Dielectric Relaxation Study on Epoxy Matrix/Polyurethane Polymer Blend

A.S. Elsammani[1], E.A.Alagag[2] and M.F. Alyas[2]

Department of Physics, Faculty of Sciences [1]Upper Nile Unversity Sudan
[2] Bagdad University Irag

ABSTRACT

A series of polymer blends are prepared by sequential mixing of epoxy resin EP with polyurethane PU. The effect of different amount of polyurethane 10%, 20%and 30% wt fraction on conduction and dielectric relaxation has been reported. It was found that all blends showed three activation energies (E_{ac}) at all frequencies, and the glass transition temperature (Tg) was increased with PU wt fraction. The exponent s values were estimated to be less than unity for all blends. Cole-Cole diagram was used to evaluate the polarizability (α), molecular relaxation time (τ) and optical dielectric constant (ε_{OP}). The thermodynamic parameters also determined, the result showed that the Gibbs free energy of activation (ΔG) and enthalpy (ΔH) are high for all blends.

(2)   (2)   (1)

(2)   (1)

.   (%30, %20, %10)

.

.

.

.   (s)

(α)   (–   )

.(τ)   (ε_{op})

10 MHz –Hz 100

Eyring   .293–453 k

(   )   (ΔG)   .

.   (ΔH)

ΔS   (   )

.

:

.

22

Introduction

Epoxy resins are an important class of thermosetting resins, because of their high tensile strength and modulus, excellent dielectric properties, good chemical resistance and dimensional stability [1-2]. The highly cross-linked nature of the epoxy network produces inherently brittle resin that has limited utility in applications, to overcome this disadvantage the modified epoxy and epoxy matrix polymer blend have been studied extensively. The blending technique will result improving the mechanical, thermal and dielectric properties of epoxy resins. Kim and Shin [3] have studied the dielectric response of 10% siloxane-90%epoxy blend. Daly and Pethrick [4] have investigated the conductivity of rubber modified epoxy resin, and they indicated that at high rubber contents, the epoxies become occluded phase and this decreased the activation energy. Patel and Suthear [5] studied the dielectric and mechanical properties of epoxy /polyurethane based on caster oil loaded with glass fiber, dielectric constant and loss behavior studied on a series specimen were investigated. Li and Mao [6] studied the glass transition behavior of Epoxy/polyurethane semi-IPNs by DSC and DMA methods, the result showed two glass transitions referring to blend components and a third T_g exist related to interface between two polymers. Ying and Suffer [7] studied the damping and dielectric properties of EP/PU IPNs; the results showed that the semi-IPNs have excellent damping properties at ordinary temperature. The maximum value of dissipation factor tanδ close to unity for the ratio 70%EP/30%PU. Literature survey reveals less amounts of work have been carried out on dielectric relaxation of EP/PU polymer blends. This article deals with the dielectric relaxation of EP matrix/PU polymer blends.

Experimental details

Materials:

The epoxy resin (diglycidyl ether of bisphenol A) used in this study is EP10 (conbextra) supplied by (Fosroc-Jordan) along with a curator an aliphatic amine catalyst (HY-956). Polyurethane resin type WEBAC 1403 (Tgb-Nr) and it's a curator isocyanate (HYG-956) are supplied by Webac-Hemie (GMBH-FAH) Germany is used in this study .

Specimen's preparation:

The polymer blend of EP/PU was synthesized by sequential mixing technique. A fixed amount of polyurethane and epoxy resins were stirred at room temperature for 20 min. After the stirring the mixture was poured into a cleaned mould sprayed with releasing agent. The mould was kept at room temperature for 24h for complete curing. Three different PU weight fractions were used to prepare 90%EP/10%PU, 80%EP/20%PU and 70%EP/30PU polymer blends. The specimens have disc like shape of diameter 30mm and thickness of 1mm.

Measurements:

The dielectric properties were measured in the frequency range $10^2 - 10^7$ Hz using a Hewlett Packard dielectric analyzers (HP 4274A and 4275A). The measurements were performed over temperature range 293-453 K using temperature controlled oven.

Results and discussion

AC conductivity:

In this part of study we report the effect of frequency, temperature, and PU wt fraction on AC conductivity. Figure1 shows the variation of conductivity (σ) with angular frequency (ω), for EP/PU blends with various PU wt fraction. The conductivity for all blends increases with frequency. We propose that two main factors influencing conductivity, they are ions motion and polymer backbone motion. Furthermore ion motion is contributed at high frequencies and temperatures only. The DC conductivity is found had a significant contribution at frequency range 10^2- 4×10^2 Hz. The exponent (s) was evaluated from equation s= d (ln σ)/d (ln ω) [8]. It is obvious that the values of exponent (s) are less than unity as shown in table (1). This result can be explained by correlated barrier hopping (CBH) model suggested by Elliott [9].

