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Thermoanalytical and biological studies of novel copolymer, derived from salicylic acid and semicarbazide

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ABSTRACT

The copolymer (SASF) was synthesized by condensation of salicylic acid and semicarbazide with formaldehyde in the presence of 2M HCL as a catalyst at 126 ± 2 ^{0}C for 5 hrs. with molar proportion of reactants. Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities by elemental analysis, FT-IR, UV-Visible 1H-NMR Spectroscopy. The thermal decomposition behavior of copolymer was studied by using TGA in static nitrogen atmosphere at a heating rate of 100C/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 thermal activation energy determined with the help of this method was in good agreement with each other. The antimicrobial activity for certain bacteria such as S. subtilis, E. coli, S. typhi, A. niger, S. aureus and C. albicans were studied.

Keywords: Synthesis, condensation, antimicrobial screening, thermogravimetric analysis; decomposition, resins.

INTRODUCTION

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*. 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 [1,2].

The non-isothermal kinetic studies 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. Terpolymers of salicylic acid, thiourea with trioxane and *p*-hydroxybenzoic acid, thiourea with trioxane have been reported in the literature [3-6].

There is a noteworthy demand to synthesize eco-friendly polymers having some biological activities like antifungal and antibacterial The invasion of polymers by fungi, bacteria and other organism is manifested by loss of mechanical properties, surface degradation, discoloration, staining and other deteriorations [7-10]. Polymers are used as biocidial agents in recent times. By incorporating biologically active organic moieties into the polymer backbone, the activities can be introduced. In terms of their biological activity, these polymers are more effective than their monomers. Such polymers are known for their biocidial activity against some bacterial, fungal and viral strains.

The present paper deals with the synthesis, characterization, and non-isothermal thermogravimetric analysis studies and relative antibacterial activity against bacteria of copolymer derived from of Salicylic acid (SA), Semicarbazide (S), with formaldehyde (F). However, the literature studies have revealed that no copolymer has been synthesized by using the said monomers. Sample is subjected to thermal degradation data with Sharp-Wentworth (S-W) and Freeman-Carroll (F-C) methods, activation energy and kinetic parameters such as ΔS, Z, S* and *n* (order of reaction) have been evaluated [11-14].

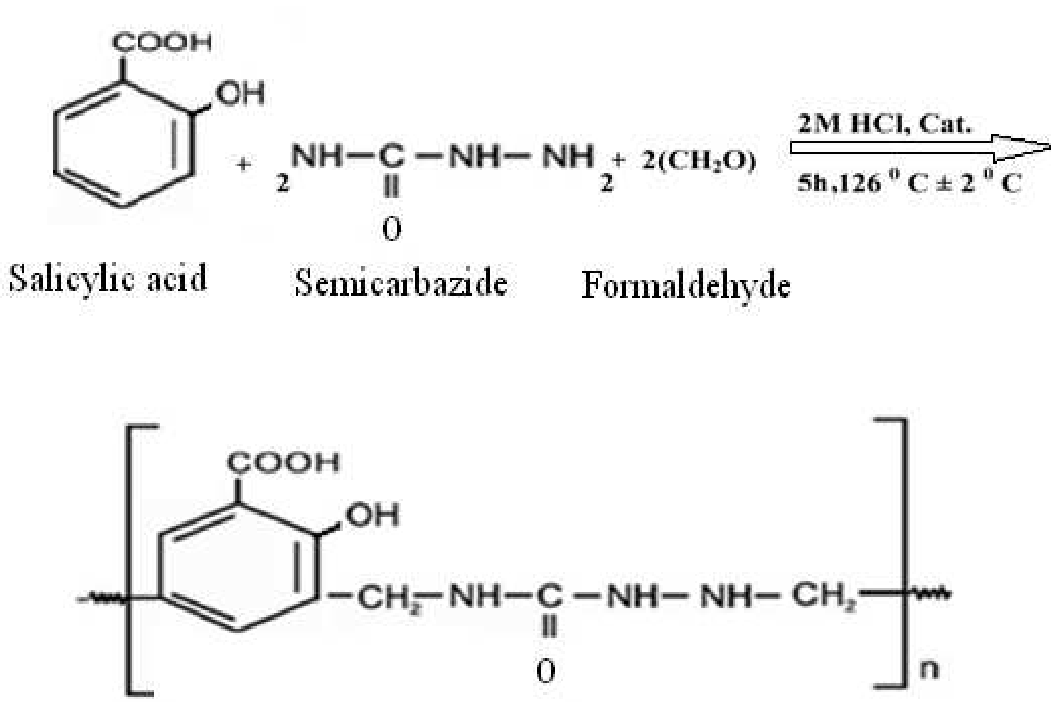

Fig.1: Synthesis of SASF copolymer resin

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 SASF Copolymer resins:
The new copolymer resin SASF was synthesized by condensing Salicylic acid (0.1 mol) and Semicarbazide (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- semicarbazide formaldehyde copolymer which might be present along with SASF 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 SASF is shown in Fig. 1

RESULTS AND DISCUSSION

The newly synthesized purified SASF 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.

