

## AC-Conductivity and Dielectric Properties of $\gamma$ -Irradiated PVA Films Doped With $Mn^{2+}$ Ions

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*The stability as well as the electrical properties of both unirradiated and  $\gamma$ -irradiated poly(vinyl alcohol)-PVA films doped with  $MnSO_4 \cdot H_2O$  at a definite concentration of 15% have been studied. The dielectric loss tangent  $\tan \delta$ , electrical conductivity  $\sigma$  and dielectric constant  $\epsilon'$  in the frequency range 100 Hz-20 KHz were measured at different temperatures. It has been demonstrated that the suitable mechanism of conduction is the correlated barrier hopping model. The exponent  $S$  according to the relation  $\sigma(\omega)=A(\omega)^S$  was estimated and found to be less than unity and decreased with increasing the temperature. Furthermore a nonlinearity of  $\log \sigma$  against  $\log f$  was observed at  $\log f$  in the range (3.7-4.3) for doses  $\geq 100$  kGy at the temperatures of 333 and 343 K.*

## Introduction

Different additives are usually added to polymer in order to modify and improve its properties. Inorganic additives such as transition metal salts have considerable effect on the optical and electrical properties of PVA polymer [1,2]. Irradiation with X-rays, alpha, beta and gamma radiation also have a significant effect on polymer properties and some physical properties are usually modified [3,4].

The aim of the present article is to study the electrical properties of the  $\gamma$ -irradiated PVA films doped with 15%  $Mn^{2+}$  ions. In this case  $\tan \delta$ ,  $\sigma$ ,  $\epsilon'$  were measured in the range (100 Hz-20 KHz).

## Experimental Work and Results

The poly (vinyl alcohol) PVA and  $MnSO_4 \cdot H_2O$  used in the present work were supplied by BDH chemicals. The components nominally free from impurities, were prepared by swelling the PVA in twice-distilled water for 24 h at room temperature. The solution was then warmed to 333 K and stirred thoroughly for about 4 h until the PVA was completely dissolved.

Manganese (II) sulphate solutions were prepared by dissolving the salt to a concentration 15% by wt in twice-distilled water. Appropriate mixtures of PVA and  $MnSO_4$  solutions were thoroughly mixed, poured onto a level glass plate and left to dry in an air oven at 309 K for about 48 h. Irradiation of samples were carried out at the National Center for Radiation Research and Technology, (NCRRT) at Nasr City, Cairo by cobalt 60 source of the type of Gamma chamber - 4000 A manufactured by Bhabha Atomic Research Center Bombay, India was used for irradiation giving a dose rate of about 4 k Gy/h in air which means that for example for a dose of 100 k Gy, the sample was irradiated continuously for 25 hours under a constant distance from the  $\gamma$ -source.

Samples of thin films of thickness 1 mm were measured perfectly within accuracy  $\pm 0.01$  mm by a micrometer. Each sample was pressed between two polished and cleaned brass electrodes coated with silver past. The capacitance C, resistance R and dielectric loss tangent  $\tan \delta$  of the investigated sample were measured in the temperature range 303-343 K and frequency range between 100 Hz-20 KHz using PM 6304 programmable automatic RCL meter Philips. A chromel-P-constantan thermocouple with accuracy  $\pm 1$  K was used for temperature measurements. The electrical conductivity  $\sigma$ , dielectric

constant  $\epsilon'$  and the dielectric loss tangent  $\tan \delta$  were estimated using the following relations [5]

$$\sigma(\omega) = \frac{L}{AR}, \quad \epsilon' = \frac{LC}{A\epsilon_0}, \quad \tan \delta = \frac{1}{R\omega C}$$

where  $\epsilon_0$  is the permittivity of free space, ( $\epsilon_0 = 8.85 \times 10^{-12}$  F/m) [6].

$\omega$ : is the angular frequency and L and A are the thickness and surface area of the sample respectively.