Table (1) The values of exponent (s) at indicated temperature for different EP/PU blends

No	T/K	100%EP/0%PU	90%EP/10%PU	80%EP/20%PU	70%EP/30%PU
1	293	0.843	0.854	0.887	0.888
2	323	0.766	0.808	0.831	0.832
3	353	0.725	0.761	0.782	0.789
4	383	0.713	0.732	0.775	0.779
5	413	0.652	0.706	0.732	0.763
6	443	0.587	0.663	0.702	0.736
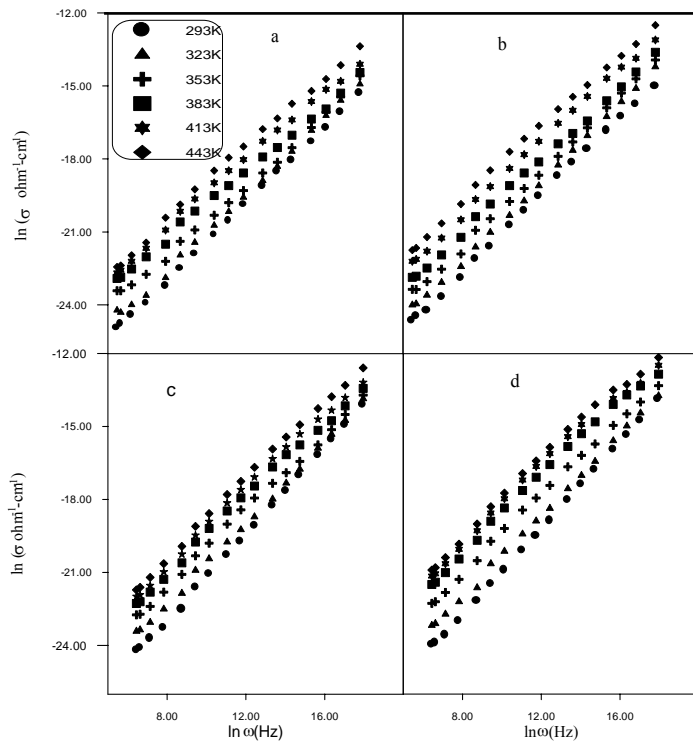
Figure (1) Variation of ln σ as a function of ln ω at various temperatures for a- pure EP, b- 90%EP/10%PU, c- 20%EP/80%PU and d- 30% EP/70% PU.

Figure 2 shows the temperature dependence of σ_{ac} for the polymer blends. Three zones are observed, the first one showed weak temperature dependence of σ_{ac} over temperature range 293-330K. This behavior is to be expected because the ion motion is likely to be governed by polymer backbone motion, which is a significant motion at low temperature range. At temperature above 330K which is approximate softening point of our blends the ion motion was grown slowly, since it has law contribution on conductivity. At temperatures above the glass transition temperature T_g (354K) the conductivity σ_{ac} increases rapidly, ion motion becomes effective mechanism of conduction. This result in a good agreement with that result reported on epoxy matrix polymer blend [10-11].
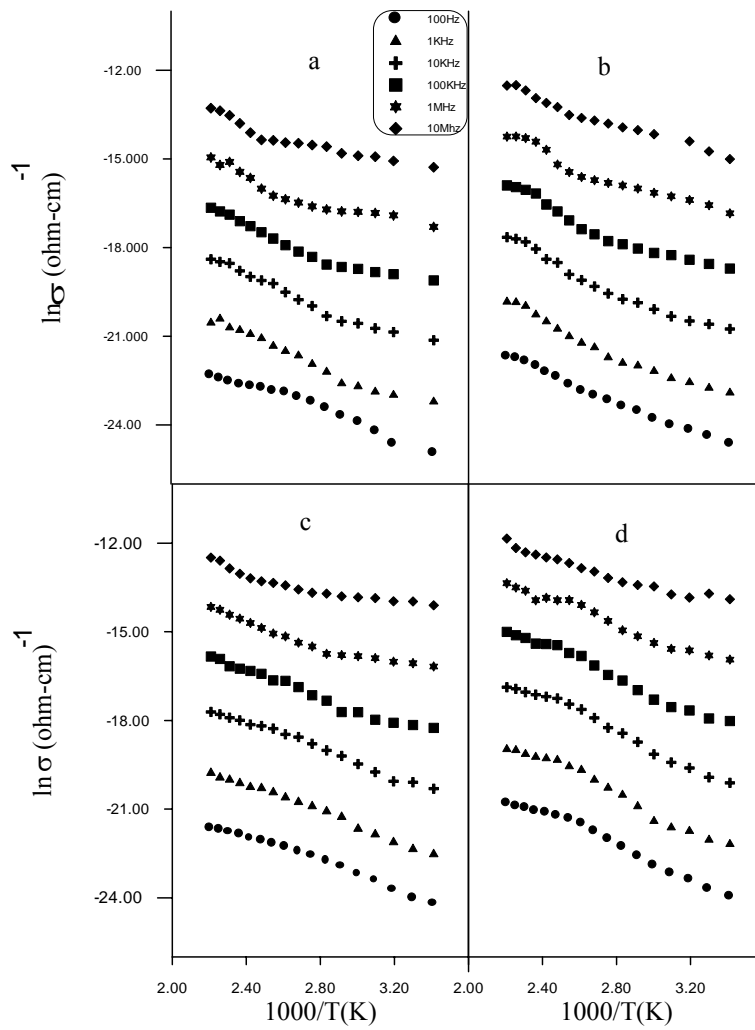
25

