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Smart Terpolymeric Materials : A Study of Thermal Degradation Behaviour

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ABSTRACT

The new terpolymer abbreviated as (PBMF-I) was synthesized by polycondensation reaction of p-hydroxy benzoic acid - Melamine - Formaldehyde monomer in 1: 1: 2 molar proportion using acid catalyst in the temperature range of 120-160 ^{0}C for 6 hrs. The terpolymeric resin synthesized has been characterized by elemental analysis, UV-visible, IR and proton NMR spectral studies. Detailed study on thermal degradation behaviour of the newly synthesized terpolymer has been carried out in order to ascertain the mode of decomposition and kinetic parameters such as order of reaction (n), frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S*). Sharp-Wentworth and Freeman-Carroll methods are used to determine activation energy (Ea) and the thermodynamic parameters. The activation energy determined by these methods is found to be in good agreement with each other. The order of reaction is found out to be 0.9841.

Keywords : Synthesis, Thermal, Thermal degradation behaviour, PBMF-I, Kinetic parameters.

I. INTRODUCTION

Polymers, in performance and characteristics, offer a variety of unique properties, application prospects and diversity which cannot be matched by any other class of materials. Polymers, though introduced in the beginning of 19th century, still play a major role in our daily life. The terpolymers reported earlier are also said to have better acid resistance, better thermal stability and electrical properties. Thermogravimetric analysis of 8-hydroxyquinoline–melamine–formaldehyde resin has been carried out by Gurnule and his co-workers (1) and have also reported the thermal degradation of resin preparing from 4-hydroxyacetophenone, catechol with formaldehyde and calculated the various kinetic parameters. Thermogravimetric analysis of copolymer obtained from p-cresol, dithiooxamide with formaldehyde has also been reported (2). The study of thermal degradation of terpolymer resins has been carried out by numerous researchers across the world. Terpolymer and their chelates possess attractive applications in the field of environment pollution control, bioinorganic catalysts, hydrometallurgy, semiconducting devices and metal recovery from dilute solutions (3-7). Our previous work on thermal degradation of terpolymers synthesized from salicylic acid/8-hydroxyquinoline and guanidine with formaldehyde has also be documented (8, 9). The thermal stabilities of some newly synthesized terpolymers derived from p-cresol, melamine and formaldehyde were determined using Freeman–Carroll method (10). The thermal decomposition pattern of the terpolymer resins was evaluated by TGA and their kinetic parameters, such as activation energy (Ea), order of the reaction (n), entropy change (ΔS), free energy change (ΔF), apparent entropy (S*) and frequency factor (Z) determined by Freeman–

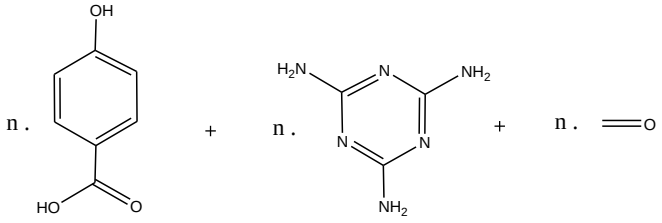
Carroll (FC) and Sharp–Wentworth (SW) methods (11, 12)

Experimental:

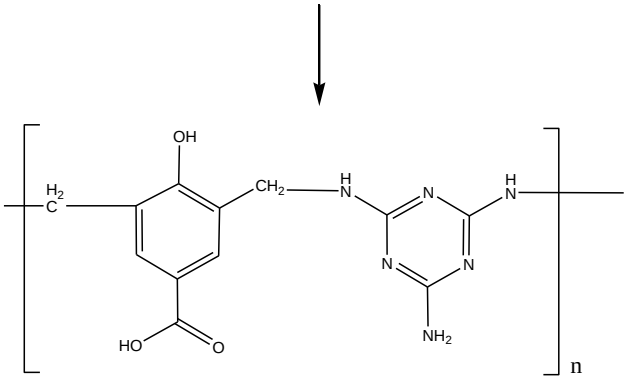
All the chemicals used were of AnalaR grade.

