

## Study of Dielectric Properties and AC Conductivity of Lignin Resin Doped with Rhodamin B

<sup>1</sup>Samah Hussein Kadhim and <sup>2</sup>Zainab J. Sweah

<sup>1</sup>Department of Chemistry, College of Science, University of Thi-Qar, Nasiriyah, Iraq

<sup>2</sup>Polymer Research Centre, University of Basrah, Basrah, Iraq

**Abstract:** Dielectric properties such as relative permittivity dielectric constant  $\epsilon'$ , dielectric loss  $\epsilon''$  and dissipation factor  $\tan\delta$  of doped Lignin Resin with different doping ratios of rhodamine B (0.02, 0.04, 0.06, 0.08, 0.1) wt.% as function of temperature in the range 30-120°C and frequency in the range 100 Hz-1 MHz. The experimental results showed that  $\epsilon'$ ,  $\epsilon''$  and  $\tan\delta$  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  $\epsilon'$  decreased with increasing frequency which indicates that the major contribution to the polarization comes from orientation polarization. Ac conductivity  $\sigma_{ac}$  and impedance ( $Z$ ) of doping polymer behaviors as function of frequency and temperature have also been investigated.

**Key words:** Lignin resin, lignosulfonate, ac conductivity, rhodamine B, dipole molecular, polarization

### INTRODUCTION

Conducting polymers have received considerable attention because of their interesting electronic, physical properties, chemical stability and their potential technological applications (Kondawar *et al.*, 2009). Polymers are typically utilized in electrical, optical and electronic devices as insulators because of their very high electrical resistivity. The dielectric properties of heterogeneous polymers (Kumari *et al.*, 2011) play an important role in device applications such as high performance capacitors, electrical cable insulation, electronic packaging, etc. Polymers are usually poly conjugated structures which are insulators in their pure state but when treated with oxidizing or reducing agents they can be converted into polymer salts having reasonable electrical conductivity. Conjugated polymers are plastic semiconductors. They have wide applications in devices such as solar cells, rechargeable batteries, light emitting diodes, micro-actuators, electrochromic displays, field effect transistors, sensors (Friend *et al.*, 1999).

Lignin is a macromolecular compound, much more active than cellulose or other natural polymers due to the functional groups contained in its macromolecule (Saraswathi *et al.*, 1999). The reactivity of lignin is determined by its particular structure which comprises specific functional groups but also, by the structural modifications induced by the methods used for its separation from wood. It is known that lignin has a very complex structure which varies depending on the plant

species on the separation method and the modification reactions that may induce particular characteristics. Regarding the functional groups, Lignin presents at least three main functional groups in its structure: methoxy, hydroxyl (alcoholic and phenolic) and a side propane chain (Ungureanu *et al.*, 2009).

### MATERIALS AND METHODS

**Experiment:** The materials tested in this study were lignosulfonate, hydrochloric acid, formaldehyde, sodium hydroxide, sodium bicarbonate, phosphoric acid, ethanol amine, dimethyl formamide, propanol and rhodamine B.

**Modification method of lignosulfonate:** A mixture of lignosulfonate 5 g and hydrochloric acid (57%,v/v), then the reaction mixture was heated under reflux for 3 h after that the reaction mixture is allowed to cooled the solid precipitate obtained was filtered, washed for many times with Deion's water dried in the oven at 60°C (Malutan *et al.*, 2007).

**Synthesis of lignosulfonate formaldehyde resin:** Modify lignosulfonate 10 g was added to 15 mL of 10% sodium hydroxide, then the mixture was heated at 80°C for 75 min after completion the reaction, the mixture was cooled then solution of formaldehyde 60 mL and sodium bicarbonate 1.6 g was added, the reaction mixture was heated with stirring at 65°C for 3 h, then the reaction mixture was

cooled, neutralized by 10% H<sub>3</sub>PO<sub>4</sub> to PH 7, excess solvent was distilled off the result mixture was dried by heating under vacuum pressure for 24 h at 40°C (Vogel, 1961).

**Synthesis of amino resin:** Shipping or distribution the reaction flask by ethanol amine 1 mL and phosphoric acid 1 mL, the reaction mixture was heated to 50°C then solution of lignosulfonate formaldehyde resin 10 g in little amount of ethanol amine was added drop wise over a period of 30 min at 50°C . After that temperature of reaction increase stepwise to 135°C, the reaction was still at this temperature for 5 h. Then the excess of ethanol was distilled off .The mixture was cooled and neutralized by saturated solution of sodium bicarbonate, the product was formed dissolved in propanol, filtered off to remove precipitate salt then excess solvent was distilled off under vacuum pressure at 90°C. Purification for many times to obtain pure resin, dried under vacuum pressure at 50°C for 24 h.

