

Synthesis, Characterization, and Curing of *o*- and *p*-Chlorophenol-Furfural Resins

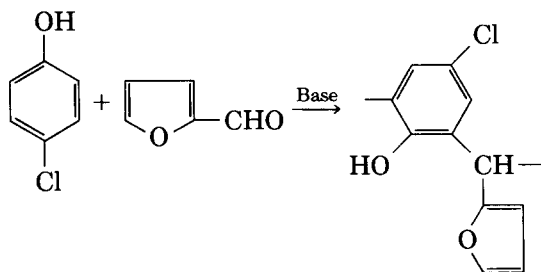
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Synopsis

Polycondensation of furfural, respectively, with *o*- and *p*-chlorophenols has been carried out under various reaction conditions. All the resin samples have been characterized by spectral studies, viscometric measurement and by the estimation of the number-average molecular weight. Thermogravimetric analysis (TGA) of selected resin samples has been carried out. The kinetics of curing reaction of selected resin samples has been investigated by differential scanning calorimetry (DSC). The properties of the glass laminates prepared using each of the two types of resins showed that the latter are much less suitable than phenol-furfural resin as matrices for the fabrication of laminates.

INTRODUCTION

Resin prepared by condensing furfural separately with phenol, isomeric cresols and naphthols, and resorcinol are reported.^{1,2} There are also reports about the condensation of isomeric chlorophenols, bromophenols, and nitrophenols with formaldehyde.³⁻⁵ The phenol-furfural (PFu) resins are known for their alkali resistance and good electrical properties.^{6,7} There is one patent report about the resin formed on condensation of *p*-chlorophenol with furfural which, however, does not provide any information about the details of synthesis and characteristics.⁸ The present communication deals with the synthesis and characterization of resins prepared by condensing furfural, respectively, with *o*- and *p*-chlorophenols. The curing of selected resin samples by hexamine is studied by differential scanning calorimetry (DSC); these resin samples are employed as matrix resins for the fabrication of glass laminates, which are characterized.



EXPERIMENTAL

Materials

The catalysts, monomers, and solvents employed for the resin synthesis and characterization were laboratory-grade reagents. Furfural, *o*- and *p*-chlorophenols, and the solvents were purified by distillation.

Resin Synthesis

The condensation of furfural, respectively, with *o*- and *p*-chlorophenol is carried out using different molar proportions of the monomers, concentration of basic catalysts, and reaction time and temperature. A typical resin synthesis is described here.

Polycondensation of *o*-chlorophenol (OCLP) with furfural (Fu) in the presence of base as a catalyst. Formation of OCLPFU-1 resin sample. A mixture of *o*-chlorophenol (6.4 g, 0.05 mol), potassium carbonate (0.128 g, 2% by weight of OCLP), water (0.32 g, 5% by weight of OCLP), and furfural (3.0 g, 0.0375 mol) was heated at 135°C for 5 h. The pasty, dark brown mass was washed with hot water and left overnight in contact with methanol (100 mL). The resulting solution was poured with stirring in cold water (1 L), containing 10 mL of concentrated HCl. The solid was filtered and washed with water until the filtrate was free from acid. It was dried in air. It was a dark-colored solid, softening in the range 85–100°C. The yield was 76%. This resin sample is labeled as OCLPFu-1. It is soluble in chloroform, acetone, methanol, dioxane, pyridine, benzene, solvent ether, methyl ethyl ketone (MEK), tetrahydrofuran (THF), dimethyl formide (DMF) and dimethyl sulfoxide (DMSO). (Calcd. for $C_{11}H_7O_2Cl$, Cl \approx 17.19%, found, Cl \approx 17%).

The other resin samples listed in Table I were synthesized following the method described above and under the reaction conditions mentioned in the same table. They are designated as OCLPFu and PCLPFu resins as shown in Table I.

