron fluences, the ε' peak is shifted toward higher temperatures. Furthermore, the maximum broadening is obtained at 7.6×10^5 and 7.6×10^6 n/cm^2, which may be related to the crosslinking formation inside the polypeptide chain of gelatin at lower fluences. The decrease of broadening at fluences above 7.6×10^5 n/cm^2 may be related to the degradation of the Co-gelatin film.[16] In addition, the oxygen from the surrounding medium reacts with the crosslinking to form peroxidic structures that decompose, causing oxidative degradation.[17]

Figure 2 shows the temperature effect on the ε'' values of Co-gelatin film before and after irradiation with the fast neutron fluences. From this figure it is clear that the ε'' values of unirradiated sample exhibit a peak at 310 K that is due to the α-relaxation process around and above the T_g of the gelatin.[8] This may be due to the micro-Brownian motion of the segmental parts in the polymer chains.[18] At the same time the polar groups that are directly attached to the main chain of gelatin cannot move independently. Also, it is clear from Figure 2 that the α-peak height decreases at lower values of fast neutron fluences (7.6×10^5 and 7.6×10^6 n/cm^2) and then increases again at higher fluences up to 0.5×10^9 n/cm^2. Moreover,

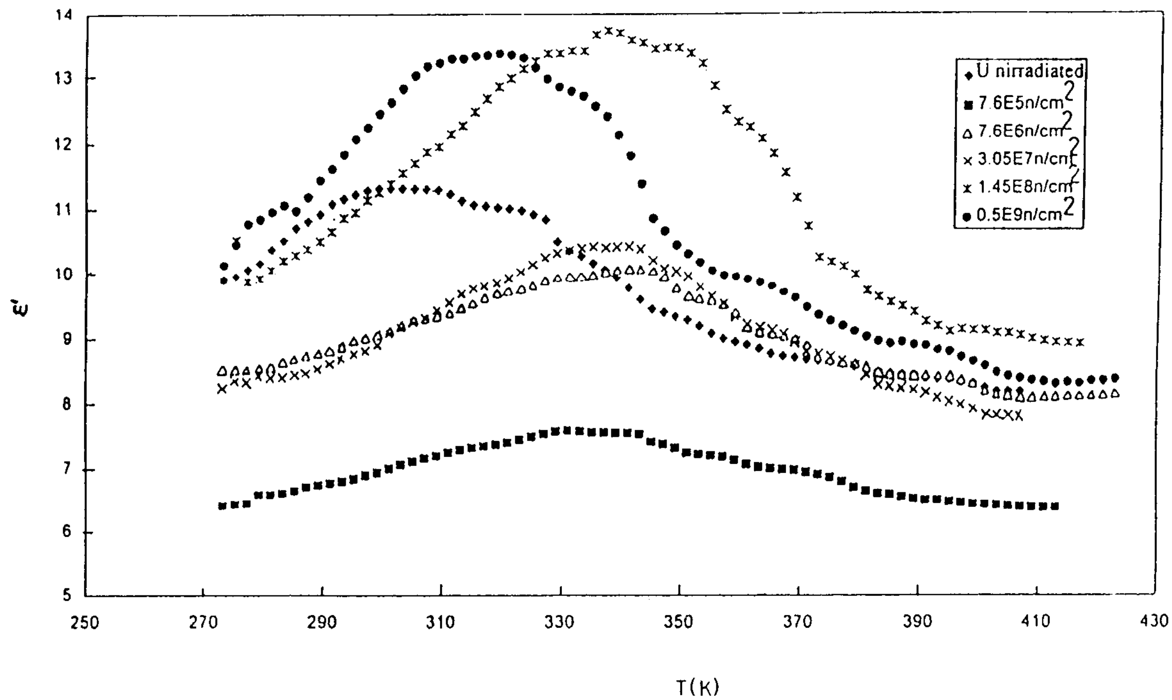

Figure 1 The variation of the ε' with the temperature at different fast neutron fluences at 10 kHz.

the broadening of the ε'' peak (Fig. 2) has a maximum value at lower doses (7.6×10^5 and 7.6×10^6 n/cm^2) and then decreases by increasing the neutron fluence up to 0.5×10^9 n/cm^2. This behavior is in good agreement with the discussion for Figure 1.

