THERMAL DECOMPOSITION OF TERPOLYMERIC RESIN DERIVED FROM P-NITROPHENOL, RESORCINOL AND FORMALDEHYDE

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Abstract:

The resin (abbreviated as PNPRF) was derived from acid catalyzed polycondensation of p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) using 1M HCl at 120-125^{0}C. The terpolymer resin was characterized by using elemental and spectral analysis. In the present paper, thermal decomposition was studied over a wide range of temperature. The thermokinetic parameters were determined using Freeman-Carroll (FC) and Sharp Wentworth (SW) method in temperature range (217-502^{0}C).The values of activation energies (Ea), entropy (ΔS^*) and free energies (ΔG^*) obtained by both method. The order of degradation reaction determined by FC method was confirmed by SW method.

Keywords: Polycondensation, resin, terpolymeric resin, thermal degradation, thermokinetic parameter, Freeman Carroll, Sharp Wentworth.

INTRODUCTION

The work on polymers has long been an interesting topic of scientific research and industrial applications due to its potential to promote improvement in some physical properties of the resultant polymer composites such as stiffness, modulus, mechanical strength, and thermal conductivity, temperature performance and dimensional stability. Thermokinetic parameters which can be used to deduce the lifetime of polymers at different temperature [1]. It is almost hard to obtain the exact kinetics parameters for each polymeric degradation reaction [2].

Recently, there has been growing interest in finding new applications for available polymers in all spheres of life [3–8].Synthesis, charectarisation and thermal study of terpolymeric resin derived from m-cresol, melamine and formaldehyde studied [9]. Structural and thermokinetic study of resin-I derived from p-hydroxyacetophenone, quinhydrone and melamine reported [10]. Thermokinetic parameters of terpolymeric resin derived from p-hydroxyacetophenone, bis-(2-amino-1, 3, 4-thiadiazole) and glycerol studied Urade *et al* [11].

An ecofriendly synthesis of terpolymeric resin anthrinilic acid-thiourea and formaldehyde were studied, the kinetic parameters were evaluated on the basis of the thermogaravemetric data [12]. Masram *et al* reported kinetic study of thermal degradation of resin derived from salicylaldehyde, ethylenediamine and formaldehyde [13]. Thermogaravemetric study of polymer provides information about the degradation pattern during heating and thermal stability reported [14]. Actually these parameters rather represent the overall weight loss behavior during the thermal decomposition as a function of temperature. Hence in literature several methods have been reported for the determination of kinetic parameters from thermal analysis. [15]. Many coworkers determined various kinetic parameters such as ΔS, A and ΔG by using Freemen Carroll and Sharp-Wentworth method [16-17].

Present paper deals with the evaluation of thermokinetic parameters of PNPRF resin by using following methods [18-19].

A) Freeman-Carroll method: In this method activation energy and order of degradation is related with following expression,

$$\frac{\Delta \lg(dw/dt)}{\Delta \lg W_r} = \left[-\frac{Ea}{2.303\,R}\right] \times \frac{\Delta \,/T)}{\Delta \lg W_r} + \iota.$$

Where,

dw/dt = rate of change of weight with time

Wr = Wc-W (difference between weight loss at completion of reaction, and at time t

Wc = Weight loss at completion of reaction

W = Total weight loss up to time t

Ea = Energy of activation

n = Order of reaction

The plot of $\dfrac{\Delta \lg dw/dt}{\Delta \lg Wr}$ vs $\dfrac{\Delta \, T}{\Delta \lg Wr}$ gives a straight line,

from slope, energy of activation (Ea) can be determined, with the help of intercept order of reaction (n) can be obtained.

B) Sharp-Wentworth method: Following expression has been used to evaluate the kinetic parameters.

$$\log \frac{(d\alpha \, dt)}{(1-\alpha^{\,n}} = \log \frac{A}{\beta} - \frac{Ea}{2.303 \, RT}$$

Where,

dɑ/dt = Fraction of weight loss with time

β = Linear heating rate

A = Frequency factor

ɑ =Fraction of amount of reactant

By plotting the graph between log $\log \dfrac{d\alpha \, dt}{(1-\chi^{\,n}}$ vs $\dfrac{1}{T}$ we

obtained the straight line which give energy of activation (Ea) from its slope and frequency factor (A) can be evaluated from intercept. The change in entropy (ΔS*), change in free energy (ΔG*) can also be calculated by further calculations.

EXPERIMENTAL SECTION

Materials

All chemicals were AR grade or chemically pure grade. p-Nitrophenol, resorcinol and formaldehyde were procured from Sd fine, India. Triple distilled water was used for all the experiments.