Synthesis

The terpolymeric resin was synthesized by refluxing a mixture of p-hydroxy benzoic acid (0.1 mol) and melamine (0.1 mol) with formaldehyde (0.2 mol) in an digital oil bath for 6 hours at 120 - 160 ^{0}C with occasional shaking. The yellowish coloured product obtained is repeatedly washed with cold and hot water to remove any soluble impurities. The resin was purified by dissolution in 8% NaOH solution and re-precipitated by drop-wise addition of 1:1 (v/v) of 2 M HCl. The terpolymer obtained was dried in an vacuum desicator over anhydrous calcium chloride. The reaction scheme in as given in the following:



p-hydroxybenzoic acid **Melamine** **Formaldehyde**



p-hydroxybenzoic acid - Melamine - Formaldehyde (PBMF I)

Terpolymer

Thermal Analysis

Theoretical Consideration. Thermogram was interpreted and analyzed to obtain information about the % weight loss at which gives information about polymer composition, product formed and kinetic parameters. Kinetics parameters have been determined using two different methods viz. Sharp-Wentworth (11), and Freeman-Carroll (12) methods as follows.

Sharp-Wentworth's:

$$\log [dc/dt] /[1 - c] = \log (A\beta) - [Ea/2.303R] \cdot [1/T], \quad (1)$$

where dc/dt is the rate of change of fraction of weight with change in temperature; β is linear heating rate, dT/dt; c is the fraction of polymer decomposed at time t. Thus, a linear plot of $\log((dc/dt)/(1 - c))$ versus $1/T$ 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 is correct.

Freeman-Carroll's:

$$[\Delta \log (dw/dt)] /[\Delta \log Wr] = (-Ea /2.303R) \cdot [\Delta (1/T)] /[\Delta \log Wr]+ n, \quad \text{----------(2)}$$

where dw/dt is the rate of change of weight with time, $Wr = Wc - W$, Wc is the weight loss at the completion of reaction; W is the total weight loss up to time, Ea is the energy of activation, and n is the order of reaction. The $\Delta \log(dw/dt)$ and $\Delta \log Wr$ values were taken at regular intervals of $1/T$. In this case, $\Delta \log(dw/dt)/\Delta \log Wr$ versus $\Delta(1/T)/\Delta \log Wr$ gives a straight line. The slope and intercept are equal to $-(Ea/R)$ and n, respectively.

II. RESULTS AND DISCUSSION

The newly synthesized PBMF-I terpolymer is found out to be insoluble in almost all organic solvents but soluble in DMF and DMSO.

Thermogravimetric analyses of all the terpolymers has been studied. TGA of the terpolymers was carried out using a NETZSCH4 thermal analyzer along with a NETZSCH STA 409 PC/PG computing system. The samples were scanned in the temperature range of 20 – 1000°C under continuous flow of nitrogen gas at a linear heating rate of 10 °C/ min using a Pt-Pt-Rh thermocouple.

The thermal degradation curve for the PBMF- I is shown in figure.1. The thermogram of the PBMF- I terpolymer exhibited three-stage decomposition in the temperature range 90–1000°C. The first-stage decomposition started at 210°C and ended at 360°C, which may have been due to the loss of the side attached to aromatic ring and carboxyl group (COOH; 55.42% Cal. and 56.8% Found). The second-step decomposition started at 405 –498°C, corresponding to a 65.96% loss, which may have been due to the degradation of hydroxyl group, calculated as 64.59%. The third-step decomposition started from 524 – 883 °C, which may have been a result of the complete decomposition of the polymer ring (100% Cal. and 99.66% Found). The half-decomposition temperature of the PBMF- I terpolymer is also given in table 2. The thermodynamic parameters for the polymers were calculated on the basis thermal *Ea* values, which are shown in table 3.

Table 1. Thermoanalytical data and decomposition data of PBMF- I terpolymer

Terpolymer	Temperature Range (°C)	Decomposition Stage	Species Degraded	% Weight Loss	
				Found	Calculated
PBMF - I	210 – 360	First	Loss of the side chain attached to aromatic ring and carboxyl group	55.42	56.8
	405 – 498	Second	Degradation of the hydroxyl group	64.59	64.59
	524 - 883	Third	Complete decomposition of the polymer ring	99.66	100

Table 2. Activation Energy & Decomposition Temperature of PBMF- I terpolymer

Terpolymer	Decomp. Temp. ^{0}c	Activation Energy (KJ / mole)	
		FC	SW
PBMF - I	498	19.35	17.39

