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Synthesis and thermogravimetric analysis of terpolymer resins derived from salicylaldoxime, melamine and formaldehyde

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ABSTRACT

Terpolymer resins (SOMF) were synthesized using salicylaldoxime, and melamine with formaldehyde in presence of hydrochloric acid as catalyst and using different molar proportions of salicylaldoxime, melamine and formaldehyde respectively. Its composition has been determined on the basis of the elemental analysis. The number average molecular weights have been determined by non-aqueous conductometric titration. Themogravimetric data was analysed to determine thermal stability of terpolymer and kinetic parameters were evaluated on the basis of thermogram of terpolymer. Freeman-Carroll and Sharp-Wentworth method have been used to calculate activation energy and thermal stabilities of these polymers. Kinetic parameters have been calculated using data of Freeman-Carroll method. the results obtained have been suitably discussed.

Keywords : Synthesis, Thermal studies, Terpolymer, Resin.

INTRODUCTION

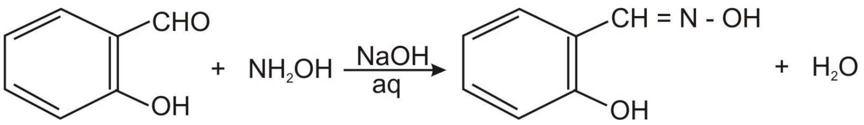
Large Number of work has been reported from these laboratories on the synthesis, characterization, structures and thermal studies of several terpolymer resins[1-5]. The present papers described detailed study of thermal degradation of polymeric resins formed with salicylaldoxime, melamine and formaldehyde.

The Freeman-Carroll [6] and Sharp-Wentworth [7] methods have been used to evaluate various kinetic parameters for these terpolymers. The methods for estimating the kinetic parameters from dynamic TG studies suffer from the difficulties that the two parameters, temperature and time can not be continuously changed. This problem is eliminated in Freeman-Carroll method where the parameters of temperature and time can be varied. Methods for estimating kinetic parameters from dynamic TG studies [8-10] are mostly based on the assumption that the Arrhenius equation is valid and that the thermal and diffusion barriers are negligible. Early numerous estimation of the thermal degradation of various polymers has shown the value of the thermogravimetric analysis with isothermal technique. With proper experimental procedure information about the degradation kinetic of decomposition can be obtained and TGA provides a method for thermal stability testing [11-14]. Suzzuki and Wilkie [15] have studied analysis in polymer degradation to evaluate the kinetic parameters. The apparent activation energy was evaluated by isothermal and dynamic thermogravimetric methods and thermal degradation behaviour was examined.

MATERIALS AND METHODS

Chemicals:
All the chemicals were obtained from Aldrich (USA), Lancaster (USA) and S. D. Fine Chem. Limited Mumbai. All the glassware is of borosilicate grade. The purity of the compound was ascertained by TLC on silica gel-G plate.

Synthesis of salicylaldoxime (salicylaldehyde oxime as a monomer)
Salicylaldehyde (20.0 g) has been dissolved in 30 ml of rectified spirit, a solution of hydroxylamine hydrochloride (15.0 g) in 10 ml of water was added to it and the mixture was rendered just alkaline with 10% sodium carbonate solution while cooling in ice. It was allowed to stand overnight, acidified with acetic acid alcohol was distilled off under reduced pressure, diluted with twice the volume of water and extracted twice with 50 ml of ether each time. The ethereal extract was dried with anhydrous magnesium sulphate, the ether was distilled off and allowed the residue to crystallize. It was recrystallized form chloroform-light petroleum (b.p. 40-60°C). The yield of salicylaldoxime, was 12.0 g.

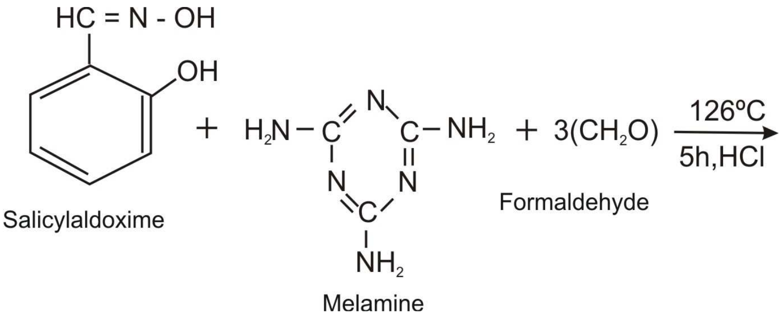


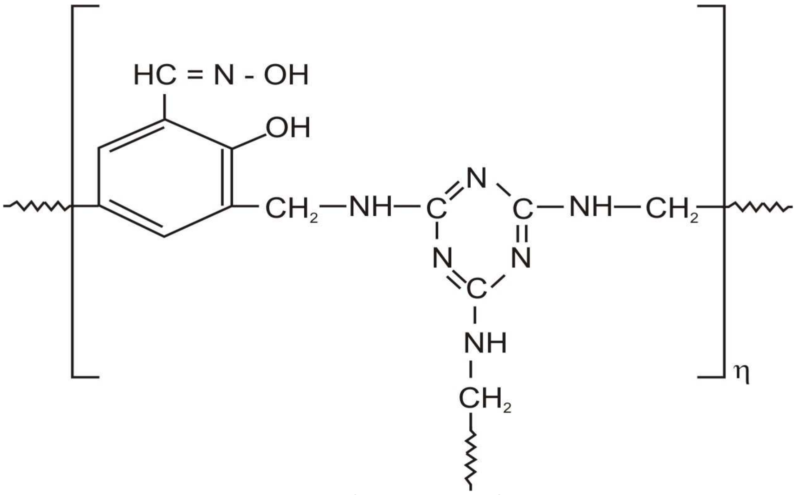
All terpolymer resins in the present; investigation were prepared by modification of procedure described by earlier workers [30] and varying composition of monomers.