Synthesis of p-Nitrophenol-Resorcinol-Formaldehyde terpolymer resin (PNPRF):

A mixture of p-nitrophenol (0.2M), resorcinol (0.1M) and formaldehyde (0.4M) was refluxed in presence of 1M HCl (150ml) in oil bath at 120-125^{0}C for six hours with intermittent shaking. The resinous reddish-brown colored product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The powder product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with diethyl ether to remove p-nitrophenol-formaldehyde co-polymer and resorcinol-formaldehyde copolymer. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipited by gradual drop wise addition of 1:1 HCl with constant and rapid stirring to avoid the lump formation. The PNPRF resin so obtained was filtered, washed several times with hot distilled water. The yield of PNPRF terpolymer resin was found to be 73.05%. Following reaction scheme was used to synthesize of PNPRF resin.
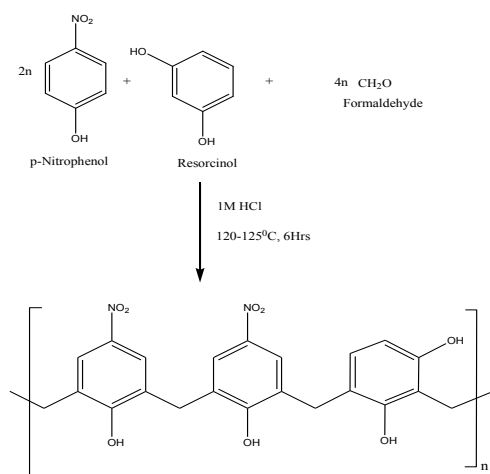
PNPRF
Figure 1. Scheme-synthesis of PNPRF resin

Table 1. Synthetic details PNPRF resin

Resin	p-nitrophenol	Resorcinol	Formaldehyde	Catalyst 1MHCL	React Temp (^{0}C)	Time (hrs)	Yield %
PNPRF	0.2M	0.1M	0.4M	150ml	120-125	6	73.00

RESULTS AND DISCUSSION

Thermogaravemetric analysis of PNPRF Terpolymer resin

Thermo gravimetric analysis (TGA) of PNPRF terpolymer resin sample have been carried out by using Perkins Elmer Diamond TGA/DTA analyzer at heating rate of 10^0C per minute in argon environment up to 1000^0C using Platinum foil crucible at Dept. of Material Science, VNIT, Nagpur, Maharashtra.

Thermogram of PNPRF terpolymer resin shown in following figure 2. The initial loss up to 150^0C was due to loss of water present in PNPRF terpolymer resin. The decomposition of resin between 217^0C to 502^0C was studied. The order of decomposition was found to be 0.72 as

determined by Freeman-Caroll (FC) method which was further confirmed by Sharp-Wentworth (SW) method. FC and SW plots of PNPRF terpolymer resin is shown in figure 3-4. Thermokinetic parameters of PNPRF terpolymer resin are tabulated in table 2.
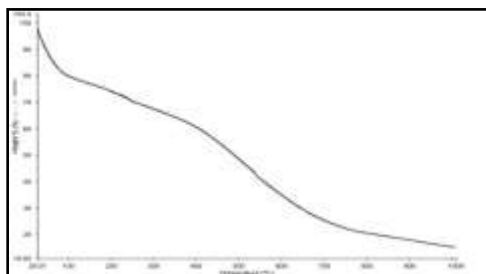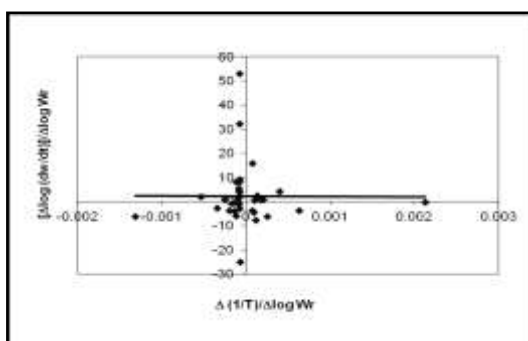

Figure2. Freeman-Carroll Plot of [PNPRF]ₙ
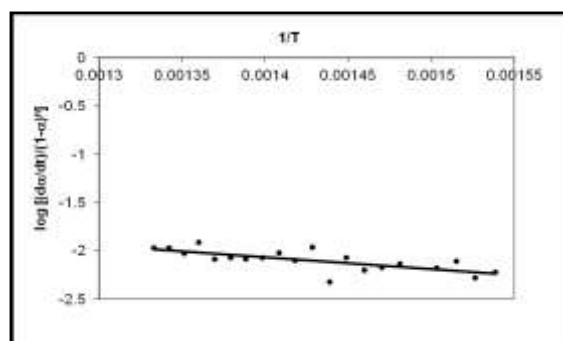

Figure 3. Freemen-Carroll Plot Of [PNPRF]ₙ

Figure 4. Sharp-Wentworth Plot Of [PNPRF]ₙ

Table 2. Thermokinetic parameters of PNPRF-II terpolymer resin

PNPRF Terpolymer resin	Decomposition Temp (°C)	E_a (kJ)	A (min^{-1})	ΔS^* (J/K)	ΔG^* (kJ)	Order (n)
FC method		15.24	189.62	-253.090	154.358	
SW method	217-502	15.12	177.93	-250.120	152.85	0.72

FC=Freemann-Carroll, SW= Sharp-Wentworth

CONCLUSION

From the results of thermal study of PNPRF terpolymer resin conclusions can be drawn.

1) The activation energy obtained by FC method is slightly higher than that obtained by SW method.
2) The values of activation energies, entropy, free energy and frequency factor of degradation are determined by Freeman-Carroll and Sharp-Wentworth methods are found in good agreement, and the values agrees with the tentative structure shown in fig 1.
3) The low value of frequency factor is due to slow degradation.
4) The resin is found to be thermally stable up to 215^0C.
5) The fractional order of degradation is attributed to solid state degradation [20].
6) In pursuance of straight line graph obtained in SW plot when placed n=0.72 confirm the said order which was obtained in FC method.

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