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Thermal Behaviour of Newly Synthesized Copolymer Derived from Salicylic acid, and Thiosemicarbazide

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ABSTRACT

The Copolymer (SATF) was synthesized by condensation of salicylic acid and thiosemicarbazide with formaldehyde in the presence of 2M HCL as a catalyst at 126 ± 2 ^{0}C for 5 hrs. with molar proportion of reactants. The copolymer (SATF) was characterized by elemental analysis, FT-IR, UV-Visible ^{1}H-NMR Spectroscopy. The thermal decomposition behavior of SATF copolymer was studied by using TGA in static nitrogen atmosphere at a heating rate of 10^{0}C/min. Freeman Carroll and Sharp-Wentworth methods were used to calculate the thermal activation energy(Ea), the order of reaction(n), entropy Change (ΔS), free energy change (ΔF), apperent entropy change (ΔS), and frequency factor (Z). The order of decomposition reaction was found to be 0.9. The thermal activation energy determined with the help of these method was in good agreement with each other.

Keywords: Thermogravimetric analysis; Decomposition, Condensation, resins, Synthesis, Sharp-Wentworth , Freeman-Carroll

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INTRODUCTION

Thermal analysis plays a vital role in studying the structure and properties of any material . Thermogravimetric analysis has been widely used to investigate the decomposition characteristics of polymeric matter . Copolymers can be used as high energy material, ion-exchanger, semiconductors, antioxidants, fire proofing agent, optical storage data, binders, molding materials *etc*. [1, 3]. Copolymers were applied in various fields of research as ion-exchangers, high thermal resistance materials, and electrical appliances [3, 4]. The study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Copolymer resins are derived from 2,4-dihydroxypropiophenone, biuret and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [5,6]. Thermal degradation of *m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol has been studied by Dash *et al*. [7] and 2-hydroxyacetophenone, oxamide and formaldehyde [8]. S. L. Oswal *et al* synthesized and studied thermal properties of copoly(maleimidemethylmethacrylate), terpoly(maleimidemethylmethacrylate- acrylicacid) and terpoly(maleimide-methylmethacrylatemethyl-acrylic acid). The thermal behaviour was studied by TG and DSC techniques [9]. Various researchers have been studied the applications of terpolymer resins of substituted phenols and formaldehyde[10]. Terpolymers of salicylic acid, thiourea with trioxane and *p*-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature[10-14]. Resins synthesized by condensation of mixtures of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [15]. The metal ion uptake capacity increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid . *o*-Nitrophenol and thiourea with paraformaldehyde terpolymer was identified as an excellent cation exchanger for Zn2+ and Co2+ ions [16]. Salicylic acid/formaldehyde /resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixtures .

The present paper describes thermal analysis of the newly synthesized resin of salicylic acid, thiosemicarbazide with formaldehyde (F), by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation (*Ea*), thermodynamic parameters viz. *Z*, Δ*S*, Δ*F*, *S**, and order of reaction/(*n*) were determined by applying Freeman-Carroll Method [17-19].

MATERIALS AND METHODS

The entire chemical used in the synthesis of various new copolymer resins were procured from the market and were analar or Fluka or chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, reprecipitation and crystallization which are generally used for the analytical purification purpose.

Synthesis of SATF copolymer resins:

The new copolymer resin SATF was synthesized by condensing salicylic acid (0.1 mol) and thiosemicarbazide (0.1 mol) with formaldehyde (0.2 mol) in a mol ratio of 1:1:2 in the presence of 2 M 200 ml HCl as a catalyst at 126 ^{0} C ± 2 ^{0} C for 5h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove salicylic acid- thiosemicarbazide formaldehyde copolymer which might be present along with SATF copolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of SATF is shown in Fig. 1.