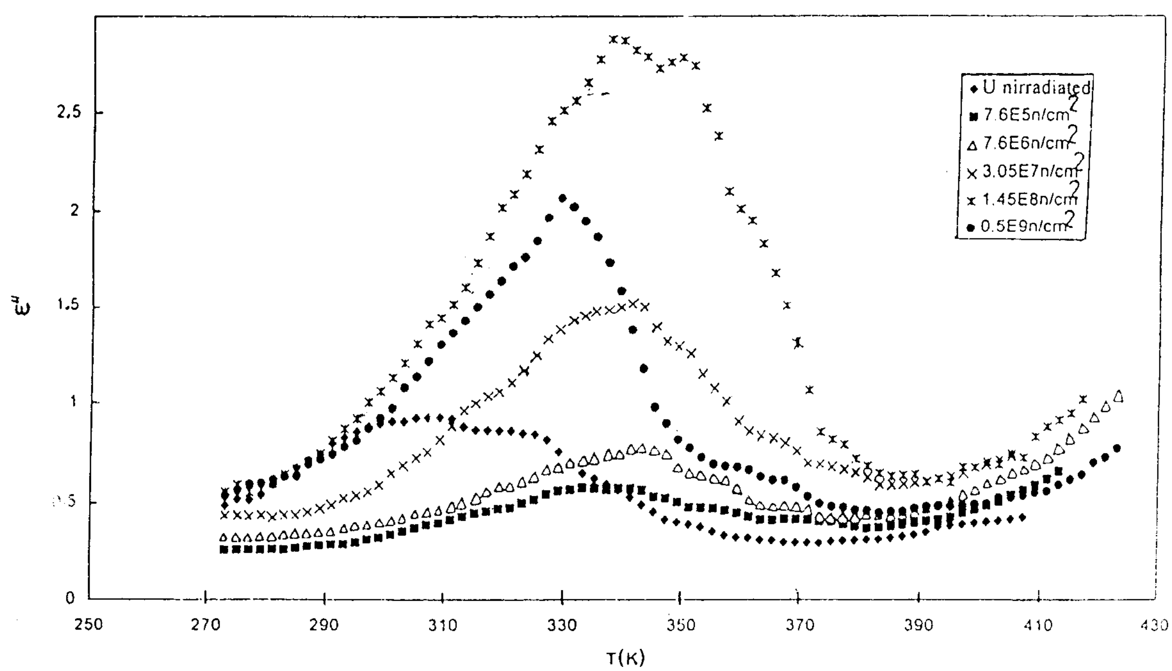

Figure 2 The variation of the ε'' with the temperature at different fast neutron fluences at 10 kHz.

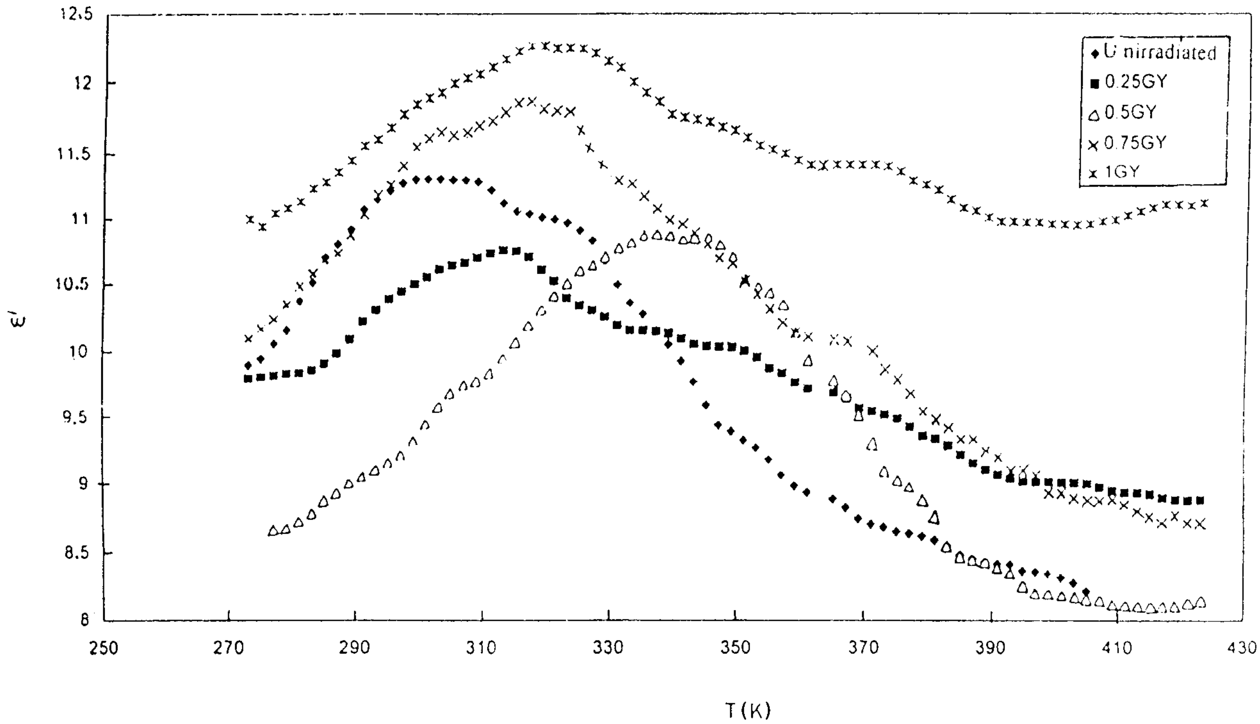

Figure 3 The variation of the ε' with the temperature at different γ doses at 10 kHz.

