Eur. Polym. J. Vol. 22, No. 10, pp. 831–834, 1986
Printed in Great Britain

0014-3057/86 $3.00 + 0.00
Pergamon Journals Ltd

SYNTHESIS, CHARACTERIZATION AND CURING OF BISPHENOL-F–FURFURAL RESIN

Pradip S. Patel and Shanti R. Patel
Chemistry Department, Sardar Patel University, Vallabh Vidyanagar 388120, India

(*Received* 5 *February* 1986; *in revised form* 11 *April* 1986)

Abstract—Polycondensation of bisphenol-F with furfural has been carried out under various conditions. The resin samples have been characterized by spectral studies and viscometry and by estimation of number-average molecular weight. TGA of selected resin samples has been carried out. The curing of three resin samples has been studied by measurement of the amount of cured material as a function of time at specified temperatures. The kinetics of curing of one resin sample have been investigated by DSC.

INTRODUCTION

This communication deals with the synthesis, characterization and results of a curing study of bisphenol-F–furfural (BF–Fu) resins prepared under various conditions. This study is in continuation of work reported earlier for bisphenol-C–furfural resins [1]. Potnis and Jambusaria have reported the characterization and application of bisphenol-F–furfural resins as matrix for composites [2, 3]. The BF–Fu resins are prepared using both acid and base as catalysts and employing monomers in three different molar ratios. Curing of three resin samples prepared using different molar proportions of the monomers in the presence of base has been studied using hexamine as curing agent following the procedure already described [4, 5]. Curing of one of the resin samples has been investigated by DSC with a view to estimating kinetic parameters of the curing reaction.

EXPERIMENTAL

Material

The catalysts and solvents employed for resin synthesis and characterization were laboratory grade reagents. Furfural (Fu) was purified by distillation. Bisphenol-F(BF) was prepared by the reported method [6].

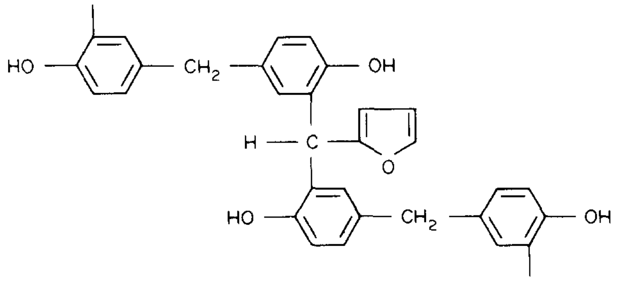
Polycondensation of bisphenol-F with furfural in presence of alkali as a catalyst: formation of BF–Fu-1 resin sample

A mixture of bisphenol-F (0.01 mol, 2.13 g), furfural (0.01 mol, 0.96 g), sodium hydroxide and water (each 5% of the weight of BF) was heated at 100°C for 3 hr. The thick red reaction mixture was poured into water with stirring. The solid was filtered, suspended in water and steam distilled for 2 hr to remove unreacted furfural. Finally the resin was washed repeatedly with hot water to remove unreacted BF. The air dried resin, BF–Fu-2 softened over the range 145°–152°C; the yield was 83%.

All the other resin samples listed in Table 1 were synthesized following the method described above under the reaction conditions specified in the table. During acid catalyzed reaction of phenol with Fu, there is simultaneous self polycondensation of furfural leading to a product of inferior quality [7]. Hence in such a reaction of BF with Fu, the catalyst was added dropwise to the ice cooled mixture of monomers and the mixture was left below 10°C for 1 hr before it was heated at 100°C for 3 hr.

Measurements

Elemental analyses of the resin samples were carried out on a Coleman C,H Analyser. The C and H contents agreed with the calculated values. The i.r. and u.v. spectral analyses were carried out on Perkin–Elmer-983 and Hitachi Spectrophotometer respectively. The number-average molecular weights were estimated by Hewlett–Packard Vapour Pressure Osmometry. The dilute solution viscosities were measured in dioxane at 35° ± 0.1°C using an Ubbelohode-type Viscometer. For the study of curing, an intimate mixture of resin and hexamine (12% of the weight of resin) was heated for various periods at certain temperatures and the proportion of cured (i.e. acetone unextractable material) was estimated [1, 4, 5]. The curing of one resin sample was investigated by DSC following the procedure described earlier [8, 9]. Unreacted furfural content in the resin sample was estimated by the Hughes–Acree method [10].



