



SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION STUDIES OF COPOLYMER DERIVED FROM P-HYDROXYBENZOICACID, ACRYLAMIDE AND FURFURAL

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Abstract

Copolymer p-HBAF has been synthesized using monomer p-hydroxybenzoic acid, acrylamide and furfural in molar ratio 1:1:2 by polycondensation method in acid medium. Various characterisation techniques, such as elemental analysis, FTIR, UV-Visible, XRD and SEM were used to evaluate the structure and characteristics of the copolymer. TGA method was used to calculate the thermal stability and kinetic parameter of copolymer resin. The Sharp-Wentworth (SW) and Freeman-Carroll (FC) were used to evaluate the activation energy. The decomposition reaction for copolymer was found to be of first order but higher order was obtained for the composite. From the results, the activation energy, frequency factor and entropy change support the good thermal stability of copolymer.

Keywords: Copolymer, Morphology, Thermal degradation, Polycondensation, Resin, Activation energy.

Introduction

In recent years, the synthesis of polymers from renewable resources has attracted the attention of many research workers [1]. A large amount of work has been reported in the laboratories on the synthesis, characterization, structure and thermal studies of several polymers [2]. The Freeman-Carroll and Sharp-Wentworth methods have been used to evaluate various kinetic parameters for the copolymer. The methods for TGA studies [3] are especially based on the assumptions of

Arrhenius equation where the thermal and diffusion barriers are negligible.

Copolymers are a very special class of polymer which are known for their versatile uses and the nature of these polymers are found to be crystalline, amorphous or resinous in nature [4]. The use of copolymer for the present generation has greatly increased in recent years, they occupy the special position in the field of polymer science [5]. The thermal decomposition kinetics of polymer 2-amino-6-nitrobenzothiazole, melamine and formaldehyde have been studied by Gupta and Co-workers [6]. Michael et al. studied synthesis characterization and thermal degradation of 8-hydroxyguanine-guanidine-formaldehyde terpolymer [7]. Rahangdale and co-workers studied thermal degradation of polymer derived from 2,4-dihydroxyacetophenone, dithioamide and formaldehyde [8-9]. It is important to note that the different methods used have been developed by considering kinetic model remains unchanged in the process. Hence it is concluded that kinetic study of is the function of reacted fraction. [10-13]. The literature studies show that no copolymer has been synthesized by using p-hydroxybenzoic acid and acrylamide and furfural. Thus, in the present paper we report the synthesis, structural characterization and thermal degradation studies of copolymer.

Experimental

Materials

p-Hydroxybenzoic acid, acrylamide and formaldehyde was procured from Central Scientific Company Nagpur. The solvents like

HCl, DMSO was procured from Himedia. Entire chemicals are of analytical grade and pure grade.

Synthesis of Copolymer Resin

Para-hydroxybenzoic acid - acrylamide - formadehyde (p-HBAF) copolymer was synthesised by polycondnsation of p-Hydroxybenzoic acid, acrylamide and formadehyde with 2M HCl in the ratio 1:1:2 in

an oil bath at a temperature of $120 \pm 2^\circ\text{C}$ with occasional shaking for about 5hrs. The copolymer obtained was black in color, washed with hot water until it was free from chloride ions, it was filtered and dried in a vacuum at room temperature. The purified copolymer was finely crushed. The yield of the copolymer was found to about 86%.