**Doping of lignin:** Doping lignin resin with dye rhodamine B is carried out by adding the weighed dye to the appropriate weight of polymer 1 g then the mixture was dissolved in Dimethyl Formamide (DMF) after the prepared directly to give a polymer/dye system containing 0.02, 0.04, 0.06, 0.08 and 0.1 g wt.% of doping reagent rhodamine B. The mixture was stirred well for 15 min to guarantee that the homogenous distribution of dye in the polymer matrix.

**Characterization and measurements:** Dielectric properties of doping lignin resin was investigated using RLC meter (Fluke PM6306) on frequency range of (100 Hz-1 kHz), RLC meter (Fluke PM6303A) was measuring capacity and dielectric loss properties at different temperatures 30-120°C.

The dielectric permittivity  $\epsilon'$  were calculated in conformity with the relation (Amir *et al.*, 2012):

$$C = \epsilon_0 \epsilon'' A/d \tag{1}$$

Where:

$\epsilon_0$  = The permittivity of the free space ( $\epsilon_0 = 8.8 \times 10^{-12}$  F/m)

d = The separation between the capacitor electrodes

A = The area of the electrodes

The dielectric loss  $\epsilon''$  are given by the relation (Kim and Shin, 2002):

$$\epsilon'' = \epsilon' \tan \delta \tag{2}$$

Ac conductivity  $\sigma_{ac}$  was calculated according to the relation (Kim and Shin, 2002):

$$\sigma_{ac} = \epsilon_0 \omega \epsilon'' \tag{3}$$

where  $\omega$  is an angular frequency given by:

$$\omega = 2\pi f \tag{4}$$

where f is frequency.

## RESULTS AND DISCUSSION

Figure 1 and 2 shows variation of dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  as a function of temperature in the range 303-393 K at constant frequency 1 kHz of pure lignin resin with different doping ratios. It is observed that dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  increases with increasing temperature. As the temperature of the sample increased there is no dispersion in dielectric constant. This is because of tight binding forces between the number of ions or atoms. As temperature increases the dipoles comparatively become free and they respond to the applied electric field. Thus, polarization increased and hence the dielectric constant also, increases with temperature (Amir *et al.*, 2012).

Figure 3 shows the variation of dielectric constant  $\epsilon'$  as a function of frequency (f) for the range (100 Hz-1 MHz) of pure lignin resin with different doping ratios at 298 K. It is observed that at low frequency dielectric constant was found to be decreased with increasing the frequency. The behavior of the dielectric permittivity with frequency is related to the applied field which assists electron hopping between two different sites of the sample. At higher frequency region, the charge carriers will no longer be able to rotate sufficiently rapidly, so, their oscillation will begin to lay behind this field resulting in a decrease of dielectric permittivity  $\epsilon'$ . The relaxation phenomena in dielectric materials are associated with frequency dependent orientation polarization. At low frequency region, the permanent dipoles align themselves along the field and contribute fully to the total polarization of the dielectric. At higher frequency region, the variation in the field is very rapid for the dipoles to align themselves, so their, contribution to the polarization and hence, to dielectric permittivity can become negligible. Therefore, the dielectric permittivity,  $\epsilon'$  decreases with increasing frequency (Singh *et al.*,

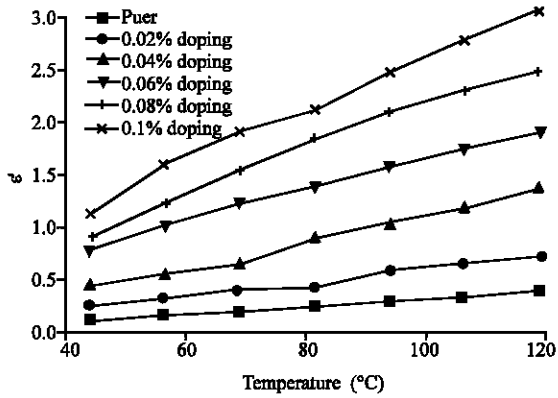


Fig. 1: Temperature dependence of dielectric constant at 1 kHz frequency for lignin resin with different ratios