Synthesis of terpolymer resins (SOMF)
A mixture of Salicylaldoxime (1.37g, 0.1 mole), melamine (1.26 g 0.1 mole), and formaldehyde (10.5 m 0.3 mole) and 2M hydrochloric acid(200 ml) was taken in a RB flask fitted with water condenser and heated in an oil bath at 126 ± 2°C for 5 hours with occasional shaking [28]. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified.

The resinous product so obtained was repeatedly washed with cold distilled water dried in air and powdered with the help of agate mortar and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air dried powder then extracted with diethyl ether and then with petroleum ether to Salicylaldoxime melamine formaldehyde polymer which might be present along with SOMF terpolymer. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipitated by gradual dropwise 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 thrice. The SOMF-I terpolymer resin so obtained was filtered, washed several times with hot powdered and kept in vacuum desicator over silica gel [29].

Similarly other terpolymer resins viz. SOMF-II. SOMF-III and SOMF-IV were synthesized by varying the molar proportions of the starting materials i.e. (2:1:4), (3:1:5) and (4:2:7) respectively with little variation of experimental conditions. The samples yields and reaction details are cited in Table-3.1.





Scheme 1. Reaction sequence of the synthesis of SOME terpolymer resin

Thermogravimetry (TG)

The dynamic (no-isothermal) thermogravimetric analysis of all the terpolymer prepared have been carried out in air atmosphere with a heating rate 5ºC/min. in a platinum crucible. The thermocouple used was chromel-Alumel in the temperature range 35-800ºC.

In the Freeman-Carroll method following expression is used :

$$\frac{\Delta \log (dw/dt)}{\Delta \log Wr} = \left[\frac{-Ea}{2.303R}\right] \quad \frac{\Delta(1/T)}{\Delta \log Wr} + n$$

Where, dw/dt is the rate of change of weight with time, Wr = Wc-W where Wc is the weight loss at the completion of reaction or at a definite time and W is the total weight loss up to time t. T is the temperature, R the gas constant and n the order of reaction. Hence by plotting

$$\frac{\Delta \log (dw/dt)}{\Delta \log Wr} \quad \text{Versus} \quad \frac{\Delta(1/T)}{\Delta \log Wr}$$

n is obtained as the intercept on the former axis and Ea is the slope of the line. The detailed procedure is clearly laid out for one representative sample as an illustration.

Using the Sharp-Wentworth method, following expression is used.

$$\log\left[\frac{dc/dt}{1-c}\right] = \log (A/\beta) - \frac{Ea}{2.303R} \quad \frac{1}{T}$$

where β is the linear heating rate, dT/dt. Thus a linear plot of

$$\log\left[\frac{dc/dt}{1-C}\right] \quad \text{versus} \quad \frac{1}{T}$$

is obtained whose slope gives the value of Ea and A may be evaluated from the intercept. The linear relationship confirmed that the assumed order (n=1) is correct.

RESULTS AND DISCUSSION

The thermogravimetric analysis of all terpolymers prepared has been carried out, but for reasons of economy of space the thermal data and kinetic plots for only one representative case have been given. The SOMF terpolymer resins are pale yellow in colour. The purified terpolymer resins are soluble in N, N-dimethyl formamide, dimethyl sulphoxide, aqueous sodium and potassium hydroxide. The melting temperatures are found to be in the range of 584 to 603K.

Elemental Analysis

The SOMF terpolymer resins were analysed for the percentage of carbon, hydrogen and nitrogen. The results are presented in Table 1. From the Table 1 it is found that the values of the percentage elements determined are in good agreement with the calculated values. The elemental analysis data suggest the empirical formula and the empirical formula weight for the repeating unit of each SOMF terpolymer resin as given in Table 1.

Table 1. Elemental Analysis Data of SOMF Terpolymer Resins

Terpolymer Resin	% of Carbon		% of Nitrogen		% of Hydrogen		Empirical Formula	Empirical Formula weight
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.		
SOMF-I	51.98	51.70	27.98	27.75	4.66	4.40	$C_{13}H_{14}O_2N_6$	300.11
SOMF-II	53.10	52.95	24.93	24.60	4.67	4.45	$C_{21}H_{21}O_4N_8$	449.17
SOMF-III	58.17	58.01	21.06	20.80	4.68	4.50	$C_{29}H_{28}O_6N_9$	598.23
SOMF-IV	55.78	55.55	25.91	25.72	4.62	4.49	$C_{41}H_{40}O_8N_{16}$	864.33

Molecular Weight Determination

The measurement of molecular weight of terpolymer resins have been carried out by conductometric titration in non-aqueous medium. Conductometric titration in non-aqueous media has been proved to be a simple method for the estimation of number average molecular weight of phenolic resins. Titrimetric study on linear phenol-formaldehyde condensation products in organic solvent indicates a stepwise neutralization of phenolic -OH group in the average chains [16].