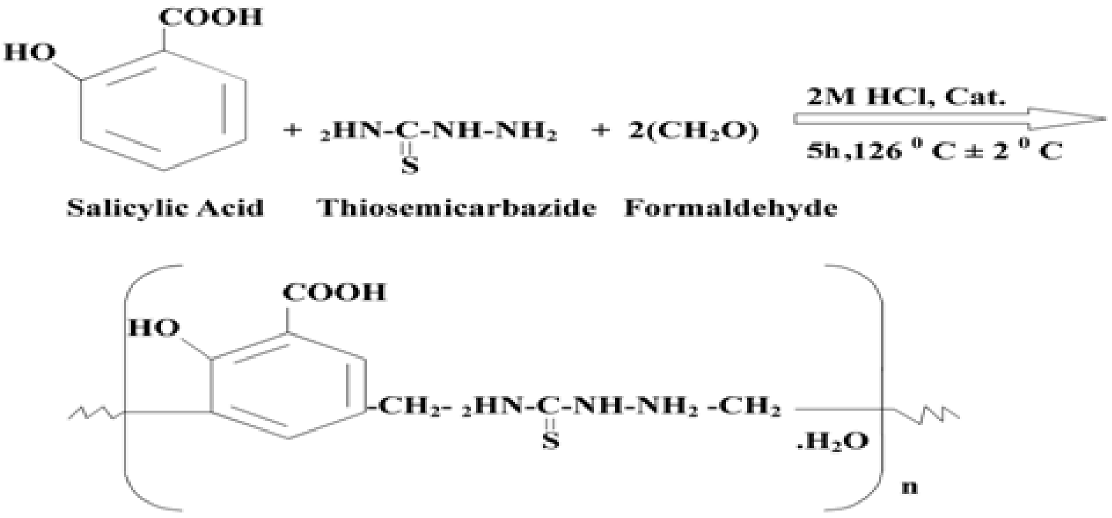

Fig.1: Synthesis of SATF copolymer resin.

The copolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample

SATF thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the copolymer resin was found to be 78 %.

RESULTS AND DISCUSSION

The newly synthesized purified SATF copolymer resin was found to be yellow in color. The copolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents.

FT-IR Spectra :
A broad band appeared in the region 2800-3200cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding . The sharp band displayed at 1600-1400 cm^{-1} may be due to the stretching vibrations of carbonyl group (C=O) of both as well as (C=S) moiety . The presence of -NH in thiosemicarbazide moiety may be assigned due to sharp band at 2800-3000 cm^{-1} . A strong sharp peak at 1625-1500 cm^{-1} may be ascribed to aromatic skeletal ring . The bands obtained at 1400 – 1200 cm^{-1} suggest the presence of methylene bridges in the polymer chain. The weak band appearing at 726 - 760 cm^{-1} is assigned to C – OH bond. 1,2,4,6 tetrasubstitution of aromatic ring is recognized from the bands appearing at 905, 1083, 1201, and 1292cm^{-1} respectively .

