Effects of the Composition Ratio, Eosin Addition, and γ Irradiation on the Dielectric Properties of Poly(vinyl Alcohol)/Glycogen Blends

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ABSTRACT: The dielectric relaxation spectra of various poly(vinyl alcohol) (PVA)/glycogen blends and irradiated blend samples with 70 wt % PVA content that were undoped and doped with eosin were measured in extended temperature (30–160°C) and frequency (1 kHz to 1 MHz) ranges. Dielectric relaxation spectroscopy separates different molecular groups of a repeating unit of a polymer with respect to the rate of its orientation dynamics. In the high-temperature range (>100°C), the σ relaxation, which is associated with the hopping motion of ions in the disordered structure of the biopolymeric material, can be measured. The electric dipole moment and the activation energy of the glass-transition temperature relaxation process were calculated. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1281–1288, 2008

Key words: activation energy; amorphous; barrier; biomaterials; blending

INTRODUCTION

Dielectric spectroscopy is sensitive to the intensity and velocity of orientational changes of mean dipole moments within a small volume unit in substances exposed to an electric field. It provides experimental results that concern the mobility of polymers bearing dipolar regions or dipolar side groups.

It is quite common in the dielectric spectroscopy of natural and synthetic polymers to distinguish between the primary relaxation (α relaxation) and several secondary relaxations. The α relaxation is related to the glass transition, and it is observed in the temperature range above the glass-transition temperature (T_g). The secondary relaxation processes observed in the range of temperatures below the glass transition (sub-T_g's) are related either to the local main-chain dynamic (β relaxation) or to different side-group motions (γ relaxation). It was found recently[1–3] that there is an additional dielectric relaxation process called σ relaxation in the higher temperature range (80–180°C) for amorphous solid systems, polysaccharides, and other polymers, which obviously cannot be assigned to any molecular dipolar group orientation. This process is associated with the hopping motion of ions in the disordered structure of the polymeric material. It is strongly related to the direct-current (dc) conductivity of the polymeric system.

The aim of this study was to perform a comprehensive study of the influence of the addition of eosin and γ irradiation on the dielectric properties and associated relaxation phenomena of PVA/glycogen compositions. We undertook a systematic investigation of the dielectric constant (ε') and dielectric loss factor (ε'') in the frequency range 1 kHz to 1 MHz and in the temperature range 30–160°C.

EXPERIMENTAL

Weighed amounts of PVA granules were dissolved in a mixture of distilled water and ethanol with a 4 : 1 ratio. Also, weighed amounts of glycogen were dissolved in distilled water at room temperature. A solution of PVA and glycogen were mixed together with different weight percentages of PVA/glycogen (100/0, 85/15, 70/30, 50/50, 30/70, and 0/100 w/w) with a magnetic stirrer at 50°C. Thin films of appropriate thickness (≈ 0.01 mm) were cast onto stainless steel Petri dishes and then dried in air at room temperature for about 6 days until the solvent was completely evaporated. The obtained glycogen film was brittle; therefore, it was used as a powder in the form of pellets with an approximate thickness of 0.136 cm for these studies. Films were cut into slab pieces and prepared to fit the cells of the measuring techniques.
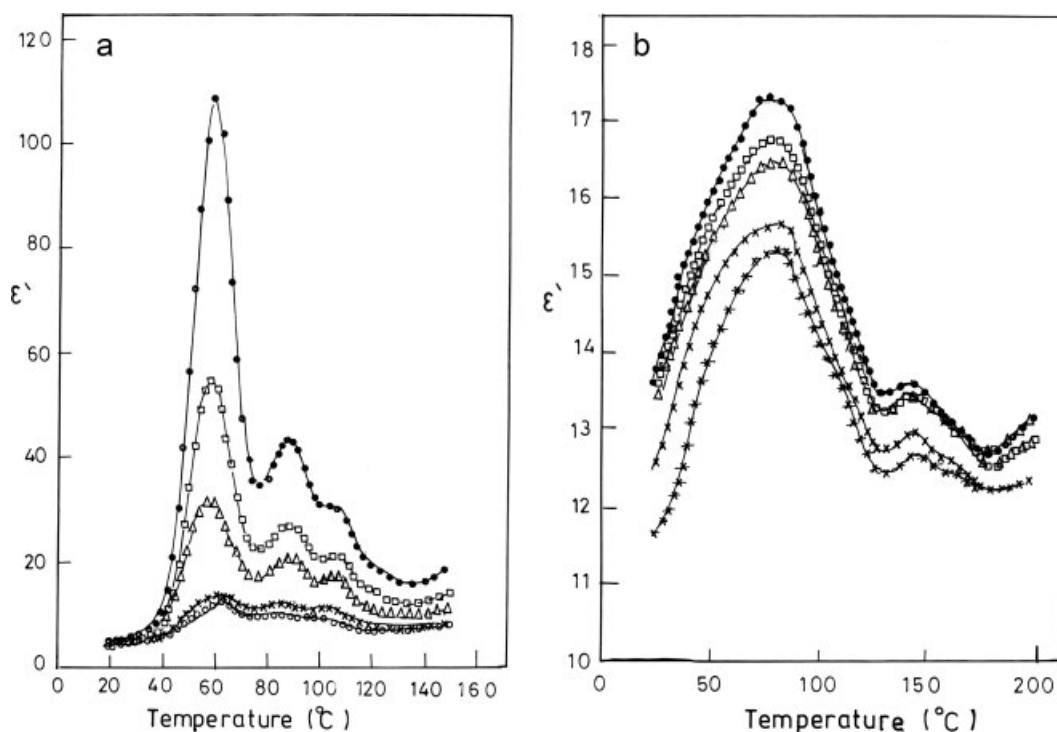
Figure 1 Variation of ε′ with temperature for (a) pure PVA and (b) pure glycogen at various frequencies: (●) 20, (□) 50, (△) 100, (×) 500, and (○) 1000 kHz.