To compare the effect of γ radiation on the dielectric properties for Co-gelatin film with that discussed above, the variation of ε' and ε'' with temperature (at 10 kHz) after exposure to γ doses ranging from 0.25 to 1 Gy were studied as shown in Figures 3 and 4. From both figures one can see that

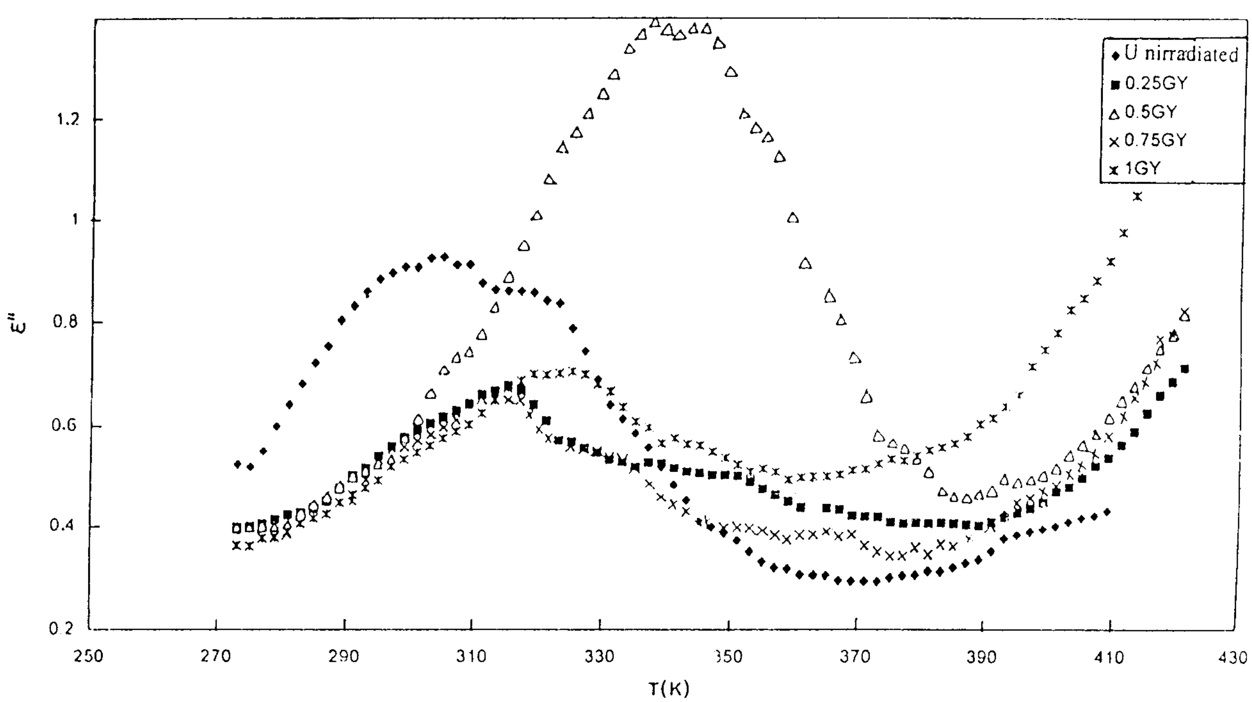

Figure 4 The variation of the ε'' with the temperature at different γ doses at 10 kHz.