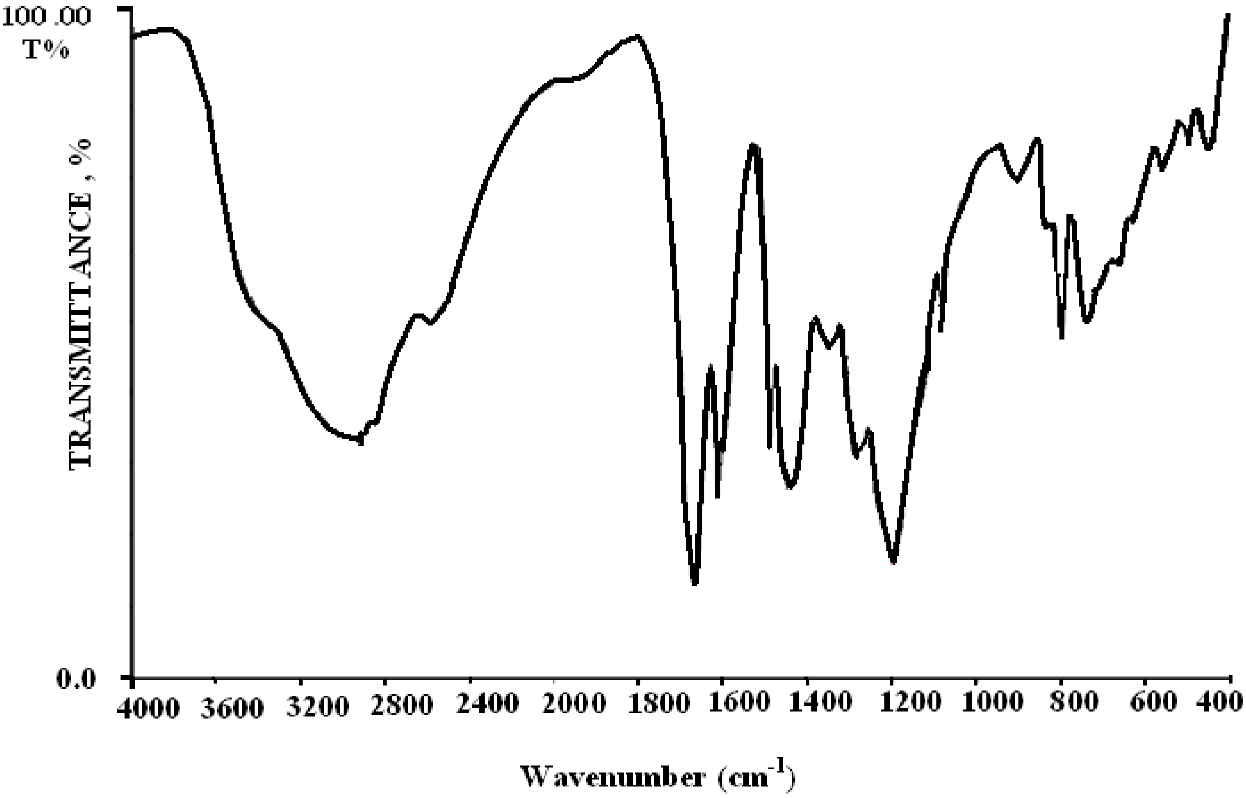

Fig.2: FT-IR Spectra of SATF copolymer

NMR Spectra:
Weak signal in the range of 8.00 to 9.0 (δ) ppm is attributed to phenolic -OH proton. The NMR spectra of SATF copolymer resins show a weak multiplate signal (unsymmetrical pattern) in the region 6.2 to 7.0 (δ) ppm which is due aromatic protons. A medium singlet peak appeared at 3.5 – 4.0 (δ) ppm may be assigned to methyl protons of Ar-CH$_2$-NH group. Intense signal appeared in the region 2 – 3 (δ) ppm may be due to Ar–CH$_2$-NH .Triplet signal appeared in the region 3.42 – 4.84 (δ) ppm can be assigned to amido proton of –CH$_2$-NH-CO- linkage.

