Thermochimica Acta, 241 (1994) 51–56
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(94)01710-X

Synthetic resins.
Part 31. Thermal properties of resin copolymers derived from semicarbazone of 4-hydroxyacetophenone–furfural–substituted benzoic acids

N.K. Mohapatra, S. Lenka and P.L. Nayak *

Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India

(Received 19 September 1993; accepted 20 January 1994)

Abstract

A number of resin copolymers have been synthesized by reacting the semicarbazone derivative of 4-hydroxyacetophenone–furfural–substituted benzoic acids in the presence of an acid catalyst. The structure of the repeat unit of the copolymer has been ascertained from the IR spectrum. The TG analysis of some resin copolymers has been studied. The kinetic parameters of the degradation have been evaluated using five different methods. A plausible mechanism is suggested.

INTRODUCTION

Phenolic resins were the first completely synthetic polymeric material to be made and they have found applications in a variety of different areas [1]. Because of their excellent ablative properties and structural integrity, they can be used as high-temperature polymers [2]. Over the past decade, an increasing number of investigations have concentrated on the development and analysis of thermally stable resins of wide ranging applicability [3–5]. Their use as structural materials for aircraft, however, is limited because of their very low solvent creep, requiring the preparation of solvent-resistant polymers. A survey of the literature has found heat-resistant copolymer compositions with benzoic acid and anilines [6]. Recently we have reported the thermal properties of resin co-polymers derived from *o*-hydroxyacetophenone [7]. This communication presents the thermal properties of resin co-polymers derived from the semicarbazone of 4-hydroxyacetophenone–substituted benzoic acid–furfural.

---

* Corresponding author.

EXPERIMENTAL

Preparation of resins

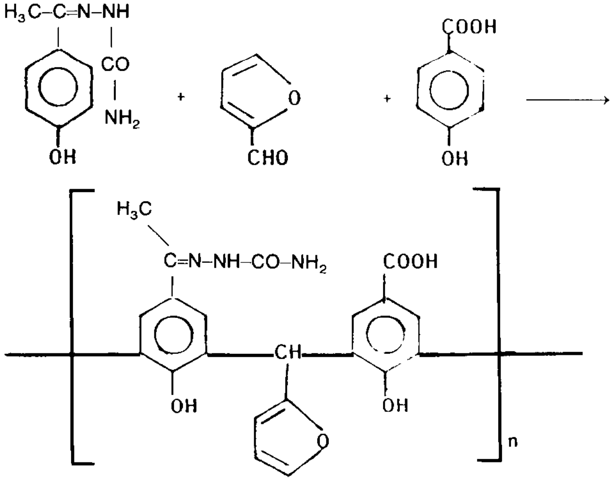
The copolymers were prepared by refluxing a mixture of the semicarbazone of 4-hydroxyacetophenone (0.025 mol), substituted benzoic acid (0.025 mol), and furfural (0.1 mol) in a round-bottomed flask in the presence of acid (2 N) as catalyst, at 120°C for 6–8 h. Hydrochloric acid and succinic acids were used as the acid catalyst. During the course of the reaction, periodic shaking was needed to ensure thorough mixing. After completion of the reaction, the contents were collected with ice-cold water. The product was filtered and washed repeatedly to drive out unreacted materials. The resins prepared by this method are reported in Table 1.

The structural characterization of the resin was made using a Nicolet DX5FT-IR spectrophotometer. A Du Pont 990 modular thermal analysis system consisting of 951 TGA and 905 DSC modules was used for thermal analysis. All the TG curves were recorded in air at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Infrared studies

The polycondensation reaction of 4-hydroxyacetophenone semicarbazone with furfural and 4-hydroxybenzoic acid may be represented as shown in Reaction 1. The structure of the repeat unit of the above resin was identified from the IR spectrum of the copolymer (Fig. 1).



Reaction 1. The polycondensation reaction of 4-hydroxyacetophenone semicarbazone with furfural and 4-hydroxybenzoic acid.

TABLE 1

Physicochemical properties of resins prepared from the semicarbazone of 4-hydroxyacetophenone and substituted benzoic acid in presence of furfural