Eosin, with a concentration of 0.1 wt %, was added only to the mixed solution of 70/30 w/w PVA/glycogen, and the same procedure were carried out to form the film. The 70/30 w/w PVA/glycogen undoped and doped samples were irradiated by different γ doses in the range 5–100 kGy with ^{60}Co source with a dose rate of 8.6 Gy/h at room temperature.

Measurements of ε′ and ε″ in the frequency range 1 kHz to 1 MHz and a controlled temperature range from 30 to 160°C were carried out with a Hioki 3531 Z Hiester programmable automatic RLC meter (Koizumi, Ueda, Nagano, Japan). The accuracy of ε′ and ε″ was ±3%.

RESULTS AND DISCUSSION

ϵ'

It is well known that the dielectric polarization in a polymer may be due to the dipole alignment rotation/motion of the main/segmental polymer chain, migration of ions within the material, or injection from electrodes.

Figure 1 shows the temperature dependence of ε′ at five frequencies (20, 50, 100, 500, and 1000 kHz) for the PVA and glycogen homopolymers. As shown in Figure 1(a), for pure PVA each ε′(T), where T is the temperature, curve revealed three pronounced peaks appearing at about 56, 85, and 110°C with

magnitudes of 110, 47, and 33, respectively, at 20 kHz. The low-temperature peak was probably related to the so-called sub-T_g, which was due either to the local main-chain dynamic or to different side-group motions. The intermediate temperature peak was located in the vicinity of T_g[4–6] and was designated as α relaxation. The high-temperature peak was a nondipolar process; it was due to the interfacial polarization or space charge polarization effects.[7,8] This peak is not always so easily visible, but it is frequently associated with the onset of ionic conductivity processes, and therefore, we labeled this process σ relaxation. Its magnitude decreased as the crystallinity of the sample increased.

As shown in Figure 1(a), ε′ decreased with increasing frequency over the whole investigated range of temperatures. This was attributed to the fact that at higher frequencies, dipoles cease to follow the changes in electric field and only ions and electrons contribute.

In case of pure glycogen [Fig. 1(b)], each ε′(T) curve exhibited two pronounced peaks at about 66 and 140°C with magnitudes of 17.5 and 13.5, respectively, at 20 kHz. The low-temperature peak corresponded to the glass transition, whereas the higher temperature peak was assigned to proton hopping in the disordered solid system of the biopolymer.[9] It was strongly related to the dc conductivity of the polymer system and has also been observed in many ionic conducting disordered solids.[10,11]
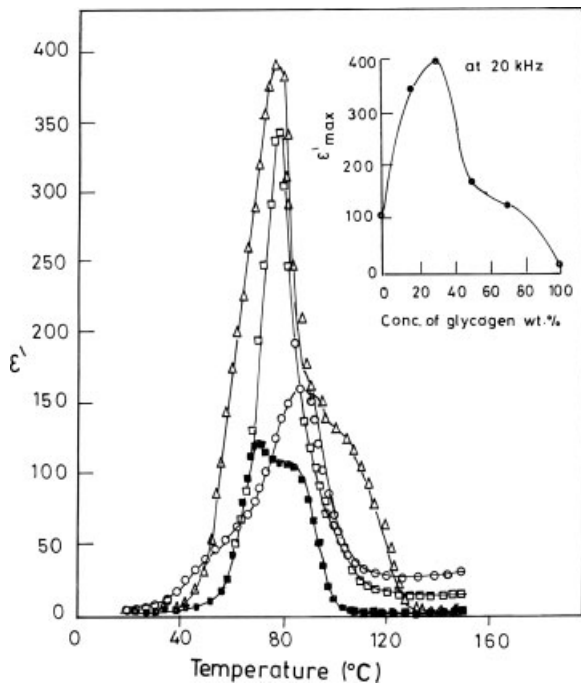
Figure 2 Variation of ε' with temperature for the PVA/glycogen blend samples: (□) 85/15, (△) 70/30, (○) 50/50, and (■) 30/70 w/w at 20 kHz.

