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Ac-Conductivity and Dielectric Properties of Neutron-Irradiated PAA films Doped with Cu^{+2} Ions

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Abstract:

The stability as well as the electrical properties of both un-irradiated and neutron irradiated poly acrylic acid (PAA) films doped with Cu^{+2} at a definite concentration of 12% have been studied. The dielectric loss tangent (tan δ) , electric conductivity (σ) and dielectric constant (Є) in the frequency range 100 Hz-20kHz 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 $\sigma(w) = A(w)^{s,}$ was estimated and found to be less than unity and decreased with increasing the temperature. Furthermore a nonlinearly of log σ against log f was observed at log f in the range (3.3 to 4.6) for doses ≥20kGy at the temperature of 300 K and 380 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 and PVC polymer [1] . Irradiation with X-rays, alpha, beta and gamma rays radiation also have a significant effect on polymer properties and some physical properties are usually modified [2, 3, 4].

The aim of this work is to study the electrical properties of the neutron-irradiated poly acrylic acid films doped with 12% Cu^{+2} ions. In this case tan δ, σ, Є were measured in the range 100 Hz- 10 kHz.

Experimental Work and Results:

The poly acrylic acid PAA and $CuSO_4.5H_2O$ used in the present work were supplied by Fluka chemicals. The components nominally free from impurities were prepared by swelling the PAA in twice-distilled water for 24 hours at room temperature. The solution was then warmed to 380 K and stirred thoroughly for about 4.30 h until the PAA was completely dissolved.

Cupper (II) sulphate solution was prepared by dissolving the salt to a concentration 12% by wt in twice-distilled water. Appropriate mixtures of PAA and $CuSO_4$ solutions were thoroughly mixed, poured onto a level glass plate and left to dry in an air oven at 300 K for about 96 h.

Irradiation of samples was carried out at irradiation center at the Visiflux Facility in Basrah University. By Am-Be (□, n) source, supplied by the radio chemical center, Amersham .The activity and the neutron flux of the source were 5Ci and $1.6*10^{11}$ n/sec respectively, as measured at Jul/2006.

This source had two channels for irradiation. The dose rate measured at a distance 2.3 cm from the source by Theroluminescence dosimeters was 0.73 Gy/min.Samples of films of thickness1mm measured perfectly within accuracy $\pm 10^{-3}$ mm by the travailing microscope. Each sample was pressed between two polished and cleaned aluminum electrodes coated with silver past . The capacitance C , resistance R and electric loss tangent tan δ of the investigated sample were measured in the temperature range 300-380 K and frequency range between 100Hz – 10kHz using Phywe automatic RLC meter. A chromel-P-constant on thermocouple with accuracy ±1K was used for temperature measurements. The electrical conductivity σ, dielectric constant Є and the electric loss tangent δ were estimated using the following relation [5].

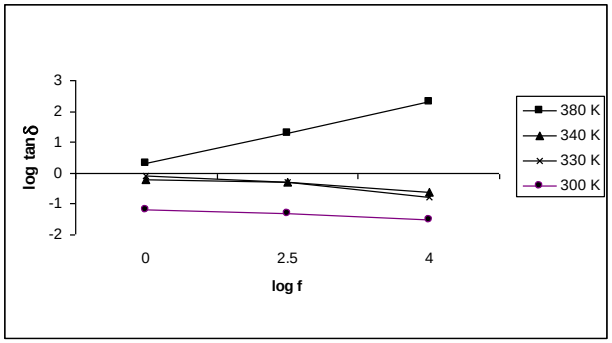
$$\sigma(\omega) = L/AR, \quad Є = LC/A\varepsilon_0, \quad \tan\delta = 1/R\omega C$$

Were ε_0 is the permittivity of free space, ($\varepsilon_0 = 8.85\times10^{-12}$F/m) [6] .

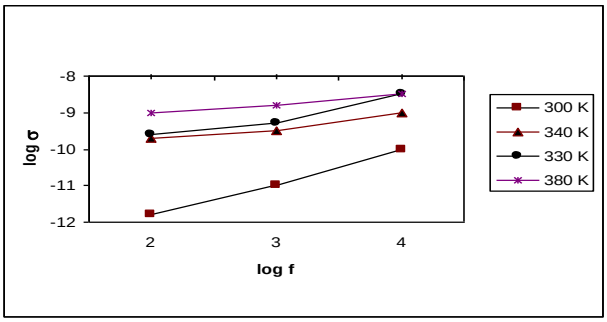
ω: is the angular frequency, L and A are the thickness and surface area of the sample respectively.