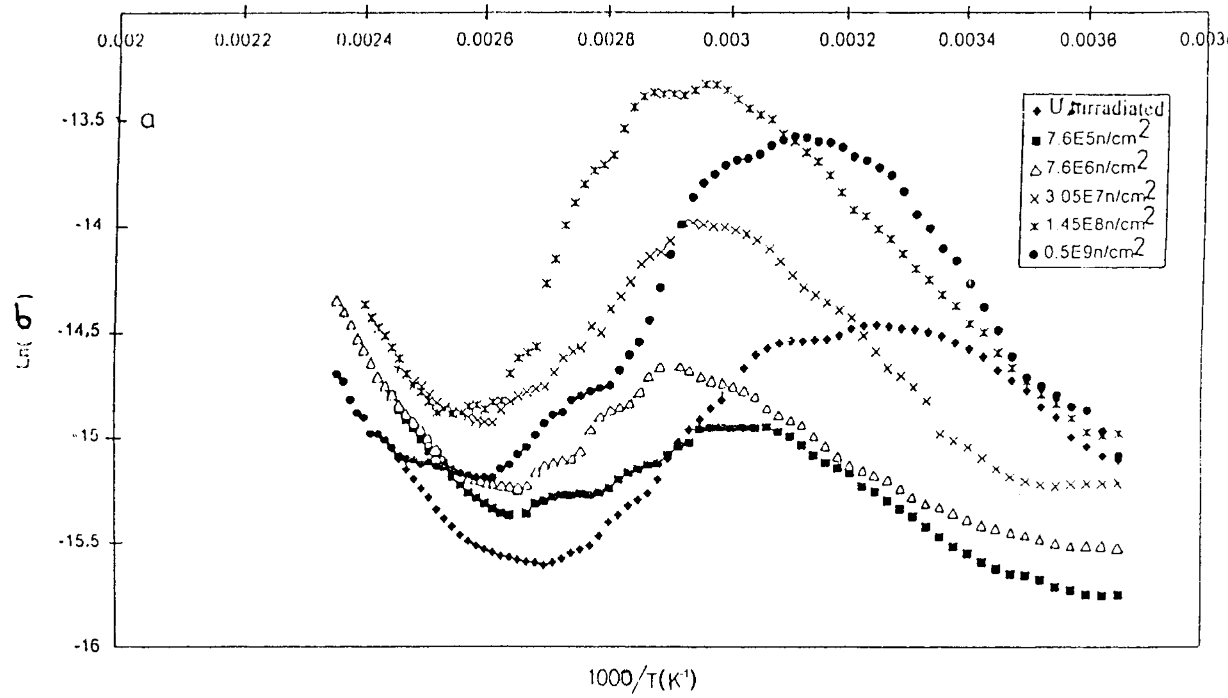

Figure 5 The variation of the ac conductivity (ln σ) with the temperature at different fast neutron fluences at 10 kHz.

the interaction of γ radiation with the polypeptide chains leads to an increase in ε' and ε'' with temperature up to 310 K. Beyond 310 K the ε' and ε'' begin to decrease to give minimum values at ~375 K, after which they increase again, especially the ε'' values. This may be due to the formation of boundary layers of blocked ions at the electrode surfaces,[17,19] a Maxwell–Wagner type effect,[20] or the cooperation of the two with each other. Moreover, the effect of γ rays is to excite the carbonyl group (C=O) in the gelatin structure and other free radicals will be formed, as well as carbon monoxide (CO), via Norrish reactions.[21] These mobile free radicals can wander through an irradiated Co-gelatin film until they meet in pairs to form a crosslink. This crosslink will directly effect the ε' and ε''. Another effect of γ rays appears as a loss of hydrogen atoms from neighboring molecules. This behavior was very clear at the γ dose of 0.25 Gy, after which the photodegradation, as well as oxidative degradation, became predominant, leading to production of more free carriers.[18] In addition, the increase of ε'' beyond 375 K may be due to the freeing of more trapped carriers by thermal agitation as a result of the heating effect.[22] Thus, the effect of both types of radiation is approximately the same at lower and higher temperature ranges.

Figure 5 represents the variation of the ac conductivity with the absolute temperature for the Co-gelatin film before and after irradiation with the same values of different fast neutron fluences. This study was carried out at 10 kHz. From the figure it is clear that the minimum values of the ac conductivity were obtained at fluences of 7.6 $\times 10^5$ and 7.6 $\times 10^6$ n/cm^2, after which it began to increase with increasing neutron fluences to reach a maximum value. The corresponding values of the activation energy (E_a) in region I (low temperature) and region II (high temperature) were calculated from experimental data and are listed in Table I. These values decreased with

Table I Activation Energies (E_a) for 5 wt % Co-Gelatin Sample before and after Irradiation with Different Fast Neutron Fluences

	E_a	
Dose	Region I	Region II
Unirradiated	0.197	0.281
7.6×10^5 n/cm^2	0.143	0.330
7.6×10^6 n/cm^2	0.155	0.313
3.05×10^7 n/cm^2	0.210	0.236
1.45×10^8 n/cm^2	0.218	0.454
0.5×10^9 n/cm^2	0.321	0.393