BF – Fu resin

Table 1. The reaction conditions and some characteristics of BF–Fu resin samples (Amount of water = 5% wt of BF, Reaction time = 3 hr)

	Reaction conditions						
Sample no.	*Reaction* temp. (°C)	*Molar ratio* BG:Fu	*Catalyst %* of BF	*Softening* range (°C)	$[\eta] \times 10^2$ *dlg*$^{-1}$ *in* dioxane	$\bar{M}_n \pm 100$ by VPO	*Unreacted* furfural (%)
1	100	1:0.8	5% NaOH	145–150	4.3	1450	6–7
2	100	1:1	5% NaOH	145–152	4.4	1450	10–12
3	100	1:1.2	5% NaOH	145–160	4.4	1500	13–15
4	100	1:1	5% Na_2CO_3	130–140	4.3	1400	14–16
5	100	1:1	5% $KHCO_3$	130–138	4.3	1400	14–17
6	100	1:1	10% NaOH	140–156	4.8	1450	12–13
7	120	1:1	5% NaOh	145–158	4.9	1450	18–11
8	100	1:1	5% CH_3COOH	148–162	4.0	1200	13–17
9	100	1:1	5% HCl	150–169	4.2	1300	14–17
10	100	1:1.2	5% HCl	156–170	4.3	1300	14–16

RESULTS AND DISCUSSION

All the BF–Fu resin samples presented in Table 1 are red solids soluble in common organic solvents. They soften between 130° and 170°C depending upon the nature of the sample. A comparative study of the softening ranges of BF–Fu resins with those of bisphenol-F–furfural (BA–Fu) [2] and bisphenol-C–furfural (BC–Fu) [1] resins prepared under identical conditions reveals that BF–Fu resins soften at lower temperatures. However all the above bisphenolic resins have higher softening ranges than those of phenol–furfural (Ph–Fu) resins prepared under identical conditions [4, 11] Due to the lower reactivity of furfural, the resin samples contain fairly large amounts of unreacted furfural which is not removed even after prolonged steam distillation. It is also observed that furfural content in the acid catalyzed resin sample is higher than that in the base catalyzed BF–Fu resin. Potnis and Jambusaria have made a similar observation about furfural content in base and acid catalyzed BA–Fu resins [2].

Table 1 shows that the yield of resin and the softening range increases as the ratio of Fu to BF increases in the base catalyzed reactions. However increase in the concentration of the catalyst and the reaction temperature have no significant effect on the yield and softening range of BF–Fu resin. Brown has made similar observations during his study on the phenol–furfural resin synthesis [11]. Comparison of the yields of the various resin samples and their characteristics reveals that 5% NaOH as a catalyst and equimolar proportions of the reagents provide the best reaction conditions for the polycondensation.

The i.r. spectra of all the resin samples are similar and exhibit the expected characteristics. The characteristics of a methylene bridge $-Ph-CH_2-Ph$ system are observed as C–H asymmetric and symmetric stretching bands at 2960 and 2860 cm^{-1} and as C–H deformation band at 1360 cm^{-1}. Some of the i.r. characteristics of the pendant α-furyl groups are distinctly observed in the spectra of both the acid and base catalyzed resins. They are sharp bands at 1220 cm^{-1} and 1000 cm^{-1} characteristic of a cyclic C–O–C system and a band at 800 cm^{-1} characteristic of aromatic three adjacent H atoms.

The u.v. spectra of all the resin samples are very similar and change similarly when the medium is rendered either acidic or basic [12]. For example, the u.v. spectrum of BF–Fu-2 resin sample in neutral medium comprises bands at 225 nm (ϵ 9.54 × 10^4) and 280 nm (ϵ 3.24 × 10^4). In the acidic medium, these bands are observed at 230 (9.31 × 10^4) and 275 (3.0 × 10^4) nm respectively. In the basic medium both bands are intensified and are shifted to longer wavelength. A new band also appears at 215 (8.0 × 10^4) nm. The u.v. spectrum of BF–Fu-2 in the basic medium comprises bands at 215 (8.0 × 10^4), 240 (1.25 × 10^5) and 300 (5.3 × 10^4) nm respectively. Surprisingly, both acid and base catalyzed resin samples exhibit similar u.v. characteristics.

Results of the curing study of BF–Fu-1,-2 and -3 resins using hexamine as curing agent at 150°, 170° and 190°C [1, 4, 5] are furnished in Table 2. They indicate that the resin sample prepared using higher molar proportion of furfural to BF is cured more rapidly and that all the three resins would cure completely within less than 10 min at 190°C.

