EFFECT OF DOPING RATIOS ON DIELECTRIC PROPERTIES OF RESOL NOVOLAC RESIN (RNR) WITH RHODAMINE 6G

Samah Hussein Kadhim[1], Anis A. Al-Najar [2], Ali H. Al-Mowali [3]

[1]Department of Chemistry, College of Science, University of Thi-Qar, Iraq
[2,3]Department of Chemistry, College of Science, University of Basrah, Iraq

ABSTRACT: *Dielectric properties and ac conductivity measurements on Resol Novolac Resin (RNR) doped with (0.01, 0.03, 0.05, 0.07, 0.1)% wt of Rhodamine 6G have been studied.The measurements were carried out in the frequency range (100Hz-1MHz) and temperature in the range (30-100) ˚C and. The experimental results showed that ε', ε″ and tanδ increased with increasing temperature, and is due to greater freedom of movement of the dipole molecular chains within polymer at high temperature. The value of ε' decreased with increasing frequency, which indicates that the major contribution to the polarization comes from orientation polarization. Ac. Conductivity σ_{ac} and impedance (Z) of doping polymer behaviors as function of frequency and temperature have also been investigated.*

KEYWORD: Dielectric properties, Resol Novolac Resin, Rhodamine 6G, ac conductivity.

INTRODUCTION

Dielectricity is a physical model focusing on interaction between the electric field and atoms/molecules of the material. All materials respond to the external disturbance in the way offsetting its effects. Likewise, all materials are polarized in response to an applied electric field, when all the dipoles in it align in the applied field so that negative end is turned towards higher potential, and positive ends towards lower. Dielectrics are mainly insulators that can be polarized by the application of electric field. When a dielectric material is placed in an electric field, electric charges do not flow through it (like in conductors) but shift from their average equilibrium positions causing polarization. The amount of polarization caused is described by a dimensionless quantity called the dielectric constant. Dielectrics are able to conduct electricity due to the impurities and imperfections within the material, but their conductivity ranges from 10^{-18} to 10^{-6} S/m. [1,2].

The ability of the dielectric materials to store energy is attributed to the polarization, i.e. electric field-induced separation and alignment of the electric charges, which can result in an increase in capacitance. There are several molecular mechanisms associated with this polarization, including electronic, ionic, molecular (dipole), and interfacial (space-charge) polarization. Polarization occurs when the electric field causes a separation of the positive and negative charges in the material. The larger the dipole moment arms of this charge separation in the direction of a field and the larger the number of these dipoles, the higher the material's dielectric permittivity. Application of a field to each of these mechanisms in a normal state will cause a displacement of charge which results in a polarization in the direction of the field. For a given material, the sum of the contributions from each mechanism determines the net polarization, *P*, of the dielectric material [3,4].

$$P = P_{electronic} + P_{ionic} + P_{molecular} + P_{interfacial} \qquad (1)$$

EXPERIMENT

Materials

The materials tested in this study were novolac, formaldehyde, sodium hydroxide, phosphoric acid, dimethyl formamide and Rhodamine 6G.

Preparation of Resol novolac Resin (RNR)

RNR can be prepared by using a three necked flask, equipped with mechanical stirrer and digital thermometer was charged with 100g (0.19mole) of novolac powder and 250 ml (3.32 mole) formaldehyde solution. The reaction mixture was mixed and 10% sodium hydroxide solution was added in order portions to control pH to about 9 while temperature of the reaction was kept at 50-60℃ for 3hrs. The reaction mixture was cooled and neutralized with 10% phosphoric acid solution, the organic layer was separated and purified by washing several times with distilled water, then curing in oven at 60c for 2hrs [5].

Doping of PFA

Doping RNRwith dye Rhodamine 6G is is carried out by adding the weighed dye to the appropriate weight of polymer (1g) then the mixture was dissolved in dimethyl formamide DMF after the prepared directly to give a polymer / dye system containing (0.01, 0.03, 0.05, 0.07 and 0.1) g wt% of doping reagent Rhodamine 6G is [6]. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of dye in the polymer matrix.

Characterization and measurements

Dielectric properties of doping RNR was investigated using RLC meter (Fluke PM6306), on frequency range of (100Hz-1kHz), RLC meter (Fluke PM6303A) was measuring capacity and dielectric loss properties at different temperatures (30-100) ˚C.

The dielectric permittivity ε' were calculated in conformity with the relation [7]:

$$C = \varepsilon_o \, \varepsilon' \, A / d \qquad (2)$$

Where ε_o is the permittivity of the free space ($\varepsilon_o = 8.8 \times 10\text{-}12$ F/m), d is the separation between the capacitor electrodes, A is the area of the electrodes.

