# Effect of γ-irradiation on the dielectric loss and A.C. Conductivity of polyvinyl Alcohol Doped with CrCl$_3$

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*Dielectric loss and a.c. conductivity have been studied for γ-irradiated polyvinyl alcohol doped with 30% by wt. CrCl$_3$. The sample was subjected to different doses of γ-rays (200, 400, 600, 800 Krad and 1 Mrad). Dielectric loss measurements revealed that γ-irradiation increases the cross-linking density in the sample. A.C. conductivity was explained in terms of the correlated barrier hopping model.*

## 1. Introduction:

The addition of transition metals to polymeric network is of considerable interest and have many applications in modern engineering (1). Special attention has been directed towards polyvinyl alcohol (PVA) containing different transition metal halides for its increasing technological importance [2-4] On the other hand, ionizing radiation of polymers causes a number of structural and chemical changes which alter their physical properties. This depends upon whether the polymer cross-links or degrades. Moreover, irradiation of polymers may cause colour changes, which are due to the formation of conjugated double bonds and/or trapped free radicals and ions. Optical absorption and microhardness of γ-irradiated PVA doped with CuCl2 and CrCl$_3$ was investigated [5]. It was found that microhardness depends on both the radiation dose and the concentration of additives.

The clean-cut understanding of the conduction mechanism of disordered polymers has not yet been reached due to the complexity of the polymer structure. A.C. conductivity ($\sigma_{a.c}$) and dielectric loss measurements may provide information about the electronic structure of these materials [6-8]. Recently [9], a.c. conductivity and dielectric constant of PVA modified by different

concentrations of $MnSO_3$ was studied. It was found that $\sigma_{a.c}$ depends linearly on frequency and the correlated barrier hopping model was the most likely operating mechanism.

The present work aimed to study the effect of $\gamma$-irradiation on dielectric loss and a.c. conductivity of PVA doped with $CrCl_3$ to provide additional information about the nature of intermolecular interactions in such heterogeneous media.

## 2. Experimental :

The solution method was used to obtain the sample film. Weighed amount of pure PVA was dissolved in distilled water. A solution o $CrCl_3$ in water (30% by wt. of polymer) was added to the polymer. The mixture was stirred throughly and then poured into dishes. Homogeneous films were obtained after drying in an air oven for 48 h. A temperature of $40^oC$ was used to minimize gelation effects.

The a.c. conductivity and dielectric loss were measured in the requency range (100 Hz to 100 KHz) using PM 6304 automatic RCL (Philips) meter. A 400 KCi cobalt - 60 source (gamma-J6000 of AECL) was used for irradiation. The sample was wrapped in Al foil and exposed to doses from 200 K rad to 1 M rad.

## 3. Results and Discussion:

### 3.1. Dielectric loss as a function of temperature:

Figures (1-4), illustrate the temperature dependence of the dielectric loss at different frequencies and different doses. It is clear that the position of maximum dielectric loss is shifted towards higher temperatures as the frequency increased. The condition of maximum dielectric loss in polar dielectrics is given by: $w \tau = 1$, where $\tau$ is the relaxation time. Therefore, as the frequency is increased, the maximum dielectric loss is shifted towards higher temperatures, since the rise of temperature facilitates segmental motion and dipole orientation. This, in turn reduces the relaxation time.