Figs. (1-3) show  $\log \tan \delta$ ,  $\log \sigma$  and  $\epsilon'$  versus  $\log f$  at different temperatures for the unirradiated sample. The Figs. reveal no anomalous effect. Both  $\tan \delta$  and  $\epsilon'$  decrease with increasing of  $\log f$  while  $\log \sigma$  increases linearly with  $\log f$ . These observations agreed with published data for different polymers and amorphous semiconductors [5,7]. In addition a decrease of the value of the exponent (S) by rising the temperature, (Fig (3a)) indicates that a C.B.H mechanism is the best be taken into account [5,8].

From Fig. 1 for the unirradiated samples a models correlating  $\tan \delta$  against  $\log f$  in the investigated frequency range  $20\text{KHz} \leq f \leq 100\text{ Hz}$  at a certain temperature value could be obtained in the forms [9]

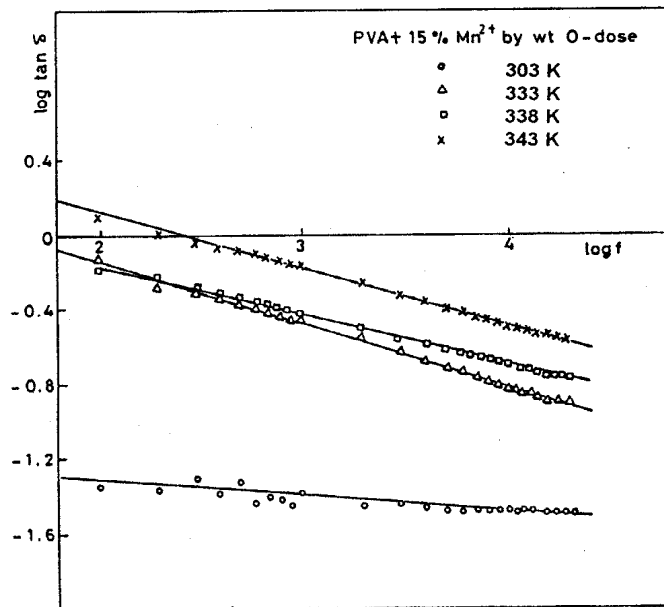


Fig. (1) Log  $\tan \delta$  versus  $\log f$  for unirradiated sample - PVA films doped with 15% by wt  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ .

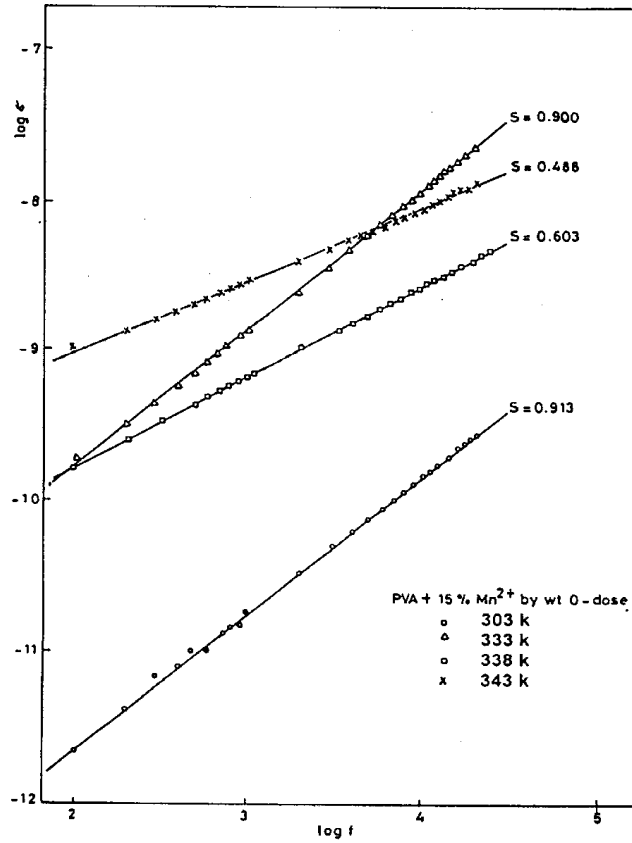


Fig. (2) Log  $\sigma$  versus log  $f$  for unirradiated sample.