Figure 2 shows the temperature dependence of ε' for the PVA/glycogen blend samples with compositions of 85/15, 70/30, 50/50, and 30/70 w/w at only 20 kHz for the sake of brevity. The analysis of $\varepsilon'(T)$ curves revealed that the lower temperature peak (sub-T_g) was missing for blend samples containing 15 and 30 wt % glycogen, whereas for the blend sample with 50 wt % glycogen, it appeared as a shoulderlike peak on the lower temperature side of the T_g peak. For the blend sample with 70 wt % glycogen content, the sub-T_g and T_g peaks were observed at 65 and 84°C, respectively. In addition, the blend sample with 70/30 w/w PVA/glycogen had only a shoulder on the high-temperature side of the T_g peak, which corresponded to σ relaxation due to dc conduction processes. Also, the value of ε' at the peak position (ε'_{max}) at the glass transition for various blend samples was higher than those in both the PVA and glycogen homopolymers; among these samples, the value of ε'_{max} for the blend sample with 70/30 w/w PVA/glycogen was the highest one (see the inset of Fig. 2).Accordingly, the mixture of PVA with glycogen polar homopolymers was expected to increase the number of ionizable charge carriers considerably in the polyblend polymer network. Furthermore, at low frequency, it was possible to consider interfacial polarization or the Maxwell–Wagner effect, which exists only in multiphase systems of inhomogeneous polymeric materials.[12]

Figure 3 shows the variation of ε' with temperature for the irradiated 70/30 w/w PVA/glycogen

blend sample with γ doses in the range 5–100 kGy at 20 kHz. All of the irradiated samples were characterized by the occurrence of two peaks corresponding to α and σ relaxations, except the irradiated samples at 50 and 100-kGy γ doses, which had only one pronounced α-glass-transition peak. The peak position of the glass-transition peak for the irradiated samples shifted toward higher temperatures than that of the pristine sample. The disappearance of the σ-relaxation peak at higher radiation doses of 50 and 100 kGy may have been due to the recombination of ions responsible for dc conduction with the ionic products of opposite sign produced upon γ irradiation.[13,14]

From room temperature up to 160°C, the $\varepsilon'(T)$ curves themselves sometimes overlapped and intersected. The width of the T_g peak was broader for the irradiated samples than for the pristine one. The greater breadth of the α relaxation was attributed to the wider range of crystalline sizes. The inset of Figure 3 shows that ε'_{max} at T_g peak rose rapidly at 5 kGy; this was followed by a decrease up to 20 kGy, but it was still higher than the value for the pristine sample and then increased up to a γ dose of 100 kGy. Crosslinking and degradation are nonequilibrium radiation chemical processes that change the structure and, hence, the physical properties of the polymers. The induced radiation effect on a polymeric material is to introduce new dipoles or cause changes in the dynamics of the existing dipoles, which result in an increase in the values of ε'. It also causes the creation of carbonyl groups, which are highly polar, anc cause a remarkable increase in ε'.[15,16]

Figure 4 shows the temperature dependence of ε' for the pristine and γ-irradiated 70/30 w/w PVA/glycogen blend samples doped with eosin at 20 kHz. ε' analysis of the irradiated samples at 6-, 10-, and 20-kGy γ doses yielded two broad peaks similar to the pristine sample; one occurred within the glass-
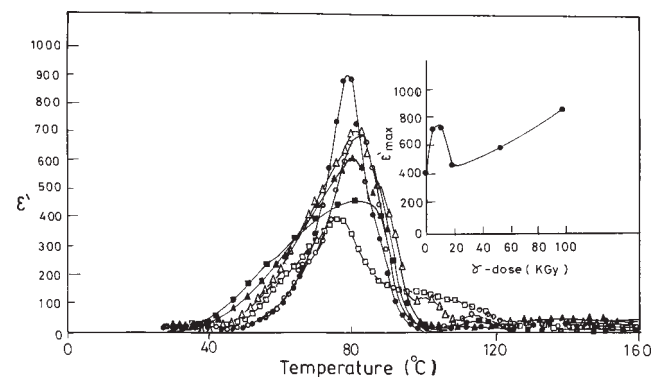