On the other hand, increasing the radiation dose, the position of maximum dielectric loss is shifted towards higher temperatures. At 200 Krad no peak is observed except at high frequenies. With the increase of the radiation dose, the maximum dielectric loss starts to appear at lower frequenies.
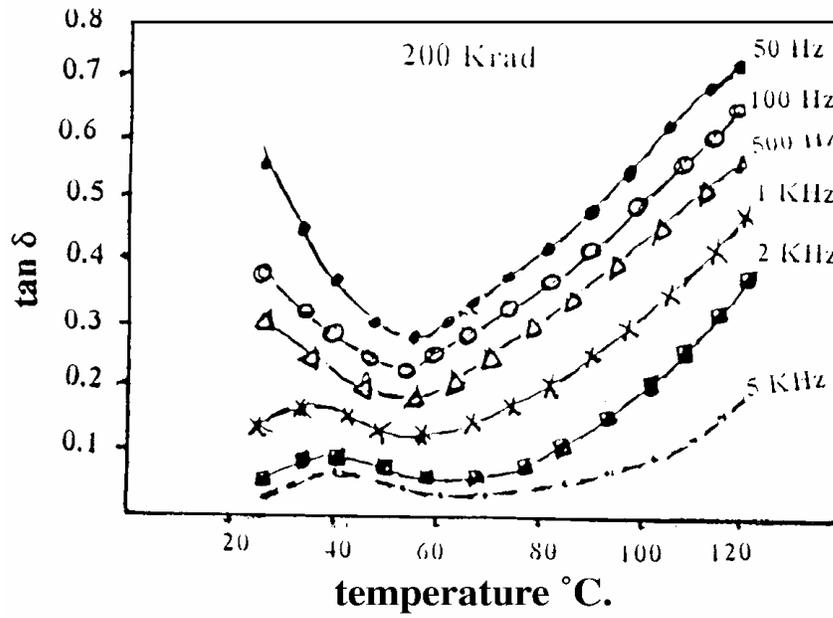
**Fig. (1):** Temperature dependence of the dielelectric loss at different
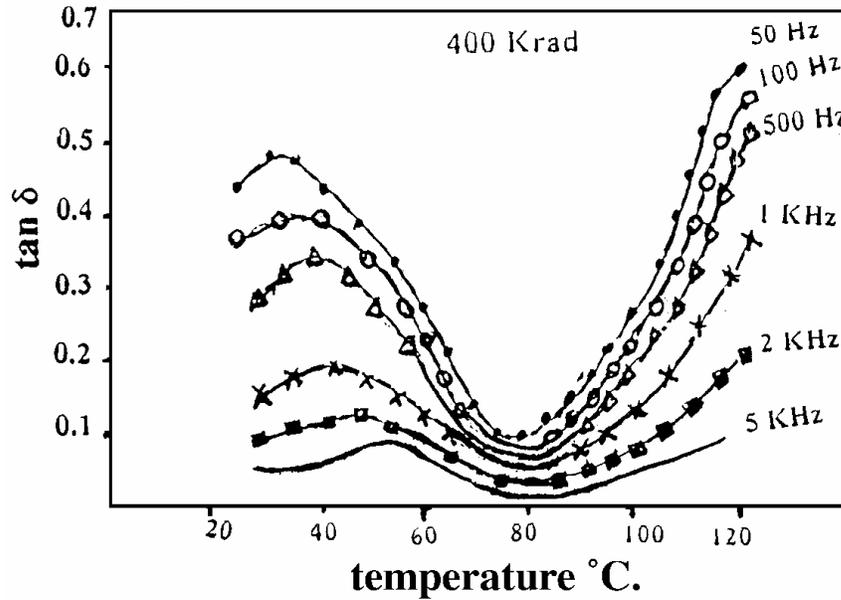frequencies and 200 krad.



**Fig. (2):** Temperature dependence of the dielelectric loss at different
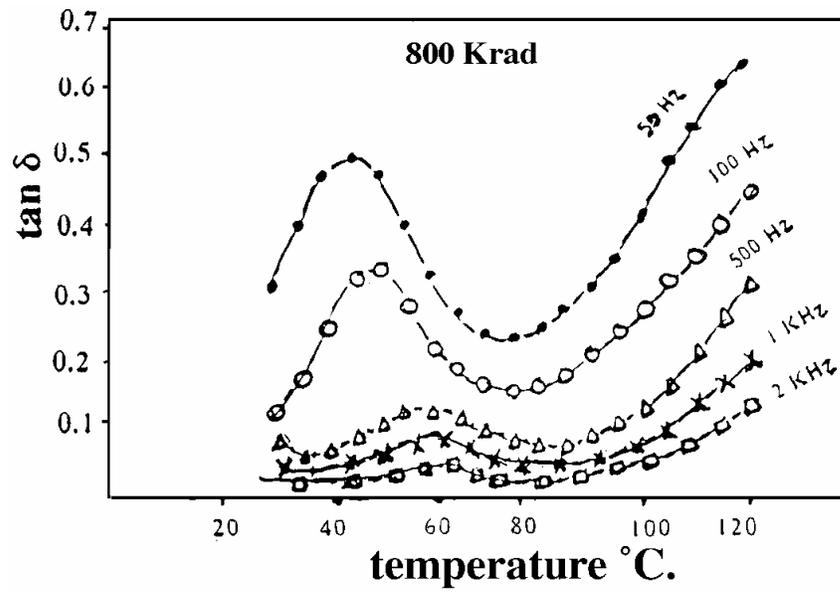frequencies and 400 krad.