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.

Antimicrobial Screening

SASF copolymer have been synthesized and agar diffusion method was employed to study their antibacterial activity (Fig.7). Test bacterial pathogens used in this study includes B. Subtilis, E. Coli , S. Typhi, A. Niger, C. Albicans and S. Aureus. The antibacterial screening of SASF is analysed at BIOGENICS, Hubli (Karnataka). Initially, the stock cultures of bacteria were revived by inoculating in broth media and grown at 37ºC for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 h old cultures (100 µl, 104 cfu) and spread evenly on the plate. After 20 min, the wells were filled with different concentrations of samples. The control wells were filled with Gentamycin. All the plates were incubated at 37ºC for 24 h and the diameter of inhibition zones were noted. Test samples were tested at different concentration to test their efficacy in inhibiting the growth of the human pathogens.

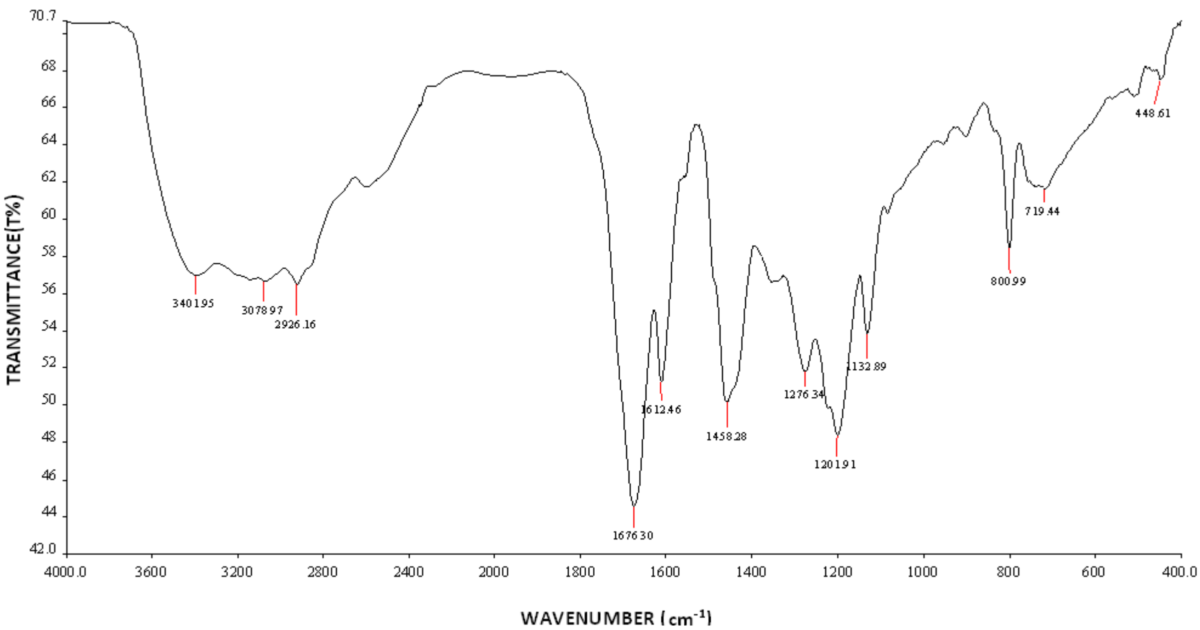

Fig.2: FT-IR Spectra of SASF copolymer

FT-IR Spectra : A broad band appeared in the region 3000-3400cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding . The sharp band displayed at 1600-1680 cm^{-1} may be due to the stretching vibrations of carbonyl group (C=O) . The presence of -NH in semicarbazide moiety may be assigned due to sharp band at 2800-3000 cm^{-1} . A strong sharp peak at 1625-1612 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 800 - 719 cm^{-1} is assigned to C – OH bond. Substitution of aromatic ring is recognized from the bands appearing between1201- 1276 cm^{-1} respectively .