Figure 3 Variation of ε' with temperature for the pristine and irradiated 70/30 w/w PVA/glycogen blend samples at γ doses of (□) 0, (△) 5, (○) 10, (■) 20, (▲) 50, and (●) 100 kGy at 20 kHz.
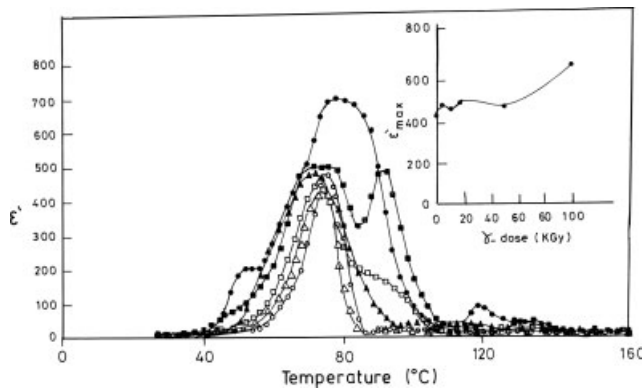
Figure 4 Variation of ε' with temperature of the pristine and irradiated 70/30 w/w PVA/glycogen blend samples doped with eosin at γ doses of ($\square$) 0, ($\triangle$) 5, ($\bigcirc$) 10, ($\blacksquare$) 20, ($\blacktriangle$) 50, and ($\bullet$) 100 kGy at 20 kHz.

transition region of the irradiated blend samples, and the other occured at higher temperatures in the range 100–140°C. An additional relaxation peak was seen at a lower temperature around 70 and 50°C for irradiated samples at 20- and 100-kGy γ doses, respectively. The ionic nature of the eosin-containing blend sample increased the number of ionizable charge carriers, so ε' increased compared to that of the undoped sample at most temperature points. Thus, we expected that the dye molecules in such a system were aligned with their molecular axes and took the orientation of the polymer side groups. A large number of eosin molecules compared to that of the side groups of polyblend polymers tends to maintain a considerable free volume and, thereby, reduces steric hindrance to side group motion and increases ε'. Also, an enhanced mobility of the chain backbone allowed by the so-called internal plastification phenomenon, which leads to a reduction in the interchain interactions, could be achieved by dye addition. However, the values of ε'_{max} for the irradiated samples were higher than that of the pristine one and changed irregularly with increasing γ dose (see the inset of Fig. 4). It was clear that the value of ε'_{max} changed slightly with increasing γ dose up to 50 kGy, whereas it changed greatly at a 100-kGy γ dose.

Dielectric properties are usually related either to the permanent or induced dipoles in the polymeric chains or to space charge effects that are found in composite materials. Classically, the relation of ε' to the permanent dipoles is given by

$$\frac{\varepsilon' - 1}{\varepsilon' + 2} = \frac{4}{3}\pi N\left[(\alpha_e + \alpha_a) + \frac{\mu^2}{3kT}\right]$$

where N is the number of molecules per unit volume, k is the Boltzmann constant, α_e and α_a are the electronic and atomic polarizabilities, respectively

and μ is the dipole moment. The slope of straight line (figure not shown) of the relation between $(\varepsilon' - 1)/(\varepsilon' + 2)$ and $1/T$ above T_g of different samples is related to the square of the dipole moment. The calculated electric dipole moments for the PVA and glycogen homopolymers and their blends with compositions of 85/15, 70/30, 50/50, and 30/70 w/w PVA/glycogen were 23.1, 31.6, 19.8, 17.6, 21.4, and 20.6 D, respectively. The value of μ_o for PVA was in good agreement with that previously reported.[17] Interestingly, the value of μ_o for the blend samples was lower than that for the individual polymers. Among these samples, the value of μ_o for the blend sample with a composition of 70/30 w/w PVA/glycogen was the lowest one. This behavior was attributed to the decrease in the chain space and free volume between dipoles in the polymer blend network due to the mixing of glycogen with PVA. It may have reflected the existence of hydrogen-bond formation in the blend sample films, which would have determined the symmetry of the translational or orientation distribution of segmental motion of the amorphous chains. For irradiated 70/30 w/w PVA/glycogen, the calculated dipole moments were 15.6, 15.9, 16.4, 15.6, and 14.8 D at 5-, 10-, 20-, 50-, and 100-kGy γ doses, respectively. The decrease in μ_o for the irradiated samples may have been due to the increasing degree of ordering of the orientation of the dipoles. In case of the irradiated 70/30 w/w PVA/glycogen blend sample doped with eosin, the calculated dipole moments were 17.4, 17.0, 17.2, 16.6, 16.9, and 16.2 D at 0-, 5-, 10-, 20-, 50-, and 100-kGy γ doses, respectively. The slight variation in μ_o reflected that the addition of eosin to the blend system enhanced its stability to γ radiolysis.