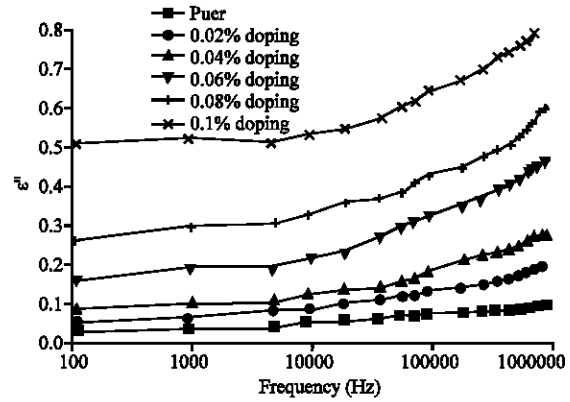


Fig. 4: Variation of dielectric loss  $\epsilon''$  with frequency for lignin resin with different ratios at 298 K

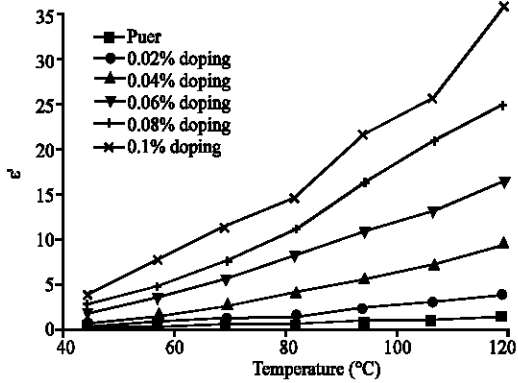


Fig. 2: Temperature dependence of dielectric loss at 1 kHz frequency for lignin resin with different ratios

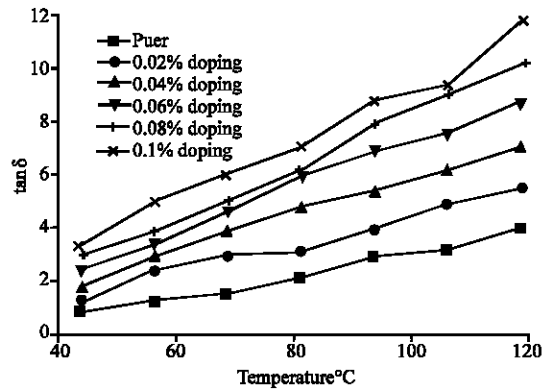


Fig. 5: Temperature dependence of dielectric  $\tan \delta$  at 1 kHz frequency for lignin resin with different ratios

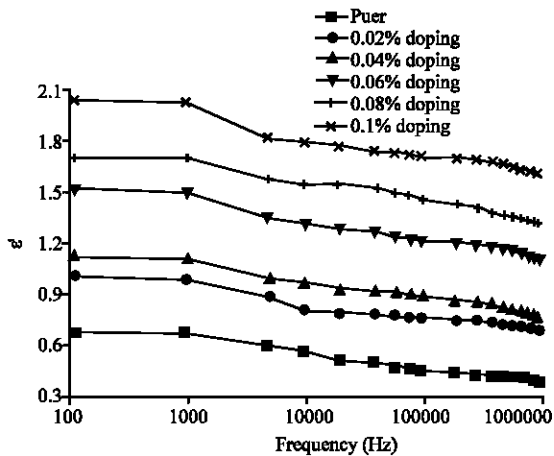


Fig. 3: Variation of dielectric constant  $\epsilon'$  with frequency for lignin resin with different ratios at 298 K

clears that the values of dielectric loss increase gradually with increasing the frequency to reach the highest value. The increase in dielectric loss may be related to ac conductivity ( $\sigma_{ac}$ ) which depends on the number of charge  $\epsilon''$ . This result is attributed to the different interface structures between dyes and polymers (Kondawar *et al.*, 2014).

Figure 5 shows the variation of loss tangent  $\tan \delta$  as a function of temperature in the range 303-393 K at a constant frequency 1 kHz for lignin resin with different doping ratios. It is noticed that  $\tan \delta$  are increased in general as doping ratios or temperature increase. This is due to the interfacial polarization. The dipole polarization on the other hand would significantly be affected during heat treatment by effectively reducing the relaxation time ( $\tau$ ), since, the polymer chain  $\tau$  would reduce as the temperature is increased, hence, the polymer segment would be better able to follow in phase with the oscillating electric field (Cheng *et al.*,

2003). Figure 4 shows the relationship between dielectric loss  $\epsilon''$  and frequency for all weight ratios at 298 K. It