The dielectric loss $\acute{\varepsilon}$ are given by the relation [8]:

$$\acute{\varepsilon} = \varepsilon' \, \tan\delta \qquad (3)$$

AC. Conductivity σ_{ac} was calculated according to the relation [8]:

$$\sigma_{ac} = \varepsilon_o \, \omega \, \acute{\varepsilon} \qquad (4)$$

where ω is an angular frequency given by:

$$\omega = 2\pi f \qquad (5)$$

where f is frequency.

RESULTS AND DISCUSSION

Figure (1) shows the variation of the dielectric permittivity ε' of pure RNR as a function of temperature in the range (303 – 373)K at a constant frequency (1 kHz) for different doping ratios. It can be seen that, permittivity increases as the temperature increases. The dielectric response of the composites may be related to the segmental mobility of polymer which increases with increasing temperature; this mechanism should lead to increase the dielectric constant due to greater freedom of movement of the dipole molecular chains within the polymer at high temperatures [7].

Figures (2) shows the relationship between dielectric permittivity ε' and frequency (f) for the range (100 Hz – 1 MHz) of pure RNR with different ratios at (298) k. It is evident from the figures that ε' Decreases with increasing frequency at fixed temperature and it is the expected behavior in most dielectric materials due to the orientation polarization and interfacial polarization which appears more effective at low frequency . In other means, all the dipole groups in the polymers molecular chains can orient themselves at low frequency. Due to the dielectric relaxation which involves the orientation and interfacial polarization, at higher frequencies the rotational motion of the polar molecules of dielectric is not sufficiently rapid for the attainment of equilibrium with the field ,hence dielectric constant seems to be decreasing with increased frequency, until reaches to a constant value depending on the fact that beyond a certain frequency of electric field the electron exchange does not follow the alternating field [9,10].

Figures (3) and (4) illustrate the variation of dielectric loss ε'' and loss tangent $\tan\delta$ as a function of temperature in the range (303 – 373)K at a constant frequency (1 kHz) for RNR with different doping ratios. It is noticed that both ε'' & $\tan\delta$ are increased in general as doping ratios or temperature increase. The increase in ε'' & $\tan\delta$ with increasing of doping ratios is attributed to the interfacial polarization, while that caused by increasing temperature may be related to the increase of segmental mobility and ionic conductivity. Since the rise in temperature (and the consequence drop in viscosity) exerts an effect on the amount of the losses due to the friction of the rotating dipoles, the degree of dipole orientation increases as well as ionic conduction increases due to the thermal dissociation of molecule [11].

Figure (5) shows the relationship between dielectric loss $\acute{\varepsilon}$ and frequency for all weight ratios at (298) K. It is apparent from both figures that dielectric loss $\acute{\varepsilon}$ increases initially with increased frequency. This kind of frequency dependency is called dielectric relaxation, being characterized by a relaxation time τ or relaxation frequency f_o corresponding to $\Delta\varepsilon/2$. This relaxation shifts to lower frequencies with the increasing of doping ratio. It clear that, the values of dielectric loss increase gradually with increasing the frequency to reach the highest value (maximum value). The increase in dielectric loss may be related to a.c conductivity (σac) which depends on the number of charge carriers, relaxation time and frequency domain when the temperature is constant, after which the dielectric loss begins to decrease gradually. This is due to the relaxation processes which were influenced by the interfacial polarization effect.This result is attributed to the different interface structures between dyes and polymers [12,13].

Figure (6) shows the relationship between dissipation factor ($\tan\delta$) and frequency for different ratios of doping at room temperature. It is apparent from figure that dielectric $\tan\delta$ increases initially with increased frequency for pure RNR with doping and than decrease until it reaches a fixed value. The increases in $\tan\delta$ may be related to a.c conductivity (σac) which depends on the number of charge carriers, relaxation time and frequency domain when the temperature is

17

constant, after that the dielectric loss begins to decrease gradually. This is may be due to the relaxation processes which were influenced by the interfacial polarization effect [14].

Figure (7) shows the variation of σ_{ac} as a function of temperature in the range (303 - 373)K at a constant frequency (1 kHz) for RNR with different doping ratios. It can be seen that the ac conductivity increases with the increasing of doping ratios for the same temperature circumstances, as well as, the σac for all cases increases as the temperature increases. The influence of temperature on σac can be explained by considering the mobility of the charge carriers responsible for hopping. As the temperature increases the mobility of hopping ions in polymers, which arises as a causal inevitably product during the synthesis processes, also increases thereby increasing the conductivity. The electrons which are involved in hopping are responsible for electronic polarization in these composites [15]. A.C conductivity is also related to the polymer segmental mobility and increases dramatically with increasing temperature.

