Bisphenol—Furfural. A High-Temperature Thermosetting Resin[†]

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ABSTRACT: Though products based on phenol—formaldehyde resins have been widely accepted in many applications, they have their own shortcomings. In order to improve their performance, studies continue to be made concerning replacement of the phenolic as well as the aldehyde component of the resin. The present paper is based on preliminary work undertaken to develop a new resin based on bisphenol-A and furfural; theoretical considerations indicated that such a resin should have highly desirable properties. Hence, a detailed study has been carried out to optimise the conditions for resin formation. Preliminary evaluations of the product in molding powders have indicated great potentialities for the resin, because of its' superior thermal, mechanical, and chemical properties. The probable industrial applications of this resin have been indicated.
KEY WORDS   Phenol—Formaldehyde / Bisphenol-A—Furfural /
Molding Powders / High-Temperature Thermosetting Resin /

Replacement of the phenolic and aldehyde components in the usual phenol—formaldehyde condensate has been attempted in order to improve the properties of the resins. The most commonly used phenols were resorcinol, alkyl substituted phenols such as cresols, xylenols, *p-tert*-butylphenol, and *p*-phenylphenol.[1] Acetaldehyde, butyraldehyde, chloral, and furfural were among the more important aldehydes used for modification, although several aromatic and aliphatic aldehydes were investigated. These modifications of the phenolic resins resulted in improvements of the flow and electrical properties and of the oil solubility and in faster curing properties. With a view to improve the thermal, electrical, mechanical, and chemical properties of the phenol resins, the possibility of the use of the condensation product of *p,p'*-

dihydroxydiphenylalkenes and furfural was therefore considered.

For a given degree of polymerization, the molecular weight of bisphenol—furfural resin is more than twice that of phenol—formaldehyde. Thus it is readily possible to obtain a polymer of molecular weight in the range of 1600—1800, as against phenol—formaldehyde resins with molecular weights of 700—800. Moreover, due to the higher functionality of bisphenol, a three-dimensional rigid crosslinked structure having a special configuration results from quick curing, which imparts specific properties to the finished products. The most striking advantage occurs from condensation of the furan ring with the bisphenol molecule, this not only increase the thermal resistance but also imparts better adhesion properties, largely due to the epoxy-type of structure in the heterocyclic furan ring. These can be seen from Figure 1.

It is noteworthy that efforts in this direction have not been made, probably because of the higher functionality of *p,p'*-dihydroxydiphenylalkenes, which normally leads to an unwanted gel during the polymerization reaction. However, recently sulphonated bisphenol-A—formaldehyde-based products have been utilized as ion exchange resins.[2]
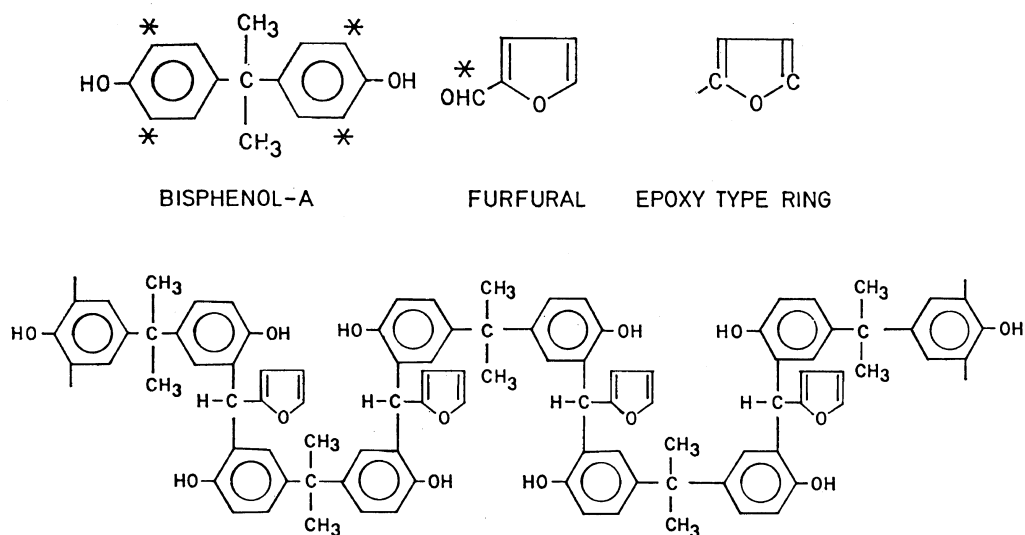
BISPHENOL-A   FURFURAL   EPOXY TYPE RING