NMR Spectra:
Weak signal in the range of 7.00 to 8.0 (δ) ppm is attributed to phenolic -OH proton. The NMR spectra of SASF copolymer resins show a weak multiplate signal (unsymmetrical pattern) in the region 6.8 to 7.0 (δ) ppm which is due aromatic protons. A sharp singlet peak appeared at 3.5 – 4.0 (δ) ppm may be assigned to methyl protons of Ar-CH2-NH group. Intense signal appeared in the region 2 – 3 (δ) ppm may be due to Ar–CH2-NH .A broad signal appeared in the region 3.42 – 4.84 (δ) ppm can be assigned to amido proton of –CH2-NH-CO- linkage.

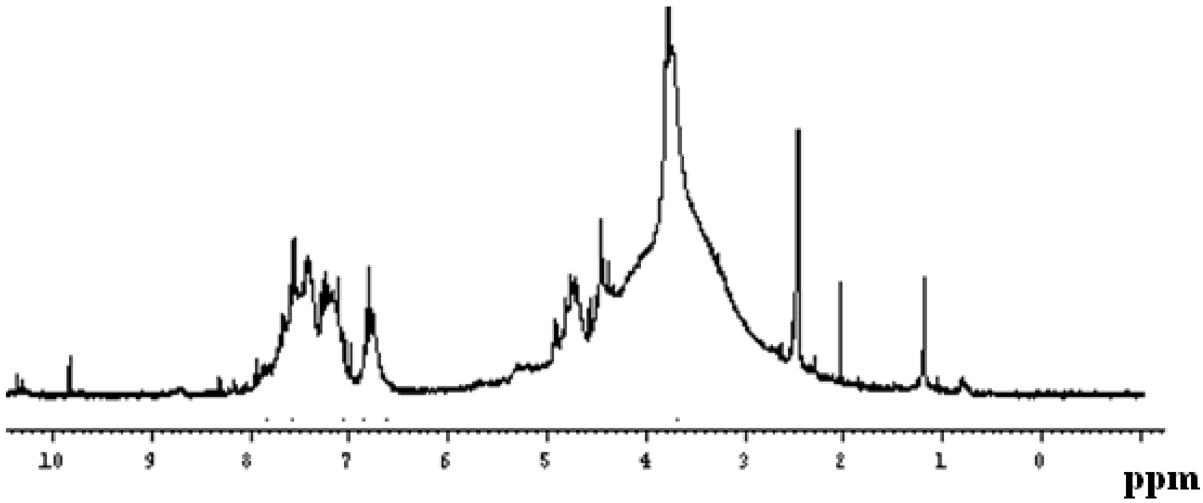

Fig.3: NMR Spectra of SASF copolymer

Thermo-analytical data
A plot of percentage mass loss versus temperature is shown in the Fig. 4 for a representative SASF 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 (22.9 KJ/mole) and 'average Ea' by Sharp*- Wentworth (22.1 KJ/mole) is nearly same. Thermogram of the copolymer resins depicts three steps decomposition in the temperature range 190- 300ºC. The slow decomposition between 0-190ºC corresponds to 9.0% loss which may be attributed to *loss of water molecule* against calculated 8.64% present per repeat unit of the polymer. The first step decomposition start from 190-250ºC which represents *loss of hydroxyl group and Acid group* (30.31% F found and 31.37% cal.). The second step decomposition start from 300-450ºC corresponding to 65.25 % F removal of *aromatic nucleus and methylene bridge* against calculated 66.27% Cal. The third step decomposition side chain from 450-540ºC corresponding to removal of *Semicarbazide moiety* (100.00% found and 100.00% cal.).