Figure (8) shows the relationship between ac electrical conductivity σ_{ac} and frequency for all ratios of doping at room temperature. The ac conductivity from both figures increases linearly with increased frequency to $(1.1*10^{-5}$ S/cm) for the RNR (0.1%) doping respectively, and this is a natural behavior for doping polymers due to increase free charge moving with increased frequency,. So, the current flow increases and causes lastly increment in ac conductivity. This increase in ac conductivity may be related to the interfacial polarization and electrical conduction .Similar trend and explanation were for another system [16].

Figures (9) shows the relationship between electrical conductivity σ_{ac} and different weight ratios of doping RNR, at frequency 1 KHz at room temperature. It is clear that the ac conductivity normally, increases with increasing weight ratio of doping. This is attributed to the increase of the charge carrier density in polymer matrix [17] where the conductivity of doping RNR rises rises from $5.32*10^{-7}$ to $1.34*10^{-6}$ for the ratios (0.01 to 0.1) wt% at temperature 373K respectively. The slight increase in ac conductivity may be attributed to the presence of the lazer dyes in RNR non-conductors matrix polymers.

Figure (10) shows the variation of impedance as a function of temperature in the range (303 – 373)K at a constant frequency (1 kHz) for RNR with different doping ratios. It can be seen that the impedance decreases with the increasing of both temperature and doping ratios due to the increased interfacial polarization. The impedance Z decreases with the temperature rise which is accompanied by clear dips near (80-100 $^{\circ}$C) for all cases in which doping were added. This decrease in Z may relate to the increased mobility of segmental molecules as the temperature increased [18].

Figure (11) shows the relationship between impedance Z and frequency for all ratios of doping at (298) K. As can be seen, there is an exponential decrease in the impedance with increased frequency . This result can be attributed to the increase in ac electrical conductivity σ_{ac} with increased frequency, therefor Z decreases until reaching a fixed and very small value. The same trend was observed with another system by Psarras et al [18].
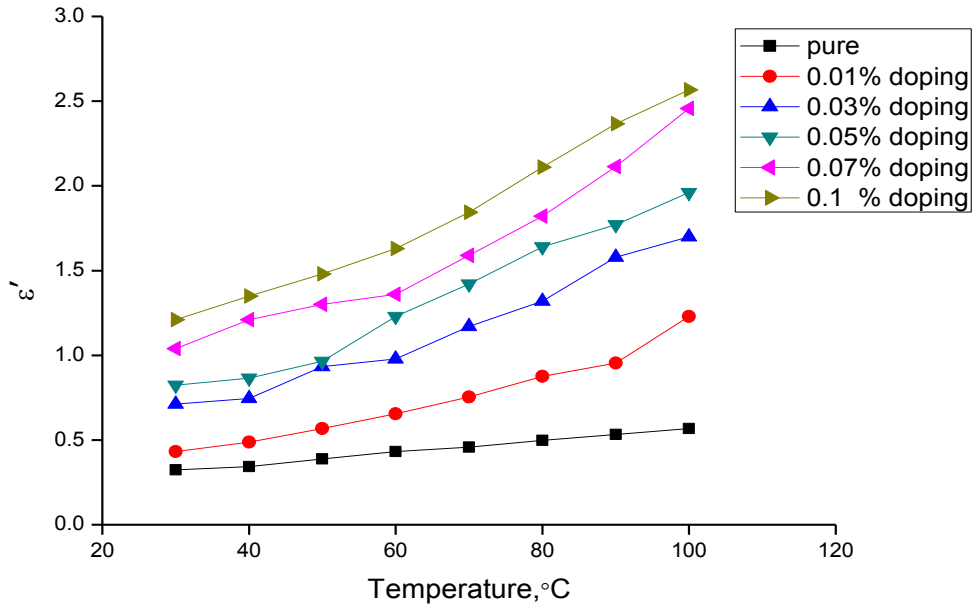
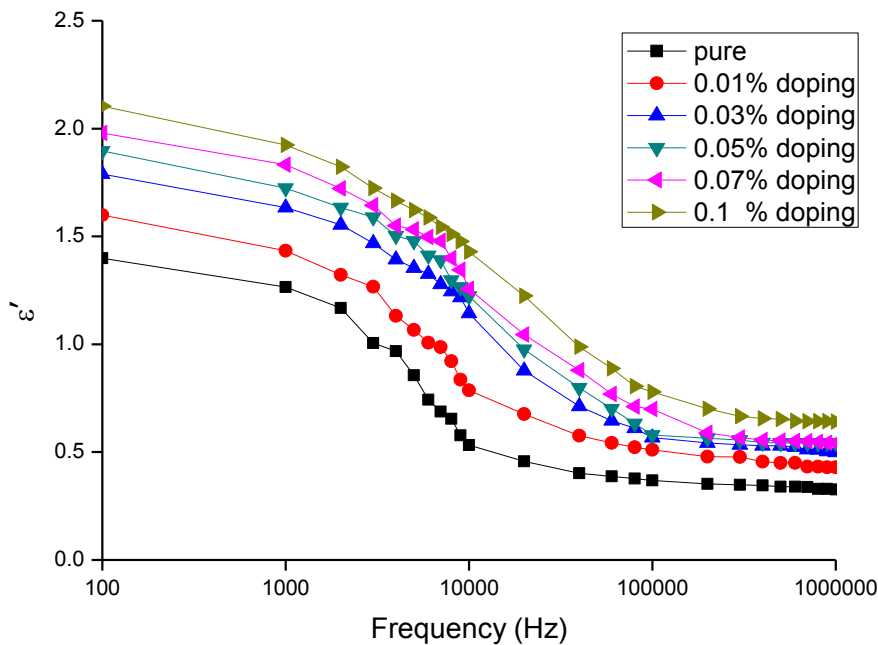**Figure(1):Temperature dependence of dielectric constant at (1kHz) frequency for RNR with different doping .**