Comonomer	Catalyst	% Yield	Decomposition temp./°C	Density	Colour/ structure [a]	Solubility parameter (δ) ranges in solvents	Solubility parameter (δ) by different methods	
							Small	Hoy
2-Hydroxybenzoic acid	HCl	67	>300	2.82	Black/Cry	23.2 [b]	23.23	23.24
4-Hydroxybenzoic acid	HCl	68	>300	2.51	Black/Cry	16.5–22.8	21.87	21.42
2-Chlorobenzoic acid	HCl	52	>300	1.85	Black/Cry	15.6–28.7	23.62	23.08
4-Chlorobenzoic acid	HCl	60	>300	1.81	Black/Cry	15.6–26.6	21.8	21.56
2-Aminobenzoic acid	HCl	70	>300	1.08	Black/Cry	24.6 [b]	24.67	24.46
4-Aminobenzoic acid	HCl	68	>300	1.10	Black/Cry	18.9–28.5	24.38	23.8
α-Naphthol	HCl	60	>300	0.886	Black/Cry	18.6–29.7	24.67	23.85
β-Naphthol	HCl	58	>300	0.831	Black/Cry	18.5–29.7	23.73	23.94
Resorcinol	HCl	62	>300	1.39	Black/Cry	18.6–24.8	22.49	21.9
Acetylsalicylic acid	HCl	70	>300	2.37	Black/Cry	21.9–24.8	22.95	22.38

[a] Cry, crystalline. [b] Swells.

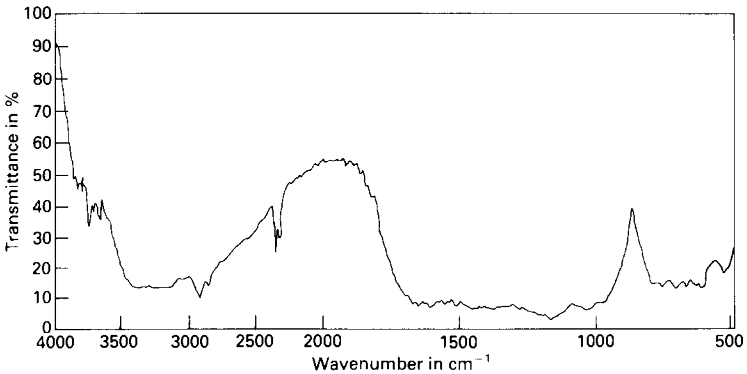


Fig. 1. FTIR spectrum of 4HAS–4HBA–FUR.

The bands in the region 3640–3619 cm^{-1} are due to O–H stretching vibrations. The band at 2568 cm^{-1} is due to the C–H stretching vibration of the CH_3 group. The peaks between 1647 and 1612 cm^{-1} are due to the COOH stretching vibration. The peak at 3441 cm^{-1} is due to the N–H stretching of the amide group. The peak between 1706 and 1676 cm^{-1} is due to the C=O stretching of the amide group. The band in the region 1564–1514 cm^{-1} is due to the C=N stretching of the amide group. The peak at 692 cm^{-1} is due to the 5-membered mono-substituted furan ring.

Thermal studies

The TG thermograms of the resin copolymers derived from the semicarbazone of 4-hydroxyacetophenone and 4-hydroxybenzoic acid, and 4-hydroxyacetophenone and 2-hydroxybenzoic acid, in the presence of furfural (4HAS–4HBA–FU and 4HAS–2HBA–FU) are shown in Fig. 2. The degra-

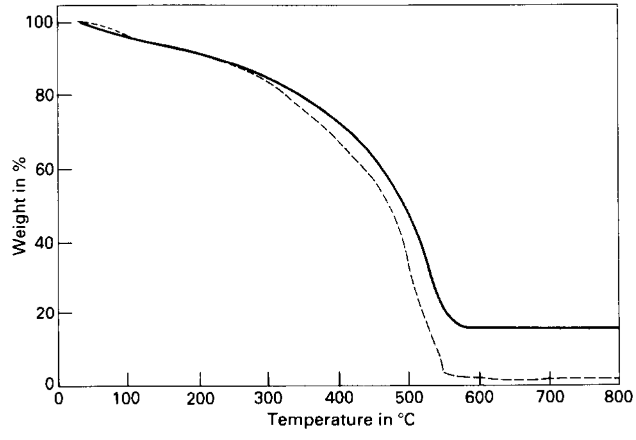


Fig. 2. TGA thermographs: ——, 4HAS–4HBA–FUR; – – –, 4HAS–2HBA–FUR.

TABLE 2

Characteristic thermal data of the resins. Oxidation index, and the percentage weight loss (±2%) at various temperatures

Resin	Temperature/°C						Oxidation index
	100	200	300	400	500	600	
4HAS–4HBA–FU	6	10	18	28	50	85	0.181
4HAS–2HBA–FU	4	10	16	34	60	95	0.176

dation of the resins follows a complex process. A cursory glance at Table 2 shows that the resins under investigation decompose in three distinct steps. The initial slow weight loss up to 200°C (about 10%) is attributed to moisture retained in the samples. A further 50% weight loss of the resins occurs at about 500°C and 80–90% weight loss occurs at around 600°C. The second stage, i.e. up to 500°C, may be due to the thermal degradation of the hydroxyl, carboxyl and the amide groups. In the third stage, cleavage of the aromatic ring occurs in an oxi-degradative manner, producing smaller molecules.