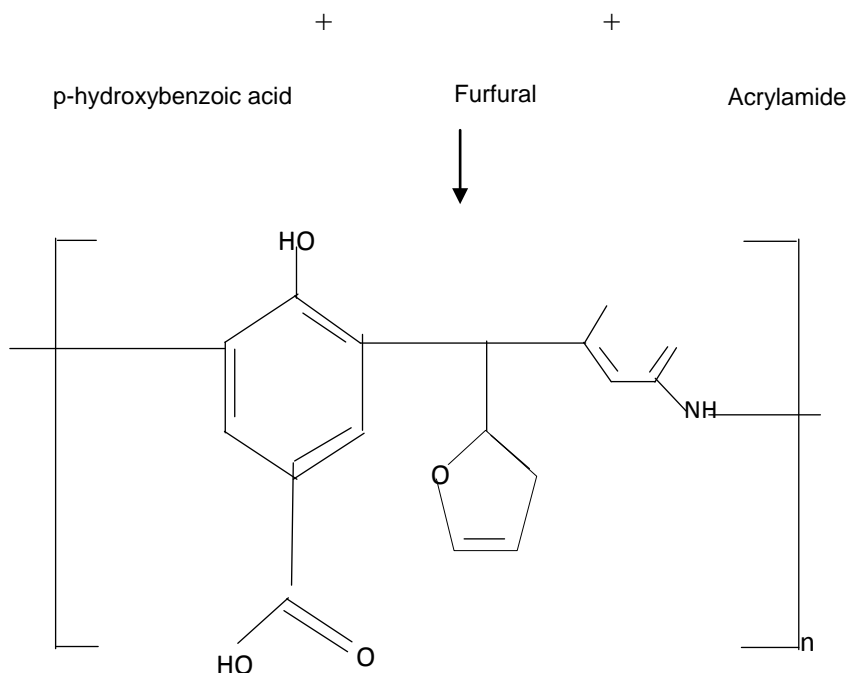


Fig.1 Synthesis of copolymer p-HBAF

Analytical and physico-chemical studies

Microanalysis for hydrogen, carbon and nitrogen content of copolymer sample was carried out on ElementarVario EL III CARLO ERBA 1108 Elemental Analyzers instrument. The UV-visible spectra of the copolymer in DMSO was scanned on automatic recording double beam spectrophotometer (UV-VIS-NIR Spectrometer) in the region of 200–800 nm. Infrared spectra was carried out on Thermo Nicolet Avatar 370, FT-IR spectrometer in KBr pellets in the region of $4000\text{--}500\text{cm}^{-1}$. Proton NMR spectra was recorded on Bruker 400 Advance-III, FT-NMR spectrometer using DMSO d_6 as a solvent. SEM has been carried out at different magnification using JEOL 6390LV, scanning electron microscope. The TGA of the copolymer was carried out using Perkin Elmer Diamond TGA/DTA thermal analyzer. All the spectral and analytical studies for the synthesized copolymer sample were

carried out at Sophisticated Analytical Instruments Facility, SAIF, Cochin University, Cochin, India.

Results and discussion

The electronic absorption spectra of p-HBAF copolymer has been scanned in pure DMSO in the range 190–800 nm and presented in Fig. 2. The spectra exhibit two absorption maxima at 285 nm and 340 nm. These observed position of absorption bands represent the presence of a carbonyl group containing a carbon oxygen double bond which is in conjugation with the aromatic nucleus.

The newly synthesized p- HBAF copolymer resin was found to be black in colour .The copolymer is soluble in solvent like DMF, DMSO, and THF while insoluble in almost all other organic solvents.

Elemental analysis:

The percentage of element present in copolymer was concluded by the calculated and experimental value found for carbon 66 %, hydrogen 4.02%, nitrogen 4.33% and oxygen is

24.76% which are in good arrangement with each other. The value of elemental analysis confirm the proposed structure of copolymer $C_{18}H_{13}O_6N$. [14-20].

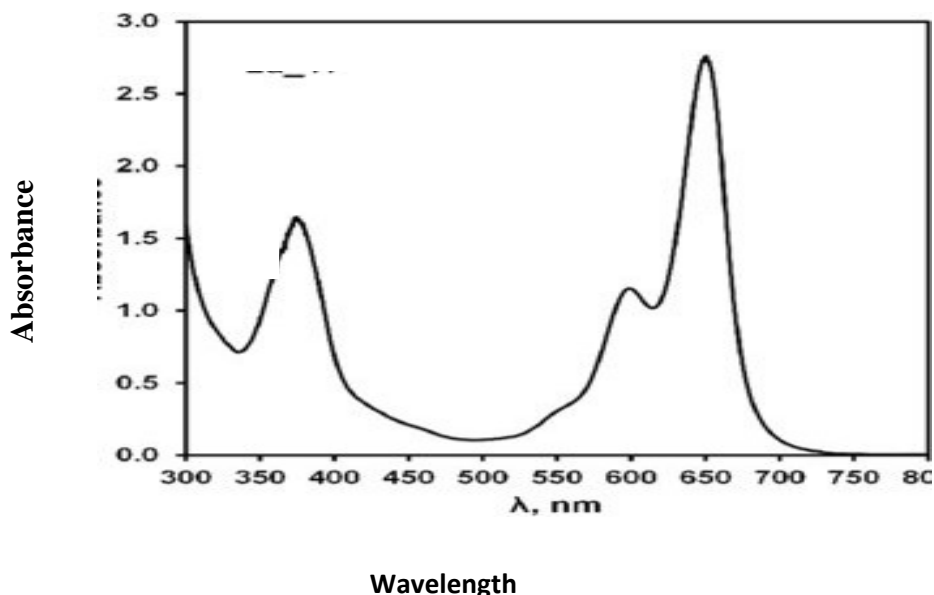
Table 1 Elemental analysis and empirical formula of copolymer resin.

