



Thermal degradation and electrical conductivity measurement study of resin derived from salicylic acid, hexamethylenediamine and formaldehyde

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ABSTRACT

The resin SHMF has been synthesized by the condensation of salicylic acid and hexamethylenediamine with formaldehyde and hydrochloric acid as catalyst. Thermal degradation curve has been discussed which shows four decomposition steps and detailed thermal degradation studies of the resin have been carried out to ascertain its thermal stability. Sharp–Wentworth and Freeman–Carroll methods have been used to calculate activation energies and thermal stability. The activation energy (E_a) calculated by using the Sharp–Wentworth (17.86 kJ/mol) has been found to be in good agreement with that calculated by Freeman–Carroll (18.96 kJ/mol) method. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*) and frequency factor (Z) have also been evaluated on the basis of the data of Freeman–Carroll method. The order of reaction (n) is found out to be 0.99. Electrical conductivity measurements have been also conducted to ascertain the semiconducting nature of the resin.

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Introduction

The resins offer novelty and versatility; hence they occupy the pivotal position in the field of material science. The progress in the field resins has been extremely rapid, as they generally useful in packaging, adhesives and coatings in electrical sensors and organometallic semiconductors [1-4]. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, protective adhesives, aerospace industries etc. because of their high thermal stability, heat and chemical resistance and electrical insulation properties [5-7]. Various researchers have been studied the applications of resins of substituted phenols and formaldehyde [8-10]. 2-Hydroxyacetophenone and its substituted derivatives have been condensed with formaldehyde to produce heat and light stabilizers. Resins of salicylic acid, thiourea with trioxane and p-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature [11-14]. Manavalan and Patel [15] synthesized resins of salicylic acid, urea and formaldehyde and also studied the various properties of resins.

Semiconductors are the most important ingredients of modern electronics. The concerted research effort was carried out to aim at developing an organic material that would possess the good electrical properties as the inorganic semiconductors. In the early days the prime attention was placed on the synthesis of highly conductive polymers, preferably of high molecular weight and the measurement of their electronic conductivity properties i.e. conductivity, mobility, thermoelectronic power, etc. The resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low [16-18]. Kand a et al reported the rubeanato –copper semiconductive polymers and studied their AC and DC conductivity [19]. Dhawan and coworkers reported the conducting polymers predicted to be the futuristic materials for

the development of light emitting diodes, antistatic and EMI materials, sensors, opto- electronic devices and rechargeable batteries due to their unique conduction mechanism and greater environmental stability [20].

In our laboratory we study on the synthesis of materials for high thermal stability and electrical conductivity measurements of resins derived from salicylic acid / p-hydroxybenzoic acid, diamide / urea / thiourea with formaldehyde [6,7, 12-14,21-24]. Our previous paper [21] describes the synthesis and characterization of SHMF resin. The present communication deals with thermal degradation and electrical conductivity properties of a newly synthesized resin derived from salicylic acid, hexamethylenediamine and formaldehyde.

Methods for the estimation of kinetic parameters from thermo gravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible. After treating the thermal degradation data with Sharp–Wentworth (SW) and Freeman–Carroll (FC) methods, activation energy and kinetic parameters such as ΔF , ΔS , Z , S^* and n (order of reaction) have been evaluated [25-27]. For the electrical conductivity measurement study the DC resistivity of the SHMF resin have been measured by applying a constant voltage (50 volts) across the pellets. The temperature dependence of the electrical conductivity of the resin has been plotted. The energy of activation (E_a) of electrical conduction is calculated from the slope of the plots. Electrical conductivity of the resin has been studied with increase in temperature.

Experimental

Chemicals

All Chemicals were AR grade. Salicylic acid, hexamethylenediamine and formaldehyde were purchased from

$$\rho = R \cdot x A/l$$

Where, R= resistance of the pellet.

A = Surface area of pellets and

l = Thickness of pellet.

The DC resistivities were measured from 313 to 423 K. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the well-known relationship.

$$\sigma = \sigma_0 \exp^{-E_a/kT}$$

Where, σ = electrical conductivity at room temperature (T)

σ_0 = electrical conductivity at temperature constant

E_a = Activation energy of electrical conduction.

K = Boltzmann constant ($1.3817 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$)

T = Absolute temperature

The relationship has been modified as

$$\text{Log } \sigma = \text{log } \sigma_0 + -E_a/2.303kT$$

According to this relation, a plot of Log σ Vs $1/T$ would be linear with negative slope. From the Slope of the plots, the activation energy was calculated [16-20, 31].