The kinetic parameters of the degradation have been evaluated using the following five methods (Table 3).

The Freeman and Anderson [7] (FA) method involves the evaluation of the quantities $\log(-\mathrm{d}w/\mathrm{d}t)$ and $\log \bar{w}$ corresponding to a constant difference in $1/T$

$$\Delta \log(-\mathrm{d}w/\mathrm{d}t) = n\Delta \log \bar{w} - \frac{E^*}{2.303K}(\Delta 1/T) \qquad (1)$$

TABLE 3

Kinetic parameters of the resins

Resin	0–350°C			350–600°C		
	System	E/(kJ mol^{-1})	A/(s^{-1})	System	E/(kJ mol^{-1})	A/(s^{-1})
4HAS–4HBA–FU	FA	108.40	67.70	FA	41.20	14.40
	BR	16.00	–	BR	12.40	–
	PN	14.40	21.60	PN	10.80	20.50
	HM	17.20	21.50	HM	4.00	4.00
	CR	28.80	79.20	CR	19.20	48.00
4HAS–2HBA–FU	FA	120.00	–	FA	38.80	–
	BR	20.40	–	BR	12.00	–
	PN	15.20	25.20	PN	12.00	21.50
	HM	20.40	50.00	HM	4.30	10.50
	CR	27.20	72.80	CR	12.00	15.20

The slope of the plot of $\Delta \log(-\mathrm{d}w/\mathrm{d}t)$ versus $\Delta \log \bar{w}$ gives n, the order of reaction, and the intercept gives E^*, the activation energy.

The Broido [8] (BR) method is based on the equation

$$\log(\ln 1/y) = \frac{E^*}{2.303R}(1/T) + K \tag{2}$$

According to the Piloyan–Novikova [9] (PN) method, the equation

$$\log(\alpha/T^2) = \log\frac{ZR}{\beta E} = \frac{E^*}{2.303RT} \tag{3}$$

where a plot of $\log(\alpha/T^2)$ versus $1/T$ gives a slope which can be used for calculating the activation energy E^*.

According to the Horowitz–Metzger [10] (HM) method, the equation is

$$\log[-\ln(1-\alpha)] = \frac{E^*}{2.303RT^2} \tag{4}$$

where a plot of $\log[-\ln(1-\alpha)]$ versus $1/T^2$ gives the slope for calculation of the activation energy E^*.

According to the Coats and Redfern [11] (CR) method, the equation

$$\log[-\ln(1-\alpha)/T^2] = \log\frac{ZR}{\beta E^*}(1 - 2RT/E^*) - \frac{E^*}{2.303RT} \tag{5}$$

is used, where a plot of $\log[-\ln(1-\alpha)/T^2]$ versus $1/T$ gives the slope for evaluation of the activation energy E^*.

The values of the activation energy calculated using the above five methods for the two stages, i.e. 0–350°C and 350–600°C, for the degradation of the resins are presented in Table 2. The values are higher in the temperature range 0–350°C. This is obvious because the degradation of the pendant groups present in the resin moiety is faster in the second stage ($\approx$350°C) for which the value of the energy of activation is lower [12, 13].

REFERENCES

1 A.A.K. Whithouse, E.G.K. Pritchett and G. Barnett, Phenolic Resins, Illiffe, London, 1967.
2 C.L. Segal, High Temperature Polymers, Marcel Dekker, New York, 1967.
3 P.D. Stanskey, Y.W. Ross and J.F. Johnson, Org. Coat. Appl. Polym. Sci. Proc., 48 (1983) 784.
4 K.K.J. Sangyo, Jpn. Kokai Tokkyo Koho JP, 5888151 May 26, 1983.
5 M. Paul, Angew. Makromol. Chem., 145 (1986) 323.
6 S.A. Yarosheveski, N.D. Kokoshkina, N.P. Paechenko, A.A. Popor and E.B. Starostina, USSR SU, 1027180, July 7, 1983.
7 D.A. Anderson and E.S. Freeman, J. Polym. Sci., 54 (1961) 253.
8 A. Broido, J. Polym. Sci., A-2, 7 (1969) 1761.
9 G.O. Piloyan, I.D. Raybchikov and O.S. Novikova, Nature, 5067 (1966), 1229.
10 H.H. Horowitz and C. Metzger, Anal. Chem., 55 (1963) 1464.
11 A.W. Coats and J.P. Redfern, Nature, 68 (1964) 201.
12 R.T. Conley, I.F. Bierum and P. Perch, J. Am. Chem. Soc., 20 (1960) 244.
13 R.T. Conley, I.F. Bierum and P. Perch, J. Appl. Polym. Soc., 7 (1963) 103.