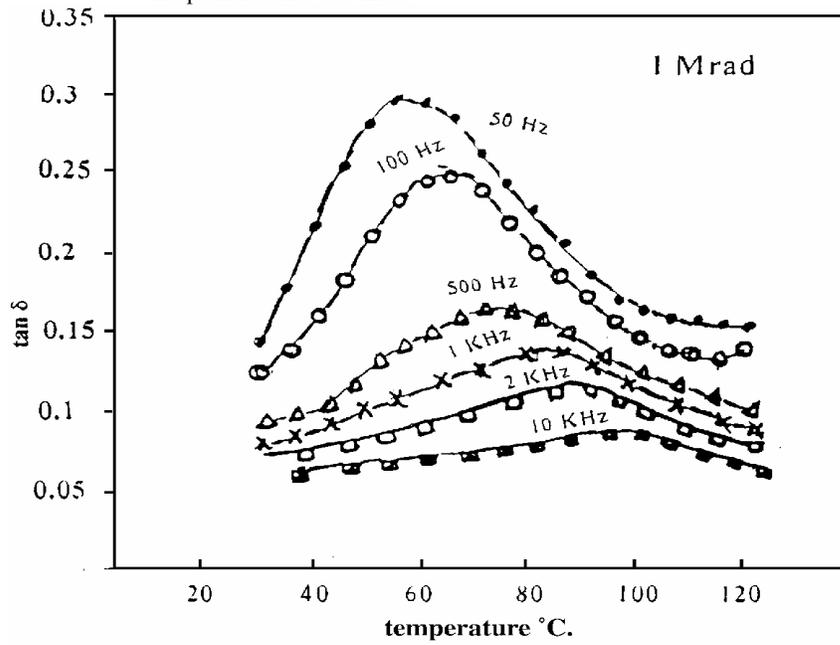**Fig. (3):** Temperature dependence of the dielelectric loss at different frequencies and 800 krad.



**Fig. (4):** Temperature dependence of the dielelectric loss at different frequencies and 1000 krad.

The above results indicate that irradiation of the sample increases the cross-linking density of macromalecule. This in turn, decreases segmental mobility and increases the relaxation time of dipole segmental loss. Fig. (5) represents the dielectric loss as function of temperature at 500 Hz for the different doses. It is obvious that the position of maximum dielectric loss is shifted towards higher temperatures as the radiation dose is increased.

### 3.2. A.C. Conductivity:

Figures (6-10) represent the frequency dependence of $\sigma_{a.c}$ at different temperatures and different doses. It can be seen that $\sigma_{a.c}$ increases linearly with frequency for all isotherms. On the other hand, a.c. conductivity is found to decrease as the rediation dose is increased. This confirms the cross-linking effect of $\gamma$-irradiation which slow down dipole orientation. The linear relations between log $\sigma_{a.c}$ and log f indicates that a.c conductivity obeys the relation.

$$\sigma_{a.c} = A\, w^S \qquad (1)$$

where A is constant and the frequency exponent S - 1. This universal character of the frequency dependent conductivity is preserved for a wide range of amorphous materials, among which are polymeric materials.

The values of S were calculated from the slope of the obtained straight lines and are plotted as function of temperature in Fig. (11). It should be noted that these values are found to be less than unity and decrease with rise of temperature. This behaviour, can be explained in terms of the correlated barrier hopping model (CBH) proposed by Elliett (10). This model considers the hopping of carriers between two neighbouring sites over a coulombic barrier separating them. Also, according to this model, the frequency exponent S is temperature dependent and is given by [10]:

$$S = 1 - \frac{6KT}{W_M - KT \ln(\frac{1}{w\tau_o})} \qquad (2)$$

where $W_M$ is the maximum height of the energy band and $\tau_o$ is the characteristic relaxation time.