Table 2. Number Average Molecular Weight Data of SOMF terpolymer resins by conductometric Titration

Terpolymer Resins	1st stage of neutralization (m.eq.of KOH/ 100g of resin	Final stage of neutralization (m.eq.of KOH/ 100g of resin	Degree of polymerization $(\overline{DP})$	Number average molecular weight $(\overline{Mn} = Emp.wt \times \overline{DP})$
SOMF-I	56	1176	21	6302.31
SOMF-II	56	1120	20	8983.4
SOMF-III	56	896	16	9571.68
SOMF-IV	56	728	13	11236.29

The number average molecular weight of all the newly synthesized SOMF terpolymer resins have been determined by conductometric titration method in non-aqueous solvent (DMF) using ethanolic potassium hydroxide as titrant. The details of the non-aqueous conductometric titrations are presented in Table 2 and titration curves are shown in Fig.1. Examination of these plots shows that there are several breaks before complete neutralization of all acidic groups [17]. The first break in the plot was the smallest of all the breaks. It was assumed that this corresponded to a stage in titration when on an average one group of each chain was neutralized. Examination of conductometric data reveals that the size of most of the breaks was nearly equal or was a whole multiple of the size of the first break. The titration curves of the terpolymer resins indicate a sharp stepwise increase in conductance till the stage of neutralization of all the -OH groups. Beyond this stage there was a continuous increase in the value of conductance. The degree of polymerisation $(\overline{DP})$ of the terpolymer samples was obtained from the ratio of total miliiequivalents of base for neutralization of first -OH group (first break). The value of $(\overline{DP})$ was multiplied by the average molecular weight of the repeating unit to give the number average molecular weight (Table 2) of SOMF terpolymer resins. Thus, the degree of polymerisation $(\overline{DP})$ and the number average molecular weight $(\overline{Mn})$ were evaluated from the conductometric titration curves. From the Table 2, it is evident that the molecular weight of SOMF terpolymer increase with the increase in salicylaldoxime content [18].

Viscosity Measurement

Viscosity measurement of all the SOMF terpolymer resins was carried out in freshly triple distilled N,N-dimethyl formamide at 303 K. The details of the experiments and calculations are furnished in Tables 3 and plots for η_{int}. determination are presented in Fig. 2. The viscometric measurements were carried out at six different concentrations ranging from 3.0% to 0.5%. The reduced viscosity of the terpolymer samples was calculated by the formula η_{sp}/C. Intrinsic viscosity $[\eta]$ was determined by the following Huggin's [19] and Kraemmer's [20] relations.