Figure (2) Variation of ln σ as a function of reciprocal temperature at various frequencies for a- pure EP, b- 90%EP/10%PU, c- 20%EP/80%PU and d- 30%EP/70%PU.

All specimens show three activation energies E_{ac}. The activation energies decreased with increases PU wt fraction as shown in table (2). The glass transition temperatures of EP/PU blends were estimated from the dielectric measurement, these results show an increase in T_g with increasing of PU wt fraction, as shown in table (2). This result is due to increasing inter-molecular forces which was caused by formation of polymer blend network. These results are good agreement with the result obtained by thermal analysis technique (DSC), H. Q. Xie: et al reported that the value of Tg of pure EP is equal 378K [12] and Al-Rawi has reported that the `Tg value of 80%EP/20%PU is equal 371.66K [14].

Table (2) The values of glass transition temperature T_g and activation energies of EP/PU blends at indicated frequency.

F/Hz	100%EP/0%PU			90%EP/10%PU			80%EP/20%PU			70%EP/30%PU		
	T_g = 354K			T_g = 370K			T_g = 375K			T_g = 378K		
	E_{ac1} (eV)	E_{ac2} (eV)	E_{ac3} (eV)	E_{ac1} (eV)	E_{ac2} (eV)	E_{ac3} (eV)	E_{ac1} (eV)	E_{ac2} (eV)	E_{ac3} (eV)	E_{ac1} (eV)	E_{ac2} (eV)	E_{ac3} (eV)
10^2	0.334	0.309	0.247	0.282	0.254	0.201	0.223	0.216	0.144	0.212	0.206	0.138
10^3	0.327	0.291	0.237	0.272	0.241	0.197	0.222	0.190	0.142	0.188	0.173	0.143
10^4	0.324	0.283	0.229	0.254	0.218	0.174	0.212	0.185	0.129	0.177	0.152	0.117
10^5	0.314	0.261	0.209	0.236	0.202	0.156	0.209	0.172	0.121	0.163	0.133	0.106
10^6	0.270	0.240	0.193	0.236	0.196	0.143	0.204	0.166	.112	0.159	0.127	0.098
10^7	0.262	0.224	0.179	0.215	0.178	0.128	0.155	0.137	0.107	0.153	0.122	0.082

Dielectric relaxation:

Figures (3a, b) and (4a, b) show the frequency and temperature dependence of real and imaginary parts (ε'), (ε'') of dielectric constant. The imaginary part (ε'') of dielectric constant is estimated by Givers formula $\tan \delta = \varepsilon''/ \varepsilon'$ [15]. We observe that these curves are symmetrical around the maximum angular frequency (w_{max}), this result is in agreement with the prediction of Debye dispersion equation $\varepsilon_i = (\varepsilon_s - \varepsilon_{op}) [w\tau/ (1+w^2 \tau^2)]$ [16], where ε_s and ε_{op} is static and optical dielectric constant respectively, τ molecular relaxation time.
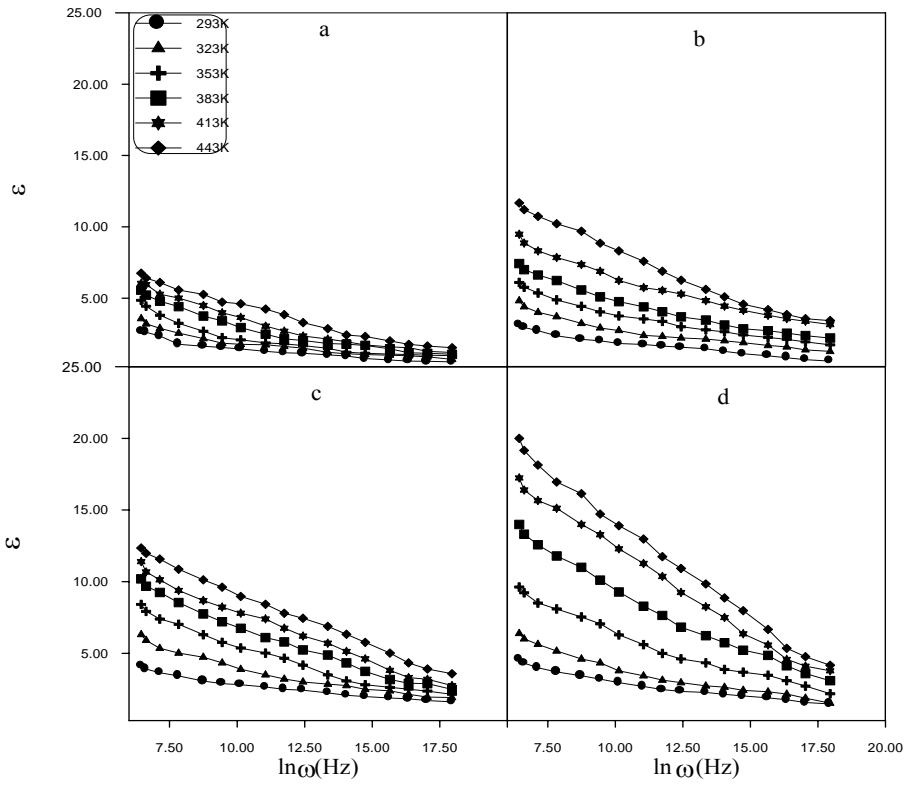
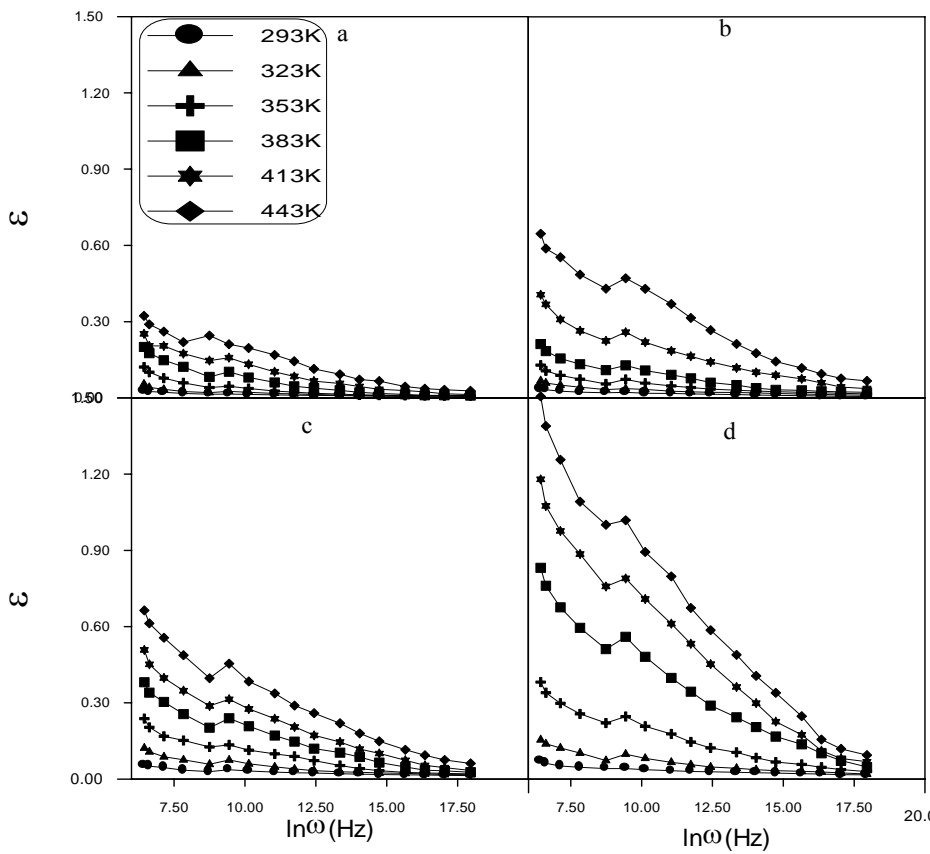**Figure (3a) Variation of ε′ as a function of ln ω at various temperatures for a- pure EP, b- 90%EP/10%PU, c- 20%EP/80%PU and d- 30%EP/70%PU.**