Equation (2) predicts that S decreases with increasing temperature at large $W_M/KT$. This agrss well with the obtained results Fig. (11). It is worth noting that, inspite of the decrease of S with temperature, it increases as the radiation dose is increased. This may be attributed to the constant A in equation (1) which is structural dependent.
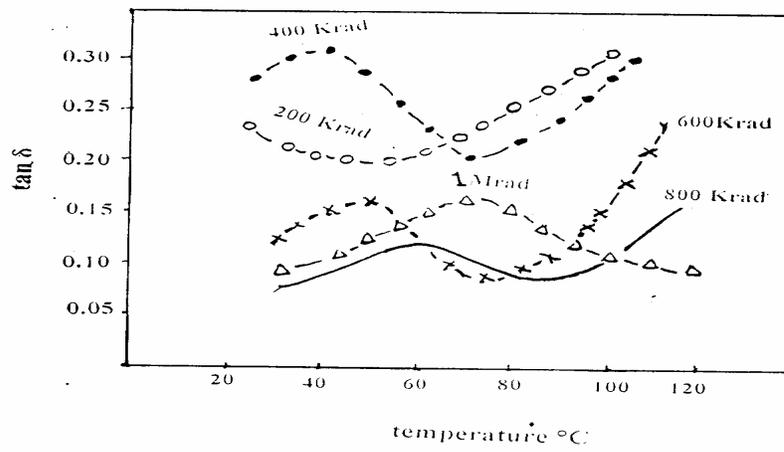
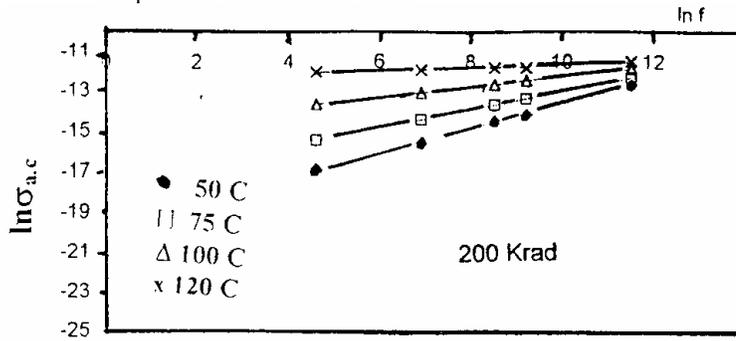**Fig. (5):** Temperature dependence of the dielelectric loss at different frequencies and different doses.



**Fig. (6):** Frequencies dependence of ln conductivity at different temperatures and at doce 200 krad.
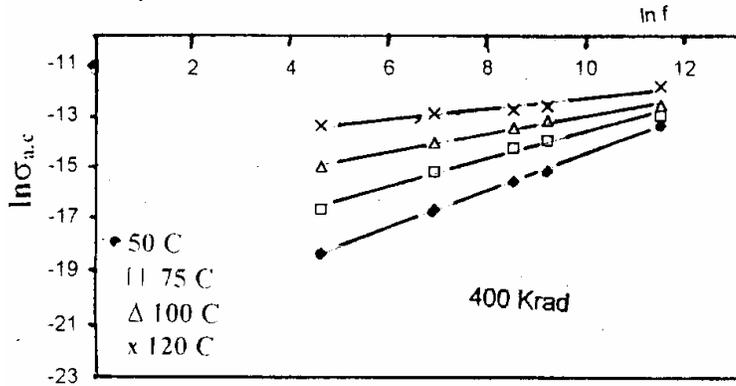


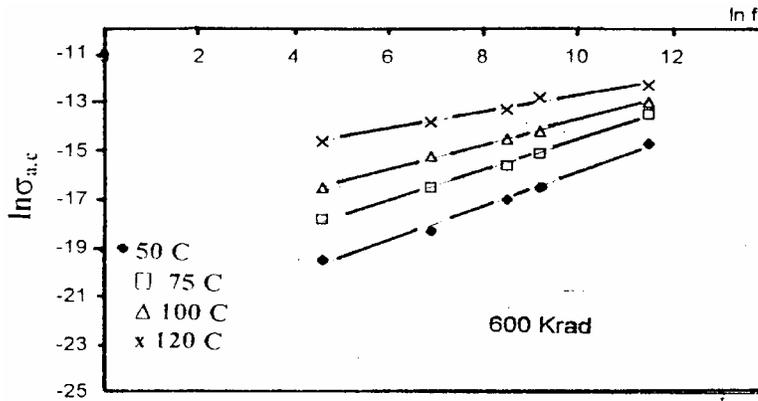**Fig. (7):** Frequencies dependence of ln conductivity at different temperatures and at doce 400 krad.

**Fig. (8):** Frequencies dependence of ln conductivity at different temperatures and at doce 600 krad.
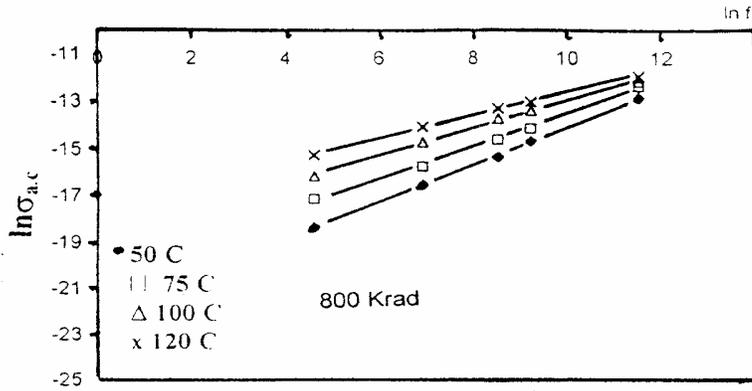