Figure 1. Probable structure of bisphenol-A—furfural resin.

EXPERIMENTAL

The condensation reactions were carried out in a three-necked, standard joint, round-bottomed flask of 500-ml capacity to which condenser, thermometer pocket, and dropping funnel were attached. The flask was heated using a constant-temperature oil bath and the reaction mixture was stirred with a glass stirrer, which was connected to a pulley and (1/2)-HP motor. Furfural was added drop by drop over a period of 40—45 min in order to prevent autooxidation. After each experiment, the resin was neutralized to pH 7 and washed first with hot acidified water and then with hot distilled water to separate the unreacted furfural from the resin. The unreacted furfural was quantitatively estimated using the Hughes—Acree[3] method. The unreacted bisphenol-A was determined using the iodimetric method. The viscosities of the resins were determined using a Corning India No. 1 Ostwald-type viscometer. Resin solutions were prepared in butyl acetate. The number-average molecular weights of the resins were determined by the Hill—Baldes differential vapour pressure method.[4-7] Benzil was used as the internal standard and acetone was used as the solvent.

RESULTS AND DISCUSSION

It was found that the condensation reaction of bisphenol-A and furfural mainly depended on the nature and the concentration of the catalyst, the reaction temperature, the reaction time, and the molar ratio of bisphenol-A to furfural. Alkali earth metal hydroxides or ammonia cannot be used as catalysts, since they react readily with furfural and thus get eliminated from the system. In the present work sodium carbonate, sodium hydroxide, triethanol amine, phosphoric acid, sulfuric acid, hydrochloric acid, oxalic acid, and iron trichloride have been used as catalysts. The results summarized in Table I show that sodium hydroxide was the best catalyst under alkaline conditions, while phosphoric acid and hydrochloric acid were satisfactory acid catalysts. The concentration of acid catalyst, however, had to be adjusted so that the self-polymerization and decomposition of furfural was kept at a minimum. This is primary to avoid gel formation and enhance the polymer chain building. Alkali catalysts, whenever employed, have to be added in predetermined concentrations to eliminate Cannizzaro reaction, which leads to formation of furoic acid. A plot of percentage yield of the resin vs. concentration of the catalyst with respect to the weight of bisphenol shown in Figure 2 indicates that the yield of the resin is directly proportional to the concentration of the sodium hydroxide catalyst, the change being very gradual, while

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Table I. Catalysts for bisphenol-A—furfural resin[a]

Catalyst	Concentration of catalyst	Unreacted bisphenol-A, %	Unreacted furfural, %	Yield of the resin, %	Viscosity of the resin, poise
NaOH	5 wt% against bisphenol-A	8.9	18.2	87.6	98.5
Na$_2$CO$_3$	//	20.8	42.2	69.6	10.9
Triethanol amine	//	45.1	81.8	43.9	12.9
H$_2$SO$_4$	3 wt% against bisphenol-A	61.8	55.9	48.7	12.9
HCl	//	20.0	43.2	46.5	36.2
H$_3$PO$_4$	//	69.1	52.1	35.8	36.2
Oxalic acid	//	75.3	43.7	34.0	8.8
FeCl$_3$	//	47.6	98.3	41.3	63.4

[a] Temperature of the reaction, 100°C; reaction time, 60 min; molar ratio, bisphenol-A : furfural=1 : 1.