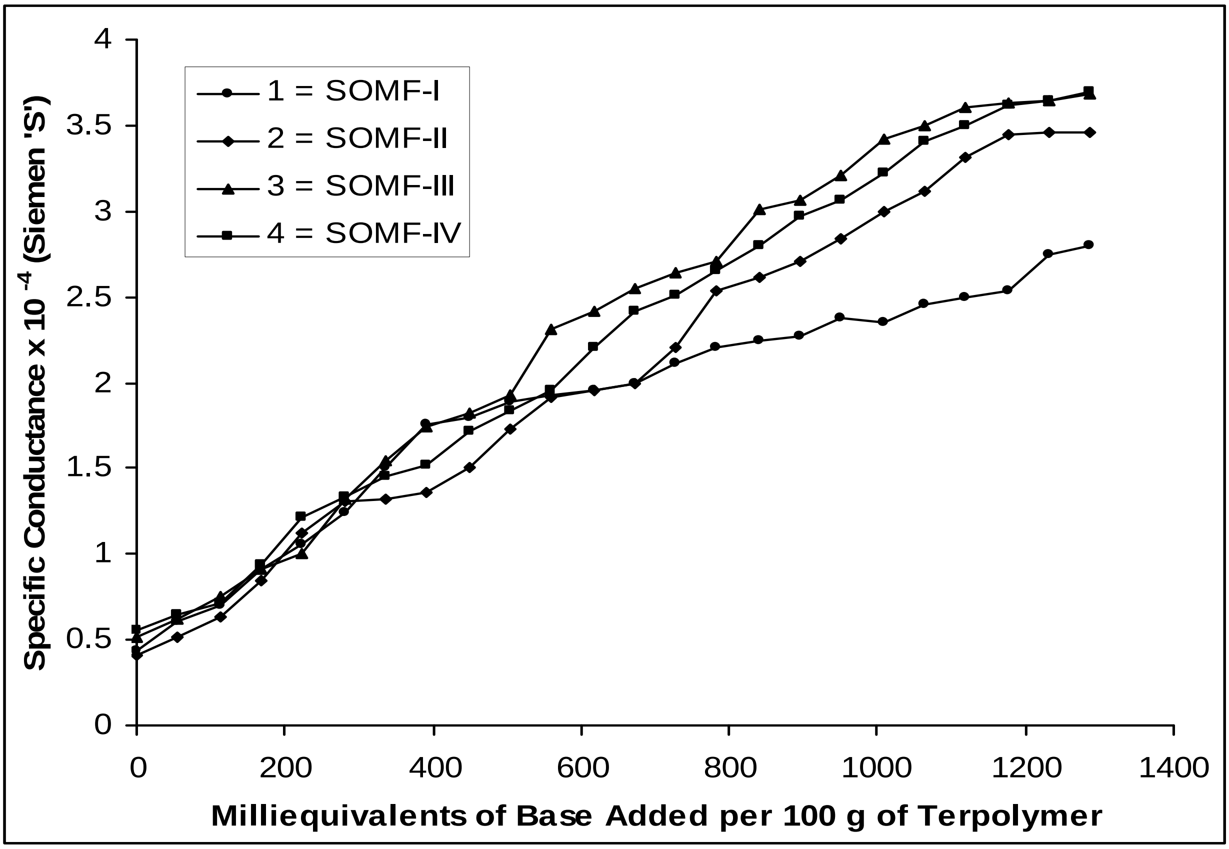


Fig. 1. Conductometric titration curves of terpolymer resins

Table 3.Intrinsic Viscosity Data of SOMF Terpolymer Resins

Solvent : Dimethyl Sulphoxide (DMSO) (t_o = 56 sec.) Temp. : 300 ±0.1K

Terpolymer Resin	Reduced Viscosity (η_{red}, dl.g^{-1})						Intrinsic Viscosity* [η] (dl.g^{-1})
	CONCENTRATION (C; g.dl^{-1})						
	3.00	2.50	2.00	1.50	1.00	0.50	
SOMF-I	0.1077	0.1085	0.1169	0.1214	0.1303	0.132	0.136
SOMF-II	0.097	0.109	0.120	0.1321	0.1464	0.157	0.162
SOMF-III	0.1202	0.1306	0.142	0.1440	0.1642	0.176	0.181
SOMF-IV	0.108	0.1235	0.1357	0.1559	0.167	0.182	0.192

** Application of Huggin's relation*

The relation between reduced viscosity and concentration is expressed by Huggin's as

$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C \qquad \text{------- Huggin Equation}$$

The relation between inherent viscosity lnη_{rel}/C and concentration is expressed by Kraemmer as

$$\frac{\ln\eta_{rel}}{C} = [\eta] + K_2[\eta]^2 C \qquad \text{------ Kraemmer Equation}$$

In accordance with the above relations the plots of η_{sp}/C and lnη_{rel}/C were found to be linear. The values of intrinsic viscosity were calculated from the intercepts on the axis of viscosity function of both the plots. Therefore, the values of η_{int} obtained from both the plots were in good agreement [21].

The results of viscometric study exhibit the following trend –
i) The plot of η_{sp}/C Vs C and lnη_{rel}/C Vs C are linear
ii)SOMF terpolymer resin having higher molecular weight has higher intrinsic viscosity. Thus the overall trend of the intrinsic viscosity of these terpolymer resins is

