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# Thermal Applications of p-Cresol-Oxamide-Formaldehyde Terpolymer Resin-III

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# ABSTRACT

Terpolymer resin p-COF-III was synthesized by the condensation of p-Cresol (p-C) and oxamide (O) with formaldehyde (F) in the presence of 2M HCl as catalyst with 3:1:4 molar ratios of reacting monomers. The resin was characterized by elemental IR and NMR spectra, the morphology was studied by SEM. Thermal study of the resin was carried out to determine its mode of decomposition and relative thermal stability. The Freeman-Carroll and Sharp-Wentworth methods have been used in the present investigation to calculate thermal activation energy and different kinetic parameter of the terpolymer resins, like frequency factor (Z), entropy change ( $\Delta$ S), free energy change ( $\Delta$ F) and apparent entropy (S\*) have been determined using Freeman-Carroll method.

Keywords: Terpolymer, Thermogravimetric analysis, synthesis, Spectra.

# **INTRODUCTION**

The synthesis of new copolymer resins attracted the attention of researcher because of versatile utility in our day-to-day life. Resins as copolymer which form special class of polymer, are widely known for their uses. Various modified phenol-formaldehyde resins have large number of practical applications [1, 2, 3] viz. high thermal conducting material, excellent abrasive, ion exchangers and many more other renowned applications are reported in the literature.

The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Zhao Hong et. al. studied the thermal decomposition behaviour of phosphorous containing copolystar [4]. The present paper explored the newly synthesized terpolymer resin p-Cresol-Oxamide-Formaldehyde (p-COF-III) in the light of its thermogravimetric study and its applications.

A Thermogravimetric analysis of p-COF-III terpolymer resin is the weight change in materials as a function of time and temperature. This measurement provides basic information about the

thermal stability of the resin. The novelty of this study is that the p-COF-III resin started degradation of high temperature nearly at 120 to 150  $^{0}$ C, indicating that this terpolymer resin is thermally stable at elevated temperature therefore can be used in the aerospace industry, automotive industry and other industry where need the polymer resistance to harsh environment and thermally stable polymers.

#### MATERIALS AND METHODS

#### Synthesis of p-COF-III terpolymer resin

The new terpolymer resin p-COF-III was synthesized by condensing p-cresol (3.24g, 0.2 mol) and oxamide (0.88g, 0.1 mol) with 37 % formaldehyde (14.8 ml, 0.3 mol) in a mol ratio of 3:1:4 in the presence of 2M 200 ml HCl as a catalyst at 140<sup>o</sup>C for 6h in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer 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 p-cresol-formaldehyde copolymer which might present remove be along with p-COF-III terpolymer. The terpolymer was purified further by dissolving in 8% 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 p-COF-III 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 terpolymer resin was found to be 70%. The reaction and suggested structure has been given in Fig. 1.



PCOF- III terpolymer



#### **RESULTS AND DISCUSSION**

#### **Infrared Spectra**

Infrared spectrum of the p-COF-III terpolymer resin is shown in Fig.2 and IR spectral data are tabulated in Table 1. Very broad band appeared in the region 2229 cm<sup>-1</sup> may be assigned to the stretching vibration of phenolic -OH groups exhibiting intermolecular hydrogen bonding between -OH and >C=O and NH group of amide. The band obtained at 1371 cm<sup>-1</sup> suggests the presence of methylene (-CH<sub>2</sub>-) bridges. A sharp strong peak at 1607 cm<sup>-1</sup> may be ascribed to aromatic skeletal ring breathing modes. The 1,2,3,5 tetrasubstitution of aromatic benzene ring can be recognized from sharp and medium/weak absorption bands appeared at 912, 1098, 1149

cm<sup>-1</sup> respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3011cm<sup>-1</sup> which seems to be merged with very broad band of phenolic hydroxyl group [5].



Fig. 2 IR of p-COF-III terpolymer resin

Observed band frequencies (cm <sup>-1</sup> ) (p-COF-III)	Assignment	Expected band frequencies (cm <sup>-1</sup> )		
3229(b,st)	-OH phenolic intermolecular hydrogen bonding	3750-3200		
3011(sh,st)	Aryl C-H stretching	3200-3000		
2917(b,sh)	>CH <sub>2</sub> , -NH, -CH <sub>3</sub> stretching	3500-2800		
1743(b,st)	>C=O stretch (oxamide moiety)	1750-1600		
1607(sh,st)	Aromatic ring (substituted)	1600-1500		
1481(sh)	-NH bending of secondary amide	1570-1490		
1379(sh,sh)	-CH <sub>2</sub> - symmetrical deformation	1390-1370		
1371(sh,sh)	-CH <sub>2</sub> - bridge	1380-1350		
1286(sh)	-CH <sub>2</sub> bending (wagging & twisting)	1370-1280		
1231(b,st)	-CH <sub>2</sub> - plane bending	1300-1250		
784(sh)	-CH <sub>2</sub> bending (rocking)	800-710		
757(sh)	-NH deformation out of plane of secondary amide	800-600		
858(sh)	Tetrasubtituted aromatic ring	830		
912(m)		950		
1098(m)	1,2,3,5 substitution in aromatic ring	1058		
1149(m)		1125		