Figure (2): Variation of dielectric constant ε´ with frequency for RNR with different ratios at (298 K).
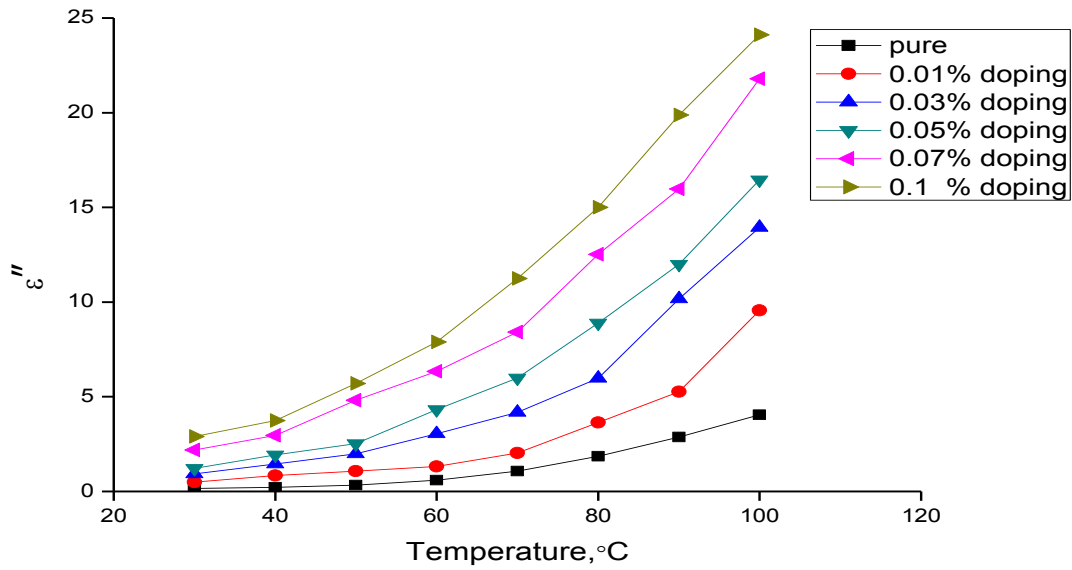
Figure (3): Temperature dependence of dielectric loss at (1kHz) frequency for RNR with different doping.
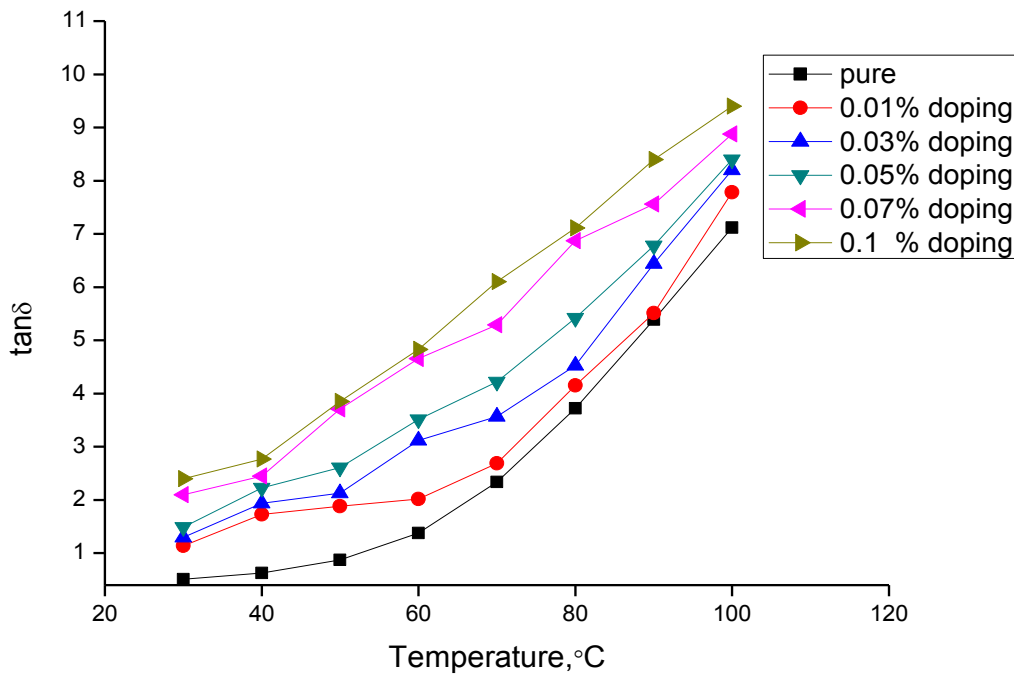