Figure (3b) Variation of ε′ as a function of ln ω at various temperatures for a- pure EP, b- 90%EP/10%PU, c- 20%EP/80%PU and d- 30%EP/70%PU.
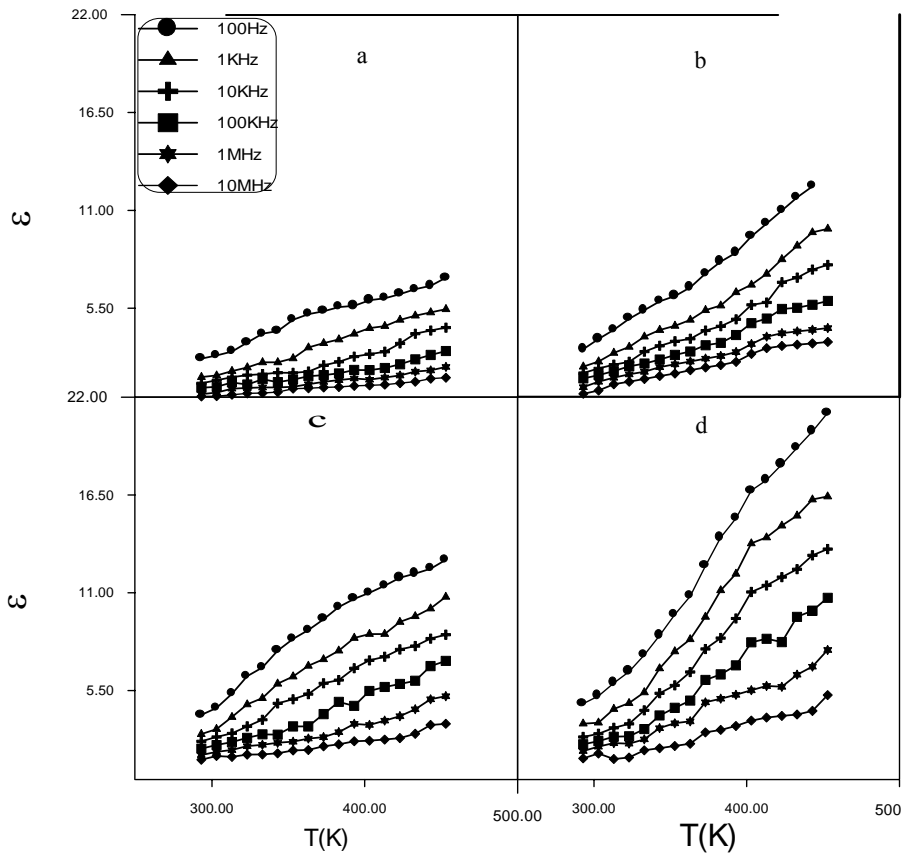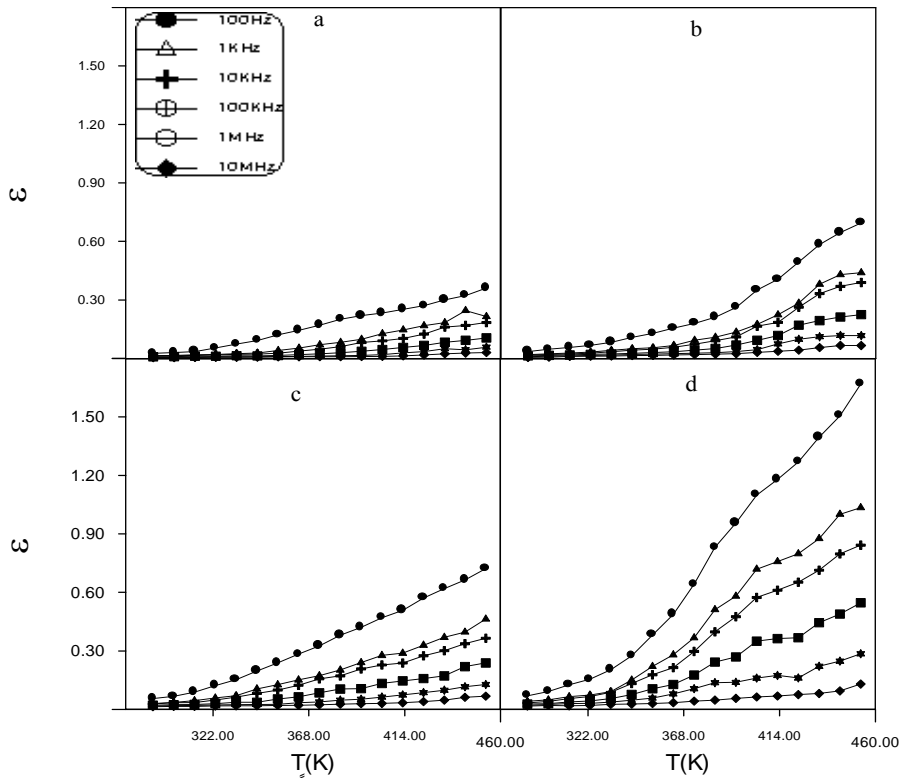
Figure 4a Variation of ε' as a function of T(K) at various frequencies for a- pure EP, b- 90%EP/10%PU, c- 20%EP/80%PU and d- 30%EP/70%PU.