$$\begin{aligned} \tan \delta &= 0.052 f^{(-0.061)} & T &= 303\text{K} \\ \tan \delta &= 0.832 f^{(-0.338)} & T &= 333\text{K} \\ \tan \delta &= 1.585 f^{(-0.183)} & T &= 343\text{K} \end{aligned}$$

According to the eq.  $\sigma(\omega) = A\omega^S$  [5,8] by considering the C.B.H model, the exponent  $S$  was found to obey the formula [8]:

$$S = 1 - \frac{6 kT}{W_M - kT \ln(1/\omega\tau_0)} \tag{1}$$

where  $W_M$  is the maximum barrier height at infinite intersite separation [5,8], which is called the polaron binding energy, i.e. the binding energy of the carrier in its localized sites [10],  $\tau_0$  is a characteristic relaxation time which is in the

order of an atom vibrational period  $\tau_0 \sim 10^{-13}$  sec [4,5,8]. For large values of  $W_M/kT$ ,  $S$  is nearer unity. Also eq. 1 predicts that  $S$  decreases with increasing temperatures in the low temperature range i.e. large  $W_M/kT$ . The above demonstrations lead to [10,11]:

$$1 - S = 6 kT/W_M \tag{2}$$

The relaxation time  $\tau$  for electrons to hop over a barrier of height  $W_H$  is given as [5,8]

$$\tau = \tau_0 \exp(W_H/kT) \tag{3}$$

The variations of  $S$  versus temperature for unirradiated sample are represented in Fig. (3a). The slight decrease of  $S$  with increasing the temperature as well as its drop at a relatively high temperatures agreed with Bhatnagar results [5].

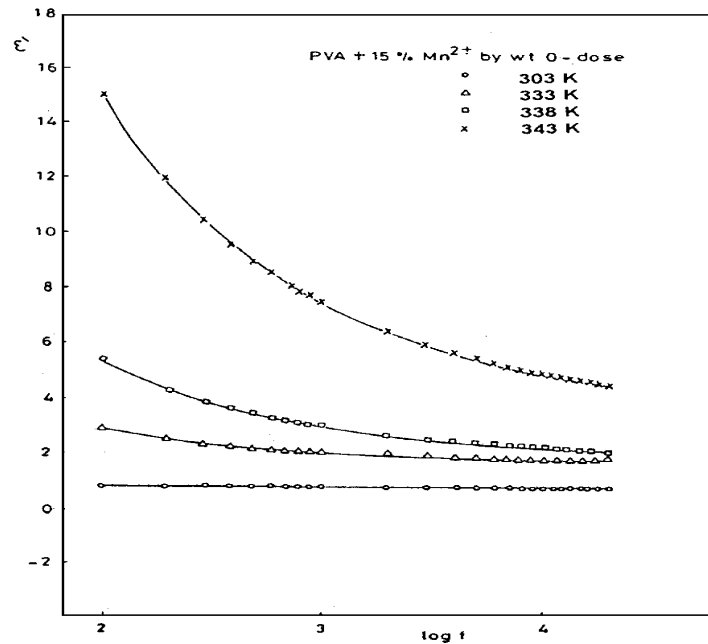
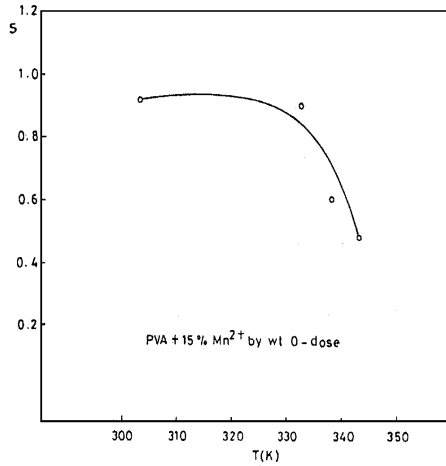