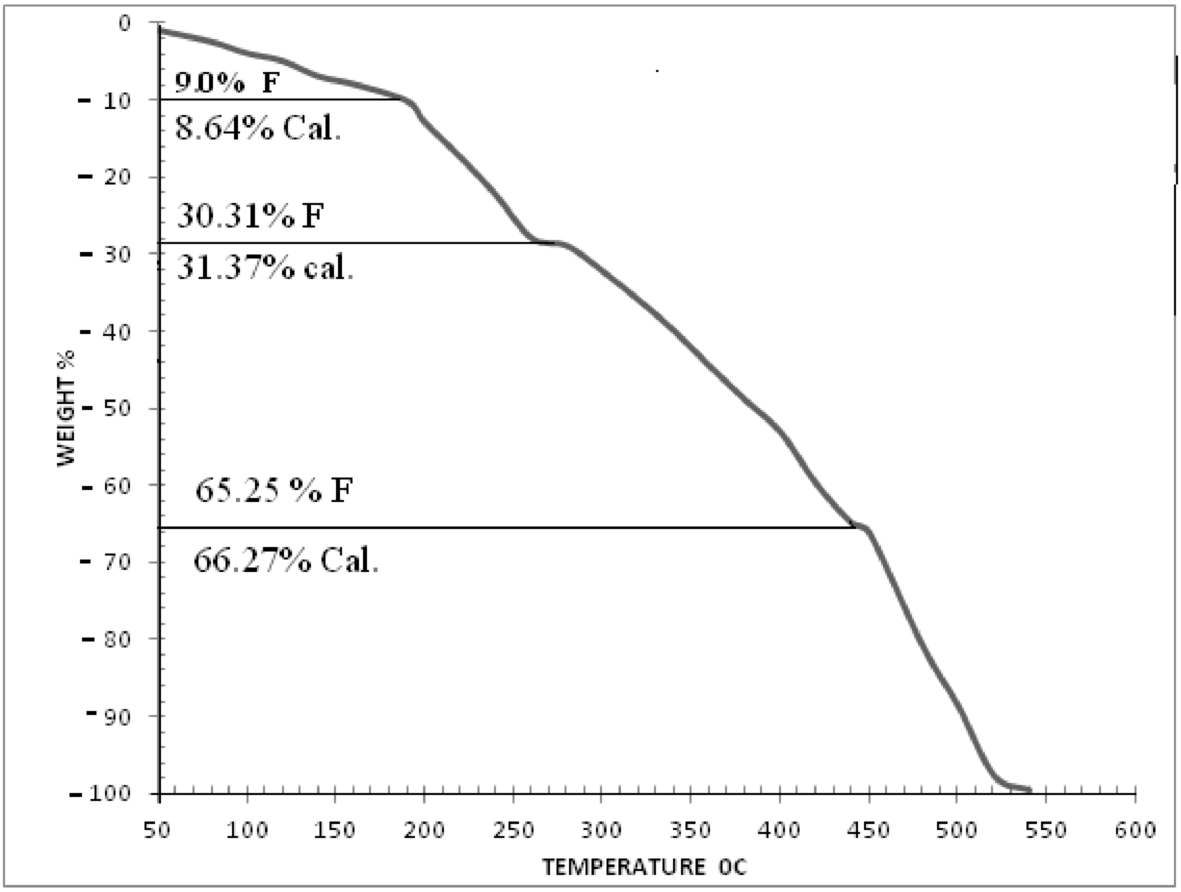

Fig.4 : Decomposition Pattern of SASF copolymer Resin

Table. 1: Results of Thermogravimetric Analysis of SASF copolymer

Copolymers	**Half Decomposition Temp.T*K**	**Activation Energy** (kJ/mol)	
		F.C	**S.W**
SASF	658	22.9	22.1

Table.2: Kinetic Parameters of SASF copolymer

Coplymers	**Entropy Change -ΔS(J)**	**Free Energy Change ΔF** (kJ)	**Frequency factor Z (S^{-1})**	**Apparent Entropy Change (S*)**	**Order of reaction (n)**
SASF	-300.53	153.11	432	-23.99	0.95