Table II. Effect of concentration of catalyst on resin formation[a]

No.	Catalyst	Concentration of catalyst, wt% against bisphenol	Yield of the resin, %	Viscosity of the resin, poise	State of polymer
1	NaOH	3	86.4	43.6	Red brown liquid
2	//	4	87.1	63.4	Red brown semisolid
3	//	5	87.6	98.5	Red brown semisolid
4	//	7	88.4	98.5	Red brown semisolid
5	//	9	89.8	98.5	Red brown semisolid
6	//	11	92.3	98.5	Red brown semisolid
7	HCl	1	43.6	12.9	Black liquid
8	//	3	46.5	36.2	Black semisolid
9	//	5	88.5	36.2	Black semisolid
10	//	7	89.4	36.2	Black semisolid

[a] Temperature of the reaction, 100°C; reaction time, 60 min; molar ratio, bisphenol-A : furfural=1 : 1.
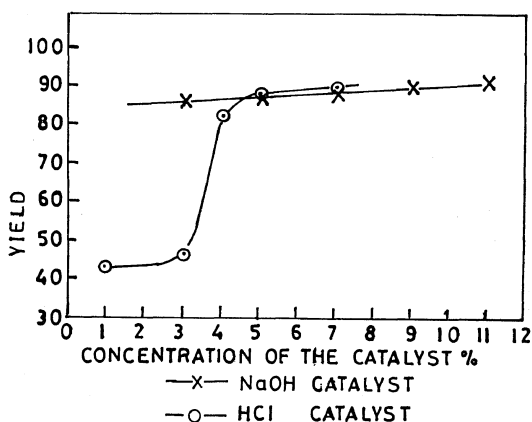

Figure 2. Effect of concentration of catalyst on resin formation.

under acidic conditions it increases rapidly at 3- to 7-% concentration of hydrochloric acid. This can be explained by noting that beyond 3% of hydrochloric acid as catalyst, the self-polymerization of furfural is very fast. The concentration of the catalyst, both alkaline and acidic, affects the yield as well as the molecular weight of the polymer, which was determined from the viscosity of its 20-% solution in butyl acetate; results are given in Table II. On the basis of both these parameters the optimum concentration of catalyst was found to be 5% for sodium hydroxide and 3% for hydrochloric acid.

The resins obtained by using the sodium hydroxide catalyst are light brown in color and of higher molecular weight than the acid-

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Table III. Effect of temperature on bisphenol-A—furfural resin formation[a,b]

No.	Reaction temperature, °C	Catalysts and wt% against bisphenol	Yield of the resin, %	Relative viscosity	State of polymer
1	100	5-% NaOH	87.6	1.45	Red brown liquid
2	105	"	91.4	1.50	Red brown solid
3	110	"	95.8	1.51	"
4	120	"	96.2	3.00	"
5	130	"	96.1	5.00	"
6	140	"	96.1	7.40	"
7	160	"	—	—	Red brown gel
8	190	"	—	—	"
9	100	3-% HCl	46.3	2.18	Black liquid
10	103	"	47.1	2.31	Black semisolid
11	105	"	48.9	2.50	"
12	108	"	—	—	Black rubber-like gel
13	110	"	—	—	Black rubber-like gel

[a] Reaction time, 60 min; molar ratio, bisphenol-A : furfural=1 : 1.
[b] Viscometer (Corning India) No. 1; least count of stop watch, 0.1 sec.