Figure 5 shows the temperature dependence of ε'' for PVA and glycogen homopolymers at five frequencies: 20, 50, 100, 500, and 1000 kHz. In the case of PVA [Fig. 5(a)], three relaxation peaks were noticed. The first relaxation peak corresponded to sub-T_g, which was reported in a nonequilibrium shoulder on the dissipation curves over the temperature range 40–80°C in low-frequency measurements.[18,19] The intermediate relaxation peak corresponding to T_g (α relaxation) was attributed to micro-Brownian motion of large chain segments. The later relaxation peak corresponded to σ relaxation, which was observed in the high-temperature range 80–180°C for amorphous solid systems and some polymers. This σ relaxation process is nondipolar; it is a result of ionic conductivity. Also, we observed that when the frequency was increased, the temperature corresponding to the maximum of ε'' shifted toward higher temperatures for only sub-T_g and T_g relaxations. However, the magnitudes of all loss peaks decreased with increasing frequency, so the
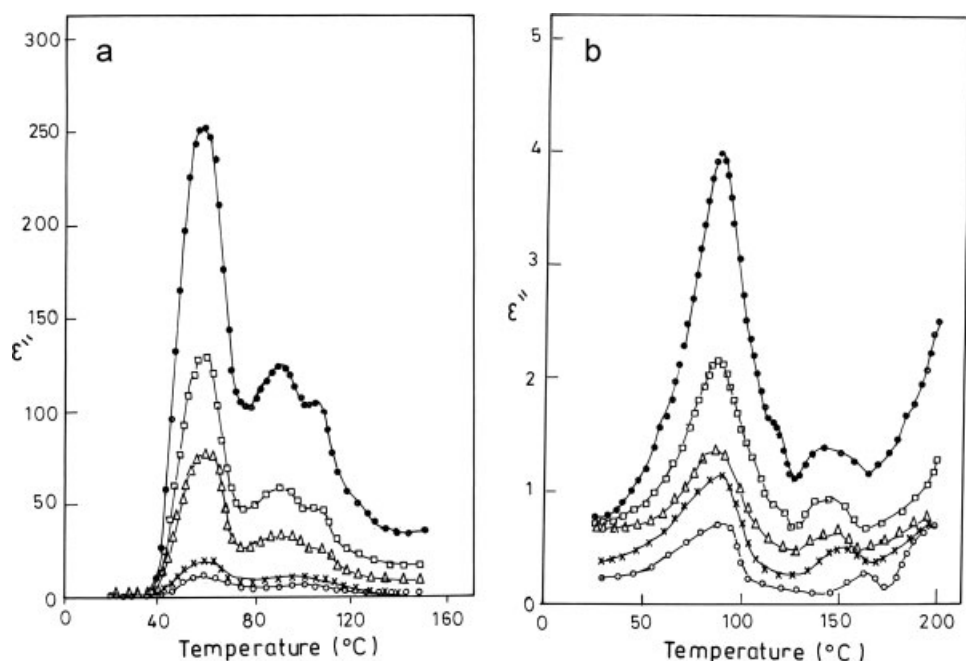
Figure 5 Variation of ε'' with temperature for (a) pure PVA and (b) pure glycogen at various frequencies: (●) 20, (□) 50, (△) 100, (×) 500, and (○) 1000 kHz.

two relaxation peaks, α and σ, overlapped with each other and appeared as a single peak at high frequency.

For glycogen [Fig. 5(b)], the $\varepsilon''(T)$ curves exhibited two pronounced relaxation peaks, the α and σ relaxations; the latter was assigned to ion migration in the disordered structure of the polysaccharide, as indicated by Einfeldt et al.[2,20] and Meßner et al.[21]

Figure 6 shows the temperature dependence of ε'' at 20 kHz for blend samples with compositions of 85/15, 70/30, 50/50, and 30/70 w/w PVA/glycogen. Two relaxation peaks were noticed. The α-relaxation process appeared as a broad peak relatively near the blend glass transition in all of the blend samples. The other relaxation process appeared as a steplike transition masked with α relaxation on the higher temperature side, σ relaxation, for blend samples with 85 and 70 wt % PVA. On the contrary, the second relaxation appeared as a shoulderlike transition because of overlapping with α relaxation on the lower temperature side, sub-T_g relaxation, for blend samples with 50 and 30 wt % PVA. It was clear that the α-relaxation was broadened in the blend samples compared to the pure components. This was attributed to disorder in the arrangement of the polar groups on one or more sites of the blend matrix and a microscopic heterogeneity environment of the relaxing dipole in the blend, which resulted in a distribution of local glass-transition points.[22,23]