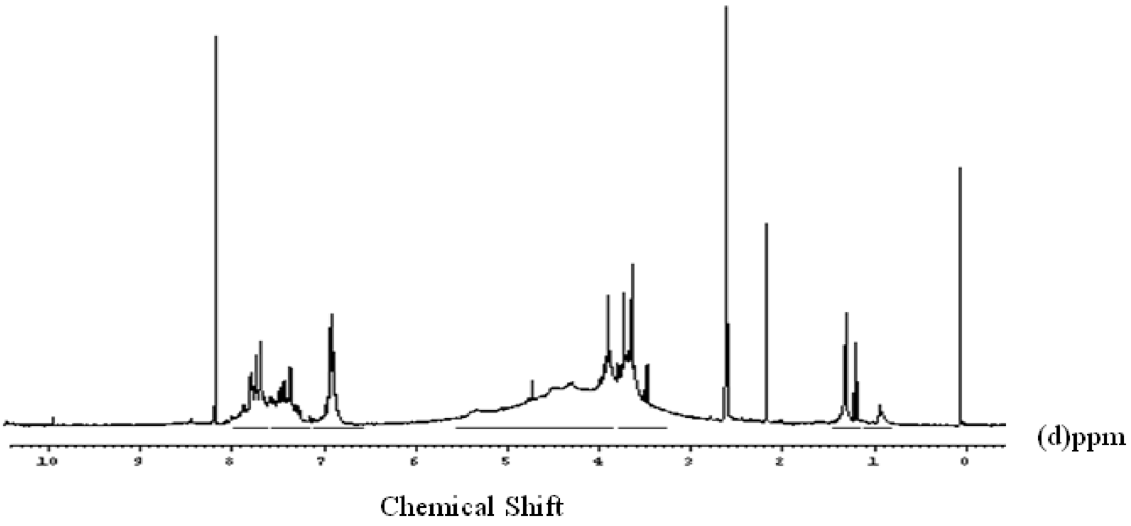

Fig.3: NMR Spectra of SATF copolymer

Thermogravimetry

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10 ^{0}C.min^{-1} from temperature range of 40 ^{0}C to 700 ^{0}C and thermograms are recorded *at SICART*, Vallabh vidyanagar, Gujrat. With the help of thermogravimetric data the thermal activation energies (Ea) and order of reaction (n) calculated. Also other thermodynamic parameters such as entropy change (DS), apparent entropy change (S*) and frequency factor (Z) are determined and reported in the Table . To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth and Freeman-Carroll.

Sharp -Wentworth method:

Using the equation derived by Sharp and Wentworth [1],

$$\log [(dc/dT)/ (1-c)] = \log (A/\beta) - [Ea/2.303R].\ 1/T \ldots\ldots\ldots\ldots..(1)$$

Where,

dc/dT = rate of change of fraction of weight with change in temperature

β = linear heating rate *dT/dt.*

By plotting the graph between (log dc/dt)/ (1-c) vs 1/T we obtained the straight line which give energy of activation (*Ea) from its slope. Where β is the conversion at time t, R is the gas constant* (8.314 Jmol-1K-1) and *T is the absolute temperature. The plots (figure 2) give the activation* energies at different stages of degradation reaction take place.

Freeman-Carroll method:

The straight-line equation derived by Freeman and Carroll , which is in the form of n

$$[\Delta\log (dw / dt)] / \Delta \log Wr = (-E / 2.303R) . \Delta (1/ T) / \Delta \log Wr + n \text{-----------------}(1)$$

Where,

dw/dt = rate of change of weight with time.

Wr = Wc-W

Wc = weight loss at completion of reaction.

W = fraction of weight loss at time t.

Ea = energy of activation.

n = order of reaction.

The plot between the terms [Δ log (dw/dt)] / Δ log Wr Vs Δ (1/T) / Δ log Wr gives a straight line from which slope we obtained energy of activation (*Ea) and intercept on Y-axis as order of* reaction (*n). The change in entropy (S), frequency factor (z), apparent entropy (S*) can also be* calculated by further calculations

(i) Entopy Change:

Intercept = [log KR/hϕE] + S / 2.303 R ------------------- (2)

Where,
K = 1.3806 x 10-16 erg/deg/mole, R = 1.987 Cal/deg/mole
h = 6.625 x 10-27 erg sec. , ϕ = 0.166
S = Change in entropy, E = Activation energy from graph.

(ii) Free Energy Change:

ΔF = ΔH – TΔS ______________________________(3)

H = Enthalpy Change = activation energy
T = Temperature in K
S = Entropy change from (i) used.

(iii) Frequency Factor:

Bn= Log ZEa / ϕR ----------------------------------(4)

B1 = log [ln 1 /1-α] – log P (x) -------------------(5)

Z = frequency factor
B = calculated from equation (5)
Log P(x) = calculated from Doyle's table corresponding to activation energy.

(iv) Apparent Entropy Change:

S* = 2.303 log Zh / KT* ------------------------- (6)

Z = from relation (4)
T* = temperature at which half of the compound is decomposed from it total loss.

Thermo-analytical data:
A plot of percentage mass loss versus temperature is shown in the Fig. 4 for a representative SATF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll adopted. The thermal stability of copolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined for different stages. The 'average *Ea' calculated by Freeman-Carroll (22.97 KJ/mole) and 'average Ea' by Sharp*- Wentworth (22.14 KJ/mole) is nearly same.

