

EFFECT OF TEMPERATURE AND DOPING RATIOS ON ELECTRICAL CONDUCTIVITY OF LIGNIN RESIN WITH RHODAMINE B

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ABSTRACT: *Electrical conductivity of lignin resin films doped with different ratios of Rhodamine B (0.01, 0.04, 0.06, 0.08, 0.1)% wt, were studied. The composite films prepared using casting method. The result showed that the conductivity increased with increasing temperature and doping ratios. The values of activation energy decreased with increasing temperature and doping ratios of dyes.*

KEYWORDS: Lignin Resin, DC Conductivity, Rhodamine B, Activation Energy.

INTRODUCTION

Conducting polymer is one of the most promising functional materials. Many scientists have extensively investigated its synthesis and applications. Due to high electrical conductivity of conducting polymers, they have attracted lots of research interest and become popular basic materials for advanced applications such as plastic batteries, light emitting diodes, EMI shields, electro chromic displays devices, gas separation membranes, smart windows and sensors [1-3].

Lignin is a macromolecular compound, much more active than cellulose or other natural polymers, due to the functional groups contained in its macromolecule [4,5]. 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 [6-10].

EXPERIMENT

Materials

The materials tested in this study were liginosulfonate, hydrochloric acid, formaldehyde, sodium hydroxide, sodium bicarbonate, phosphoric acid, ethanol amine, dimethyl formamide, propanol and Rhodamine B.

Modification method of liginosulfonate

A mixture of liginosulfonate (5gm) and hydrochloric acid (%57 ,v/v), then the reaction mixture was heated under reflux for (3hr). after that the reaction mixture is allowed to cooled .the solid

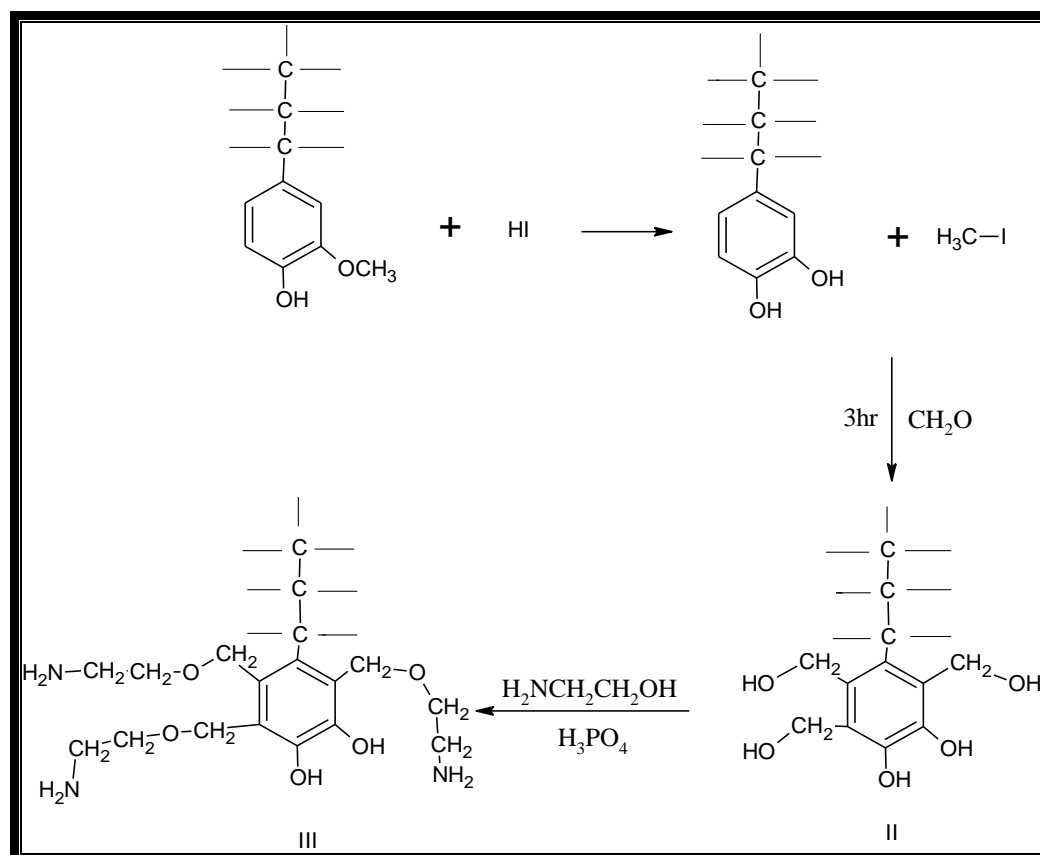
precipitate obtained was filtered, washed for many times with Deion's water dried in the oven at 60°C [11].