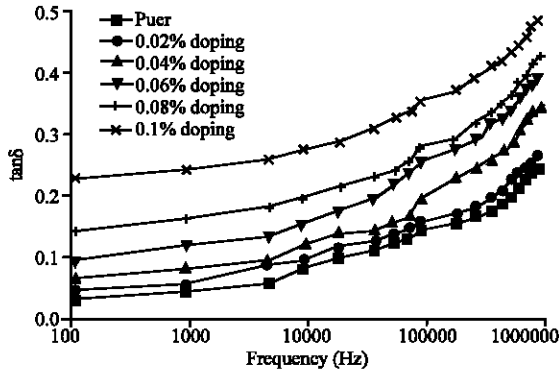


Fig. 6: Wavelength variation of  $\tan\delta$  with frequency for lignin resin with different ratios at 298 K

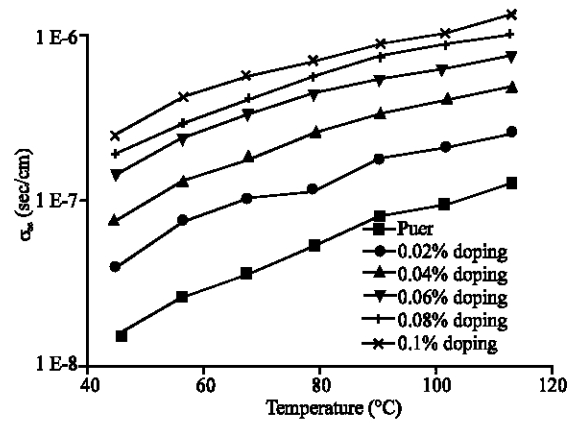


Fig. 8: The variation of ac conductivity  $\sigma_{ac}$  with temperature at 1 kHz for lignin resin with different ratios

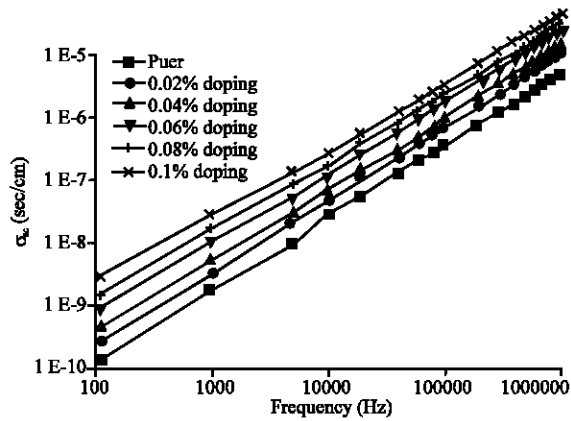


Fig. 7: Variation of conductivity  $\sigma_{ac}$  with frequency for lignin resin with different ratios at 298 K

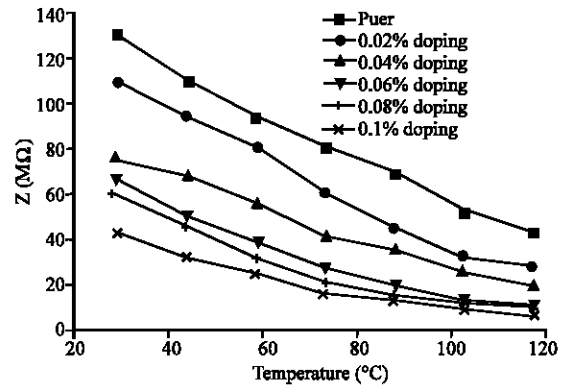


Fig. 9: Variation of impedance  $Z$  with temperature at 1 kHz for lignin resin with different ratios at 298 K

2007). Figure 6 shows the relationship between dissipation factor ( $\tan\delta$ ) and frequency for different ratios of doping at 298 K. It is apparent from figure that  $\tan\delta$  increases with increased frequency for pure lignin resin with doping. The increases in  $\tan\delta$  may be related to a.c conductivity ( $\sigma_{ac}$ ) which depends on the number of charge carrier. This is may be due to the relaxation processes which were influenced by the interfacial polarization effect (Hassan *et al.*, 2007).

Figure 7 and 8 show the variation of  $\sigma_{ac}$  as a function of frequency and temperature for lignin resin with different doping ratios, respectively. It is clear from the figures that the conductivity is found to be high for higher frequencies at a given temperature which confirms small polaron hopping in the present sample (Popielarz *et al.*, 2001) As the frequency of the applied field increases, hopping of charge carriers also increases thereby increasing the conductivity. A similar variation is observed for other temperatures. The ac conductivity is much more sensitive to temperature in the higher

temperature regime than the lower temperature regime. The low temperature ac. conduction can be due to bipolar hopping mechanism whereas the high temperature conduction is due to thermally activated single polaron hopping.

Figure 9 shows the variation of impedance as a function of temperature in the range 303-393 K at a constant frequency 1 kHz for lignin resin 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 90-120°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.