Figure 7 shows the variation of ε'' with temperature at a frequency of 20 kHz for irradiated 70/30 w/w PVA/glycogen blend samples with 5–100-kGy

γ doses. $\varepsilon''(T)$ curves for the irradiated samples with 10 and 20-kGy γ doses contained two relaxation peaks at about 85 and 116°C in both γ doses similar to that of the pristine sample, except that the step-like peak (σ relaxation) at the higher temperature side of α relaxation appeared as a clear peak by γ
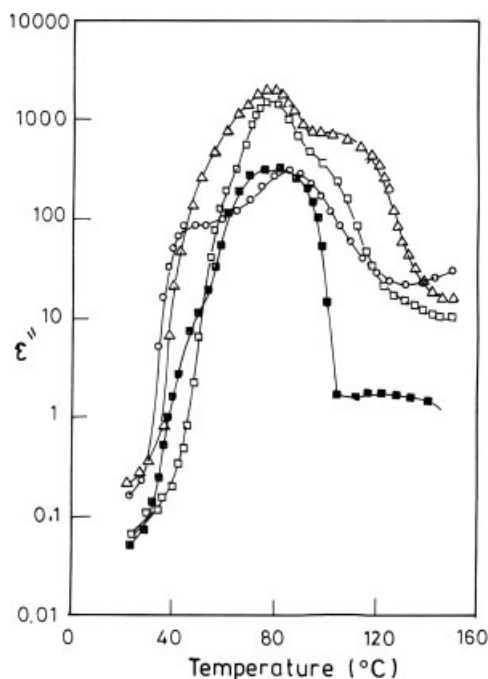

Figure 6 Variation of ε'' with temperature for the PVA/glycogen blend samples: (□) 85/15, (△) 70/30, (○) 50/50, and (■) 30/70 w/w at 20 kHz.
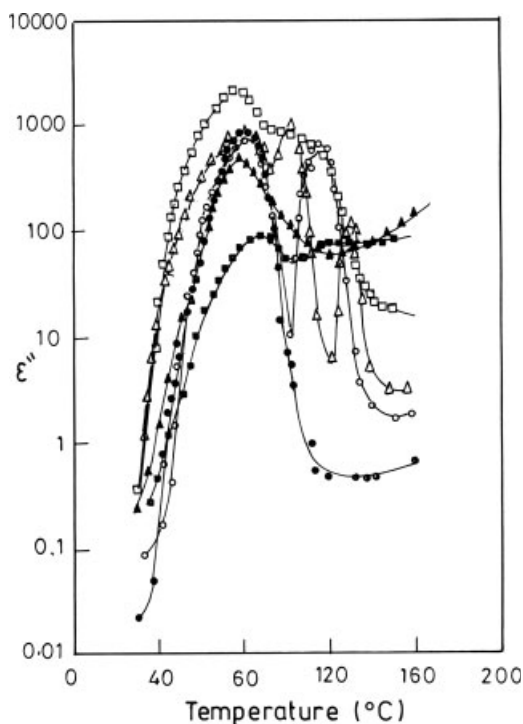
Figure 7 Variation of ε'' with temperature for the pristine and irradiated 70/30 w/w PVA/glycogen blend samples at γ doses of ($\square$) 0, ($\triangle$) 5, ($\bigcirc$) 10, ($\blacksquare$) 20, ($\blacktriangle$) 50, and ($\bullet$) 100 kGy at 20 kHz.

ε'' as a function of frequency at various temperatures (60, 70, 80, and 90°C) for the homopolymers and their blends as well as the irradiated samples undoped and doped with eosin with a composition of 70/30 w/w PVA/glycogen were studied. Each group of the investigated samples showed the same behavior. Accordingly, Figure 9 with $\varepsilon''(f)$, where f is the relaxation frequency, is given here for homopolymers and their blends as a representative of the whole groups (as an example for the sake of brevity). The variation of ε'' with frequency provided evidence for a very distinct dipolar peak (although not a Debye-type because they were broad and showed a distribution of relaxation times) whose position depended on the temperature. The existence of a peak at low frequency was an indication of the longer relaxation times pertinent to polymers composed of macromolecules. The peak in $\varepsilon''(f)$ shifted to lower frequencies, which meant an increase in relaxation time, as the temperature decreased, which indicated the dielectric relaxation character of the ε'' in these samples. These well-known features are characteristic of the freezing of dipolar motion with no longer range correlations (i.e., glasslike).