Synthesis of lignosulfonate formaldehyde Resin II

Modify lignosulfonate (10gm) was added to (15ml) 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 (60ml) and sodium bicarbonate (1.6gm) was added, the reaction mixture was heated with stirring at 65°C for 3hr, then the reaction mixture was cooled, neutralized by % 10 H₃PO₄ to PH 7, excess solvent was distilled off, the result mixture was dried by heating under vacuum pressure for 24 hr at 40°C [12].

Synthesis of amino resin III.

Shipping or distribution the reaction flask by ethanol amine (1mole) and phosphoric acid (1ml), the reaction mixture was heated to 50°C then solution of resin(II) (10gm) 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 hr. 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 hr [13].



Scheme (1): Preparation of lignin resin.

Doping of Lignin

Doping lignin resin with dye Rhodamine B 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, 0.04, 0.06, 0.08 and 0.1) g wt% of doping reagent Rhodamine B [14]. The mixture was stirred well for 15 minutes to guarantee that the homogenous distribution of dye in the polymer matrix.

Characterization and measurements

The electrical measurements for the already prepared samples as Al/polymer/Al were performed by two point probe method. Electrical conductivity measurements were carried out by using Keithley 2400 instrument in different temperatures (30-120) °C for lignin resin with different weight ratios of Rhodamine B.

RESULTS AND DISCUSSION

Figures (1) - (6) show the relationship between current-voltage characteristics of lignin resin films with different ratios at the temperature range (303-393) K. Ohmic behavior was noticed at low voltage of less than 10V at all ratios. This can be explained by the fact that there is a negligible injection of charge carriers from the aluminum electrode to the polymer film, because the thermally generated charge carriers are greater than the injected charge from electrodes [15]. The current increases with increasing temperature and the applied voltage is identical to the characteristics of semiconductor materials.

When temperature increases, more localized electrons have the energy to bridge the gap and the system becomes more ordered, then decreasing amount of localized states present allowing for more mobile of charge carriers [16]. On other hand, the molecular structure of the polymer greatly influences the charge carriers mobility according to the (I-V) characteristics. Namely, lignin resin do not has side chain that lead to higher charge carriers mobility compared to the polymers with long side chains [17].

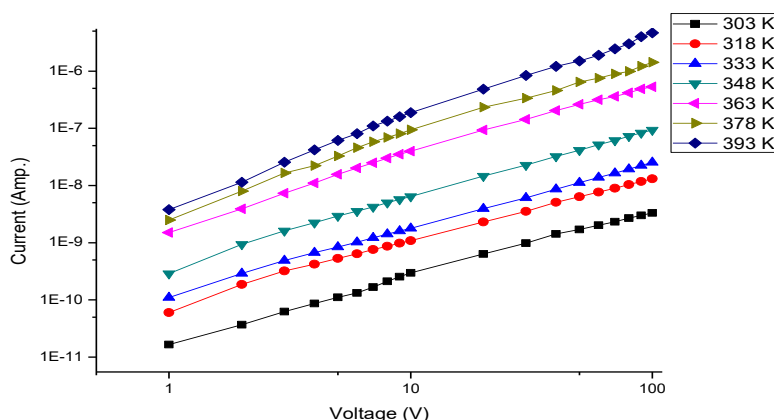


Figure (1): (I-V) Characteristics at different temperatures for pure lignin resin.