Characterization of resins. Carbon and hydrogen contents of the polymer samples estimated by Coleman C and H Analyzer and the chlorine content estimated by Carious method agreed with the calculated values. The infrared (IR) spectra were measured in KBr on UR-10 spectrophotometer. Ultraviolet (UV) spectra were measured using 10^{-6} M methanolic solutions containing 10 mL of water, 0.1 M NaOH, and 0.1 N HCl per liter of solution, respectively. The number-average molecular weight was estimated by conductometric titration in pyridine against 0.1 M NaOMe in pyridine. The dilute solution viscosities were measured in dioxane at $35^\circ \pm 0.1^\circ\text{C}$ using Ubbelohde-type Viscometer. The curing of OCLPFu-2 and PCLPFu-2 resin samples by hexamine was investigated by differential scanning calorimetry (DSC) following the procedure described earlier.^{9,10}

The glass laminates were prepared using OCLPFu-2 and PCLPFu-2 as matrix resins. A solution containing the resin (100 g) and hexamine (12 g) in methanol (100 g) was applied on each side of the cut piece of 10 mil E glass plane weave fabric. Twelve such sheets were prepared and were allowed to dry in air and stacked one over the other and pressed between flat plates at a constant pressure of 50 psi at 100°C for 30 min, then at 135°C for 30 min, and

TABLE I
 Base-Catalyzed *o*- and *p*-Chlorophenol-Furfural Polycondensation : Reaction Conditions
 and Preliminary Characteristics
 Medium : Water (5% by weight of CLP)
 Reaction temperature : 135°C
 Reaction time : 5 h
 Catalyst : K₂CO₃ (2% by weight of CLP)

Resin sample	Molar ratio CLP : Fu	OCLPFu			PCLPFu		
		Yield (%)	Softening range °C	Number average molecular weight \bar{M}_n	Yield (%)	Softening range (%)	Number average molecular weight \bar{M}_n
1	1 : 0.75	76	86-100	1600	38	102-117	1200
2	1 : 1	78	88-103	1600	40	121-135	1300
3	1 : 1 : 25	88	107-122	1950	56	150-160	1800
4 ^a	1 : 1	41	76-88	1500	25	117-132	1120
5 ^b	1 : 1	93	106-120	2100	93	250	1600
6 ^c	1 : 1	11	81-90	1100	11	74-86	1300
7 ^d	1 : 1	85	104-119	1600	63	164-180	2000
8 ^e	1 : 1	40	74-88	1400	17	88-99	1300
9 ^f	1 : 1	78	96-104	2050	41	122-137	1400
10 ^g	1 : 1	81	103-120	2100	61	178-190	2600

^a Catalyst 1% K₂CO₃.

^b Catalyst 3% K₂CO₃.

^c Reaction temp. 120°C.

^d Reaction temp. 150°C.

^e Reaction time 4 h.

^f Reaction time 6 h.

^g Catalyst 2% NaOH.

at 180°C for 1 h. The whole system was allowed to cool slowly to room temperature over a period of 12 h. The laminate was released from the plates and cut to the required size. The glass content and thickness of the laminates were measured. Flexural strength of the laminate was measured before and after dipping the laminate in boiling water for 2 h and also in water at room temperature for 7 days. It is observed that there is delamination when the laminate were kept in 10% aqueous NaOH for 72 h.

RESULTS AND DISCUSSION

All the OCLPFu and PCLPFu resin samples presented in Table I are brown-colored solids. They are soluble in most of the common organic solvents. The OCLPFu resin samples soften over a range somewhere between 74° and 120°C and the PCLPFu resins soften over the range somewhere between 74° and 190°C. The softening range, percentage yield and the value of \bar{M}_n of the resin samples of each series are found to increase with increase in the ratio of furfural to phenol, the reaction temperature, the percentage of the catalyst (K₂CO₃), and the reaction time period. Such a change in the property of the resin was also observed when sodium hydroxide was used in place of potas-

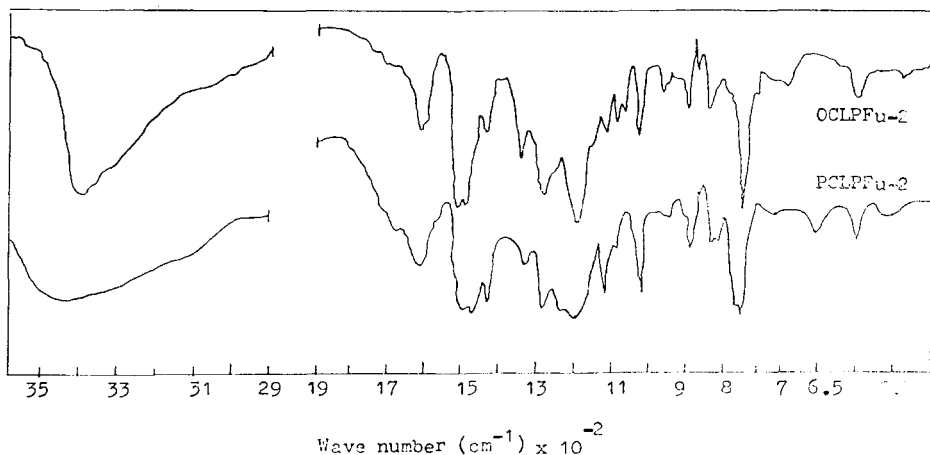


Fig. 1. IR spectra of OCLPFu-2 and PCLPFu-2 resin samples.