Table. 1: Results of Thermogravimetric Analysis of SATF copolymer

Coplymer	Half Decomposition Temp.T*K	Activation Energy (kJ/mol)	
		F.C	S.W
SATF	551	22.97	22.14

FC = Freeman-Carroll, SW = Sharp-Wentworth

Table.2: Kinetic Parameters of SATF copolymer

Coplymers	**Entropy Change -ΔS(J)**	***Free Energy Change ΔF (kJ)***	***Frequency factor Z (S_{-1})***	**Apparent Entropy Change (S*)**	**Order of reaction (n)**
SATF	-277.17	*155.01*	*427*	-24.01	0.9

Thermogram of the copolymer resins depicts three steps decomposition in the temperature range 190-575ºC. The slow decomposition between 0-190ºC corresponds to 7.0% loss which may be attributed to *loss of water molecule* against calculated 6.64% present per repeat unit of the polymer. The first step decomposition start from 190-250ºC which represents *loss of hydroxyl group and Acid group* (32.67% found and 29.52% cal.). The second step decomposition start from 250-500ºC corresponding to 66.54% removal of *aromatic nucleus and methylene bridge* against calculated 68.26%. The third step decomposition side chain from 500-575ºC corresponding to removal of *Thiosemicarbazide moiety* (100.00% found and 100.00% cal.).