Results and discussion

Thermal Degradation Study for SHMF Resin

The thermal degradation curve for SHMF resin is shown in Figure 1 exhibits four-stage decomposition and its ranges are given in Table 1. The first stage decomposition which was slow and ranged from 40-160 °C corresponding to loss 6.3% which may have been due to entrapped H₂O molecule. The second stage decomposition represents degradation of side chain attached to aromatic nucleus. [Observed 57.9% against calculated 57.6%]. The third stage decomposition at 240-420 °C which may be due to the loss of phenolic -OH and -COOH groups [observed 64.9% and calculated 65.54%]. The fourth stage decomposition is probably total decomposition of resin. The Half Decomposition temperature for SHMF resin is found to be 225°C.

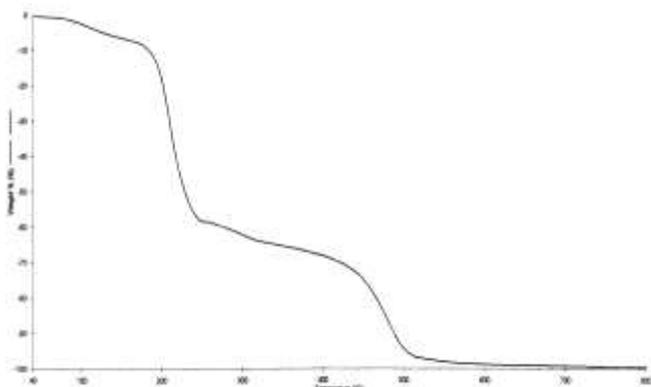


Fig.1: Thermogram of SHMF resin

A representative thermal activation energy plot [Figure -2] and Freeman-Carroll plot [Figure -3] for the polymer has been shown. By using thermal decomposition data and then applying the Sharp-Wentworth method [shown in Figure - 4] activation energy has been calculated which is in agreement with the activation energy calculated by Freeman-Carroll method. The thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are incorporated in [Table - 2].

Due to abnormally low value of frequency factor [Z] it may be classified as a slow reaction and no other obvious reason can be given. The value of entropy [ΔS] indicates that the activated polymer has more ordered structure than the reactants and the reaction are slower than normal. This is further supported by low Z values [22- 24, 28, 29]. It is very difficult to draw any unique

conclusion from the magnitude of thermal activation energy [E_a] as decomposition mechanism is expected to be complicated. Positive values of activation energy under present investigation correspond to the energy of activation due oxidation-reduction process of resin in the higher temperature range [22- 24, 28, 29].

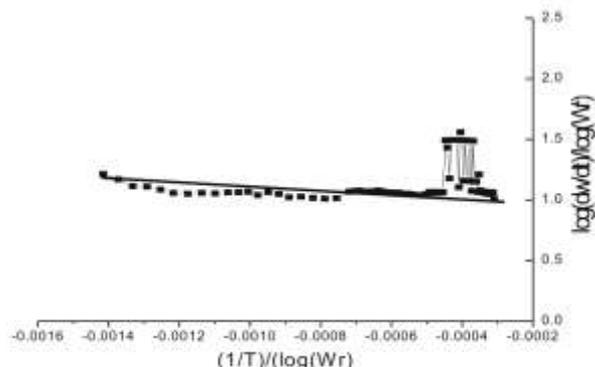


Fig .2: Thermal Activation Energy Plot of SHMF Resin

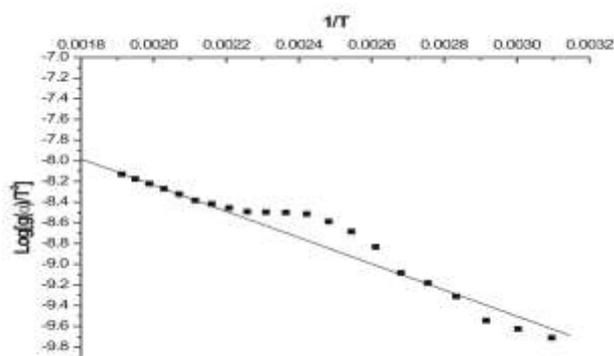


Fig .3: Freeman – Carroll Plot of SHMF Resin

Fairly straight line plots are obtained using the two methods. However, using the Freeman- Carroll method some abnormal points were ignored to get a clear picture about most of the points. Similarly, in the Sharp- Wentworth method, some points at the beginning or the end did not fall on straight line. This is expected, since, the decomposition of resin is not obeying first order kinetics perfectly. These observations are in harmony with the findings of Jacobs and Tompkin and other earlier workers [30].