Table IV. Effect of mole ratio bisphenol-A : furfural[a]

No.	Catalyst	Reaction temp, °C	Molar ratio of bisphenol-A : furfural	Relative viscosity	Yield, %	Melting point range, °C	State of polymer
1	3-% HCl	100	1 : 0.5	1.75	64.9	—	Black semisolid
2		"	1 : 0.75	1.85	86.1	—	"
3		"	1 : 0.85	1.88	86.3	—	"
4		"	1 : 1	1.90	88.4	—	"
5		"	1 : 1.25	1.89	80.9	—	Black liquid
6		"	1 : 1.5	1.75	63.9	—	"
7		"	1 : 2	1.74	59.1	—	"
8	5-% NaOH	120	1 : 0.5	1.62	65.5	—	Red brown liquid
9		"	1 : 0.85	1.87	68.3	105—119	Red brown solid
10		"	1 : 1	2.08	96.2	124—149	"
11		"	1 : 1.25	1·92	90.1	109—123	"
12		"	1 : 1.5	1.93	89.9	118—129	"
13		"	1 : 2	2.53	90.3	130—139	"
14		"	1 : 3	1.85	64.7	—	Red brown semisolid
15		"	1 : 4	1.81	61.3	—	"

[a] Reaction time, 2.5 hr; viscometer (Corning India) No. 1; least count of stop watch, 0.1 sec.

catalyzed resins, which are of low molecular weight and dark steel-grey in color. The physical nature of the resin depends on the reaction time, reaction temperature, and molar ratio of bisphenol-A to furfural, as indicated in Tables III and IV.

The reaction times depend mainly on the temperature of the reaction. Using 5-% sodium hydroxide catalyst and 3-% hydrochloric acid catalyst at temperatures 120°C and 100°C respectively, on the basis of the previous results (Table III) polymerization reactions were carried out for different reaction times where the duration of the individual reactions was increased by 30 min. Time of flow, in seconds, of 10 ml of 20-% resin solution in butyl acetate was
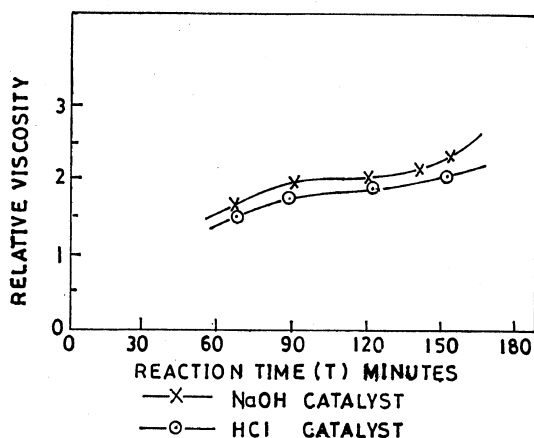
Figure 3. Effect of reaction time on resin formation.

measured in each case. The plot of relative viscosity of the resin (20-% solution in butyl acetate) *vs.* the reaction time (Figure 3) indicates that a maximum degree of polymerization can be achieved after 150 min and that the molecular weight of the alkali-catalyzed resin is higher than that of the acid-catalyzed product. At higher temperatures the reaction is very rapid and if not controlled leads to gel formation. Since furfural is less active than formaldehyde, during the initial stages the reaction is very sluggish, while during the latter part the rate of reaction increases rapidly, due to the exothermic nature of the reaction. The reaction temperature must be carefully controlled at this stage, otherwise water formed during the condensation reaction vaporizes along with the furfural, resulting in frothing of the mass in the reaction kettle. In order to control the reaction rate, it is desirable to add 2—3-% water (based on the weight of bisphenol-A) during the reaction. This can be achieved by preparing an aqueous solution of catalyst of the required strength.

The effect of temperature on the formation of bisphenol-A—furfural resin is shown in Table III, where the optimum temperature of reaction appears to be 120°C for 5-% sodium hydroxide-catalysed resin and 100°C for 3-% hydrochloric acid-catalysed resin. At temperatures higher than 100°C, acid-catalyzed reactions are too vigourous and hence are not recommended.

The formation of the polymer was studied

using various molar ratios of bisphenol-A to furfural; these change and both the physical state of the resin and its molecular weight, as shown in Table IV. Irrespective of the catalyst used in the preparation of bisphenol-A—furfural novolacs, it was found that these resins do not behave as true novolacs.