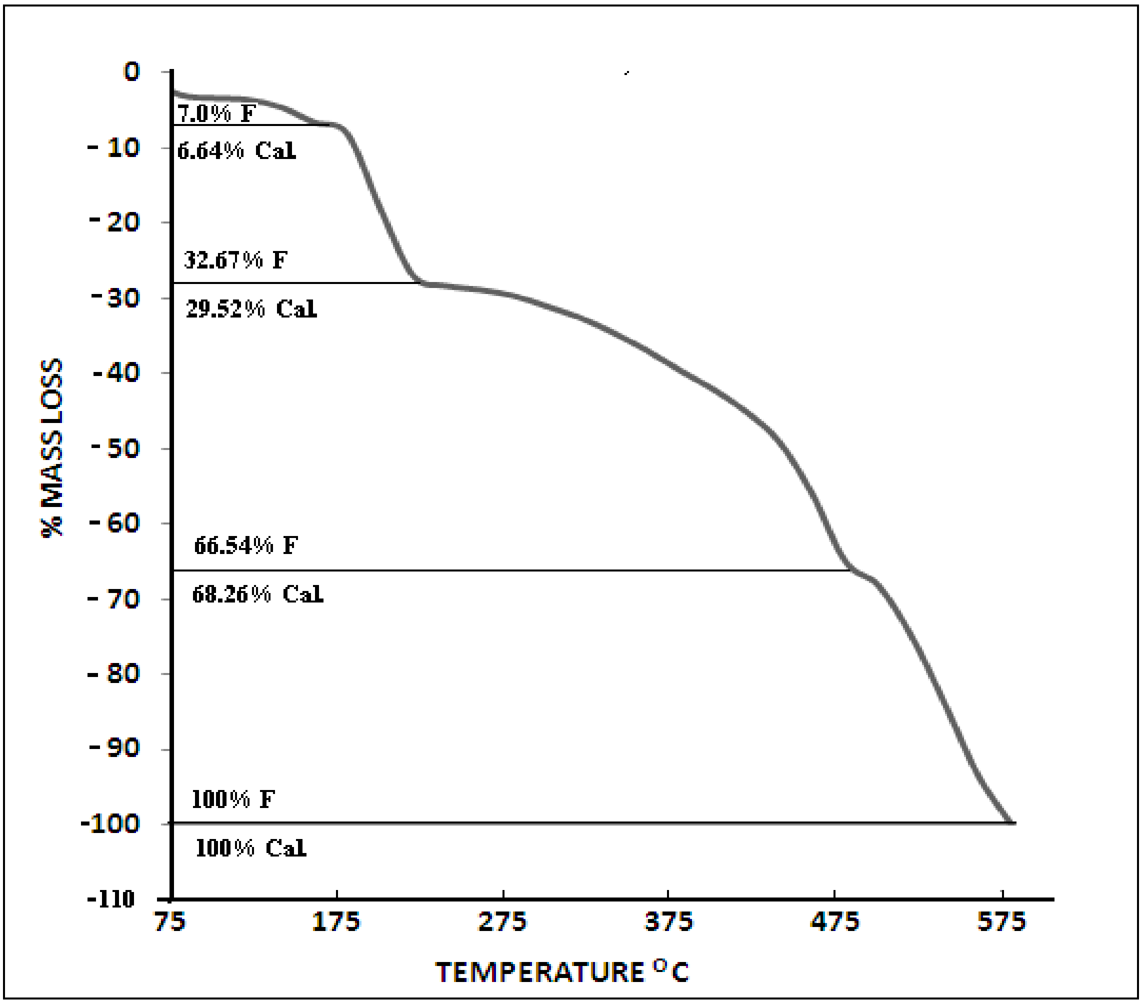

Fig. 4: Decomposition Pattern of SATF copolymer Resin.