**Fig. (9):** Frequencies dependence of ln conductivity at different temperatures and at doce 800 krad.
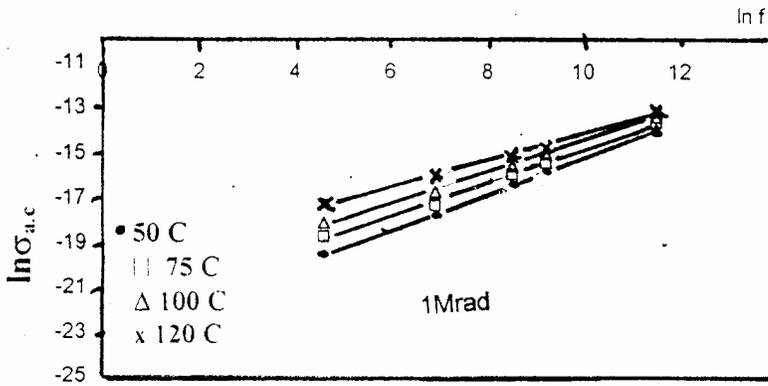


**Fig. (10):** Frequencies dependence of ln conductivity at different temperatures and at doce 1000 krad.
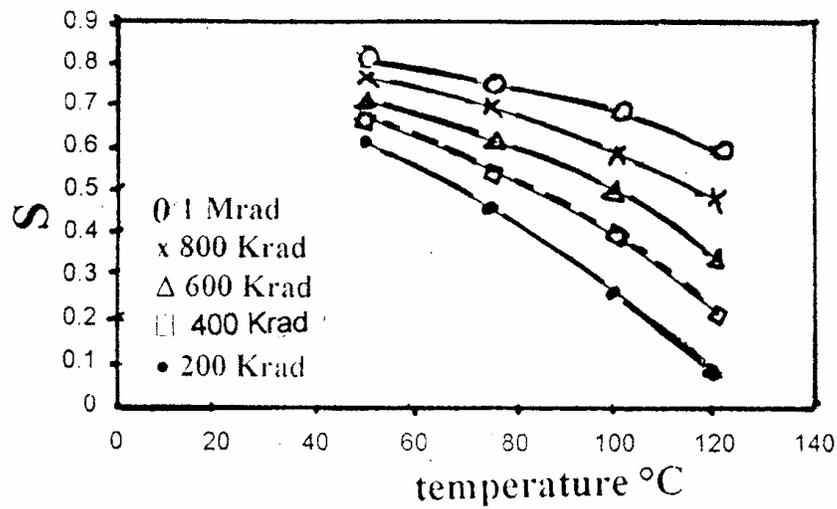
**Fig. (11):** temperatures Dependence of S at different doses.

Figure (12) illustrates the temperature dependence of a.c conductivity at dose of 1 Mrad and at different frequencies. It is clear that, $\sigma_{a.c}$ increases with both temperature and frequency. The last two factors enhance dipole polarization and hence a.c conduction is improved.
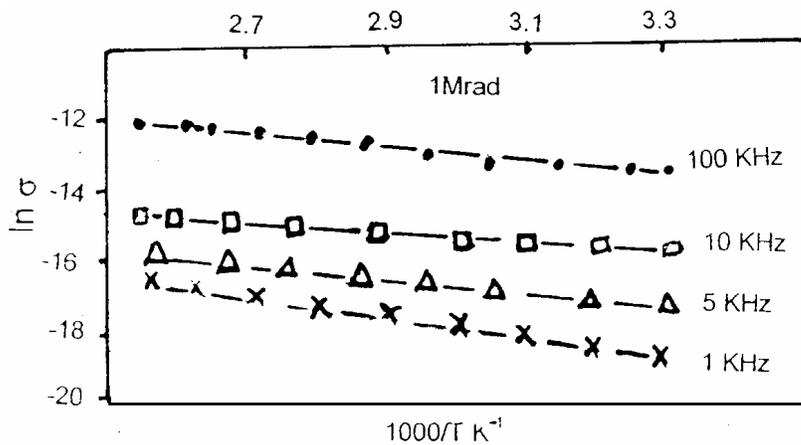


**Fig. (12) :** ln conductivity versus 1000/T at different frequencies.

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