Copolymer resin	% of C Observed (Cal.)	% of H Observed (Cal.)	% of O Observed (Cal.)	% of N Observed (Cal.)	Emperical formula	Emperical formula weight
p- HBAF	65.81% (66%)	2.33 (4.02%)	23.90% (24.76%)	4.01% (4.33%)	$C_{18}H_{13}O_6N$	339

UV-visible spectra

The appearance of more intense band can be account for $\pi \rightarrow \pi^*$ electronic transition while the less intense band may be due to $n \rightarrow \pi^*$. The extra shift of absorption to the longer

wavelength region from basic value (viz. 240 nm and 310 nm respectively) may be because of conjugation effect and existence of phenolic hydroxyl group which is responsible for hyper chromic effect i.e. max higher value.

**Fig.2.** UV-visible spectra of p-HBAF Copolymer**FT-IR spectral analysis**

The structure of synthesized resin was analysed by FTIR Spectrum of p-HBAF in fig-3. A broad peak appeared in the region of 3423.12cm^{-1} is assigned to the amine group of Ar-NH group and -OH merged in the copolymer. A peak appeared at 2755cm^{-1} is attributed to aromatic

ring stretching modes. A peak appeared in the region 2825cm^{-1} is attributed to -CH₂ linkage present in copolymer. The specific adsorption band at 3258.21 was caused by -NH bridge from copolymer. A band at 2927 indicates -CH₂ stretching involved in the copolymer. [21]

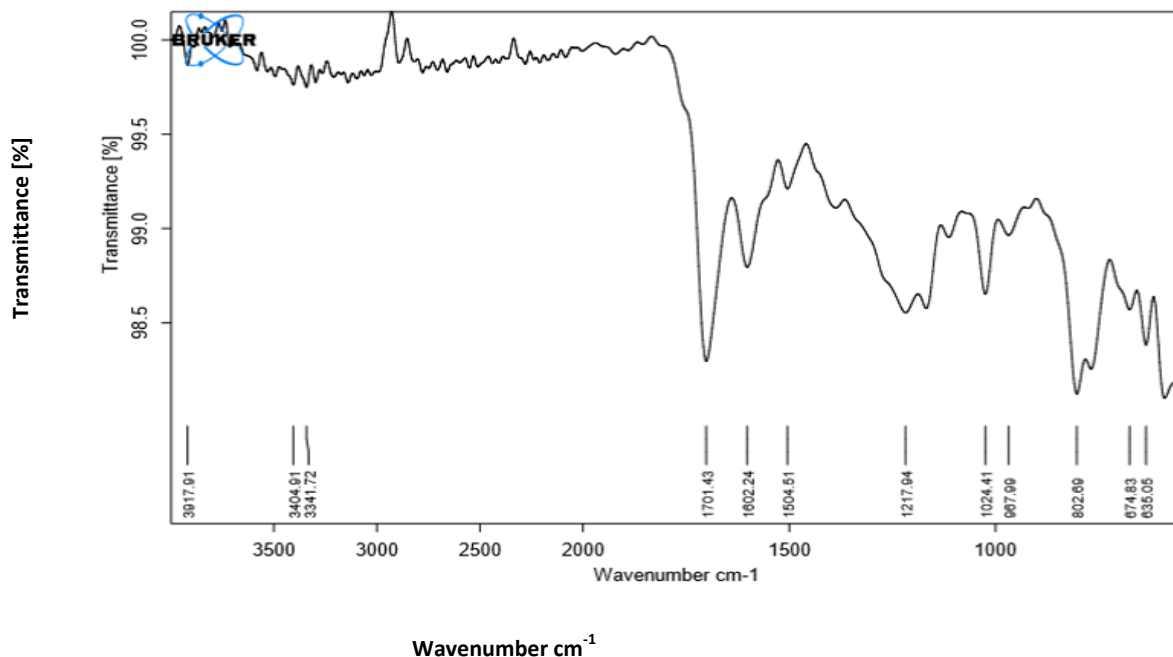


Fig.3.FT-IR spectra of p-HBAF Copolymer

SEM morphological details

The morphology of the synthesized p-HBAF copolymer was studied by scanning electron micrograph at distinct magnification which is presented in Fig. 4. The morphology of the resin displays spherules and fringed model. The spherules are complex polycrystalline formation smooth surface. This shows the copolymer resin is

crystalline in nature. It also shows a fringes model of the amorphous-crystalline structure. The level of crystalline character depends on the acidic nature of monomer. The copolymer shows an additional amorphous character with a closed packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix. The existence of few holes and cracks are noted which may be because of air voids useful for ion exchange studies. [22-27]