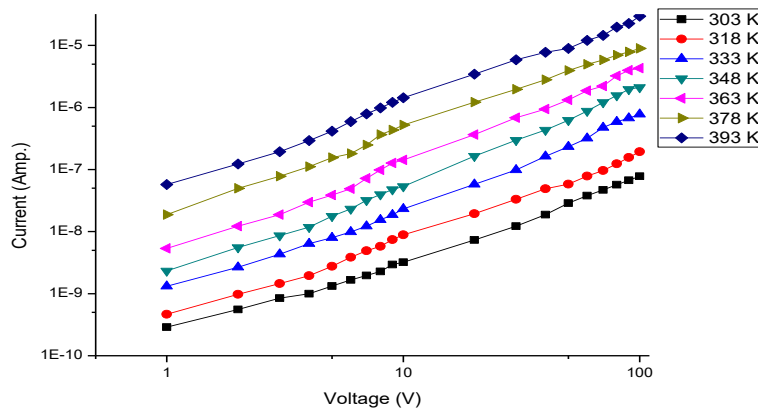


Figure (2): (I-V) Characteristics at different temperatures for weight ratio (0.01%) of doping lignin resin .

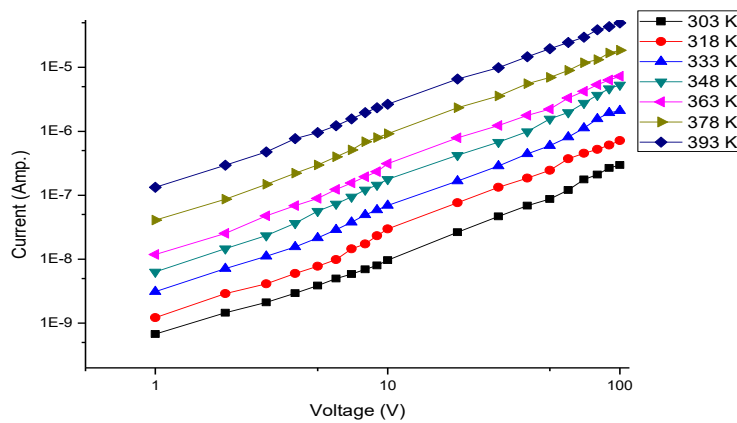


Figure (3): (I-V) Characteristics at different temperatures for weight ratio (0.04%) of doping lignin resin .

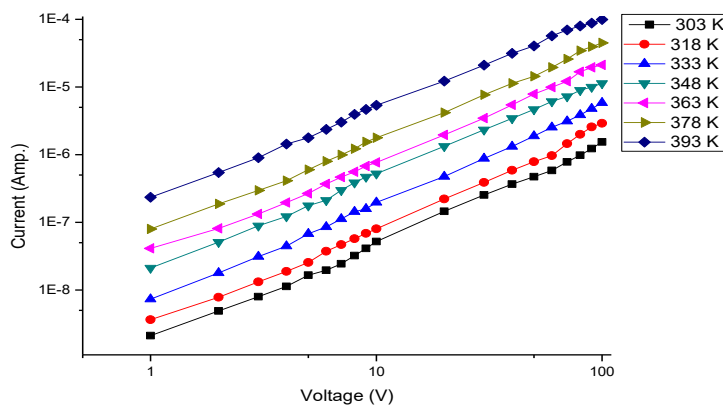


Figure (4): (I-V) Characteristics at different temperatures for weight ratio (0.06%) of doping lignin resin.