The TGA data of BF–Fu-2 and -10 resin samples were analyzed by the method of Doyle [13] to estimate the temperature of maximum rate of degradation (T_{max}) and integral procedural decomposition temperature (IPDT). For the resin samples BF–Fu-2 and -10, the values of T_{max} are 520°C and those of IPDT are 510° and 498°C respectively, indicating similarity in the thermal stabilities of acid and base catalyzed BF–Fu resin samples.

Examination of the DSC thermograms of the curing reaction of BF–Fu-1–hexamine mixture studied at three scan rates in static air (Fig. 1) reveals that the peak-exotherm (T_p) is shifted to a higher temperature and curing time decreases with increase in the scan rate (β °C min^{-1}). Such a trend is commonly observed during study of curing of epoxy and pheno-

Table 2. Isothermal curing study of BF–Fu resin samples

Resin no.	Temp. (°C)	% Unextracted at time (min)			
		5	10	15	20
1	150	10	24	38	46
2		12	28	40	52
3		18	32	43	58
1	170	35	53	67	77
2		38	56	70	82
3		46	63	80	93
1	190	73	86	100	—
2		87	98	100	—
3		98	100	—	—

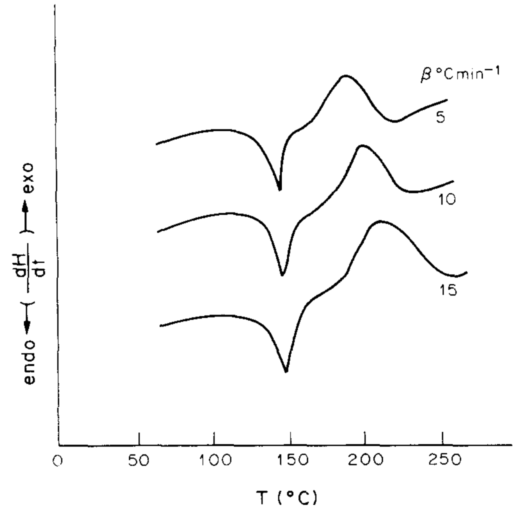


Fig. 1. DSC thermogram of BF–Fu–hexamine mixture at different scan rates.

lic resins [14–16]. The $T_p^0 - \beta$ data are analyzed by the treatments suggested by Ozawa through relations 1–3 [17], by Kissinger through relation 4 [18] and by Crane *et al.* through relation 5 [19].

$$E = 2.19R\frac{d\log\beta}{d(1/T_p)} \quad (1)$$

$$A = \frac{\beta . E . e^{E/RT}}{RT_p^2} \quad (2)$$

$$k = A . e^{-(E/RT_p)} \quad (3)$$

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{R}\left(\frac{1}{T_p}\right) \quad (4)$$

$$\frac{d\ln\beta}{d\ln(1/T_p)} = -\left[\frac{1}{n}\cdot\frac{E}{R}\right] \quad (5)$$

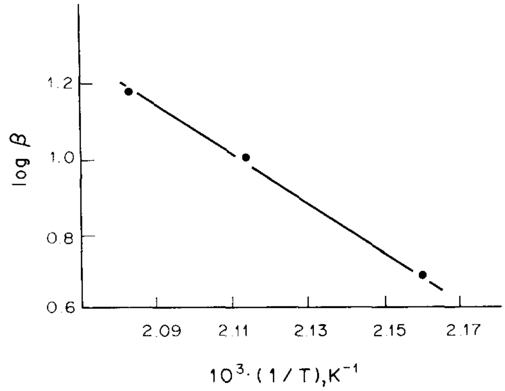


Fig. 2. Plot of log β vs $1/T_p$.

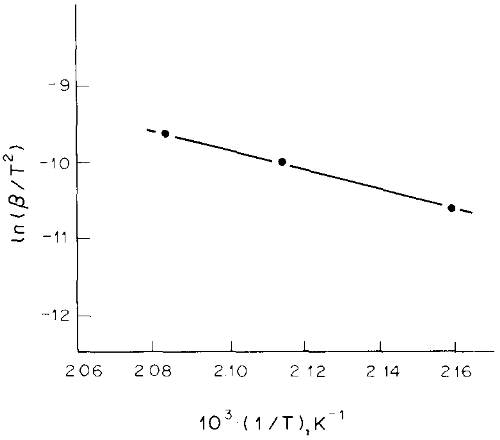


Fig. 3. Plot of $\ln(\beta/T_p^2)$ vs $1/T_p$.

The plots of log β vs $1/T_p$ (Fig. 2)

$$\ln\left(\frac{\beta}{T_p^2}\right) \text{vs} \frac{1}{T_p} \text{(Fig. 3)}$$

and ln β vs $1/T_p$ were made. From the estimated slopes and employing the appropriate relation 1, 4 or 5, the energy of activation of the curing reaction (E) was estimated. The values of E estimated by the three methods presented in Table 3, are very similar.