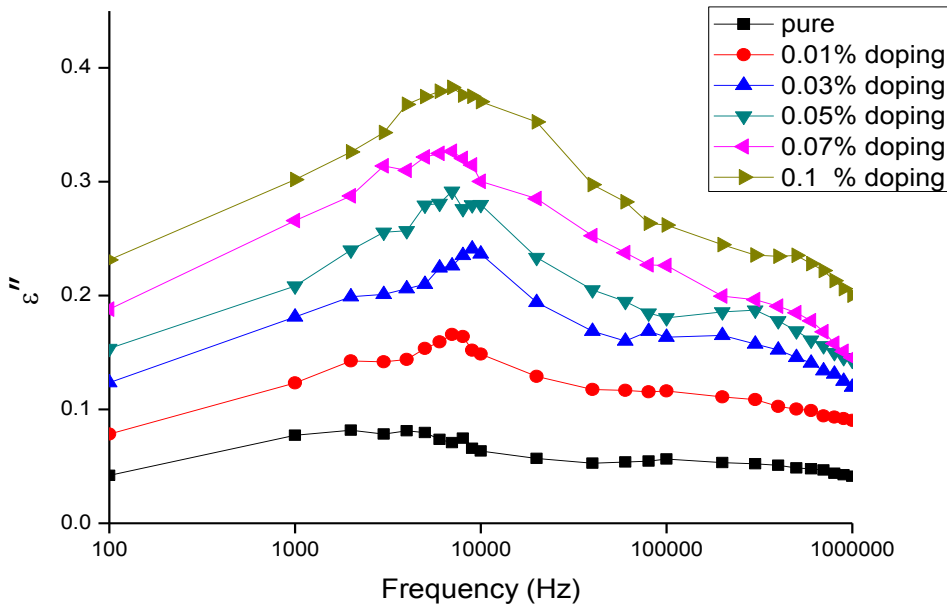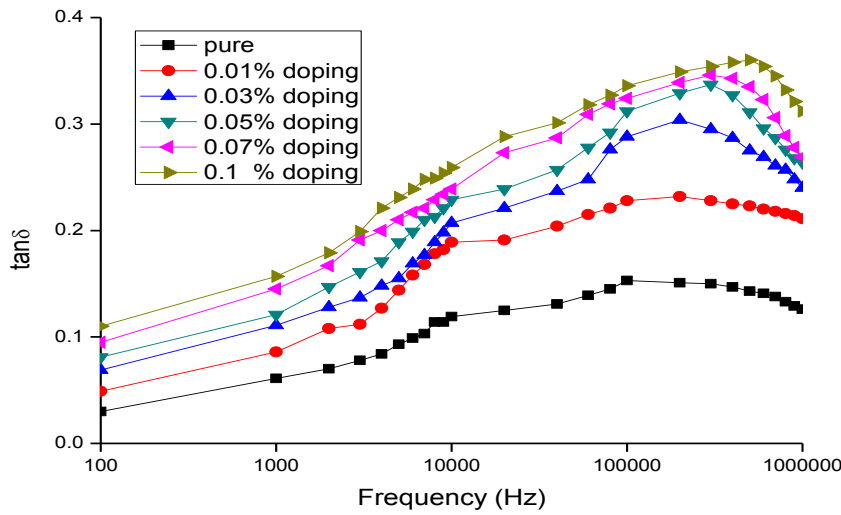**Figure (4): Temperature dependence of dielectric tan δ at (1kHz) frequency for RNR different doping .**

Figure (5): Variation of dielectric loss ɛ̋ with frequency for RNR with different ratios at (298K).