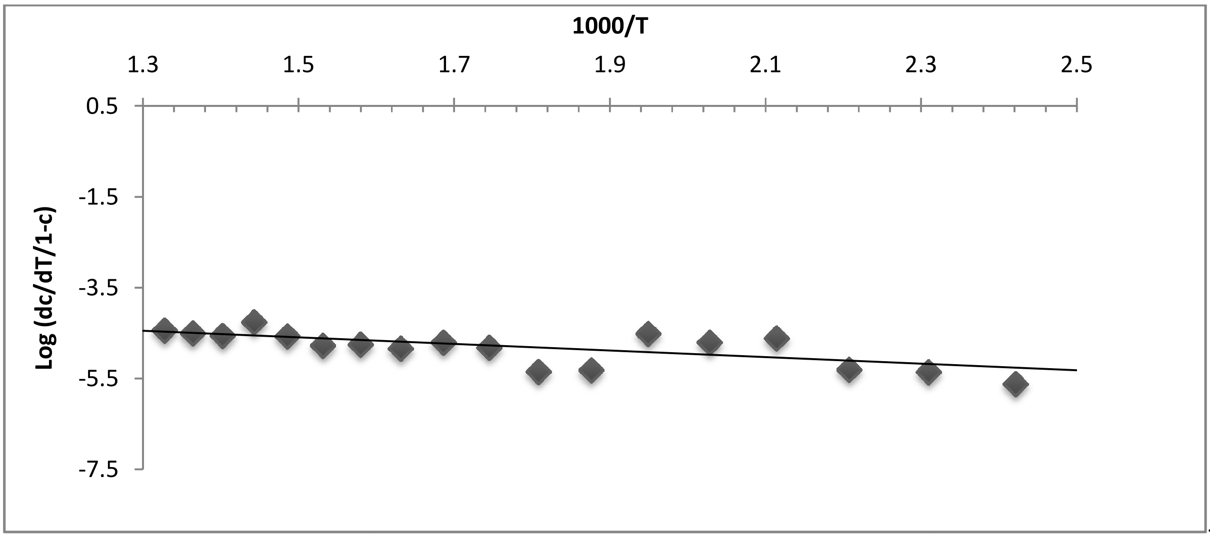

Fig.5 : Sharp-Wentworth plot of SASF copolymer

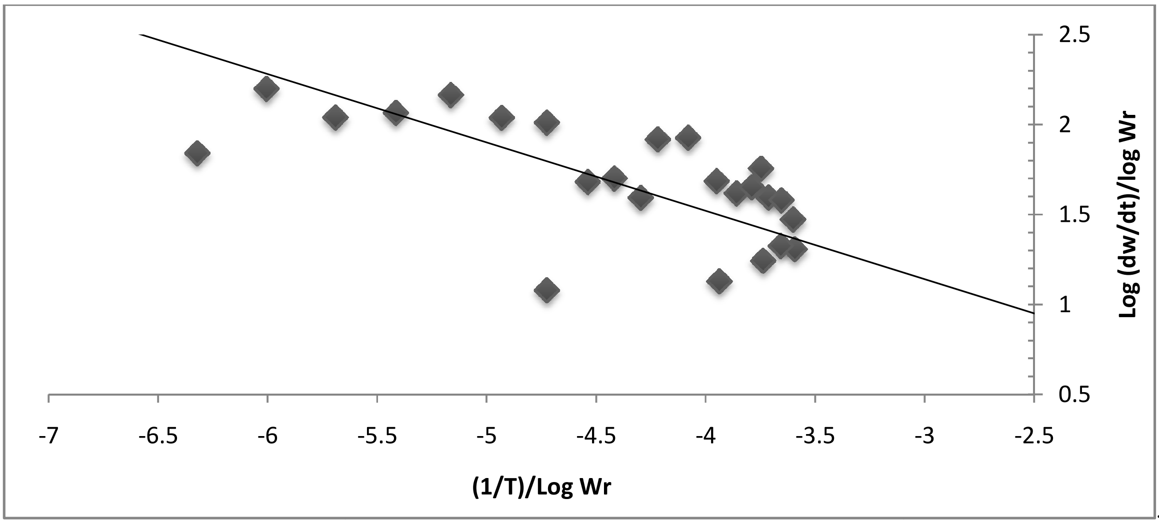

Fig.6 : Thermal activation energy plot of SASF copolymer

Biological Activity:
It depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with the known concentration of standard antibiotic. For the antimicrobial analysis of SASF copolymer the agar diffusion method was employed. During the course of time, the test solution diffuses and the growth of the inoculated microorganisms such as B. subtils , S. aureus, S. typhi, A. niger, were tested only E. coli is found to be affected. The activity developed on the plate was measured by measuring the diameter of the inhibited zone in millimetres. The drug gentamycin was used as the standard for bacteria.

In the present work, SASF copolymer were tested at different concentration to test their efficacy in inhibiting the growth of the human pathogens. The bacterial activity of SASF was assayed against B. subtilis, S. aureus, E. coli , S. typhi . The diameters for the zone of inhibitions at different concentration against the test bacteria are given in Table 3. The standard antibiotic disc (Gentamycine disc 5µg ⁄disc) inhibited the growth of B. subtilis by 8-25 mm E. coli by 18-25 mm, S. auresus by 13-25 mm and S. typhi by 2-25 mm.