SOMF-I < SOMF-II < SOMF-III < SOMF-IV

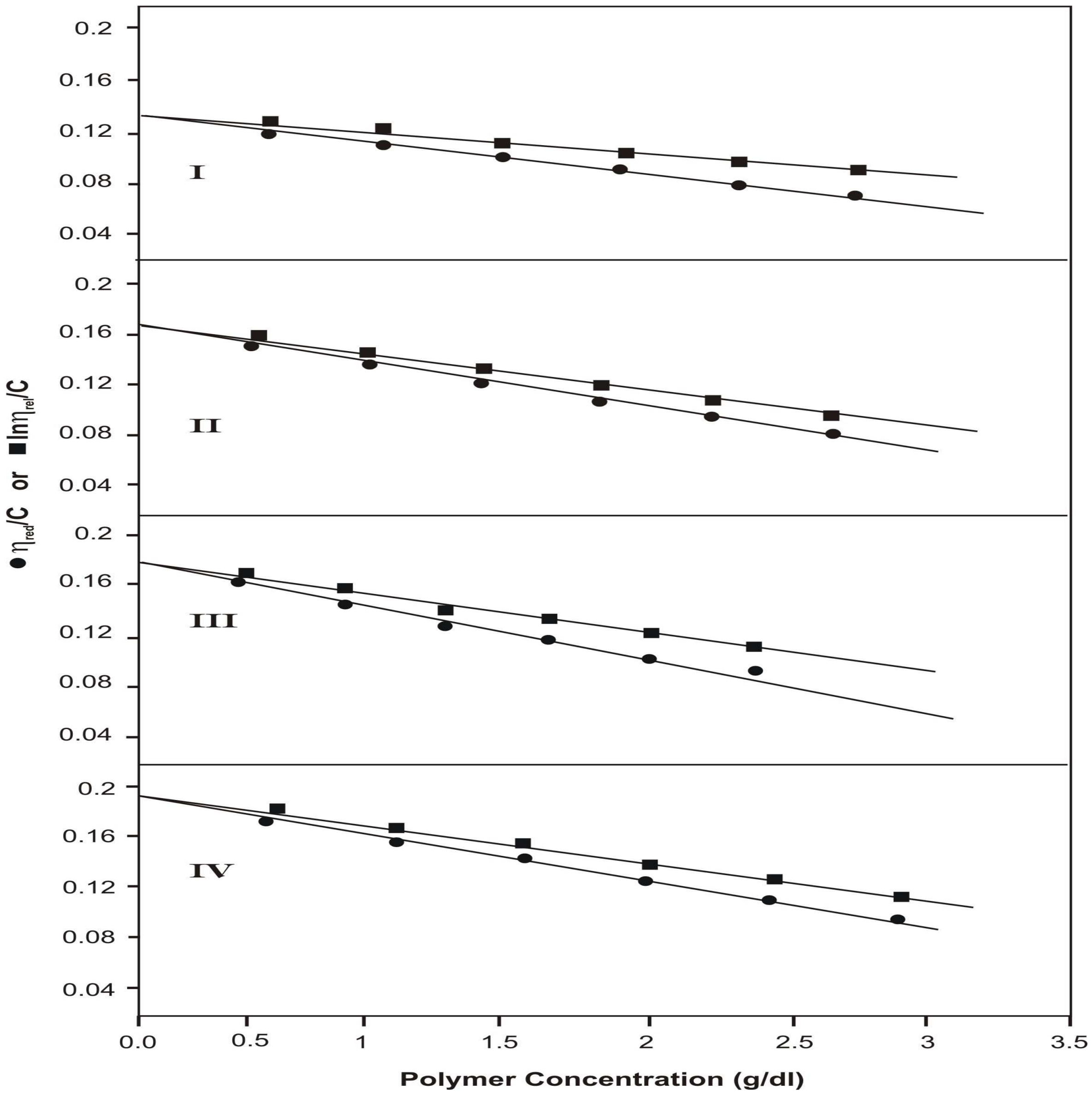


Fig. 2. Viscometric Plots of Terpolymer Resins-SOMF-I, II- SOMF-II, SOMF-III, SOMF-IV.

Thermogravimetry

The data on the thermogravimetric analysis of terpolymers of SOMF-I, SOMF-II, SOMF-III and SOMF-IV were analysed using the methods described below. These methods were used to determine the kinetic parameters like activation energy Ea, and order of reaction n of the products formed. Also on the basis of the decomposition pattern hydrated/ coordinated water molecules attached to the polymers have been suggested. From the values of activation energy, the thermal stability and the mechanism of degradation of polymers have been interpreted.

TG of SOMF-I Terpolymer

Thermogram of this terpolymer is shown in Fig.3. Thermogram of the terpolymer resins depicts four steps decomposition in the temperature range 35-715ºC. The first step slow decomposition between 35-110ºC corresponds to 5.5% loss which may be attributed to loss of water molecule against calculated 6.0% present per repeat unit of the polymer. The second step decomposition start from 110-250ºC which represents degradation of hydroxyl and oxime moiety (35.1% found and 26.0% cal.). The third step decomposition start from 250-420ºC corresponding to 50.1% loss of aromatic nucleus against calculated 51.33%. The four step decomposition side chain from 420-715ºC corresponding to removal of side chain of triazine polymer (80.5% found and 80.33% cal.) and consequently residue remained may be assigned as 1, 3, 5, S-triazine (19.5% found and 19.67% cal.).