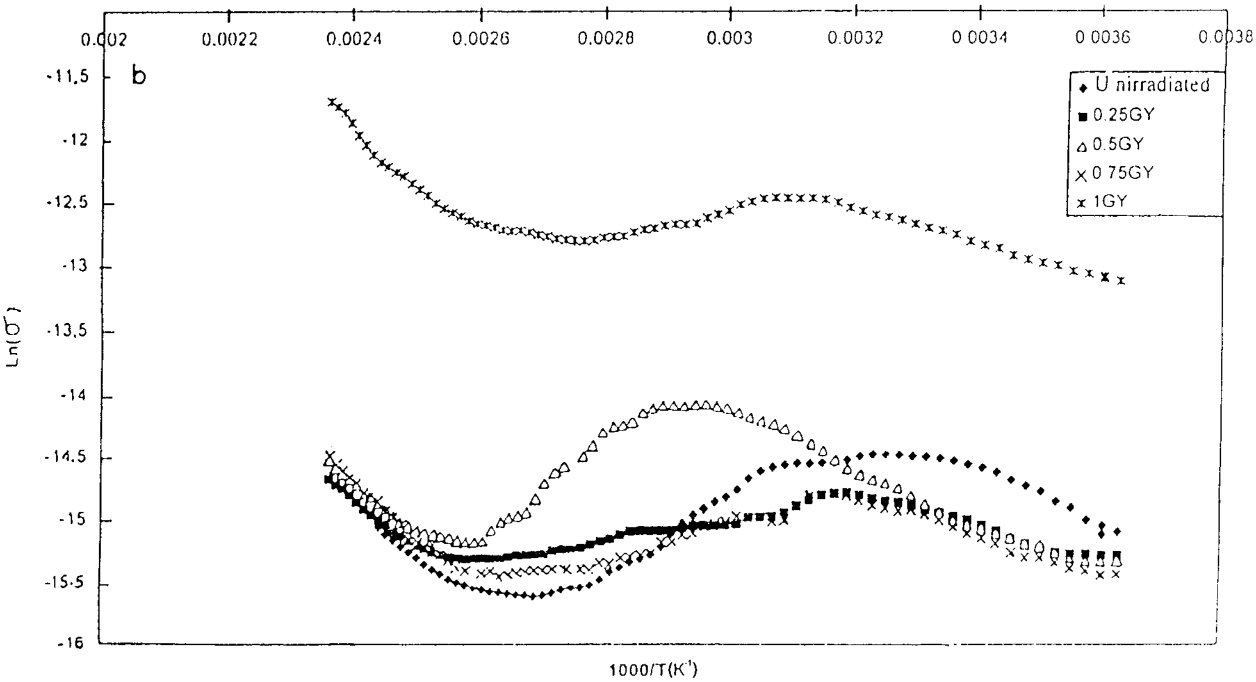

Figure 6 The variation of the ac conductivity (ln σ) with the temperature at different γ doses at 10 kHz.

decreasing neutron fluence down to 7.6 $\times$ 10^6 n/cm^2, which indicates that the conduction is partially electronic (mainly ionic) as a result of crosslink formation inside the secondary and tertiary structure of the Co-gelatin film. The increase in the E_a with increasing fluences (more than 7.6 $\times$ 10^6 n/cm^2) is probably due to degradation that occurs as a result of neutron irradiation, as well as oxidative degradation.[18,23]

The above study was repeated before and after irradiation with different γ doses (0.25, 0.5, 0.75, and 1 Gy) as shown in Figure 6. One can observe from this figure that the minimum value of the ac conductivity was obtained at 0.25 Gy while the maximum one was obtained at higher values of the γ doses up to 1 Gy. This may be due to rupturing of the chemical bonds of the Co-gelatin film and creation of free radicals that are able to migrate through the network structure, leading to this change in ac conductivity.[24] The E_a values listed in Table II for regions I and II indicate that the crosslinking is predominant at 0.25 Gy while the photodegradation process appears at higher values (0.5–1 Gy).

In conclusion, the dielectric properties (ε' and ε'') and the ac conductivity exhibited approximately the same behavior at higher and lower doses of both types of radiation (fast neutrons and γ ray). Moreover, Tables I and II indicate that the values of the activation energies had nearly the same trend with an increasing dose, which agrees well with the expected characteristics of the samples under investigation.

Table II Activation Energies (E_a) for 5 wt % Co-Gelatin Sample before and after Exposure to Different γ Doses

	E_a	
Dose	Region I	Region II
Unirradiated	0.179	0.281
0.25 Gy	0.141	0.304
0.50 Gy	0.191	0.433
0.75 Gy	0.419	0.457
1.00 Gy	0.130	0.315

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