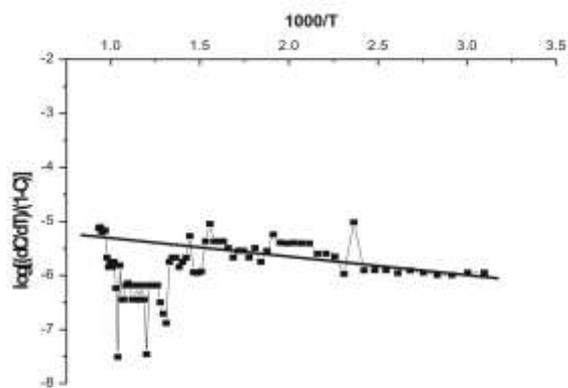


Fig .4: Sharp-Wentworth Plot of SHMF Resin
Electrical Conductivity for SHMF Resin

The results of electrical conductivity and activation energy are incorporated in Table 3. The temperature dependence of the electrical conductivity of the resin has been mentioned in

Figure.5. The electrical conduction of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation, atmosphere etc; activation energy (E_a) is not affected by these parameters and, therefore, it is fairly reproducible [31-35]. The magnitude of activation energy depends on the number of electrons present in semiconductor materials. The more the number of π – electrons lowers the magnitude of activation energy and vice versa. Generally polymers containing aromatic nuclei in the backbone exhibit lower activation energy than those with aliphatic system. Thus, the low magnitude of activation energy may be due to the presence of large number of π -electrons in the polymer chain. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation [16-20, 31-35].

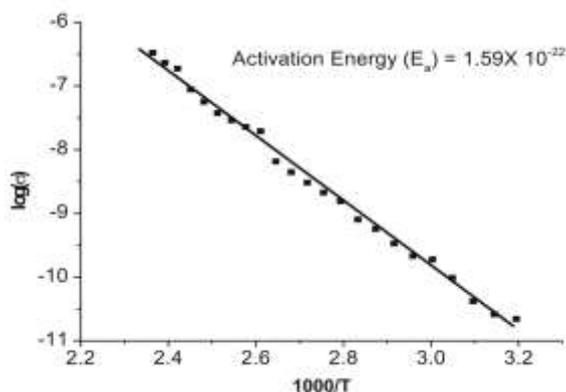


Fig.5: Electrical Conductivity Plot of SHMF Resin

The carrier motilities of the organic semiconductors might decrease due to:

- The forces between the adjacent molecules are relatively weak as organic compounds from molecular crystals.
- Due to little electronic coupling that exists between the adjacent molecules, it becomes difficult for the electrons to jump from one molecule to other.
- As a consequence of the disordered structure which is due to amorphous nature, the electrons get scattered while traveling through the materials, when they try to flow through it and hence lowers the conductivity.

The study shows following results of electrical conductivity-

- The electrical conductivity of SHMF resin lies in the range of 2.29×10^{-11} to 2.36×10^{-7} Siemen.
- The plots of $\log \sigma$ versus $1/T$ is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma_0 \exp(\Delta E/kT)$ is obeyed.
- The energy of activation (E_a) of electrical conduction calculated from the slopes of the plots is found to be in the range of 1.59×10^{-22} J/K.

These observations and results are in harmony with the findings of other earlier workers [16-20, 34, 35]

Conclusion

Thermogram of the resin depicts four stages of decomposition. The observed weight loss is little higher than the calculated. This may be due to the degradation of side chain of resin. Activation energy by both Sharp-Wentworth and Freeman-Carroll method are in good agreement with each other. Low value of frequency factor [Z] it may be concluded that the reaction of decomposition of resin can be classified as a slow reaction. The negative values for entropy indicate that the

activated polymer has more ordered structure than the reactants which are further supported by low Z value. The decomposition of resin is following first order kinetics although not perfectly.

Electrical conductivity of this resin increases with increase in temperature which is the important property essential for the resin may be ranked as semiconductors. Hence, this new polymer may be semiconducting in nature.