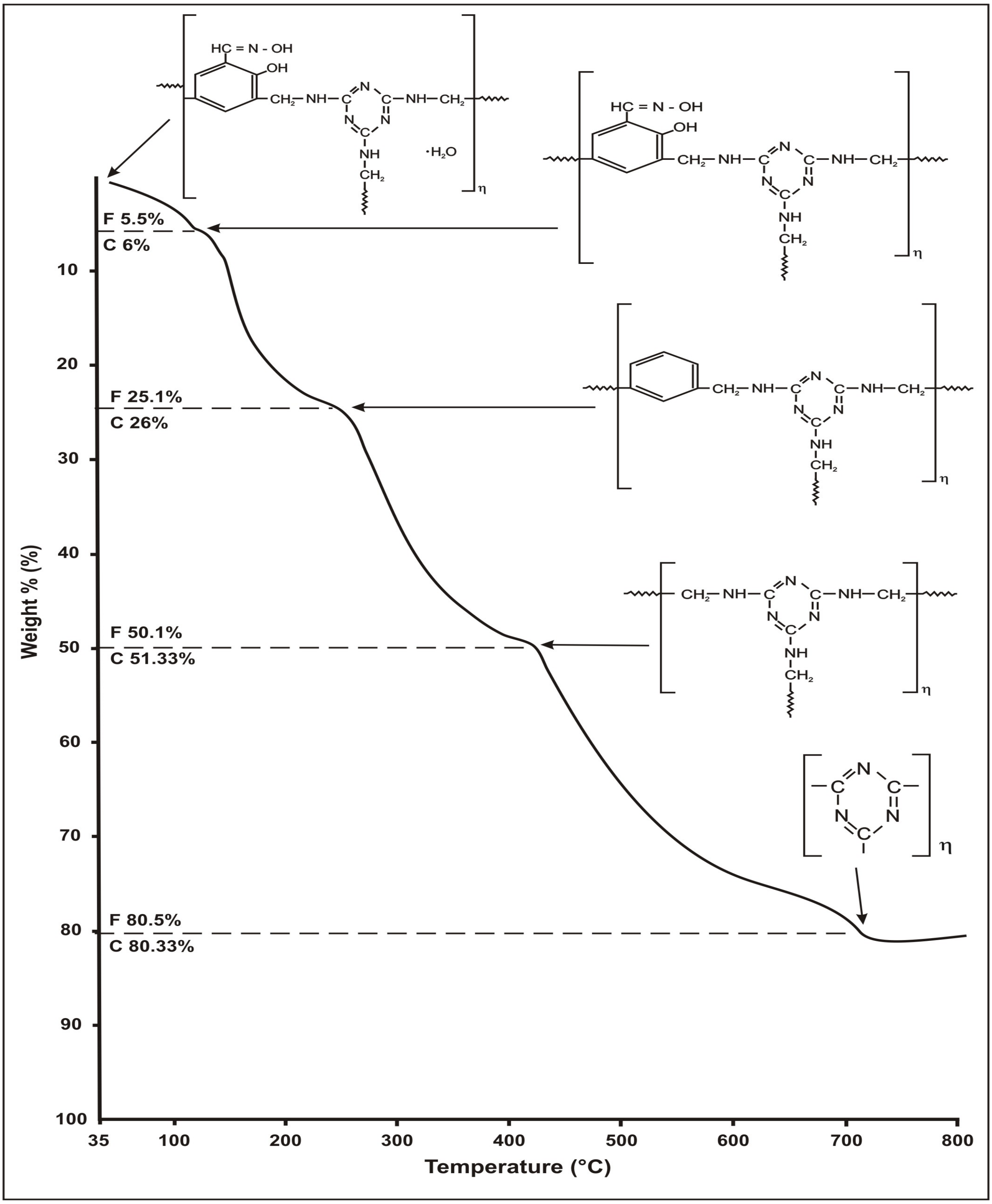


Fig. 3. Thermogravimetric Analysis of SOMF-I terpolymer

Table 4..Results of thermogravimetric analysis of terpolymers of SOMF (Kinetic Parameters)

Terpolymer Resins	Decomposition Temperature (°C)	Activation Energy Ea, (KJ)		□S (J)	□F (KJ)	Z (Sec.$^{-1}$)	S* (KJ)	n
		SW	FC					
SOMF-I	311	14.36	14.87	8.37	14.74	179.3	-25.06	0.99
SOMF-II	315	17.40	17.23	8.61	14.40	174.5	-25.11	0.98
SOMF-III	320	18.56	18.18	8.42	14.60	180.5	-25.07	0.99
SOMF-IV	330	23.65	23.74	8.65	14.28	178.3	-25.11	0.97

SW – Sharp-Wentworth Method
FC – Freeman–Carroll Method

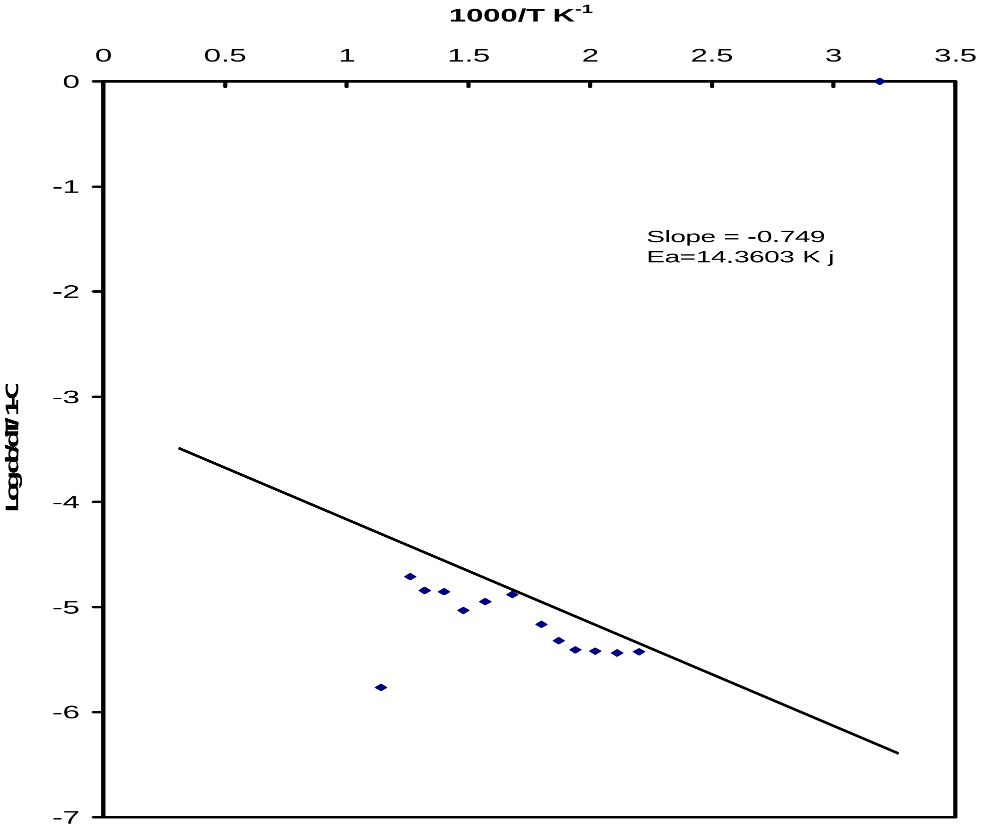


Fig. 4. Sharp-Wentworth Plots SOMF-I

TG of SOMF-II Terpolymer:

Thermogram of this terpolymer is shown. Thermogram of the terpolymer resins depicts four steps decomposition in the temperature range 35-700ºC. The first step slow decomposition between 35-100ºC corresponds to 5% loss which may be attributed to loss of water molecule against calculated 4.0% present per repeat unit of the polymer. The second step decomposition start from 100-290ºC which represents degradation of hydroxyl and oxime moiety (31.3% found and 30.73% cal.). The third step decomposition start from 290-500ºC corresponding to 64.2% loss of aromatic nucleus against calculated 64.58%. The four step decomposition side chain from 500-700ºC corresponding to removal of side chain of triazine polymer (86.3% found and 87.08% cal.) and consequently residue remained may be assigned as 1, 3, 5, S-triazine (13.7% found and 12.92% cal.).