FC- Freeman-Carroll, SW- Sharp Wentworth

1) Table No. 3 Kinetic Parameter of PBMF- I terpolymer

Terpolymer	Entropy Change ΔS (J)	Free Energy Change ΔF (kJ)	Frequency Factor Z (sec^{-1})	Apparent Entropy Change S*(kJ)	Order of Reaction n
PBMF - I	-251.45	130.27	406.31	-23.91	0.9841

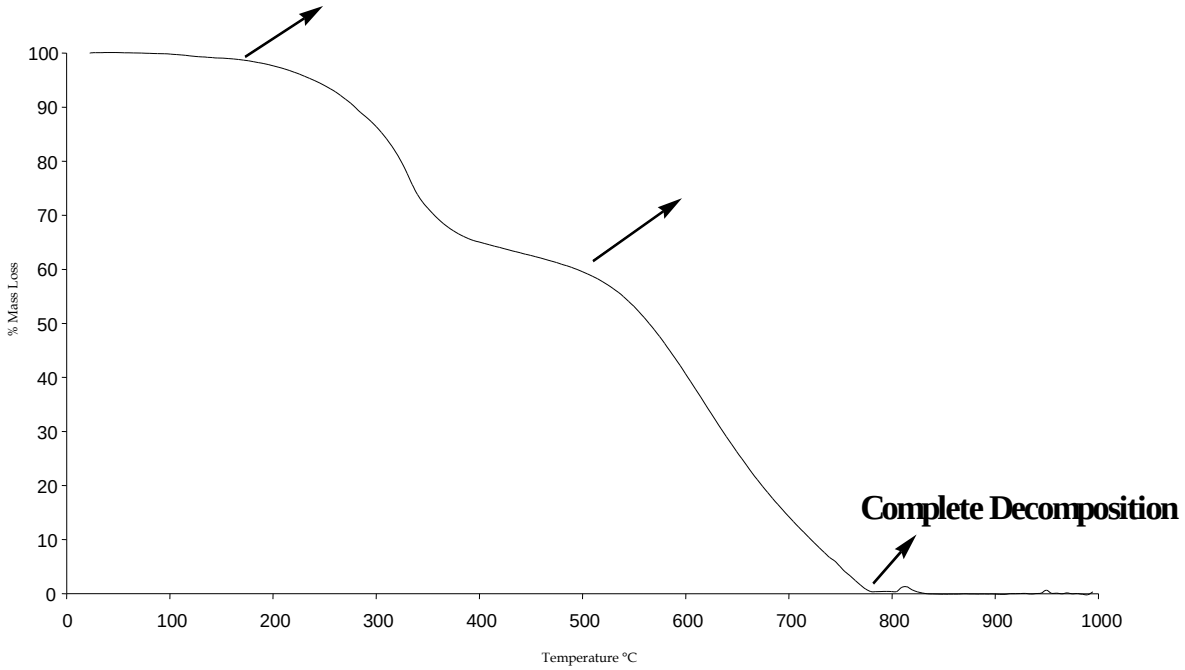


Fig. 1 Thermogram of p-hydroxybenzoic acid , melamine , formaldehyde terpolymer

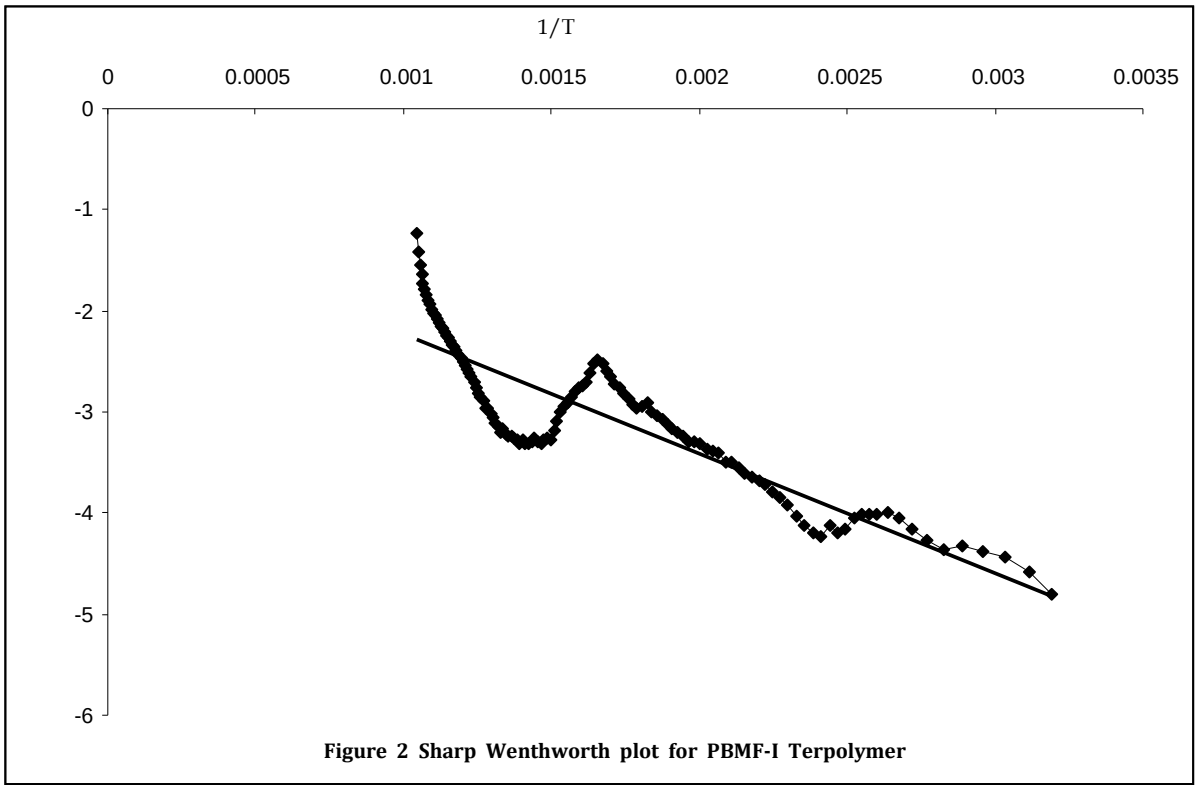