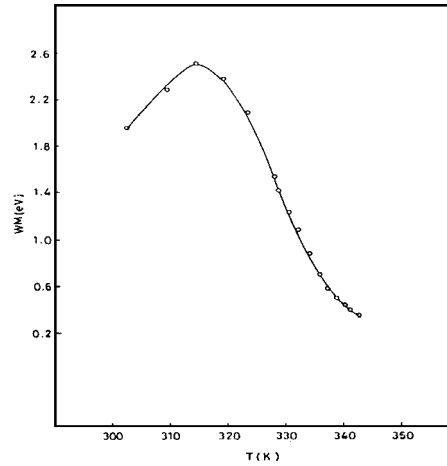
Fig. (3)  $\epsilon'$  versus  $\log f$  for unirradiated sample

A model for electron transfer by thermal activation over the barrier between two sites each having a coulombic potential well associated with it has been proposed by Pike [11]. For neighbouring sites, the coulomb wells overlap [8] resulting in a lowering of the effective barrier from  $W_M$  (the value at infinite intrinsic separation) to the value  $W_H$ , where the condition  $W_H/W_M < 1/2$  was satisfied [11]. For a relatively high strength of overlap which gives  $W_H \approx 1/4$

$W_M$ ,  $W_M$  as well as  $\tau$  were evaluated at different temperatures using equations 2 and 3 and Fig.(3a), results are listed in Table 1.

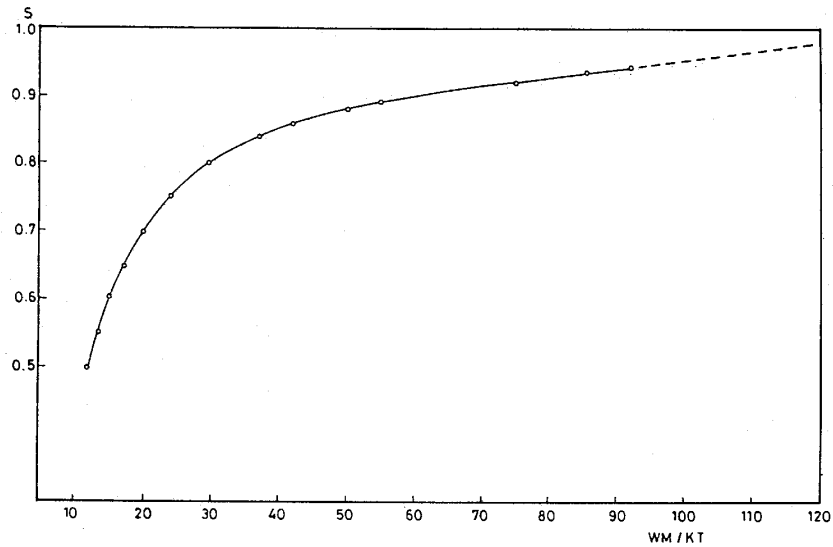


**Fig. (3a)** The exponent  $S$  versus the absolute temperature  $T$  for unirradiated sample.



**Fig. (3b)**  $W_M$  versus the absolute temperature  $T$ .

Fig. 3b illustrates the variation  $W_M$  as a function of absolute temperature. A drop of  $W_M$  with increasing the temperature corresponds to a decrease of the exponent  $S$ . Fig. 3c indicates an increase of the ratio  $W_M/kT$  with increasing  $S$ . It is also observed that  $S$  approaches unity, at  $W_M/kT \geq 100$  agrees well with the previous work [8].



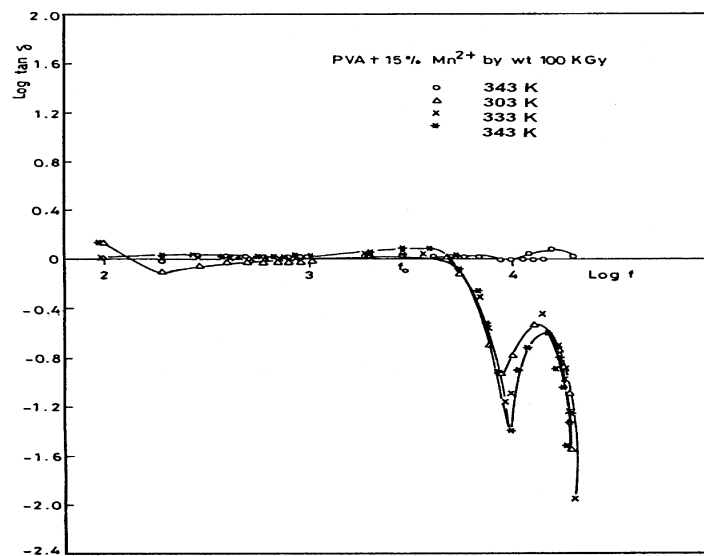
**Fig. (3c)**  $S$  versus  $W_M/kT$ .