TG of SOMF-III Terpolymer:

Thermogram of this terpolymer is shown. Thermogram of the terpolymer resins depicts four steps decomposition in the temperature range 35-625ºC. The first step slow decomposition between 35-60ºC corresponds to 2.4% loss which may be attributed to loss of water molecule against calculated 3.01% present per repeat unit of the polymer. The second step decomposition start from 60-280ºC which represents degradation of hydroxyl and oxime moiety (32.2% found and 31.11% cal.). The third step decomposition start from 280-495ºC corresponding to 77.3% loss of aromatic nucleus against calculated 76.25%. The four step decomposition side chain from 495-625ºC corresponding to removal of side chain of triazine polymer (89.5% found and 90.46% cal.) and consequently residue remained may be assigned as 1, 3, 5, S-triazine (10.5% found and 9.54% cal.).

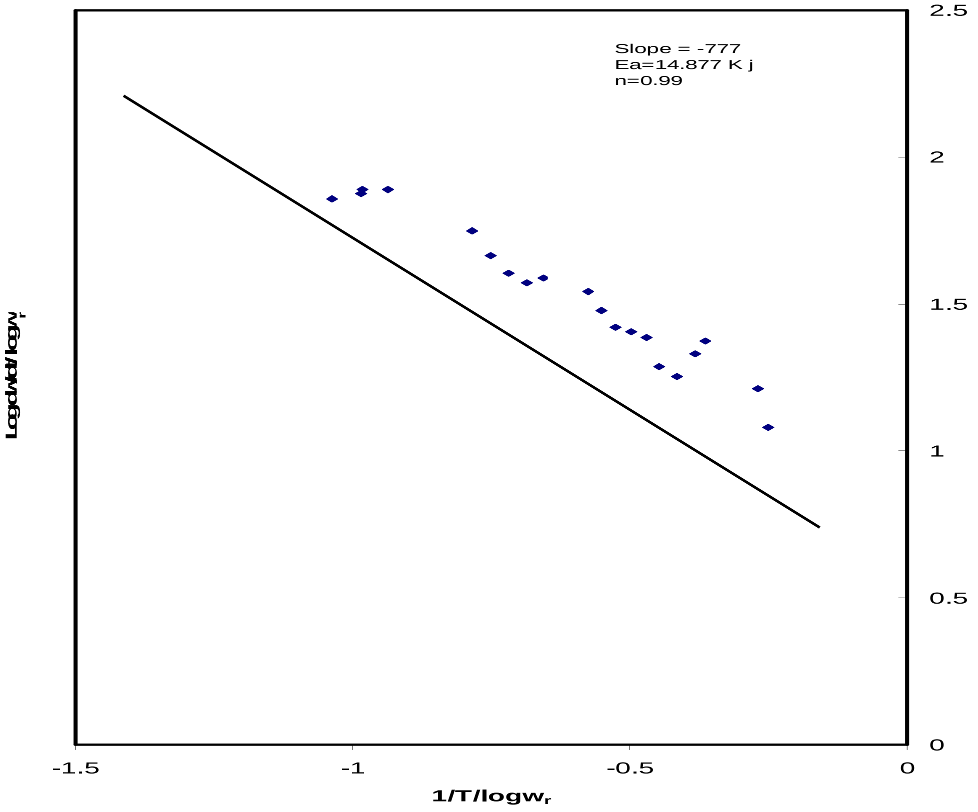


Fig. 5 Freeman-Carroll Plots SOMF-I

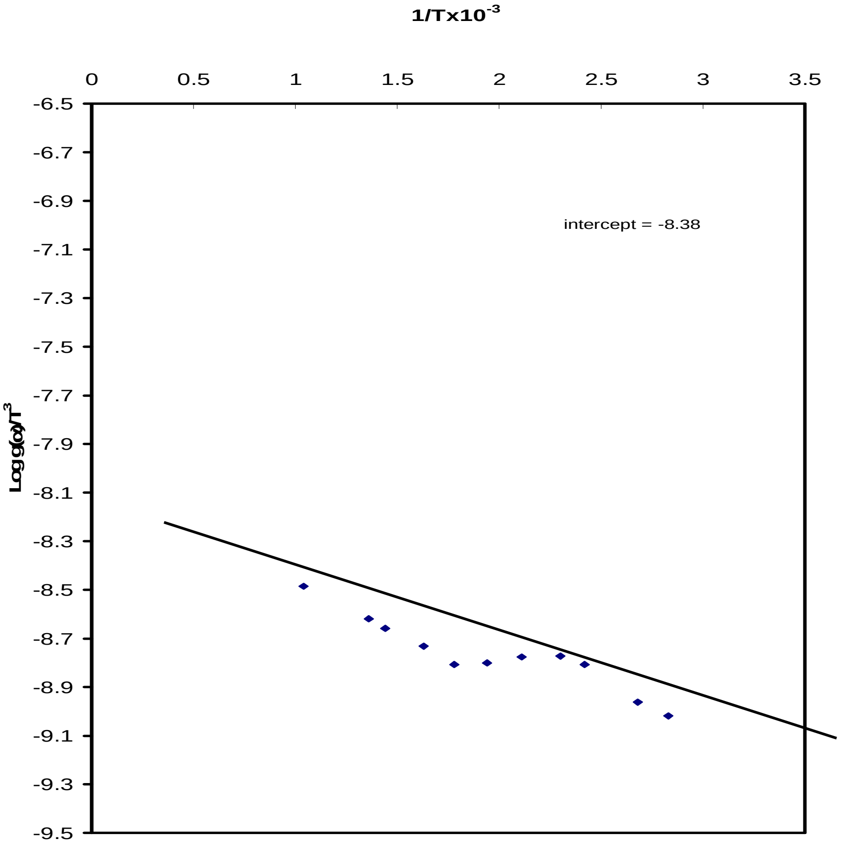


Fig. 6 Freeman-Carroll Plots SOMF-I

TG of SOMF-IV Terpolymer:
Thermogram of this terpolymer is shown. Thermogram of the terpolymer resins depicts four steps decomposition in the temperature range 35-670ºC. The first step slow decomposition between 35-60ºC corresponds to 3.1% loss which may be attributed to loss of water molecule against calculated 2.08% present per repeat unit of the polymer. The second step decomposition start from 60-280ºC which represents degradation of hydroxyl and oxime moiety (30.4% found and 29.86% cal.). The third step decomposition start from 280-470ºC corresponding to 64.3% loss of aromatic nucleus against calculated 65.04%. The four step decomposition side chain from 470-670ºC corresponding to removal of side chain of triazine polymer (85.2% found and 86.80% cal.) and consequently residue remained may be assigned as 1, 3, 5, S-triazine (14.8% found and 13.20% cal.).

DISCUSSION

In the present study, in case of SOMF terpolymer the removal of water from the polymer is complete around 100 ^{0}C. The water is probably crystal water loss correspond to water molecule in SOMF-l, SOMF-II, SOMF-III and SOMF-IV. The observed weight loss is a little higher than required in the region and this may be due to some other chain degradation reaction involved in the pyrolysis of the terpolymers [22].

By using thermal decomposition data and then applying the Sharp- Wentworth method (Fig.4) activation energy is calculated, which is in agreement with the activation energy calculated by Freeman-Carroll method (Table 4). A representative thermal activation energy plot and Freeman - Carroll plot have been shown in Fig.5-6 respectively. Thermodynamic parameters have been calculated on the basis of thermal activation energy and these values are cited in Table 4.