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Table1: Thermoanalytical data and decomposition temperature of SHMF resin

Terpolymer	Temperature Range (°C)	Stage of Decomposition	Species Degraded	% Weight loss	
				Observed	Calculated
SHMF	40-160	First	Loss of entrapped - H ₂ O molecule	6.3	6.1
	160-240	Second	Loss of side chain attached to aromatic nucleus and -COOH group.	64.2	64.5
	240-420	Third	Loss of phenolic -OH group.	70.0	70.2
	420-800	Fourth	Complete decomposition	100	100

Table2: Result of thermogravimetric analysis of SHMF resin

Decomposition Temp. (T)	Half Decomposition Temp. (T*)	Activation Energy kJ/mole		Kinetic parameters by FC				
		Freeman-Carroll FC	Sharp-Wentworth SW	Entropy change ΔS(J)	Free energy change ΔF(kJ)	frequency factor Z (S ⁻¹)	Apparent entropy S*(J)	n
220	225	18.96	17.86	7.9	17.18	2089.296	-22.0411	0.99

Table 3: Evaluation of Activation Energy of Conduction SHMF Resin

Diameter of the pellet = 1.289

Surface area of the pellet (A) = $\pi r^2 = 3.142 \times (0.645)^2 = 1.305 \text{ cm}^2$

Thickness of pellet (l) = 0.191 cm.

A/l = 6.832 cm.

Temp (K)	1000/T (K ⁻¹)	Resistance in Ohm 'R'	Resistivity $\rho = RA/l$ (Ohm.cm)	Electrical Conductivity $\sigma = 1/\rho$ (Siemen.cm ⁻¹)	Log σ
313	3.1949	6.38 X 10 ⁹	4.36 X 10 ¹⁰	2.29 X 10 ⁻¹¹	-10.6394
318	3.1447	4.56 X 10 ⁹	3.12 X 10 ¹⁰	3.21 X 10 ⁻¹¹	-10.4935
323	3.0960	2.81 X 10 ⁹	1.92 X 10 ¹⁰	5.21 X 10 ⁻¹¹	-10.2833
328	3.0488	1.24 X 10 ⁹	8.47 X 10 ⁹	1.18 X 10 ⁻¹⁰	-9.9280
333	3.0030	8.67 X 10 ⁸	5.92 X 10 ⁹	1.69 X 10 ⁻¹⁰	-9.7726
338	2.9586	6.86 X 10 ⁸	4.69 X 10 ⁹	2.13 X 10 ⁻¹⁰	-9.6709
343	2.9155	4.41 X 10 ⁸	3.01 X 10 ⁹	3.32 X 10 ⁻¹⁰	-9.4790
348	2.8736	1.73 X 10 ⁸	1.18 X 10 ⁹	8.46 X 10 ⁻¹⁰	-9.0726
353	2.8329	1.81 X 10 ⁸	1.24 X 10 ⁹	8.09 X 10 ⁻¹⁰	-9.0923
358	2.7933	8.71 X 10 ⁷	5.95 X 10 ⁸	1.68 X 10 ⁻⁹	-8.7746
363	2.7548	6.03 X 10 ⁷	4.12 X 10 ⁸	2.43 X 10 ⁻⁹	-8.6149
368	2.7174	4.94 X 10 ⁷	3.38 X 10 ⁸	2.96 X 10 ⁻⁹	-8.5283
373	2.6810	3.61 X 10 ⁷	2.47 X 10 ⁸	4.05 X 10 ⁻⁹	-8.3921
378	2.6455	2.53 X 10 ⁷	1.73 X 10 ⁸	5.78 X 10 ⁻⁹	-8.2377
383	2.6110	1.49 X 10 ⁷	1.02 X 10 ⁸	9.82 X 10 ⁻⁹	-8.0078
388	2.5773	9.01 X 10 ⁶	6.16 X 10 ⁷	1.62 X 10 ⁻⁸	-7.7893
393	2.5445	7.46 X 10 ⁶	5.10 X 10 ⁷	1.96 X 10 ⁻⁸	-7.7073
398	2.5126	5.66 X 10 ⁶	3.87 X 10 ⁷	2.59 X 10 ⁻⁸	-7.5874
403	2.4814	3.30 X 10 ⁶	2.25 X 10 ⁷	4.44 X 10 ⁻⁸	-7.3531
408	2.4510	2.14 X 10 ⁶	1.46 X 10 ⁷	6.84 X 10 ⁻⁸	-7.1650
413	2.4213	1.21 X 10 ⁶	8.27 X 10 ⁶	1.21 X 10 ⁻⁷	-6.9174
418	2.3923	8.14 X 10 ⁵	5.56 X 10 ⁶	1.80 X 10 ⁻⁷	-6.7452
423	2.3641	6.21 X 10 ⁵	4.24 X 10 ⁶	2.36 X 10 ⁻⁷	-6.6277