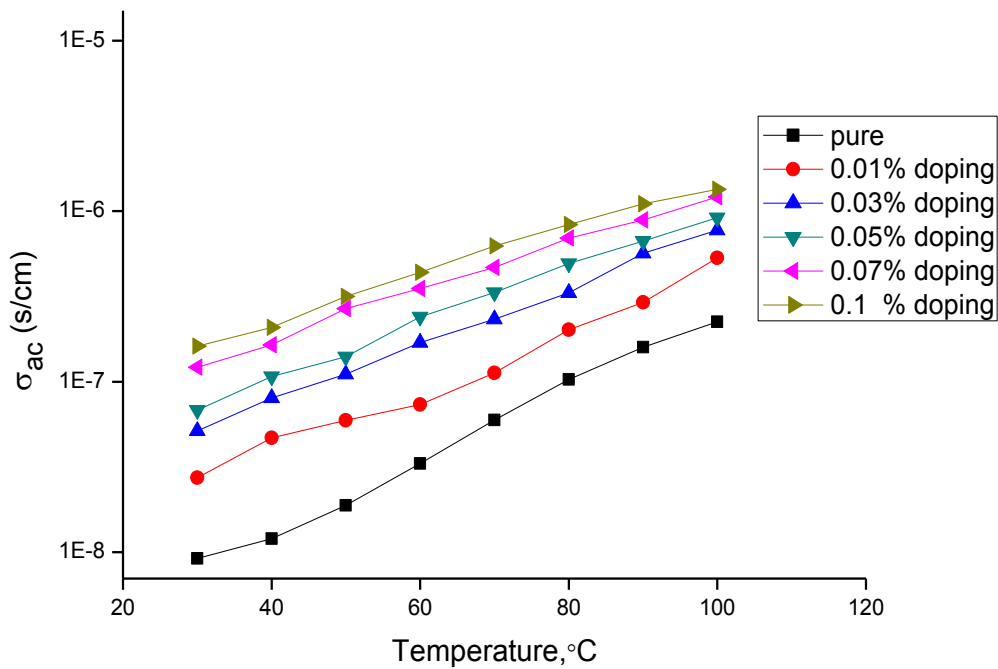**Figure (6): Wavelength Variation of tan δ with frequency for RNR with different ratios at (298 K).**

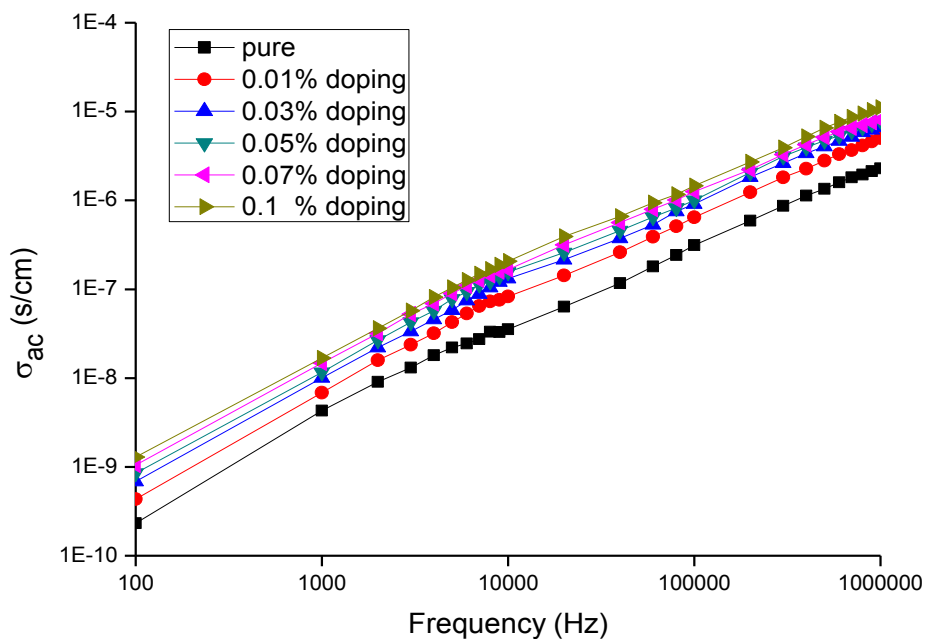**Figure (7): The variation of ac conductivity σ$_{ac}$ with temperature at (1kHz) for RNR different doping .**