Figure 4b Variation of ε' as a function of T(K) at various frequencies for a- pure EP, b- 90%EP/10%PU, c- 20%EP/80%PU and d- 30%EP/70%PU.

The Cole - Cole Diagrams for different EP/PU blends are illustrated in figure5. These curves were used to determine the values of polarizabillity (α), static dielectric constant (ϵ_s), optical dielectric constant (ϵ_{op}), macroscopic relaxation time (τ_0) and molecular relaxation time (τ) are inserted in table (3). Hence the Cole-Cole diagram represent an arc of a circle intersecting the abscissa axis at values ϵ_s, ϵ_∞ respectively and having it is center lying below the abscissa axis thus the diameter drawn through the center from ϵ_∞ makes an angle $\alpha\pi/2$ with ε' axis. The formula $v/u = (\omega \tau_0)^{1-\alpha}$ where v is the distance on the Cole-Cole diagram between ϵ_S, the experimented point and u is the distance between that point and ϵ_∞ and ω is angular frequency [17], was used to evaluate the values of macroscopic relaxation time (τ_0) and molecular relaxation time (τ) was estimated dependence on τ_0 using equation $\tau = [(2 \epsilon_S + \epsilon_{OP})/3 \epsilon_S]$

31

τ_0 [17] where ϵ_S is static dielectric constant and ϵ_{OP} is optical dielectric constant. A look at table (3) reveals that the values of α, τ systematically decreased with temperature for all blends, these results are another agreement with the concept of molecular relaxation this behavior can explained by the fact that the dominated type of the polarization in those samples is orientation polarization, since this type of polarization is very sensitive to the temperature and the molecular explanation of this temperature dependence is that the relative influence of the segmental molecular interaction energy decreased with respect to the temperature increasing.
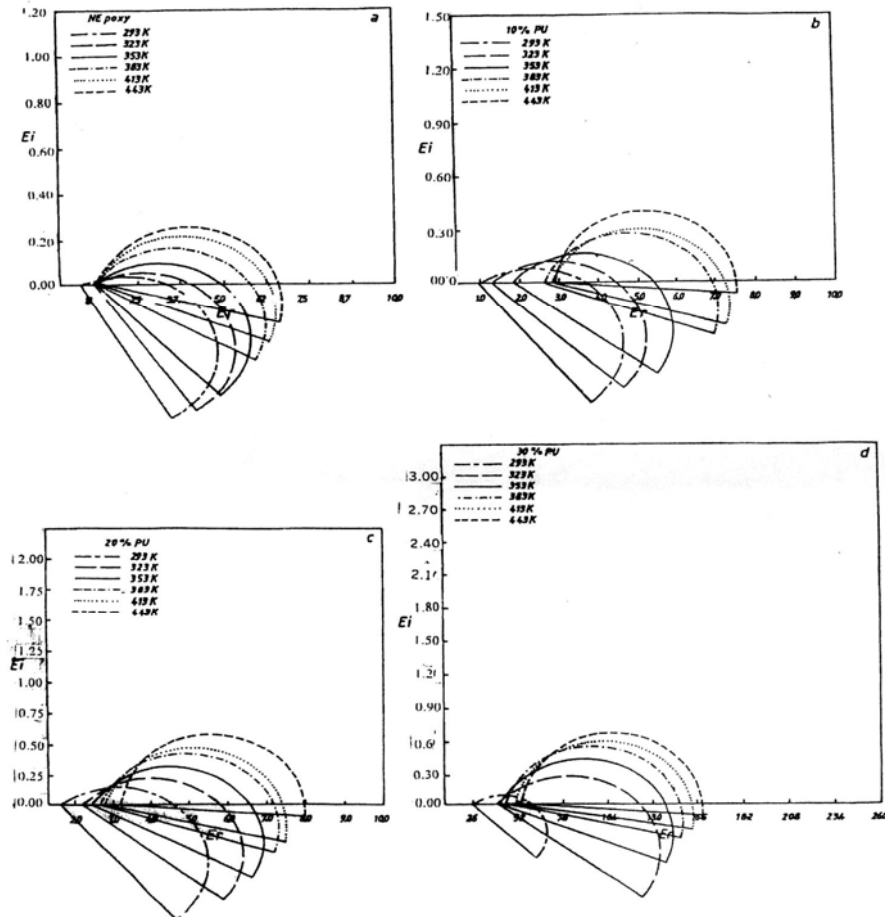