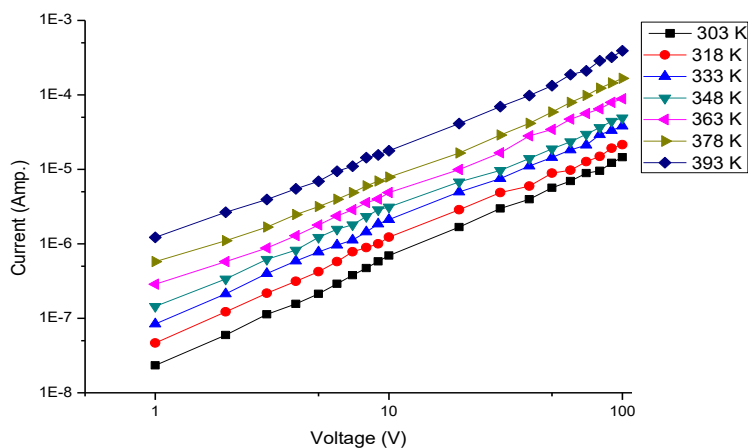


Figure (5): (I-V) Characteristics at different temperatures for weight ratio (0.08%) of doping lignin resin .

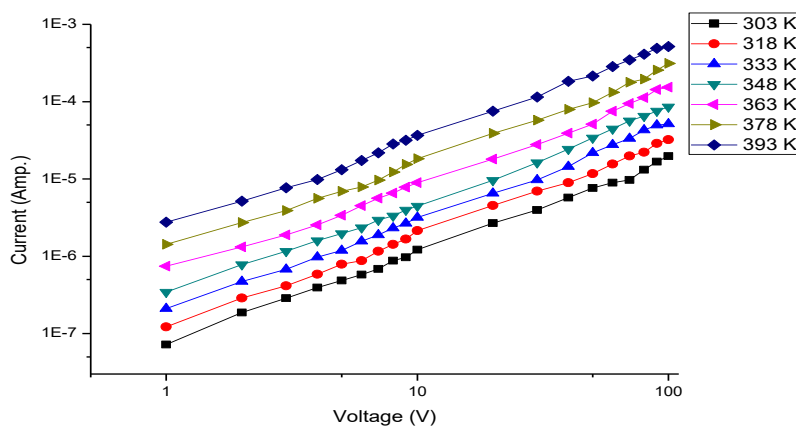


Figure (6): (I-V) Characteristics at different temperatures for weight ratio (0.1%) of doping lignin resin .

Figure (7) shows the effect of doping ratio with Rhodamine B enhanced electrical conductivity in this order: (pure < 0.01 < 0.04 < 0.06 < 0.08 < 0.1) % wt. This is due to electrostatic interaction in emulsion and powder between laser dye and lignin resin, and the small amount of dye which make it diffuse within the matrix of lignin resin.

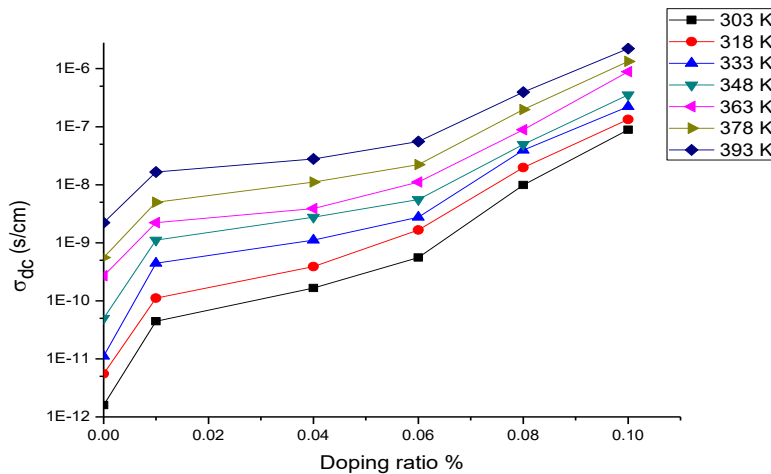


Figure (7): The relationship between σ_{dc} and weight ratio of doping lignin resin at different temperatures.

Figure (8) shows the relation between effect of temperature and dc conductivity for lignin resin with doping ratios. The σ_{dc} increases with increased temperature from (30-120) °C and that was because of the increasing charge carrier in conduction band, this indicating semiconductor-like behavior, which is fit to the following Arrhenius exponential equation [18]

$$\ln \sigma_{dc} = \ln \sigma_0 - E_a/kT \quad (1)$$

The sharp increase of dc conductivity between 363 K to 393 K can be related to segmental motion as a result of increasing temperature. However, the electrical conductivity increases linearly beyond 363 K as exactly detected for another system [18].