Figure (8): Variation of conductivity σ_{ac} with frequency for RNR with different ratios at (298 K).
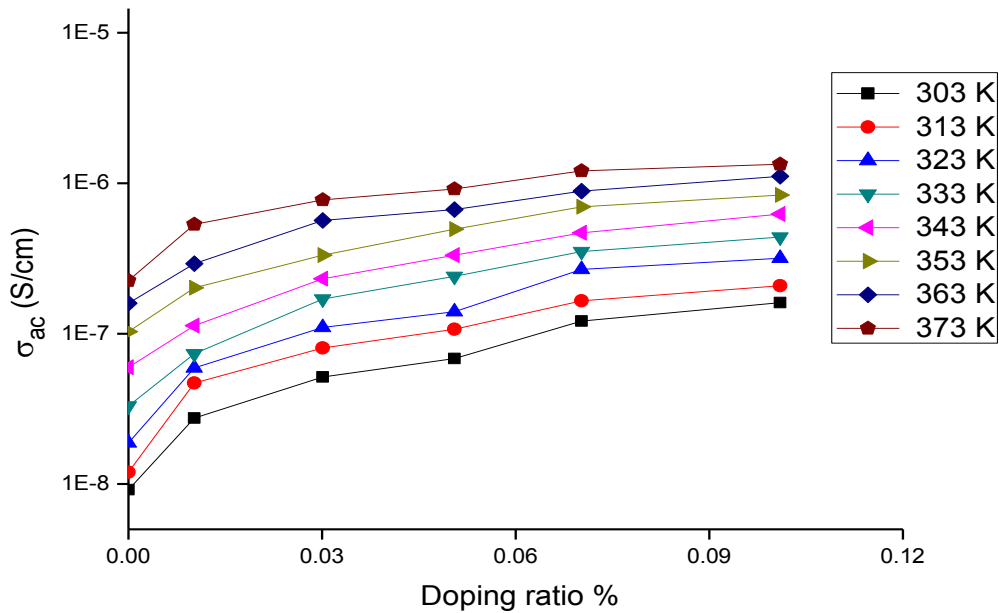

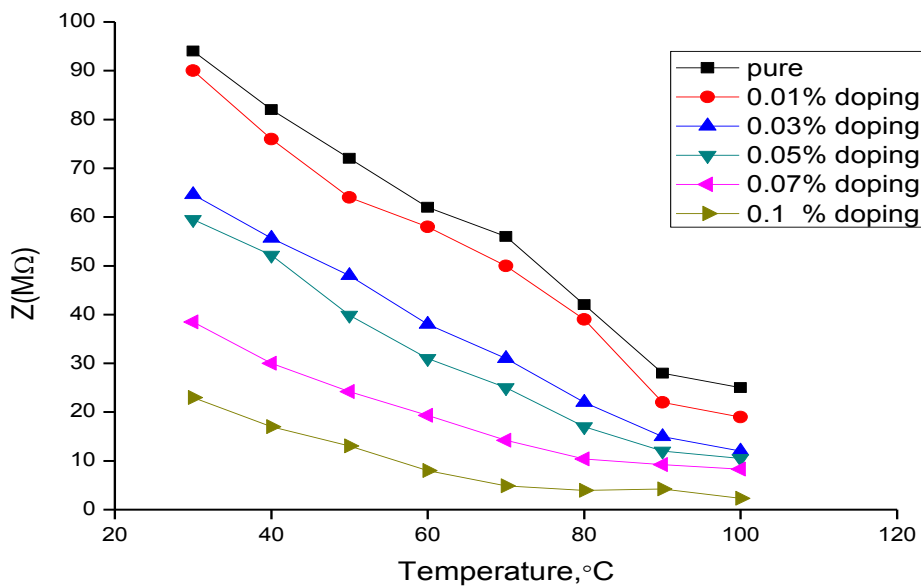**Figure (9) Variation of σ_{ac} for RNR with wt% of doping at 1kHz.**