Table 3. Antimicrobial activities of SASF copolymer resin

Organism	0.0625 mg	0.125 mg	0.25 mg	0.5 mg	1.0 mg	2.0 mg	MIC mg
B. subtilis	-	-	-	-	-	-	NF
E. coli (ETEC)	-	-	-	-	-	9	2
S. aureus	-	-	-	-	-	-	NF
S. typhi	-	-	-	-	-	-	NF
A. niger	-	-	-	-	-	-	NF
C. albicans	-	-	-	-	-	-	NF

Table.4: Antibacterial activity of standard antibiotic (Gentamycin)

Organism	25 µg	50µg	100µg	200µg	400µg	800µg	MIC µg
B. subtilis	8	10	15	19	22	25	25
E. coli (ETEC)	18	20	23	26	28	31	25
S. aureus	13	18	21	25	27	34	25
S. typhi	2	13	16	21	25	27	25

S. Typhi ***S. Aureus*** ***S. Subtills***

C. Calbicans ***A. Niger*** ***E. Coli***

Fig.7. Antibacterial activity of SASF copolymer

SEM micrographs of SASF copolymer is 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 .

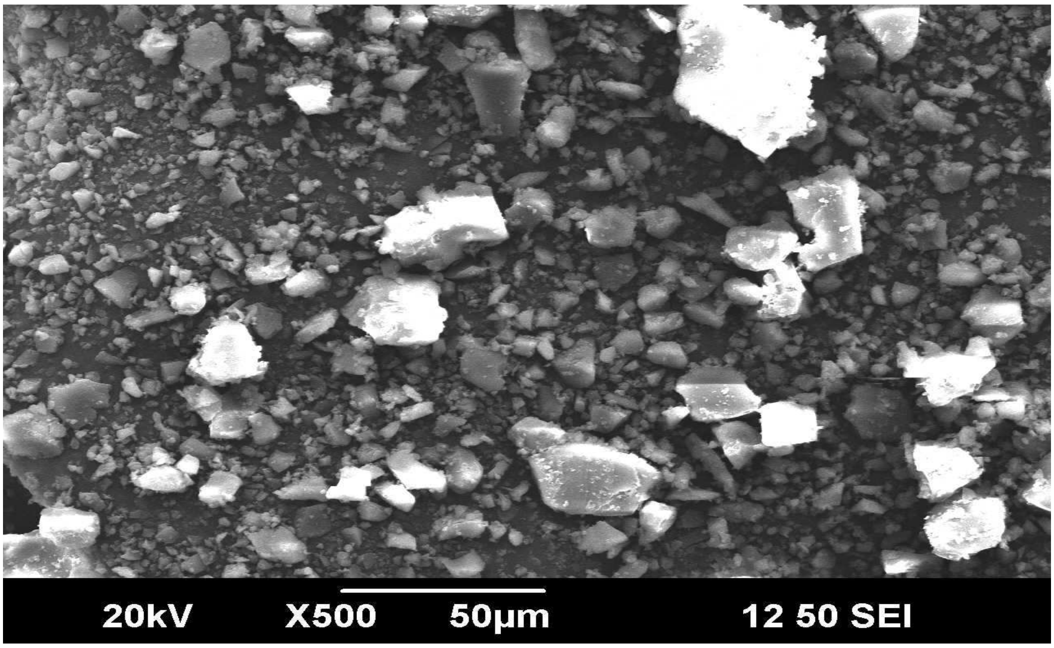

Fig.8: SEM of SASF copolymer

CONCLUSION

On the basis of dynamic TGA study of SASF copolymer shows the kinetic parameters like energy of activation, order etc. have been calculated from the Isothermal TG data using the methods which are widely used for finding the kinetic parameters in the thermal degradation of organic polymers and the values are incorporated in Table 2. A copolymer SASF, based on the condensation reaction of salicylic acid -Semicarbazide-formaldehyde in the presence of acid catalyst was prepared. The energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the kinetic parameters obtained from Freeman-Carroll method are found to similar, indicating the common reaction mode. Low values of collision frequency factor (Z) may be concluded that the decomposition reaction of salicylic acid, Semicarbazide-formaldehyde copolymer can be classified as 'slow reaction'. The decomposition reaction was started at higher temperature, indicating a copolymer SASF is thermally stable at higher temperature.

The results of present antimicrobial assay revealed that the SASF copolymer showed inhibitory activity against E. Coli pathogen only , suggesting that the presence of semicarbazide group may enhances antibacterial activity.

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