Figure 2 Sharp Wenthworth plot for PBMF-I Terpolymer

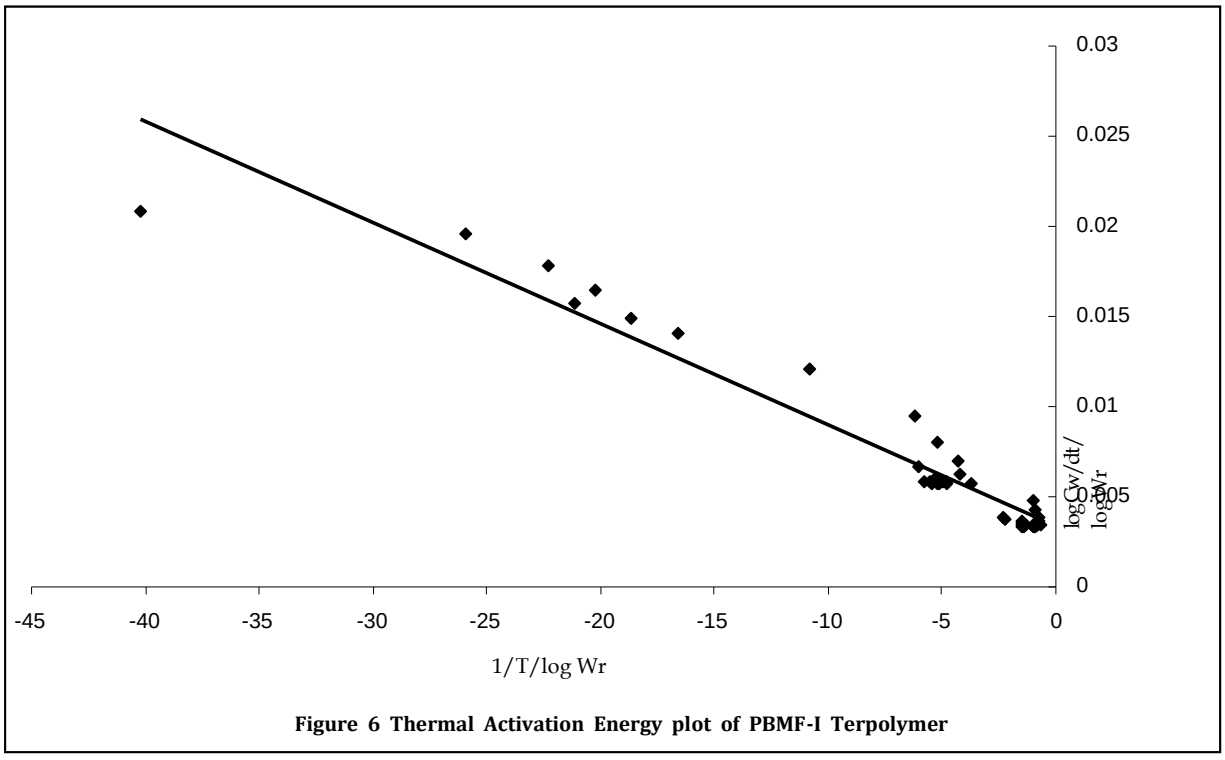


Figure 6 Thermal Activation Energy plot of PBMF-I Terpolymer

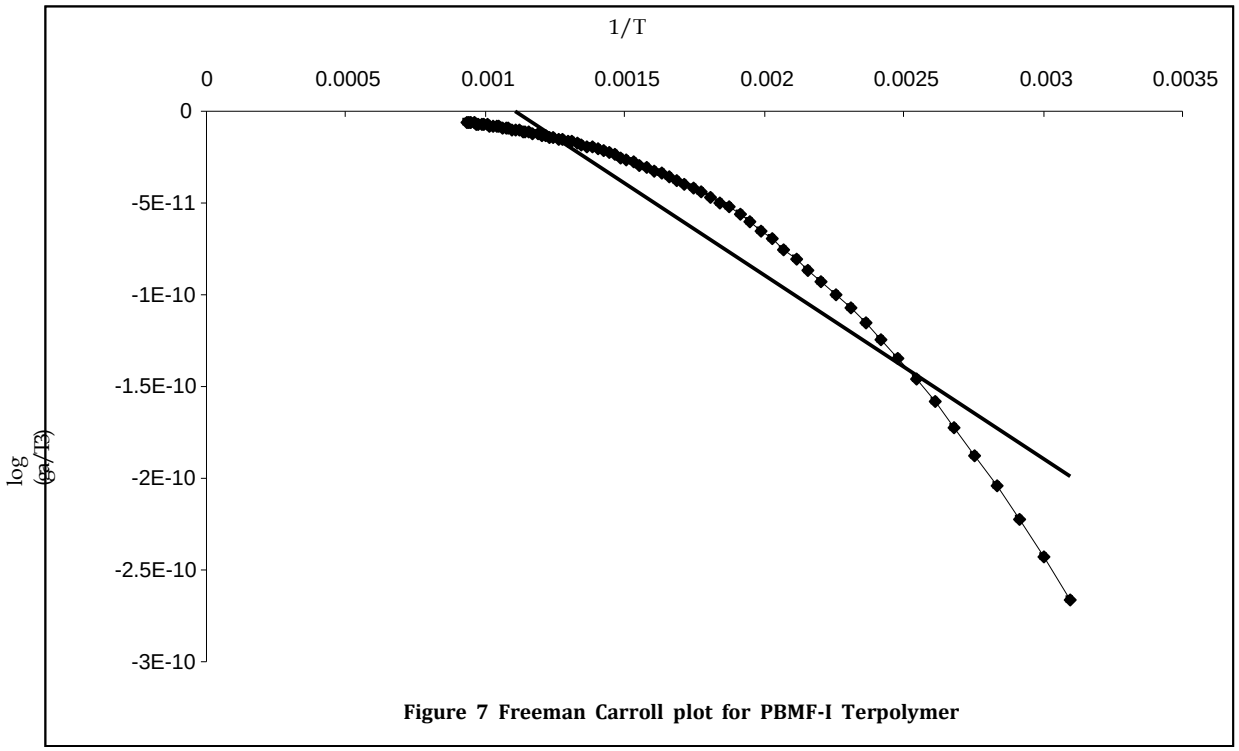


Figure 7 Freeman Carroll plot for PBMF-I Terpolymer

III.CONCLUSION

The thermogram of PBMF- I shows three degradation steps and the terpolymer molecule degrades completely at around 883 ^{0}C.

The TGA pattern indicates that the terpolymer has good thermal stability. The Ea (activation energy) calculated are found to be in good correlation with each other.

The negative entropy and low values of frequency factor calculated by Freeman Caroll method is indicative of the fact that the thermal stability of the terpolymer is a slow reaction.

The decomposition of the PBMF- I terpolymer almost follows first order kinetics but not completely.

IV.Acknowledgment

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