Fig.4. SEM of p

X-RAY Diffraction

The three major aspects of investigating the crystal structure are degree of crystallinity, crystalline orientation and lattice size. Herman,

Karst and Flaschner developed a quantitative method for determination of the degree of the

crystallinity ie relative proportion of crystalline domain in the crystalline-amorphous composite structure[28-32].

In the above investigation Ruland and Vonk method has been employed for calculating the degree of crystallinity value. All

sharp peaks around $2\Theta = 12^{\circ}, 14^{\circ}, 18^{\circ}, 21^{\circ}, 26^{\circ}, 28^{\circ}, 30^{\circ}$ indicates highly crystalline nature of polymeric material Based on data analysis the polymer synthesized can be considered as crystalline in nature.

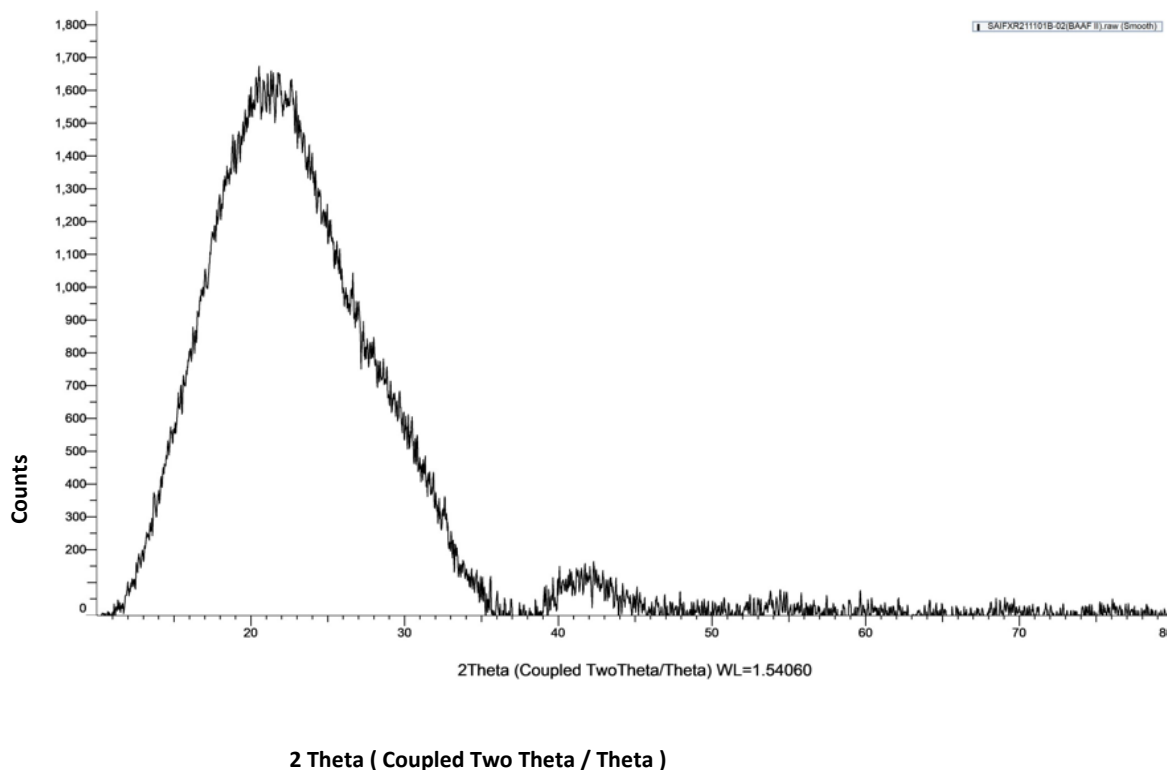


Fig.5. XRD of p-HBAF Copolymer

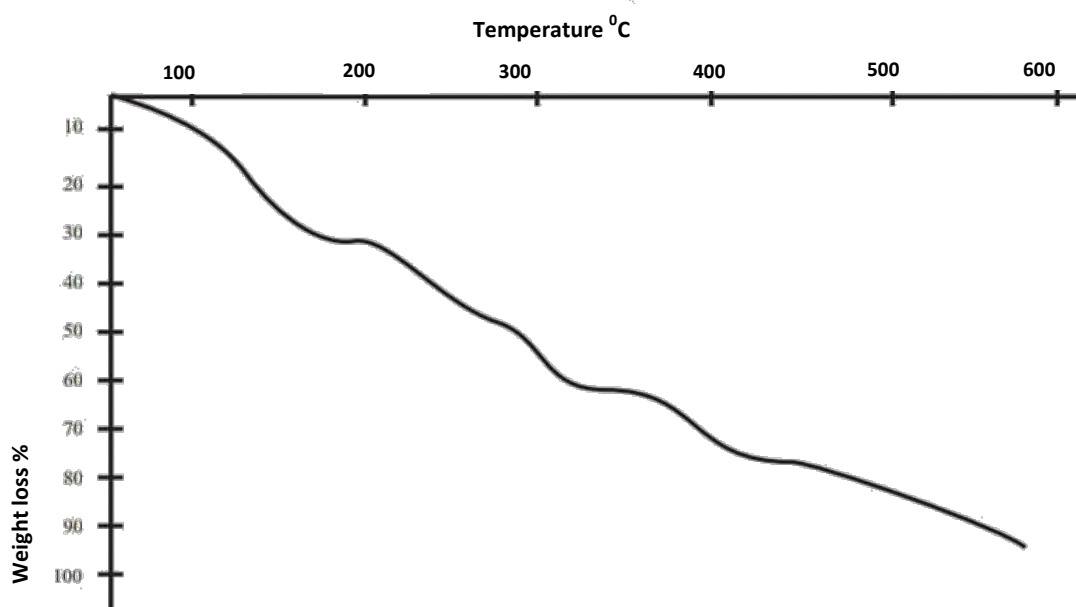
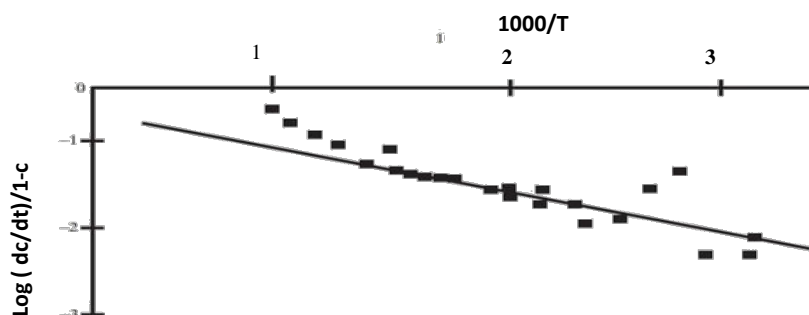
Thermogravimetric analysis

Thermogram of copolymer p-HBAF is presented and shows three steps in degradation reaction, after loss of one crystalline water molecule entrapped in the copolymer molecule, in the temperature range 50°C – 100°C . The initially decomposition take place between 50°C – 70°C corresponds to 2.04% loss which may be due to loss of water molecule against calculated 2.01% present per repeat unit of the polymer. The first stage degradation starts from 70°C – 530°C which may be due to gradual loss

of phenolic $-\text{OH}$, $-\text{CO}-\text{C}_6\text{H}_5$ and $-\text{O}-\text{CH}_3$ groups (found 52.08% and calculated 52.53%) attached to aromatic benzene ring. The second step of decomposition begins from 510°C – 585°C corresponding to 83.09% due to degradation of aromatic ring along with methylene group against calculated 82.81%. The third step of degradation begins from 585°C – 670°C corresponding to removal of naphthalene moiety (97.50% found and 100% calculated). The half decomposition temperature for copolymer resin is found to be 510°C . [33-39]

Table2 Thermal degradation behaviour of p-HBAF

Copolymer resin	Stages of de-composition	Temperature range ($^{\circ}\text{C}$)	Group degraded	%Weight Loss	
				Observed	Calculated
p-HBAF	First	50-70	One water molecule	2.01	2.04
	Second	70-510	Three-OH, Three COC_6H_5	52.08	52.53
	Third	510-585	Three aromatic ring, four $-\text{CH}_2$	83.09	82.81
	Fourth	585-670	Naphthalene moiety	97.50	100

**Fig.6.**TGA Plot of p-HBAF Copolymer**Fig.7.**Sharp-Wentworth plot for p-HBAF Copolymer**Reference**

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