Figure (10): Variation of impedance Z with temperature for RNRat different doping.
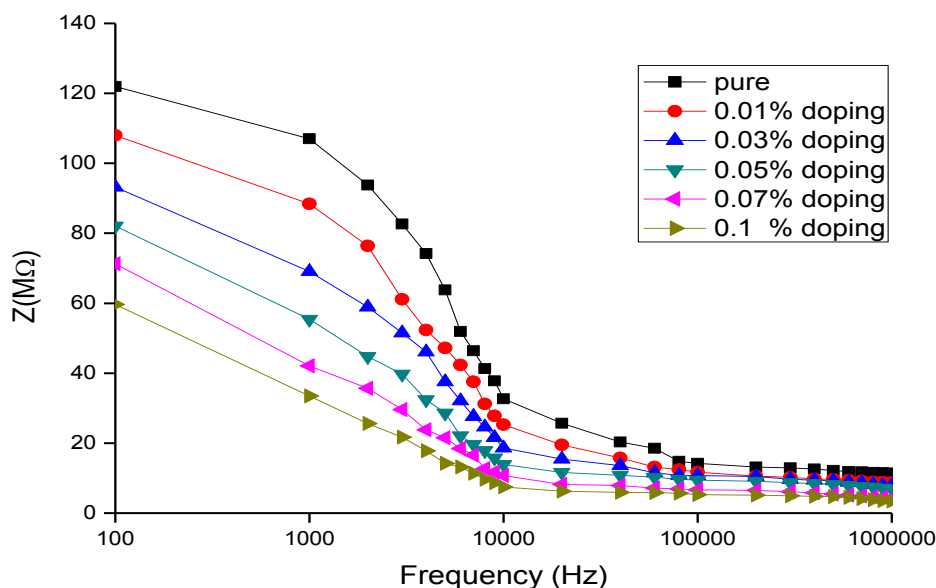
Figure (11): Variation of impedance Z with frequency for RNR with different ratios at (298 K).

CONCLUSION

Frequency and temperature dependence of dielectric constant ε' , dielectric loss ε'' and dissipation factor $\tan\delta$ in doping RNR has been investigated in the frequency rang 100Hz-1kHz and temperature range (30-100) ˚C. the experimental results indicate that ε', ε'' and $\tan\delta$ increase with increasing doping ratios and temperature is attributed to the interfacial polarization and segmental mobility of the polymer molecules , the permittivity decreases with increasing frequency, while ε'' and $\tan\delta$ increase with increasing frequency. The ac conductivity for all doping ratios increase with increasing temperature and frequency. The impedance Z decrease with increase temperature and frequency.

REFERENCES

[1] H.Stoyanov , D.Sc. thesis, University of Potsdam, (2010).

[2] G.Kofod, Ph.D. thesis, The Technical University of Denmark (2001).

[3] L.Jiongxin , PhD. Thesis,Georgia Institute of Technology ,December (2008).

 [4] D. L. Chung, Applied Materials Science, CRC Press LLC, (2001).

[5] M.A. Jabir, Ph.D. thesis , University of Basrah, (2003).

 [6] E. Amir, P. Antoni, L. M. Campos, D, Damiron, N. Gupta, R. J. Amir, N. Pesika, E. Drockenmuller and C. J. Hawker, Electronic Supplementary Material (ESI), The Royal Society of Chemistry Journal (2012).

[7] C.H. Kim, and J.S. Shin, Bulletin of the Korean Chemical Society, 23(2002) 413-416.

[8] V. Singh, A. R. kumar, and T.R. Ramamohan, J. Appl. Sci., 90 (2003) 3602-3608.

[9] S.A. Saq'an, A.S. Ayesh, A.M. Zihlif, E. Martuscelli and G. Ragosta, Polym.Test., 23 (2004) 739-745.

[10] P. Gonon, A. Sylvester, J. Teysseyre and C. prior, J. Mater. Sci., 81 (2001).

[11] K.-C. Cheng, C.-M. Lin, S.-F. Wang , S.-T. Lin, and C.-F. Yang, Materials Letters, 61 (2007) 757-760.

[12] S.Singha and M. J. Thomas, "IEEE Trans. Dielect. Elect. Ins.", 15(1), (2008).

[13] D. K. Pradhan, R.N.P. Choundhary, B.K. Samantaray, "Int. J. Electro. Sci,", 3(2008) 597-608.

[14] R. Popielarz, C.K.Chiang, R.Zozaki and J.Obrzut," J. of Am. Chem." Soc.", 34 (2001) 5910-5915.

[15] S. Sindhu, M.R. Anantharaman, B.P. Thampi, K.A. Malini and P. Kurian, Bull.mater. Sci., 25, 599 (2002).

[16] N.Chand and D. Jain, "Bull. Mater. Sci.", 27 (2004) 227-233.

[17]   A.A.Hussain, A.A.Sultan,H.K.Mousa, A.H.Al-Mowali, Chemistry and Mteials Research, 3(3), (2013) 57-65.

[18]   G.C. Psarras, E . Manolakaki and G.M. Tsangaris, Composites part A, (2002) 375.