Figs.(1,2,3a) show log tan δ, log σ and Є versus log f at different temperatures for the un-irradiated sample . The Figures reveal no anomalous effect. Both tan σ and Є decreases with increasing of log f while log σ 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(3b) indicates that a correlated barrier hopping(C.B.H.) mechanism is the best be taken into account [5,8] .

From Fig.1 for the un-irradiatesd samples models correlating tan δ against log f in the investigated frequency ranges. 100 Hz □ f □□10k Hz at a certain temperature value could be obtained in forms [9].



Fig(1): Log tanδ vs. log for unirradiated sample-PAA Films doped with 12% by CuS04.5 H_2O



Fig(2): logσ vs. log for un-irradiated sample

$\tan \delta = 0.052\ f^{(-0.016)}$ T=300 K

$\tan \delta = 0.832^{(-0.413)}$ T=340 K

$\tan \delta = 1.585^{(-0.201)}$ T=380 K

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 [10] :

$$S = \frac{1 - \sigma kT}{W_m - kT \ln(1/\omega\tau_0)} \quad . \qquad (1)$$

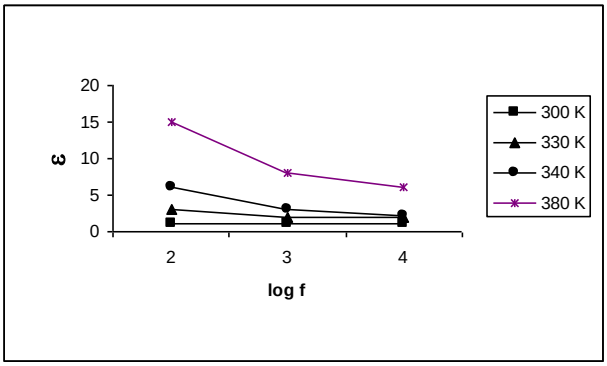
Were W_M is the maximum barrier height at infinite intersite separation [8,10] , which is called the polaron binding energy , i.e. the binding energy of the carrier in its localized sites [10] , τ_0 is the characteristic relaxation time which is the order of an atom vibration period $\tau_0 \sim 10^{-13}$sec [4,5,8] . For large values of Wm/kT, S is nearer unity. Also eq.1 predicts that S decreases with increasing temperatures in the low t temperature range i.e. large Wm/kT. The above demonstrations lead [12].

$1- S = 6\ kT/ W_m$ …… (2)

The relaxation time τ for electrons to hop over barrier of height W_H is given as [10, 12].

$\tau = \tau_0 \exp(W_H/ kT)$…… (3)

The variations of S vs. The temperature of un-irradiated samples are represented in Fig. (3b). The slight decrease of S with increasing the temperature as well as its drop at a relatively high temperature agreed with Gadou and Bhatnagar results [3] and [8] respectively.



Fig(3a) : ε versus logf for unirradiated

A model for electron transfer by thermal activation over the barrier between two sites each having a columbic potential well associated with it has been proposed by pike [13]. For neighboring 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 [14] . For a relatively high strength of over lap which gives $W_H = 1/4\ .\ W_H$, W_m as well as τ were evaluated at different temperatures using equs.2 and 3 and Fig.(3b) , listed in Table 1.

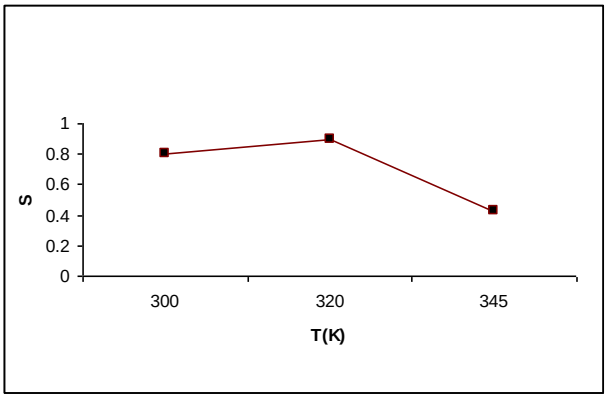


Fig (3b): The exponent S Vs. the absolute Temperature T for un-irradiated samples