Figure 5. Variation of ε′ as a function of ε′ at various temperatures for pure EP and EP/PU blends

This work perhaps for the first time reports the measured values of optical dielectric constant ϵ_{OP} for epoxy matrix polymer blend. We observed that (ϵ_{OP}) increased with temperature, this behavior can explained as the follows, when the temperature arises the segment dipoles slowly get activated and attain freedom of rotation even though the blend remains in sold state.

Table (3) lists the values of α, ϵ_{OP}, ϵ_S, and τ for various polymer blends at indicated temperatures

T/K	100% EP/0%PU				90%EP/10%PU				80%EP/20%PU				70%EP/30%PU			
	α	ϵ_{op}	ϵ_s	$τ×10^4$	α	ϵ_{op}	ϵ_s	$τ×10^4$	α	ϵ_{op}	ϵ_s	$τ×10^4$	α	ϵ_{op}	ϵ_s	$τ×10^4$
293	0.689	0.77	2.14	141	0.600	1.00	3.75	109	0.567	1.93	4.58	81.66	0.489	2.60	5.94	49.92
323	0.633	1.25	4.02	59.84	0.511	1.25	4.42	37.40	0.467	2.21	5.75	25.18	0.433	3.99	12.16	10.40
353	0.489	1.25	5.18	23.7	0.422	1.83	5.38	12.19	0.344	2.50	6.46	8.41	0.294	4.18	13.74	3.01
383	0.360	1.25	5.80	9.52	0.245	2.63	6.83	5.37	0.233	2.71	7.17	3.26	0.167	4.55	14.67	1.15
413	0.267	1.25	6.34	4.13	0.211	2.83	7.21	2.24	0.200	2.79	7.42	1.30	0.122	5.01	15.28	0.46
443	0.166	1.25	6.66	2.03	0.111	2.92	7.50	1.23	0.080	3.25	7.96	0.65	0.067	5.39	15.88	0.26

Thermodynamic parameters:

The thermodynamic parameters obtained in this work using the method suggested by Eyring [18]. The Gibbs free energy of activation (ΔG) for dipoles relaxation was calculated using relation ΔG = RT ln (k Tτ/h) where R is general constant of gases, T the temperature k is Boltizman constant, τ is molecular relaxation time and h is Blanck constant , and ΔG is related to enthalpy (ΔH) and entropy (ΔS) by the following equation ΔG = ΔH- TΔS, these equations predict that the plot of log (τ) versus reciprocal temperature give a linear behavior with slop ΔH/R as shown in figure (6). The thermodynamic parameters evaluated by above method were inserted in table (4). The values of both ΔG and ΔH are highly this result support our explanation on relaxation time behavior, in other hand side this result confirm a stronger inter molecular force for our blend. Also it is obvious that the values of ΔG decreased when ΔH and entropy ΔS were increased with increasing PU wt fraction, this is another confirms of Debye dispersion equation.
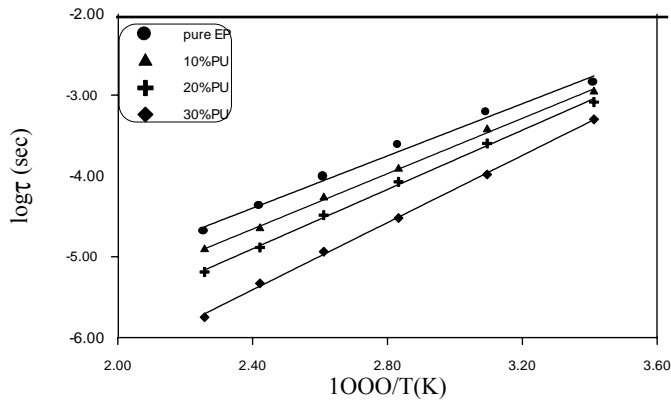
Figure 6. Variation of log τ as a function of reciprocal temperature for pure EP and EP/PU blends

Table (4) the values of thermodynamic parameter estimated by Cole-Cole diagrams for different EP/PU blends at indicated temperatures.