Fairly good straight line plots are obtained using both methods. However, in the Freeman-Carroll method (Fig.5-6) some abnormal points were ignored to get a clear picture about most of the point. Similarly, in the Sharp-Wentworth method, (Fig. 4) some points at the beginning or at the end did not fall on the straight line. This is expected since the decomposition of terpolymer is known not to obey first order kinetics perfectly [23]. These observations are in harmony with the findings of Jacobs and Tomkin[24] and other earlier workers [25].

On the basis of Dynamic TGA of the Terpolymers of SOMF-I, SOMF-II, SOMF-III and SOMF-IV the order of thermal stability based on the initial decomposition temperatures and the activation energies, may be given as, SOMF-IV > SOMF-III > SOMF-II > SOMF-I. 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 4. From the table it is observed that the activation energy values calculated by the two different methods are close to each other. Hence these methods which are familiar amongst organic polymers, may also be used in obtaining the kinetic parameters for the, thermal degradation of terpolymers. Finally it is again observed from the Table 4 that the thermal stability of terpolymers follow the same order as has been predicted earlier from the non-isothermal TG data.

The order thermal stability is SOMF-IV > SOMF-III > SOMF-II > SOMF-I. From the results of kinetic parameters it is concluded that the terpolymer resins prepared from a higher molar ratio of salicylaldoxime exhibited a lower rate of decomposition suggesting the order of stability as: SOMF-I< SOMF-II < SOMF-III < SOMF-IV. This fact is further supported by the increasing order of melting points (viz, SOMF-I < SOMF-II < SOMF-III < SOMF-IV) of these terpolymer resins. The above mentioned order of stability may be due to the possibility of an almost linear structure of the terpolymer having higher molar ratio of salicylaldoxime which may give rise to a stable structure to the terpolymer chain[26]. The negative values for entropy (ΔS) indicate that the activated polymer has a more ordered structure than the reactants and the reactions are slower than normal. This is further supported by low Z values [23]. Higher value of activation energy suggest the higher stability [23]. Thus the order of thermal activation energy is : SOMF-l < SOMF-II < SOMF-III< SOMF-IV.

CONCLUSION

SOME terpolymer resin was prepared from salicylaldoxime and melamine with formaldehyde in HCl medium by polycondensation method. Thermogravimetric data reveals that the degradation of the terpolymer involves three stages and showing good thermal stability. Higher value of activation energy suggest the higher stability. Thus the order of thermal activation energy is : SOMF-l < SOMF-II < SOMF-III< SOMF-IV.

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