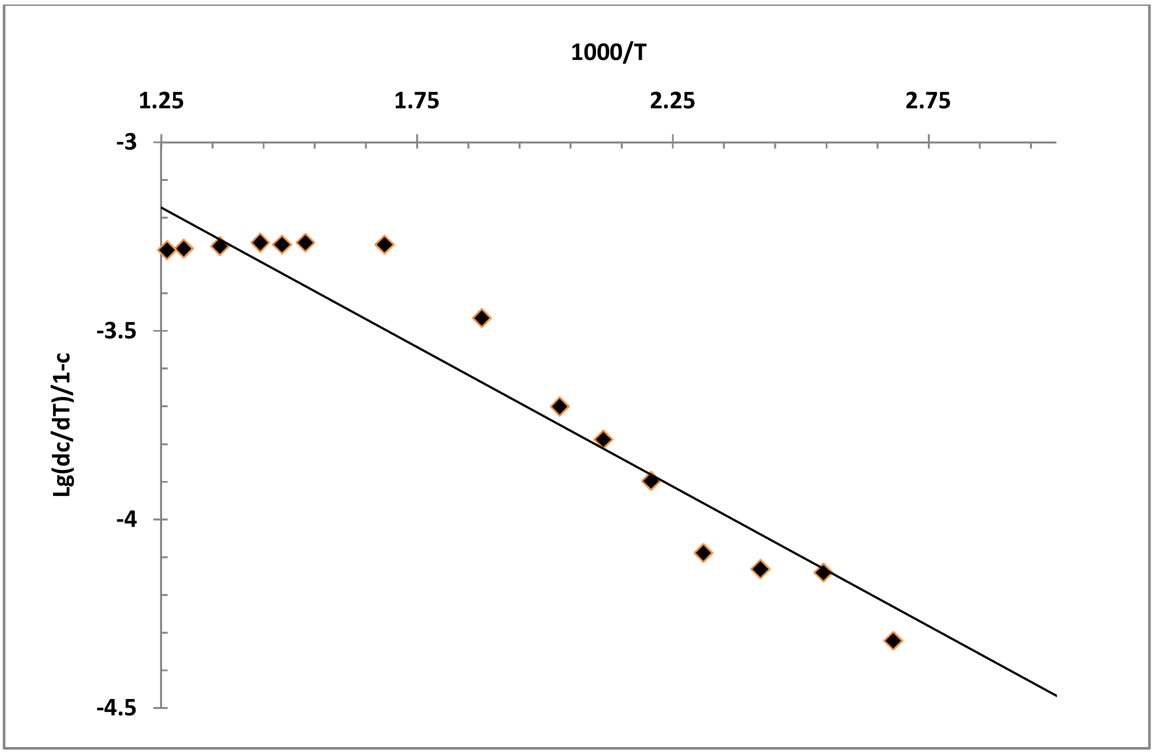

Fig. 5: Sharp-Wentworth plot of SATF copolymer

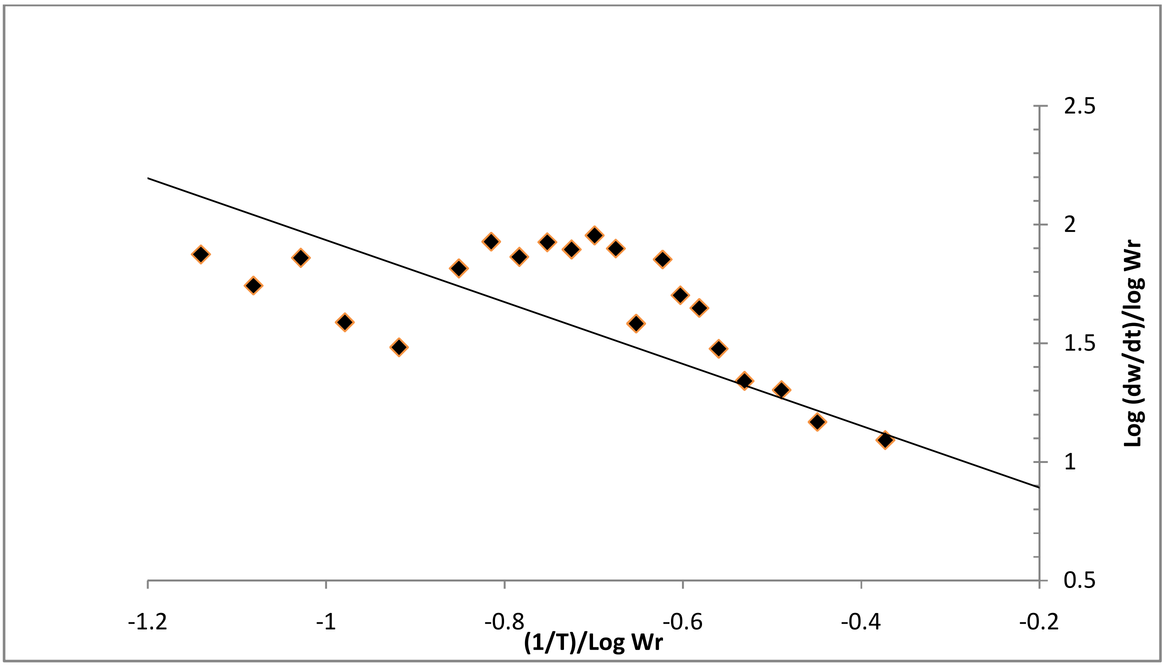

Fig. 6: Thermal activation energy plot of SATF copolymer

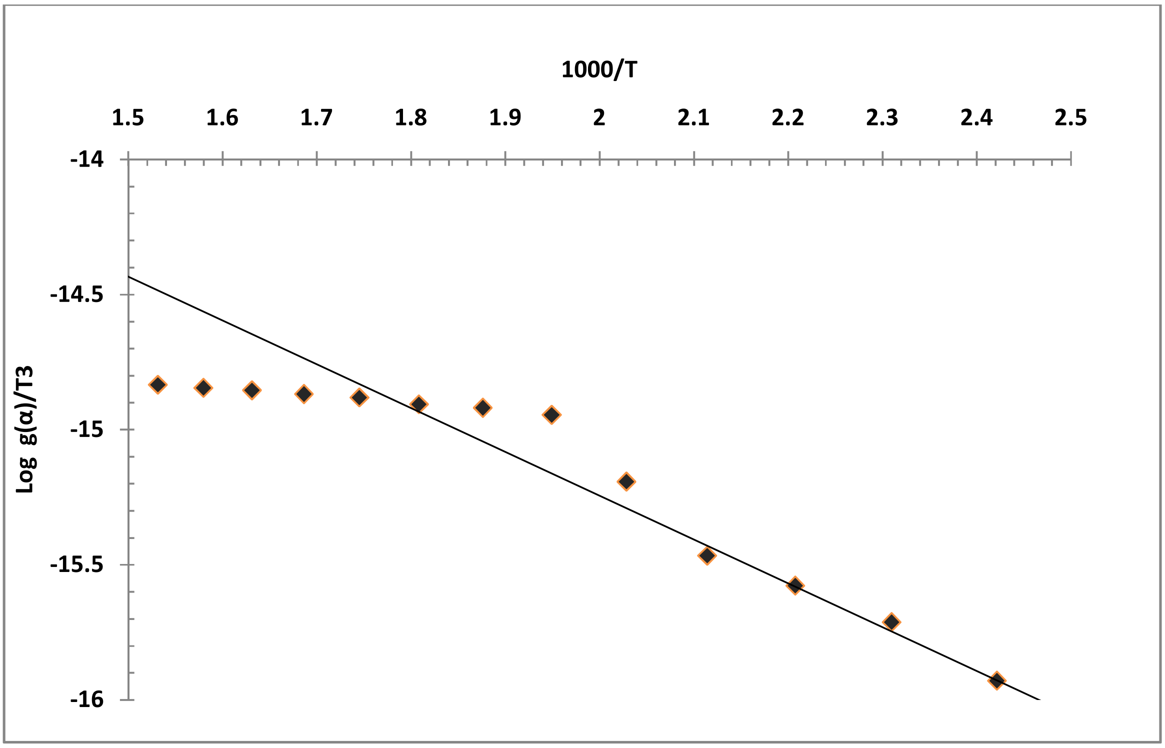

Fig. 7: Freeman-Carroll plot of SATF copolymer

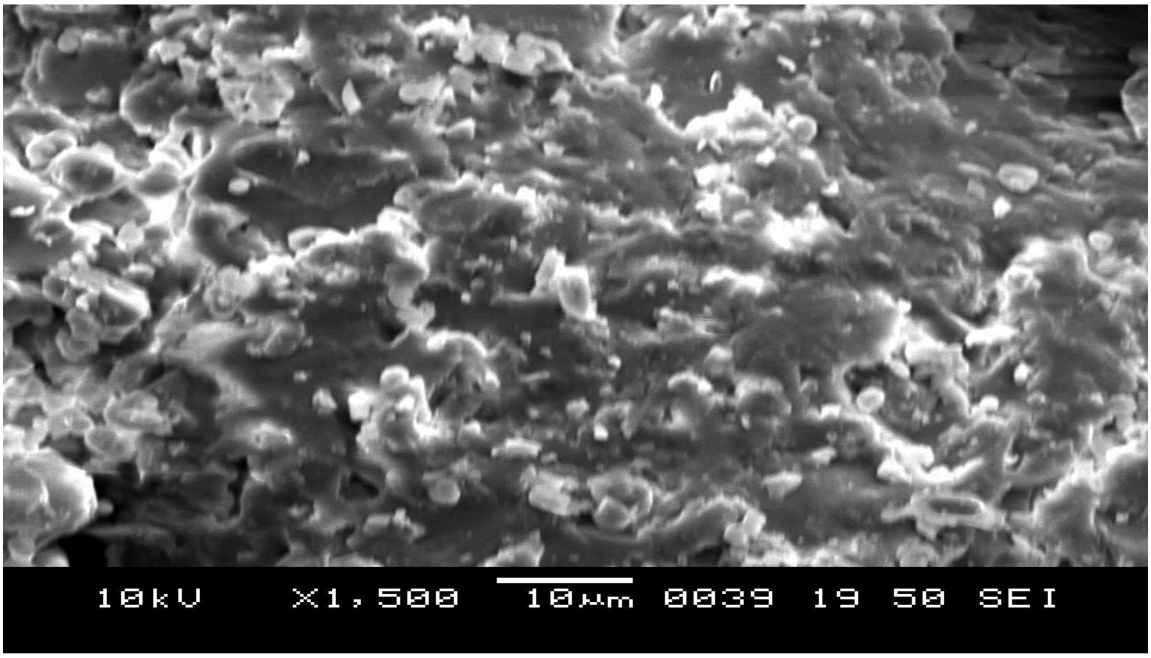

Fig.8: SEM of SATF copolymer

SEM micrographs of SATF copolymer are shown in Fig.8. The morphology of pure sample shows spherulites with deep pits. This is the transition of crystalline and amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structures at the beginning of the reaction but during course of condensation polymerization the crystalline structures of monomers lost into amorphous nature in copolymer resin .

CONCLUSION

A copolymer, SATF, based on the condensation reaction of salicylic acid -thiosemicarbazide-formaldehyde in the presence of acid catalyst was prepared. Low values of collision frequency factor (Z) may be concluded that the decomposition reaction of salicylic acid thiosemicarbazide-formaldehyde copolymer can be classified as ‘slow reaction’. The decomposition reaction was started at higher temperature, indicating a copolymer SATF is thermally stable at higher temperature.

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