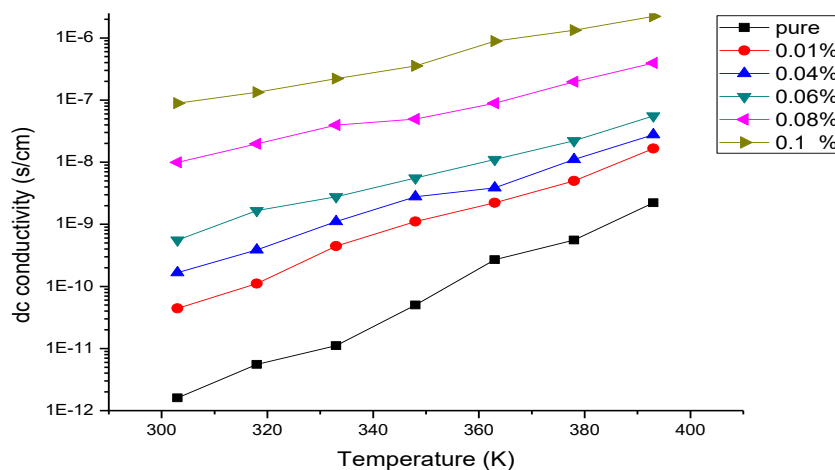


Figure (8): DC conductivity for doping lignin resin with different temperatures.

Figure (9) shows the relation between $\ln \sigma$ and $1/KT$ (eV) (equation 1) from where activation energy of lignin resin with different ratios of doping can be calculated from the slope of the

straight line. It was found that the values of activation energy decrease with the increase of the ratios of doping for all ratios.

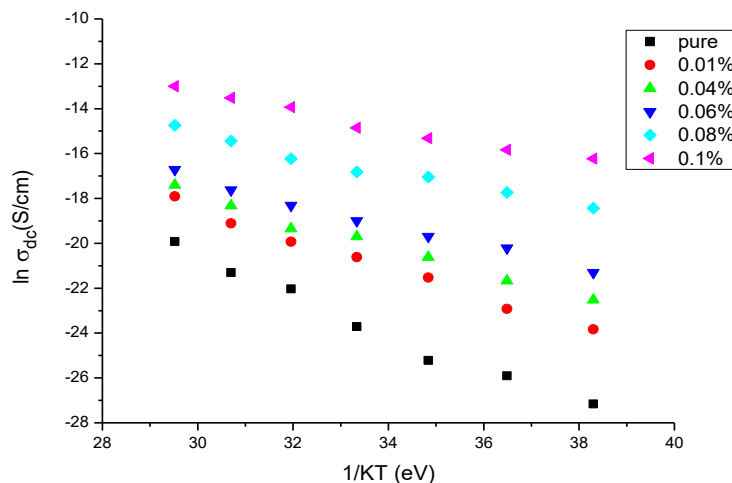


Figure (9):The relationship between $\ln \sigma_{dc}$ and $1/kT$ for lignin resin with different ratio.

The results of activation energies E_a and R^2 and their standard deviations are listed in the Table (1).

Table 1. Activation energies, R^2 and S.E values for doping lignin film with different doping ratio.

Doping ratio %	E_a	R^2	S.E
0.00	0.82	0.980	0.049
0.01	0.65	0.984	0.041
0.04	0.56	0.989	0.032
0.06	0.49	0.993	0.027
0.08	0.40	0.997	0.025
0.10	0.38	0.999	0.023

CONCLUSION

Temperature dependence of conductivity of doped lignin resin with different ratios of dye suggests a transition from insulator nature to semiconductor nature with increase in temperature. The conductivity is increase with increasing the ratio of Rhodamine B as the temperature increase the conductivity is increase too in a behavior similar to the semiconducting materials.

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