A novolac-type of resin was prepared using a sodium hydroxide catalyst and the number-average molecular weight of the resin was found to be 1773; the corresponding degree of polymerization was 6. The number-average molecular weight of the acid-catalysed resin obtained was found to be 829. The acid-catalysed resin was mainly of academic interest and detailed investigations regarding its industrial application were not undertaken due to the low molecular weight and the limited control during the reaction. 4,4′-dihydroxy-3,3′-di(2,α-hydroxyfurfuryl)-diphenylmethanes were isolated and the structural investigations of these resins have been carried out using NMR, IR, elementary analysis, and chemical analysis methods. It was found that the polymer formation takes place in a manner very similar to that of phenol—formaldehyde resins.

PROPERTIES AND APPLICATIONS

The curing rate of the resin was investigated using 3- to 12-% hexamethylenetetramine and 5-% boric acid at 120°C to 180°C. The resin completely cures at 170°C after 5 min. The curing rate was evaluated using the acetone extraction method.[8-9] The graphs shown in Figure 4 for the curing rate of the different resins indicate that the resin based on bisphenol-A—furfural has a reasonably fast curing rate and resembles the faster-curing phenol—formaldehyde resin. Depending on the conditions of preparation, different type of resins could be prepared which could be used for moldings, lamination, castings, and coatings.

Preliminary investigations carried out with molding-grade resin using different fillers like wood flour, coconut fibers, α-cellulose, silica, asbestos, mica dust, carbon, etc., showed that the molded article takes 3—7% more filler than the phenol—formaldehyde resin. The mold shrinkage, which partly depends on the mold

A - PHENOL FORMALDEHYDE
B - 50-50 PHENOL FORMALDEHYDE
C - BISPHENOL-FURFURAL
D - PHENOL FURFURAL
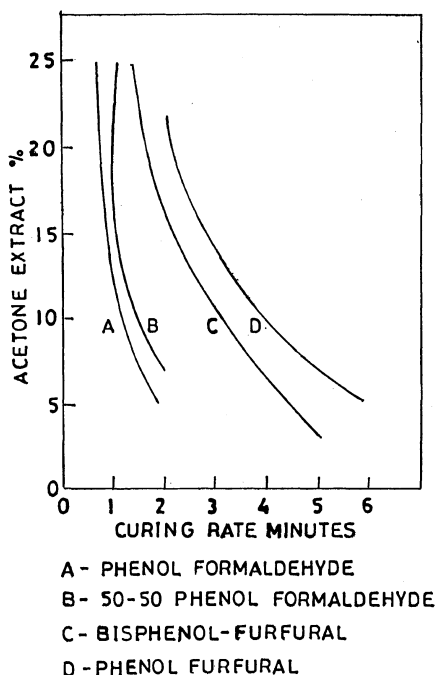
CURVES A, B, & D. HAVE BEEN TAKEN FROM PUBLISHED INFORMATION REF. 10, 11.

Figure 4. Curing rate of various phenolic resins.

design, was found to be very much less in the case of this resin. The thermal resistance was investigated and found to be 350°C—500°C for 12 hr against 170°C—200°C for the phenol—formaldehyde resin. The flame resistance was determined and it was found that the molded articles had a low burning rate (low flammability) and self-extinguishing properties. Both the thermal resistance and flame resistance could be improved by incorporating aluminium chloride, antimony chloride, and salts of titanium, and by halogenating the resin or starting materials. In general, molded articles had 10% more physicomechanical strength and comparable electrical properties. An improvement in electrical properties can be achieved by eliminating the presence of furoic acid, unreacted bisphenol-A, and the ionizable salts derived from the catalyst. The water absorption of the molded article was 2—6% less than that of phenol—formaldehyde resin. The chemical resistance properties of this resin were also studied. The articles molded with appropriate fillers were