**Table 1. Unirradiated polymer**

T(k)	S	$\tau(\text{sec})$	$W_H(\text{eV})$	$W_M/kT$
343	0.50	$2.031 \times 10^{-12}$	0.089	12
340	0.60	$4.271 \times 10^{-12}$	0.110	15
338	0.70	$1.503 \times 10^{-11}$	0.146	20
335	0.80	$1.839 \times 10^{-10}$	0.217	30
333	0.84	$1.179 \times 10^{-9}$	0.269	37
329	0.88	$2.648 \times 10^{-8}$	0.354	50.5

It is worthy noted that unirradiated samples are pale pink due to the  $\text{Mn}^{2+}$  ions because of d-d transitions [12]. It was observed that the pale pink colour became clear by increasing  $\gamma$ -irradiation dose, This was explained by the formation of conjugated double bonds and/or trapped free radicals and ions [3]. Considering the new physical properties of the irradiated polymer.

We now deal with the hopping mechanism for a dose of 100 kGy. The values of the exponent S for a dose of 100 kGy at temperature 303K is obtained from the linearity of  $\log \sigma$  against  $\log f$  - as well as - for every temperature 333 and 343K in the range of  $\log f$  at (2-3.7) as shown in Fig5 and Table (2). It is observed that both S &  $W_H$  decrease with increasing the temperature which indicates a C.B.H mechanism [5,8,13,14]. For the irradiated polymer a drop of  $W_H$  from 0.8eV at 303 K to 0.1 eV at temperature  $\geq 333$  K is occurred. The lowering of  $W_H$  by increasing the temperature is due to thermal agitation which leads to an increase of the degree of overlap of coulombic potential wells of the considered sites.



**Fig. (4)** Log tan  $\delta$  versus log f for 100 kGy irradiated sample.

Moreover for a dose 100kGy, an infinitesimal change for the quantities  $S$ ,  $W_H$ ,  $W_M/kT$  for a raise of temperature from 333 k to 343 K is observed from Table (2) which corresponds to an appreciable decrease of the mentioned quantities for the unirradiated sample, Table (1). In this case these quantities are nearly the same for either unirradiated - or irradiated - sample at the temperature 343 K, which may be attributed to that, the overlap of coulombic potential wells of the considered sites is the more pronounced effect at high temperatures in comparing to cross linking reaction and/or dipole reorientation of the perturbed polymer molecules as a result of the irradiation process.

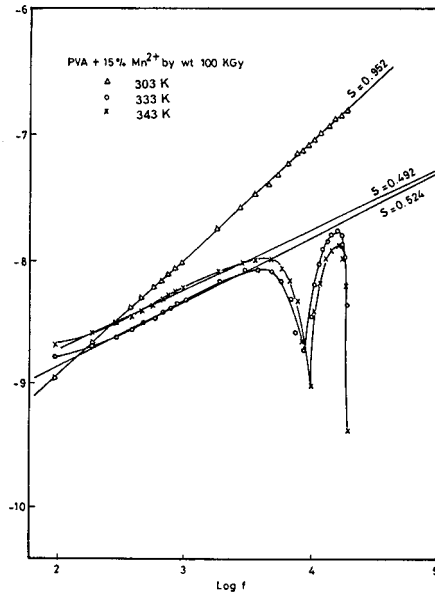


Fig. (5) Log  $\sigma$  against log f for 100 kGy irradiated sample.