Table 1 IR frequencies of p-COF-III terpolymer resin

*sh=sharp; b=broad; st= strong; m= medium; w=weak* 

# Nuclear Magnetic Resonance spectra

The NMR spectrum of p-COF-III terpolymer was scanned in DMSO-d<sub>6</sub><sup>-</sup> The spectra are given in Fig.3. The spectral data are given in Table 2. The chemical shift ( $\delta$ ) ppm observed is assigned on the basis of data available in literature [6]. The p-COF terpolymer sample shows an intense weakly multiplate signals at 2.16 ( $\delta$ ) ppm may be attributed to methyl proton of Ar-CH<sub>3</sub> group. The medium singlet at 2.56 ( $\delta$ ) ppm may be due to the methylene proton of Ar-CH<sub>2</sub> bridge. The singlet obtained in the region of 3.46 ( $\delta$ ) ppm may be due to the methylene proton of Ar-CH<sub>2</sub> bridge. The weak multiplate signals in the region 5.22 ( $\delta$ ) ppm are attributed to protons and –NH bridge. The weak multiplate signals (unsymmetrical pattern) in the region at 6.95 ( $\delta$ ) ppm may be due to terminal methylene group. The signals in the range at 8.5 ( $\delta$ ) ppm may be due to phenolic hydroxy protons. The much downfield chemical shift for phenolic –OH indicates clearly the intramolecular hydrogen bonding on -OH group. The signal at 0 ( $\delta$ ) ppm is due to TMS (tetra

methyl silane) the signal at 1.20 ( $\delta$ ) ppm may due to -CH<sub>3</sub>-C= moiety. The signal at 2.80 ( $\delta$ ) ppm and 3.37 ( $\delta$ ) ppm may due to CH<sub>2</sub>-N $\langle$  moiety. The signal at 4.60 ( $\delta$ ) ppm may due to >CH-O group. The signal at 7.30 ( $\delta$ ) ppm may due to aromatic proton (Ar-H) [6].





Table 2	$^{1}$ H	NMR	data	of	p-COF-	·III	terpolymer	resin
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Observed Chemical Shift ( $\delta$ )	Nature of proton	Expected chemical		
ppm (p-COF-III)	Assigned	shift (δ) ppm		
2.16	Methyl proton Ar-CH₃ group	2.00 to 3.00		
1.20	-CH <sub>3</sub> -C≡C	1.00 to 2.00		
2.56	Methylenic proton of Ar-CH <sub>2</sub> moiety	2.00 to 3.00		
2.80 3.37	-CH <sub>2</sub> -N< group	2.00 to 4.00		
3.46	Methylenic proton of Ar-CH <sub>2</sub> -N moiety	3.00 to 3.5		
4.60	>CH-O group	5.00 to 5.5		
5.22	Proton of -NH bridge	5.00 to 8.00		
6.95	Terminal -CH <sub>2</sub> group	6.00 to 7.00		
7.30	Aromatic proton (Ar-H)	6.2 to 8.5		
8.5	Proton of phenolic – OH involved intramolecular hydrogen bonding	8.00 to 10.00		



Fig. 4 SEM micrographs of p-COF-III terpolymer resin

# Scanning Electron Microscopy (SEM)

Fig. 4 shows the scanning electron microscopy (SEM) [7] micrographs of the pure p-COF-III terpolymer sample at 1500X and 3000X magnification. The morphology of resin exhibits growth of crystals from polymers solution corresponding to the most prominent organization in

polymers on a large scale such as in size of few millimeters spherulites. The morphology of resin shows a fringed micelle model of the crystalline-amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. The micrograph of pure sample shows the presence of crystalline-amorphous layered morphology which is the characteristic of polymer. The monomers have crystalline structure but during condensation polymerization of some crystalline structure lost into amorphous nature.

The polymers under study are terpolymer and hence, it is very difficult to assign their exact structures. However, on the basis of the nature and reactive position of the monomers, elemental analysis, IR, NMR spectral studies and taking into consideration the linear structure of other phenol formaldehyde and the linear branched nature of urea-formaldehyde polymers, the most probable structure has been proposed for p-COF-III terpolymer resin, has been shown in Fig.1. The morphology of the resin shows the transition between crystalline and amorphous nature.