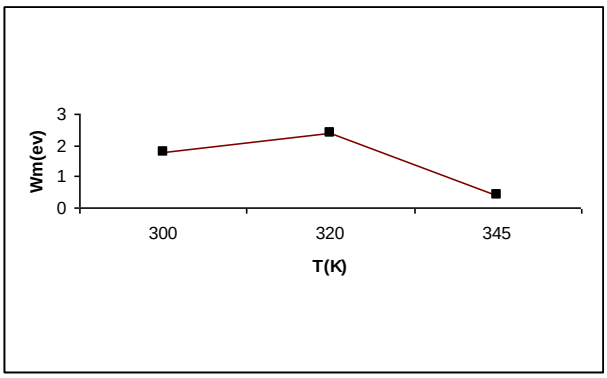


Fig (3c): Wm VS. The absolute temperature T.

Fig. 3c 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. 3d indicates an increase of ratio W_m/kT with increasing S. It is also observed that S approaches unity, at $W_M/kT \geq 100$ agree with what done in reference [8].

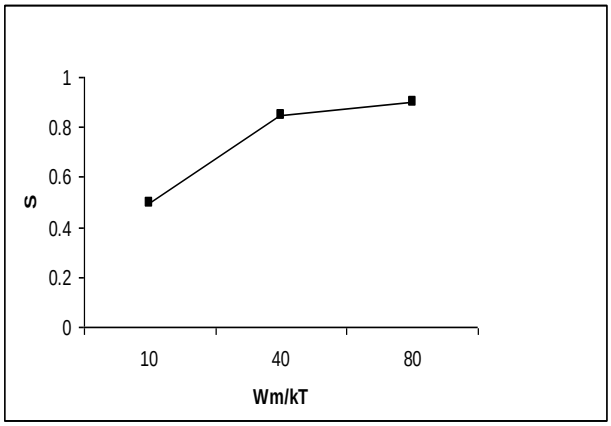


Fig (3d): S vs. Wm/kT

Table(1): Un-irradiated polymer

T(k)	S	τ (sec)	W_H(eV)	W_M/kT
300	0.96	1.12*10^-7	0.354	50.1
330	0.88	2.64*10^-8	0.217	37
340	0.6	4.27*10^-12	0.110	15
380	0.41	2.03*10^-12	0.069	11

It is worthy noted that unirradiated samples are blue due to theCu^{+2} ions because of d-d transitions [15]. It was deserved that the blue colour will change to more deep by increasing neutron-irradiation dose. This was explained by the formation at 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 20kGy . The values of the exponent S for a dose of 20kGy at temperature 300K is obtained from the linearity of log σ against log f as well as for every temperature 340 K and 380 K in the range of log f (2-3-7) as shown in Fig.5 and Table (2). It is observed that both S and W_H decrease with increasing the temperature which a C.B.H. mechanism [5, 8, 13, 14]. For the irradiated polymer a drop at W_H from 0.7 eV at temperature 300K to 0.13eV at temperatures ≥ 340 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 columbic potential wells of considered sites.

Moreover for a dose 20 kGy , an infinitesimal change for the quantities S , W_H, W_M/KT for a raise of temperature from 300K to 340K 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 un-irradiated – or irradiated sample at temperature 340K, which many be attributed to that, overlap at columbic potential wells of considered sites is the more pronounced effect at high temperatures in comparing to cross linking reaction and /or dipole re-orientation at the perturbed polymer molecules as a result of the irradiated process

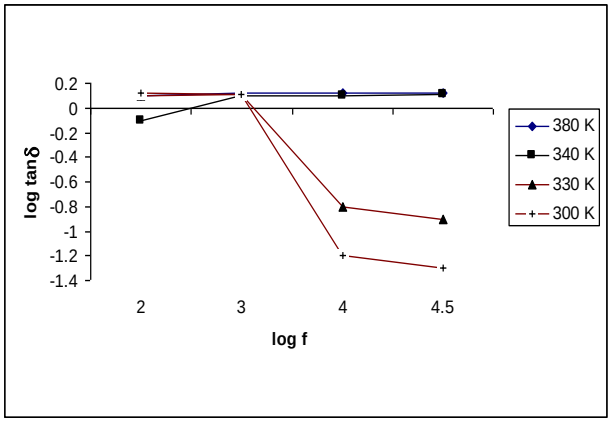
Table(2): Irradiated polymer with a dose of 20 kGy.