Figure 10 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

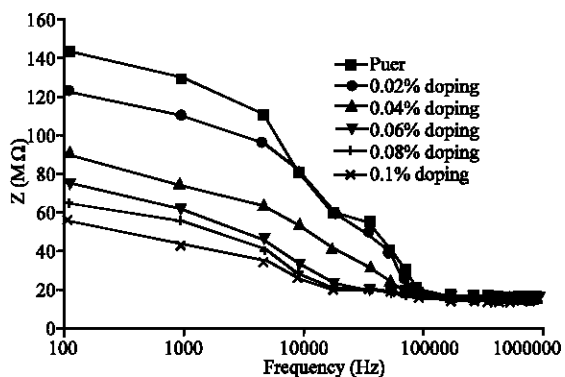


Fig. 10: Variation of impedance  $Z$  with frequency for lignin resin with different ratios at 298 K

impedance with increased frequency. This result can be attributed to the increase in ac electrical conductivity  $\sigma$  ac with increased frequency, therefore,  $Z$  decreases until reaching a fixed and very small value.

### CONCLUSION

Frequency and temperature dependence of dielectric constant  $\epsilon'$ , dielectric loss  $\epsilon''$  and dissipation factor  $\tan\delta$  in doping lignin resin has been investigated in the frequency rang 100 Hz-1 kHz and temperature range 30-120°C. The experimental results indicate that  $\epsilon'$ ,  $\epsilon''$  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  $\epsilon''$  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

Amir, E., P. Antoni, L.M. Campos, D. Damiron and N. Gupta *et al.*, 2012. Electronic Supplementary Material (ESI) for organic and biomolecular Chemistry. R. Soc. Chem. J., 1: 1-31.  
Cheng, K.C., C.M. Lin, S.F. Wang, S.T. Lin and C.F. Yang, 2007. Dielectric properties of epoxy resin-barium Titanate composites at high frequency. Mater. Lett., 61: 757-760.

Friend, R.H., R.W. Gymer, A.B. Holmes, J.H. Burroughes and R.N. Marks *et al.*, 1999. Electroluminescence in conjugated polymers. Nat., 397: 121-128.  
Hassan, J., F.M. Yen, M. Hashim, Z. Abbas and Z.A. Wahab *et al.*, 2007. Dielectric permittivity of nickel ferrites at microwave frequencies 1 MHz to 1.8 GHz. Ionics, 13: 219-222.  
Kim, C.H. and J.S. Shin, 2002. Dielectric relaxation of siloxane-epoxy copolymers. Bull. Korean Chem. Soc., 23: 413-416.  
Kondawar, S.B., A.D. Dahegaonkar, V.A. Tabhane and D.V. Nandanwar, 2014. Thermal and frequency dependence dielectric properties of conducting polymer/fly ash composites. Adv. Mater. Lett., 5: 360-365.  
Kondawar, S.B., S.R. Thakare, V. Khati and S. Bompilwar, 2009. Nanostructure Titania reinforced conducting polymer composites. Intl. J. Mod. Phys. B, 23: 3297-3304.  
Kumari, K., V. Ali, G. Rani, S. Kumar and G.B.V.S. Lakshmi *et al.*, 2011. DC conductivity and spectroscopic characterization of poly (o-Toluidine) doped with binary dopant ZrOCl<sub>2</sub>/AgI. Mater. Sci. Appl., 2: 1049-1057.  
Malutan, T., R. Nicu and V.I. Popa, 2007. Contribution to the study of hydroxymetylation reaction of alkali lignin. BioResources, 3: 13-20.  
Popielarz, R., C.K. Chiang, R. Zozaki and J. Obrzut, 2001. Dielectric properties of polymer/ferroelectric ceramic composites from 100 Hz to 10 GHz. J. Am. Chem. Soc., 34: 5910-5915.  
Saraswathi, R., M. Gerard and B.D. Malhotra, 1999. Characteristics of aqueous polycarbazole batteries. J. Appl. Polym. Sci., 74: 145-150.  
Singh, V., A.R. Kumar and T.R. Ramamohan, 2003. Dielectric properties of Aluminum: Epoxy composites. J. Appl. Sci., 90: 3602-3608.  
Ungureanu, E., O. Ungureanu, A.M. Capraru and V.I. Popa, 2009. Chemical modification and characterization of straw lignin. Cellul. Chem. Technol., 43: 263-269.  
Vogel, A.I., 1961. A Text Book of Quantitative Organic Analysis. 3rd Edn., Longman Publisher, London, England, UK., Pages: 392.