Fig. 5 Decomposition Pattern of p-COF-III Terpolymer Resin

# Thermogravimetric of p-COF-III terpolymer resin

Thermogram of p-COF-III terpolymer resin is shown in Fig. 5, in the temperature range of 40°C to 800°C, showing three stage decomposition reaction with initial loss of one water molecule corresponding the loss of 3.09% found and 3.16% calculated. The first step of decomposition starts from 150°C to 400°C, corresponding to the loss of mass equal to 26.33% found and 26.71% calculated, which may be due to the degradation of two hydroxyl and two methyl groups

attached to two aromatic benzene rings, may be due to increasing cross linking, strain and unstability by thermal vibrations. The second step decomposition starts from 400°C to 580°C, when the molecule loss it's fine structures, cross linking, strain and unstability may increased, which result of showing the mass loss equal to 74.22% found and 74.47% calculated which may be due to the degradation of two aromatic benzene rings. The third step starts from 580°C to 800°C, when the strained molecule suffer unzipping of cross linking, leading to the mass loss of 80.12% found and 80.33% calculated, may be due to degradation of side chain of oxamide consequently the residue left behind (19.88% found and 19.67% calculated) which may be oxamide moiety [8,9].

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been used to determine the kinetic parameters of p-COF-III terpolymer sample.

Sharp-Wentworth method: In this method following expression is used.

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

Where,  $\beta$  is the linear heating rate. The graph of  $\log \left[\frac{dc/dt}{\Delta(1-c)}\right]$  versus 1/T has been plotted. The graph is a straight line with Ea as slope and A as intercept. The linear relationship confirms that the assumed order (n) = 1 is correct.

Freeman-Carroll method: In this method following expression is used.

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_{r}} = (-Ea/2.303R) - \frac{\Delta(1/T)}{\Delta \log W_{r}} + n$$

where dw/dt = rate of change of weight of terpolymer sample with respect to time Wr = Wc-W, where Wc is the weight loss at the completion of the terpolymer reaction or at definite time and W is the total weight loss upto time t. T is the temperature, R is the gas constant and n is the order of reaction. Hence the graph of

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_{r}} \text{ versus } \frac{\Delta(1/T)}{\Delta \log W_{r}}$$

Should give on Y axis (x=0) an intercept for the value of n, the order of reaction and the slope m = -Ea/2.303R.

Using thermal decomposition data and then applying the Sharp-Wentworth method (Fig. 6) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method [10,11] (Fig. 7 and 8). Thermodynamic parameters such as entropy change ( $\Delta$ S), free energy change ( $\Delta$ F), frequency factor (Z) and Apparent entropy (S\*) calculated on the basis of thermal activation energy are given in Table 3.

The analysis of the thermograms indicates that the decomposition of the terpolymers is three stage processes after a loss of water molecule at 150°C. In the first step side chain attached to aromatic nucleus and hydroxyl groups decompose. In the second step, aromatic nucleus decompose while in the third step side chain attached to oxamide polymer and oxamide itself

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degraded and finally there is no residue remained after completion of degradation. Decomposition is completed at about  $800^{\circ}$ C in all terpolymer resins. The degradation with increasing temperature may be due to increasing strain in the molecule due to the thermal vibrations, which in increased the cross linking among the chain and increase unstability. To maintain stability and to decrease strain, the molecule undergoes degradation slowly.

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 3). From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of p-COF-III terpolymer can be classed as a 'slow' reaction. There is no other obvious reason [12].

Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is known not to obey first order kinetics perfectly [12, 13].

Table 3 Results of Thermogravimetric Analysis of p-COF-III Terpolymer

Terpolymer	Half decomposition Temp. (K)	Activent ent Ea (K FC	vation ergy J)/mol SW	Entropy change $\Delta S$ (J)	Free energy ΔF (KJ)	Frequency factor (Z) (Sec. <sup>-1</sup> )	Apparent entropy (S*) (KJ)	Order reaction (n)
p-COF-III	793	27.576	27.514	-165.092	102.548	785	-19.03	0.94
	CW Sharp Wanter outh Mathad			EC Ena	aman Camall	Mathad		

SW – Sharp-Wentworth Method

- Freeman–Carroll Method



#### CONCLUSION

1. In TGA 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, indicate that the resin is stable at elevated temperature.

2. Low values of frequency factor may be concluded that the decomposition reaction of p-COF-III terpolymer resin can be classified as 'slow reaction.

Contribution of the results to the development of an important area of research because of the remarkable properties and the lower cost of manufacturing p-COF-III terpolymer resin can have major potential application in various sectors.

Thermogravimetric analyses of p-COF-III terpolymer resin the weight change in materials as a function of time and temperature. This measurement provides basic information about the thermal stability of the resin. The p-COF-III resin started degradation of high temperature, indicating that this terpolymer resin is thermally stable at elevated temperature therefore can be used in the aerospace industry, automotive industry and other industry where need the polymer resistance to harsh environment and thermally stable polymers.

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