Range of logf	T(K)	S	W_M(eV)	W_HeV	W_M /KT
2-4.3	300	0.95	3.26	0.081	125
2-3.7	340	0.52	0.36	0.091	12.60
2-3.7	380	0.49	0.34	0.087	11.80

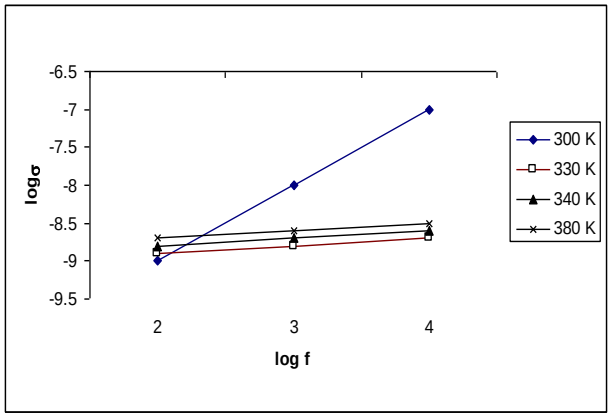
Further more for a dose of 20kGy at temperature 300K, the hopping mechanism should be considered which is observed from the linearity of log σ against log f in which the condition S<1 must be satisfied Fig.5. Which may be attributed to the value of S = 0.87 accompanied with a relatively large values of W_M =3.52 eV and W_H = 0.93 eV. Table (2) which mean a decrease of the degree at overlap of columbic potential wells of the considered sites at low temperature from which the C.B.H. mechanism must not be perturbed [16]. The linear increase of log σ against log f at 300K corresponds to a general decrease of Є with the increase of log f, Figs. (3, 4, 5). A nonlinearity of log σ against log f at (3.7-4.3) for a dose of 20 kGy at temperatures ≥ 340K are shown in Fig.5. This associated with a drop at tan δ accompanied with a respective minimum and maximum value. Fig.4. As a result of the irradiation process liberation of electrons would be occurred, as well as, 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 [17]. This may interpret the anomalous behavior of log δ and Є at log f = 3.8 for a dose of 20kGy irradiated samples at temperatures ≥ 340K as illustrates in Figs (5, 6) respectively. On the other hand by increasing radiation doses from 25 to30 kGy, the same constant behaviors of log σ , log tan δ , Є , have been observed without appreciable changes .

In this case the stability of the radiation induced new physical properties for dose ≥20 kGy, where in an l^{st} order approximation the graphs follow the same constant behavior under the given conditions for either tan δ or log σ or Є along the investigated frequency range Fig. (4, 5, 6).

From the above arguments the behavior of the polymer for a certain neutron-dose at definite temperature range may be due to the formation of ladder polymer with a high strength and a high thermal stability [18].



Fig(4): log tanδ vs. log f for kGy irradiated samples



Fig(5): Logσ vs. log f for 20 kGy irradiated Sample

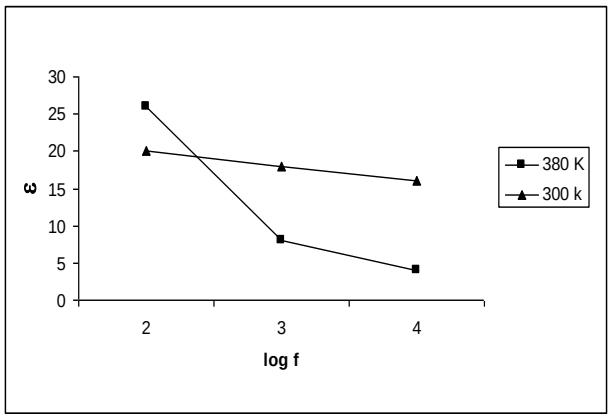


Fig (6): ε vs. log f for 20kGy irradiated Sample

Conclusion:

The electrical properties as well as the stability of neutron-irradiated films doped with Cu^{+2} ions-accompanied with colour change due to the formation of conjugated double and/or trapped free radicals and ions-could be investigated using measured parameters tan δ , σ , Є in view of C.B.H. mechanism.