Table V. Properties of phenol—formaldehyde resin

Properties	Wood flour-filled	Mineral-filled	Fiber-filled
Molding qualities	Excellent	Good	Excellent
Molding temp, °F	266—320	290—350	290—350
Mold shrinkage	0.002—0.007	0.004—0.006	0.010—0.014
Tensile strength, psi	6500—9500	3800—4000	5000—7000
Impact strength, ft lb/in of notch	0.24—0.40	1.3—1.6	0.32—0.50
Hardness rockwell	B65—B75	B55—B65	B65—B75
Heat resistance temp, °F	250—300	300—350	290—300
Burning rate	Low	Low	Low
Chemical resistance	Poor	Fair	Poor

Table VI. Properties of phenol—furfural resins

Properties	Wood flour-filled	Mineral-filled	Fiber-filled
Molding qualities	Excellent	Good	Good
Molding temp, °F	280—400	270—360	270—360
Mold shrinkage	0.005—0.01	0.002—0.006	0.0025—0.007
Tensile strength, psi	5,000—8,500	4,000—8,000	5,500—8,000
Impact strength, ft lb/in of notch	0.2—0.4	0.22—1.0	0.6—4.8
Hardness rockwell	B65—B75	B65—B65	B65—B75
Heat resistance temp, °F	240—300	240—300	240—285
Burning rate	Very low	Nil	Approx. nil
Chemical resistance	Fair	Good	Good

found to resist hot or cold concentrated hydrochloric acid, 85-% phosphoric acid, 80-% sulphuric acid, glacial acetic acid, chloroacetic acid,

Table VII. Properties of bisphenol-A—furfural resin

Properties	Wood flour-filled	Mineral-filled	Fiber-filled
Molding qualities	Excellent	Good	Excellent
Molding temp, °F	350—400	350—400	350—400
Mold shrinkage	0.001	0.009	0.002
Tensile strength, psi	6500	5900	8500
Impact strength, ft lb/in of notch	0.30—0.5	0.7—1.5	1.6
Hardness rockwell	80D	90D	85D
Heat resistance temp, °F	500	900	800
Burning rate	Very low	Nil	Nil
Chemical resistance	Good	Excellent	Good

50-% sodium hydroxide solution, saturated potassium permanganate solution, saturated potassium nitrate solution, benzene, toulene, xylene, petroleum, chlorobenzene, acetone, and methyl ethyl ketone for attacks up to 12 hr. Due to the phenolic nature, bisphenol-A has been used as a fungicide, hence the resins derived from it are also likely to resist fungus growth.[2] Some properties of phenol—formaldehyde, phenol—furfural, and bisphenol-A—furfural moldings have been compared in Tables V to VII which bring out the superiority of the bisphenol-A—furfural resins.

It was also found that the alkali-catalyzed low-molecular-weight liquid resin is oil-soluble. The oil solubility of the resin can be further enhanced by modifying it with rosin. Phenol—furfural resins have been extensively studied and they are found to be compatible with thermoplastic vinyl compounds.[10] Bisphenol-A—furfural resins are also likely to show similar performance. This could naturally lead to a new range of heat- and chemical-resistant coatings and lacquers. Due to the incorporation of the epoxy-type furan ring, the coatings should have better adhesion, while the presence of methyl groups in bisphenol-A should make it more flexible. Like resorcinol—furfural resins, these could be used for glass[11] or asbestos reinforced plastics and in adhesives for rubber.[12—17]

Systematic investigations on the possible industrial applications of this new resin are in progress.

CONCLUSION

Bisphenol-A—furfural resins have advantages over phenol—formaldehyde resins as regards thermal, chemical, physicomechanical, and electrical properties. The comparatively simple process and longer self-life are added advantages. The bisphenol-A—furfural resins have better properties and an extended range of applications and can advantageously replace phenol—formaldehyde resins for improved performance.

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