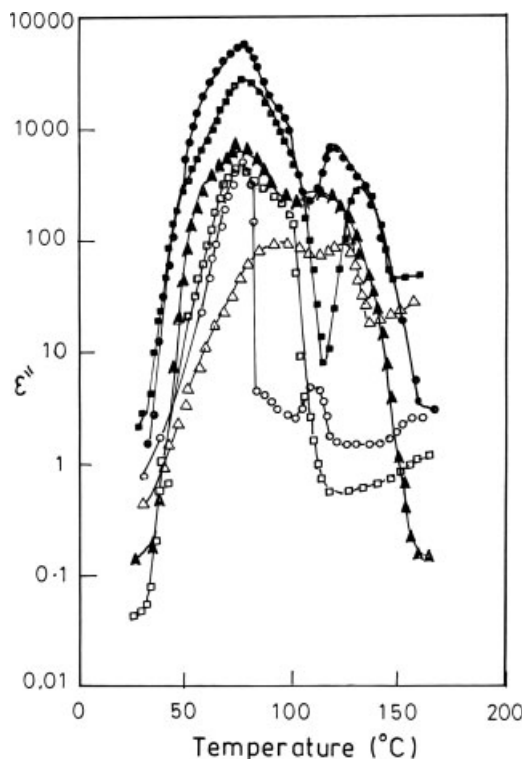The relaxation process can be modeled by an Arrhenius temperature dependence as follows:

irradiation. The σ relaxation observed for the pristine sample disappeared for irradiated samples at 20- and 50-kGy γ doses. For irradiated samples at a 5-kGy γ dose, three pronounced relaxation peaks were observed. The new relaxation peak appearing at about 98°C seemed to be related to dose and was probably due to local dipoles that were formed by radiation. These results indicate that γ irradiation caused induced changes in the orientation and microstructure of the 70/30 w/w PVA/glycogen blend matrix.

Figure 8 shows the temperature dependence of ε'' at 20 kHz for the pristine and γ-irradiated 70/30 w/w PVA/glycogen blend sample doped with eosin. The ε'' curve of the pristine sample contained only one broad relaxation peak corresponding to α relaxation. The disappearance of the steplike relaxation peak observed for the undoped blend sample may have been due to structural changes in the blend polymer matrix due to the addition of eosin. For all of the irradiated samples, two clearly separated peaks corresponding to α and σ relaxations were observed. The position of the σ relaxation peak changed irregularly with increasing γ dose, whereas the α-relaxation peak position for the irradiated samples was close to the pristine one, except the irradiated sample at 5-kGy γ dose shifted toward a higher temperature.

Figure 8 Variation of ε'' with temperature for the pristine and irradiated 70/30 w/w PVA/glycogen blend samples doped with eosin at γ doses of ($\square$) 0, ($\triangle$) 5, ($\bigcirc$) 10, ($\blacksquare$) 20, ($\blacktriangle$) 50, and ($\bullet$) 100 kGy at 20 kHz.

$$f = f_o \exp(-E_a/kT) \qquad (1)$$

where f is the relaxation frequency at which $\varepsilon''(f)$ is maximum, E_a is the energy barrier for dipole relaxation (activation energy), and f_o is the constant parameter characteristic for a particular relaxation process. The frequency of the maximum in ε'' is plotted in Figure 10 as a function of the reciprocal temperature for both homopolymers and their blends (as representative for all groups for the sake of brevity). The data were fitted to straight lines whose slopes gave the apparent activation energy for the α-relaxation process. The straight line suggested that the origin of the relaxation should have been seen in individual rearrangements of single noninteracting dipoles rather than in the collective behavior of cooperating species, which was likely to correspond to the Vogel–Fulcher–Tamman law.[24] The activation energies of the PVA and glycogen homopolymers and their 85/15, 70/30, 50/50, and 30/70 w/w PVA/glycogen blends were 0.41, 0.58, 0.54, 0.45, 0.47, and 0.48 eV, respectively. It was obvious that the values of the activation energy for various blend samples occurred between the values for the individual homopolymers. The lower activation energy values associated with the dipoles for pure PVA and
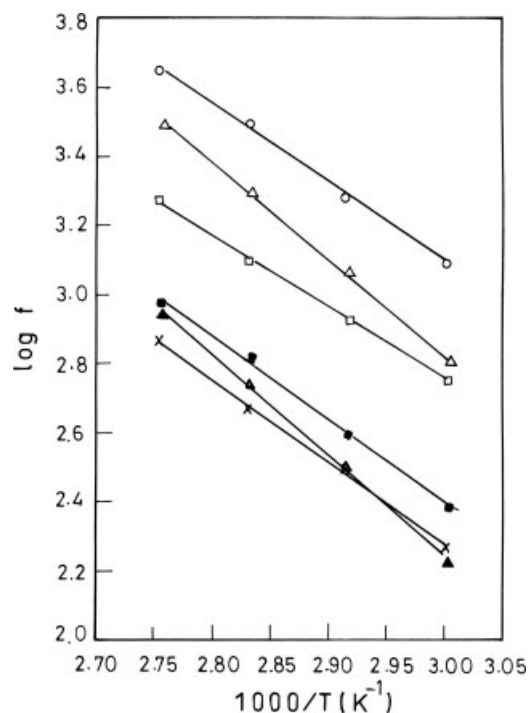