References:

1. R.I.Mohamed and A.M.Gadou, Egypt.J.Sol. Vol. (23), No.(1),(2000).
2. M.A. Kaled, A.E. Basha, M.M. El-Ocker and H.Abdel-Samad, Ind, J.Phys. 63A, 399(1989).
3. A.M.Gadou,Egypt.J.Sol.,Vol.(26),No.(4),(2003).
4. A.F. Baha, M. Amin, K. Darwish and H.Abdel-Samad, J. Polymer Mater , 5,115,(1989).
5. U.Suryavanshi,J.Applied polymer science, Vol. (68), Iss2, p255, (1998).
6. M.A.Khaled,F.Sharaf,M.S.Risk and M.M. El-Ocker, Polymer Degradation and stability 40, 385 (1993).
7. Barakat,N; El-Hennawi, H.A; El-Ocker, M and Sharaf, F , J. Phys. D: Appl. Phys. 22, 786(1989).
8. V.K. Bhatnagar and K.L. Bhatia, Journal of non-crystalline solids 119, 214 (1990).
9. B.M. Jaworski, A.A. Detlaf, Physik griffbereit im Verlag NAUKA, Moskau, p.325(1972).
10. M. El-Shahawy, A. Hussein, Journal of Material Science 27, 6605(1992).
11. S.R. Elliott, A.vances in Phys. Vol. 36, no. 2, 135-218 page 152(1987).
12. N. Bronshtein and K.A. Semendyayev, A Guide Book to Mathematics.
13. Pike, G.E; Phys. Rev. B6, 1572(1972).
14. J.D. Lee, Concise Inorganic Chemistry, Published by Blackwell Science Ltd, Osney Mead, Oxford OX2 OEL, 25 John, Street, London WC1N2BL, p. 734(1991).
15. B.K.Chaudhuri,J.K.Chaudhuri andK. K. Som, J. Phy. Chem. Solids. Vol.(50),11,1149,(1989).
16. Polla, K.M; Phil. Mag. 23, 519(1971).
17. A.D. Jenkins, Polymer Science, North-Holland Publishing Company – Amsterdam – London, p. 1219, 1223(1972).
18. Ulf W-Gehddge, Polymer Phys., published by Chabman & Hall, 2-6 Boundary, London SEI 8HN, UK,p. 6, 138, 163, 224(1995).

التوصيلية المتناوبة والعازلية الكهربائية لاغشية PAA المشعة بالنيوترونات والمطعمة بايونات النحاس

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الملخص:

اختبرت الصفات الكهربائية كدالة لمعرفة مدى التأثيرات التي تحدثها النيوترونات السريعة لثبوتية وتركيب حامض البولي اكريليك المطعم باملاح كبريتات النحاس خماسية ماء التبلور ولدرجات حرارة ختلفة . ان بوليمر الحامض الاكريليكي المطعم باملاح معدنية مثل النحاس يستخدم في مجالات صناعية كثيرة ، منها صناعة حشوات الأسنان ، صناعة الاغشية النصف ناضجة وكذلك في السبائك البوليمرية (IPNS) الاكريلية. تم التطعيم بالنسبة الوزنية ١٢% . وعند دراسة العلاقات بين مقدار الفقد في العازلية (tan δ) ، التوصيلة الكهربائية (σ) وثابت العزل (ε) لمدى الترددات من١٠٠ هرتز ولغاية ١٠ كيلو هرتز . ولجرعة إشعاعية قدرها ٢٠ كيلوكراي ولمدى درجات الحرارة من ٣٠٠كلفن ولغاية ٣٨٠ كلفن .بينت النتائج ان اليكانيكية الأمثل لوصف التغيرات الحاصلة هو أنموذج حاجز الجهد المتبادل والمترابط (C.B.H) . حيث ان ما يدعم هذا الانموذج هو قيمة (S) والذي يمثل الخسائر الكلية للمجال المار في العينة .ومن العلاقة $\sigma(\omega) = A(\omega)^s$

صار واضحا ان قيمة S هي اقل من الواحد ، كما تقل قيمتها مع زيادة درجة الحرارة. بالإضافة الى العلاقة اللاخطية بين log σ و log f لقيم log f بين (٣,٣-٣,٦) و ان الجعة الإشعاعية اكبر أو تساوي ٢٠كيلو كراي ولدرجات حرارة ٣٠٠كلفن، ٣٨٠ كلفن.