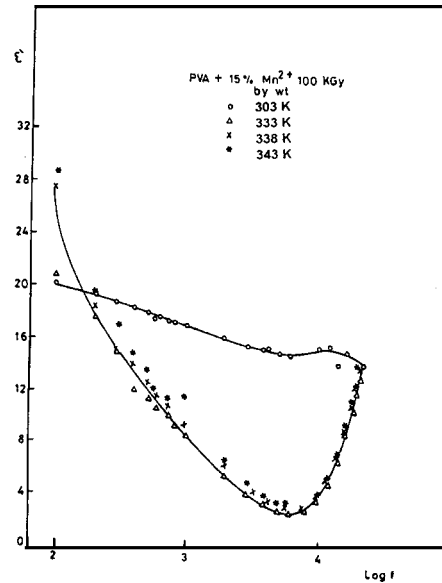


Fig. (6)  $\epsilon'$  against log f for 100 kGy irradiated sample.

Table 2. Irradiated polymer with a dose of 100 kGy.

Range of logf	$T_K$	$S$	$W_M$ eV	$W_H$ eV	$W_M/KT$
2-4.3	303	0.952	3.264	0816	125
2-3.7	333	0.524	0.362	0.091	12.605
2-3.7	343	0.492	0.349	0.087	11.811

Furthermore for a dose of 100 kGy at temperature 303 K, the hopping mechanism should be considered which is observed from the linearity of log  $\sigma$  against log f in which the condition  $S < 1$  must be satisfied, Fig. 5. Which may be attributed to the value of  $S \sim 0.952$  accompanied with a relatively large values of  $W_M \sim 3.264$  eV and  $W_H \sim 0.816$  eV Table (2) which means a decrease of the



degree of overlap of coulombic potential wells of the considered sites at low temperatures from which the C.B.H. mechanism must not be perturbed. The linear increase of  $\log \sigma$  against  $\log f$  at 303 K corresponds to a general decrease of  $\epsilon''$  with the increase of  $\log f$ , Figs. (13-15). A nonlinearly of  $\log \sigma$  against  $\log f$  in the range of  $\log f$  at (3.7-4.3)- for a dose of 100 kGy at temperatures  $\geq 333$  K are shown in Fig. 5 This associated with a drop of  $\tan \delta$  accompanied with a respective minimum and maximum values, Fig. 4. As a result of the irradiation process liberation of electrons would be occurred, as well as, the randomly oriented polymer chain must be perturbed. Consequently, the conduction hopping mechanism proposed by Pike in which the depth of the potential well will be a time dependent function related to the rotational or vibrational modes of the polymer must be perturbed [11,15]. This may interpret the anomalous behaviour of  $\log \delta$  and  $\epsilon''$  at  $\log f \sim 3.8$  for a dose of 100 kG irradiated - samples at temperatures  $\geq 333$  K as illustrated in Figs. (5,6), respectively. It is worthy noted that, the results of 338 K are not shown in Fig. 5 because it is difficult to be distinguished from the results at either 333 K or 343 K, from which the separate tangent lines will be more difficult to be obtained. On the other hand by increasing radiation doses from 100 to 150 and 200 k Gy, the same constant behavior of  $\log \sigma$ ,  $\log \tan \delta$ ,  $\epsilon''$ , have been observed without appreciable changes.

In this case the stability of the radiation induced new physical properties for doses  $\geq 100$  kGy at 303 K or at temperature  $\geq 333$  K, where in a 1<sup>st</sup> order approximation the graphs follow the same constant behavior under the given conditions for either  $\tan \delta$  or  $\log \sigma$  or  $\epsilon''$  along the investigated frequency range Figs. (4,5,6).

From the above arguments the behaviour of the polymer for a certain  $\gamma$ -dose and a definite temperature range may be due to the formation of Ladder polymer - with a high strength and a high thermal stability [16].

## Conclusion

The electrical properties as well as the stability of  $\gamma$ -irradiated PVA films doped with  $Mn^{2+}$  ions - accompanied with colour changes due to the formation of conjugated double bonds and/or trapped free radicals and ions - could be investigated using the measured parameters  $\tan \delta$ ,  $\sigma$ ,  $\epsilon''$  in view of C.B.H mechanism.

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