Figure 10 Plot of log f versus reciprocal temperature for the PVA/glycogen (w/w) blend samples: (□) 100/0, (△) 85/15, (○) 70/30, (×) 50/50, (■) 30/70, and (▲) 0/10.
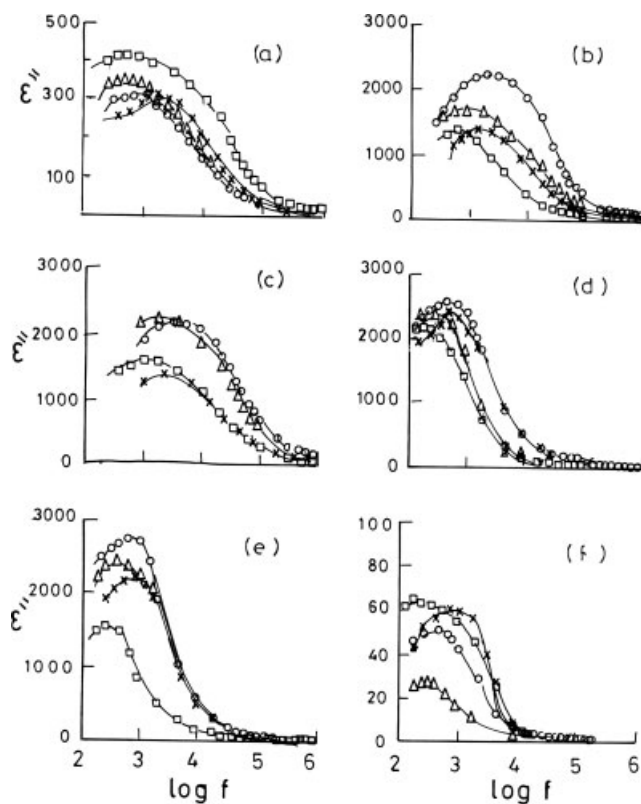

Figure 9 Variation of ε'' with log f for the PVA/glycogen blend samples (a) 100/0, (b) 85/15, (c) 70/30, (d) 50/50, (e) 30/70, and (f) 0/100 w/w at different temperatures: (□) 60, (△) 70, (○) 80, and (×) 90°C.

the blend sample of 50 wt % PVA may have been due to the increase in chain separation and free volume, which facilitated dipolar orientation that mainly contributed to polarization.

In case of irradiated 70/30 w/w PVA/glycogen, the values of activation energy at 0-, 5-, 10-, 20-, 50-, and 100-kGy γ doses were 0.45, 0.35, 0.34, 0.42, 0.36, and 0.30 eV, respectively. It was clear that the values of activation energy of the irradiated samples were lower than that of the pristine one. The lower values of activation energy associated with the dipoles for the irradiated samples indicated that γ irradiation caused the dipoles to be more free. However, for the irradiated 70/30 w/w PVA/glycogen blend doped with eosin, the values of activation energy at 0-, 5-, 10-, 20-, 50-, and 100-kGy γ doses were 0.44, 0.41, 0.42, 0.38, 0.39, and 0.35 eV, respectively. The values of activation energy for of the all of the irradiated samples were relatively smaller than that of the pristine sample.

CONCLUSIONS

The α-relaxation process exhibited typical Arrhenius behavior for the individual polymers and their blends as well as the irradiated blend sample with 70 wt % PVA undoped and doped with eosin. The lower apparent activation energy values associated with the dipoles for the investigated samples may have been due to the increase in chain separation

and free volume, which facilitated dipolar orientation that mainly contributed to polarization. The obtained values of electric dipole moment were sensitive to both blend composition and γ-irradiation doses for the blend sample with 70 wt % PVA, whereas a slight variation of μ_o was observed for the irradiated blend sample doped with eosin.

According to the previously mentioned results and considerations, blending PVA with glycogen and adding eosin and γ irradiation caused considerable changes in the dielectric properties of the polymeric system. This, together with the conditions of sample preparation, must be taken into account in the development and determination of the properties of solvent-cast polymeric films with specific characteristics.

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