Barrett [20] proposed a method for the analysis of a single DSC thermogram in which the value of the rate constants (k) of curing at various temperatures are estimated employing the relation

$$k = \frac{dH/dt}{A - a}$$

where A is the total area under the exotherm, a is the area under the exotherm up to a given point decided by the temperature and dH/dt is the rate of heat

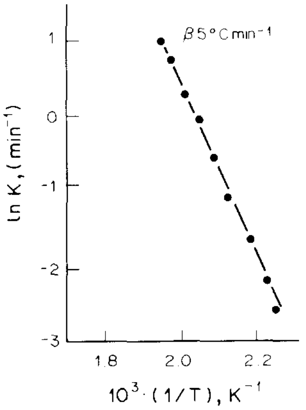


Fig. 4. Plot of ln k vs $1/T$ at 5°C min⁻¹ scan rate.

Table 3. Kinetic parameters of curing reaction of VF–Fu-1 resin–hexamine mixtures

Scan β rate (°C min^{-1})	T_p(K)	k (min^{-1}) Eqn 1, 2 and 3	E ± 5 (kJ mol^{-1}) Eqn (1)	Eqn (4)	Eqn (5)	Barrett method
5	463	0.30				97
10	473	0.58	104	100	105	100
15	480	0.85				97

generation, given by the ordinate at the same point. From the Arrhenius plots of log k vs $1/T$ (Fig. 4 at $\beta = 5°\text{C min}^{-1}$), the values of E were estimated using data for experiments carried out at each of the three scan rates (see Table 3). All three values agree very closely and the average value agrees reasonably with each of the three values estimated by the above three methods. The values of the rate constants at three peak temperatures estimated by the Ozawa [17] and Barrett [20] methods agree very closely. The values of the Arrhenius factor (ln A) estimated by the Ozawa and Barrett method are almost of the same order of 25 ± 2. Such close agreement in the estimated values of kinetic parameters by four methods for treatment of the DSC data supports the assumptions that the curing reaction is first order and that the mechanism is the same irrespective of the scan rate.

REFERENCES

1. P. S. Patel and S. R. Patel, *Eur. Polym. J.* **22,** 525 (1986).
2. R. B. Jambusaria and S. P. Potnis, *Polym. J.* **6,** 333 (1974).
3. S. P. Potnis and B. V. Sharma, *Pop. Plast.* **13,** 25 (1968).
4. L. H. Brown and D. D. Watson, *Ind. Engng Chem.* **51,** 683 (1959).
5. C. S. Chen, B. J. Bulkin and E. M. Pearce, *J. appl. Polym. Sci.* **27,** 3289 (1982).
6. John K. Stille and T. W. Camphel, *Condensation of Monomers*, Chap. 27, p. 597. Wiley–Interscience, New York (1972).
7. A. I. Kogan and E. Y. Kerman, *Kunststoffe* **25,** 222 (1935); cf. C.A. **28,** 49217*a*.
8. P. P. Shah, P. H. Parsania and S. R. Patel, *Br. Polym. J.* **17,** 64 (1985).
9. P. P. Shah, P. H. Parsonia and S. R. Patel, *Br. Polym. J.* **17,** 354 (1985).
10. E. E. Hughes and S. F. Acree, *Ind. Engng Chem. Analyt. Edn* **6,** 126 (1934).
11. L. H. Brown, *Ind. Engng Chem.* **44,** 2673 (1952).
12. *UV Atlas of Organic Compounds*, Vol I and II, Butterworths–Verlag Chemie, London (1966).
13. C. D. Doyle, *Analyt. Chem.* **33,** 77 (1961).
14. R. A. Eava, *Polymer* **9,** 137 (1968).
15. A. Siegmann and M. Narkis, *J. appl. Polym. Sci.* **21,** 2311 (1977).
16. R. Ray and A. R. Westwood, *Eur. Polym. J.* **11,** 25 (1975).
17. T. Ozawa, *J. Thermal Analysis* **2,** 301 (1970).
18. H. E. Kissinger, *J. Res. Natn. Bur. Stand.* **57,** 217 (1956).
19. L. W. Crane, P. J. Dynes and D. H. Kaelbel, *J. Polym. Sci. Polym. Lett. Edn* **11,** 533 (1973).
20. K. E. Barrett, *J. appl. Polym. Sci.* **11,** 1617 (1967).