T/K	100%EP/0%PU		90%EP/10%PU		80%EP/20%PU		70%EP/30%PU	
	ΔH = 12.888KJ		ΔH = 12.939KJ		ΔH = 13.610KJ		ΔH = 16.482KJ	
	ΔG/ K J	ΔS/ J	ΔG/ K J	ΔS/J	ΔG/ K J	ΔS/ J	ΔG/ K J	ΔS/ J
293	56.10	-147.49	55.11	-143.92	54.41	-139.23	53.21	-125.32
323	59.39	-143.98	58.13	-139.91	57.07	-134.55	54.69	-118.30
353	62.44	-140.38	60.49	-134.71	59.41	-129.73	56.38	-113.04
383	65.12	-136.37	63.30	-131.48	61.71	-125.57	58.40	-109.44
413	67.62	-130.61	65.52	-127.32	63.65	-121.15	60.14	-105.71
443	70.17	-129.30	68.32	-125.02	66.65	-119.73	62.56	-104.01

34

Conclusion

1- The addition of dispersive phase PU to epoxy resin improve the values of $\sigma_{ac}(\omega)$,s, ε and ε while it reduce the values of E_{ac}.

2- The values of glass transition temperatures (T_g) of pure EP and EP/PU blends estimated by dielectric measurements (DM) and the results show the addition of dispersive phase PU improves T_g.

3- The values of α, ε_S, ε_{OP} and τ are estimated by Cole-Cole diagram and the adding of PU reduce the values of α and τ and improves the values of ε_S and ε_{OP} .

4- The thermodynamic parameters (ΔG, ΔH and ΔS) evaluated by dielectric measurements according to Eyring theory. It found that blends show high values of ΔG and ΔH and the values of ΔH increases with dispersive phase concentration increasing.

REFERENCES

1- Dyson, R.W. (1987)."specialty polymers' Blackic and son; New York,

2- Biswas, S. Srikanth, G. and Nangia, S. (2001). "Composites 2001 Convention and Trade Show", Composites Fabricatoris Association, Tampa, FL, USA,

3- Kim, C. H. and Shin, J. S. (2002). "Bull, Korean Chem, Soc." V 23 PP (413-416).

4- Daly, J. H. and Pethrick, R. A. (1981). "Polymer" V. 22, PP (37-42).

5- Patel, M. and Suthar, B. (1987). "J. Appl. Polym. Sci" V33, PP (67-75).

6- Li, Y. and Mao, S. (1996). "J. of. Polym. Sci, part A: Polym chem" V 34, PP (2371-2375).

7- Ying, L. and Sufen, M. (1996). "J. Appl., Polym. Sci", Vol. 61 PP (2059-2063),

8- Saha, K. Abbi, S. C. and Pohl, HA. (1976)."J. Non- Cryst. Solids" V 22 PP (291-303).

9- Elliot, S.R. (1987)."Adv. Phy." V, 36, No. 2, PP (135-218).

10- Jeevananda, T. and Siddaramaiah, (2003). "Euro, Polym, Journal", V. 39, PP (569-578).

11- Daly, J. H. and Pethrick. R.A. (1982)."Polymer". V. 23, PP (1619-1621).

12- Xie, H.Q. Huany, X. D. and Guo Jun-Shi, (1996). "J. Appl. Polym. Sci", V. 60, PP (537-542).

13- Douglas, H. J. Schafe, and John, B.S. (1996)."J. Appl. Plym. Sci" V.60 PP (2409-2417).

14- Al Rawi, K. E. (1998). "Ph. D. Thesis submitted to Bayhdad univ".

15- Tareev, B. (1980). "Physics of Dielectric Materials", Mir Publishers, Moscow.

16- Srivastava, K. K. Kumar, A. Pan war, O. S. and Lakshminarayan, K. N. (1979). "J. Non crys. Solids", V 66, PP (205-224).

17- Powles, J. G. (1953). "J. chem. Phys", V. 21, P (633).

18- Eyring, H. (1936). "J. chem. Phys." V. 4, P (2831).