sium carbonate as a catalyst. Brown has also made similar observations during the study of phenol-furfural (PFu) resin synthesis.¹¹

It is found that the softening range of a PCLPFu resin is higher, and its yield is lower, than those of OCLPFu resin samples prepared using similar experimental conditions. The intrinsic viscosity of the dioxane solution of the resin samples is found to lie between 0.02 to 0.04 dL. g⁻¹. The value of intrinsic viscosity estimated by the application of Huggins, Kraemer's¹² and Martin's¹³ relations agree very well. The Mark-Houwink relation between intrinsic viscosity and \bar{M}_n of the resin samples of each series worked out as:

$$[\eta] = 3.13 \times 10^{-4} \times M^{0.61} \quad \text{-OCLPFu series}$$

$$[\eta] = 2.52 \times 10^{-4} \times M^{0.66} \quad \text{-PCLPFu series}$$

It is reported that for the solution of Novolak's in methanol,¹⁴ the value of constant K and α are 10^{-4} and 0.7 and for solution of phenol-furfural resins in dioxane,¹⁵ these constants are reported to be 10^{-4} and 0.79, respectively.

The IR spectra of the resin samples of each series are found to be identical. The spectra of two resin samples, one from each series, are shown in Figure 1. The bands at 1606, 1508, 1395, and 1235 cm⁻¹ are assigned to α -furyl system.¹⁶ The band observed at 1340 cm⁻¹ is most probably due to the —CH— bonding of the bridge —CH(Fu)—. A sharp band observed at 850 cm⁻¹ is attributed to the system of isolated (aromatic) H atoms. The band observed around 755 cm⁻¹ is attributed to aromatic C—Cl stretching. The shape of the band observed at 755 cm⁻¹ suggests that two bands are placed on vicinal positions, one of which is due to the system of three adjacent H atoms of α -furyl system and other is most probably due to aromatic C—Cl stretching. It is observed by the present author that C—Cl stretching appears at 760 cm⁻¹ in the spectrum of *p*-chlorophenol-formaldehyde resin.

The UV spectra of 10^{-6} M solutions of resins of both series exhibit a strong band at 230 nm and a broad and strong band extending from 285 to 325 nm with a maximum around 290 nm. Each of these bands is shifted to a higher

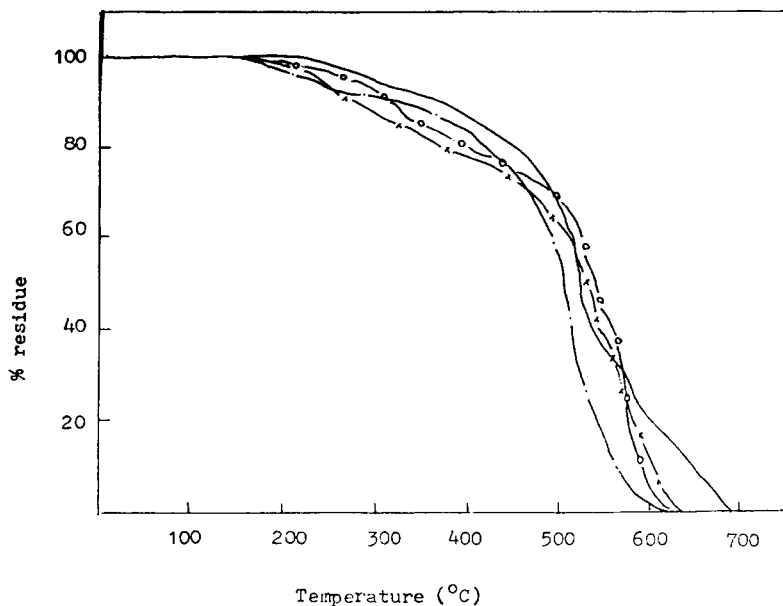


Fig. 2. TG thermograms. Plot of % age-weight residue at different temperature ($^{\circ}\text{C}$). Sample: OCLPFu-2 —; OCLPFu-10 -x-x-x-x; PCLPFu-2 -o-o-o-o; PCLPFu-10

wavelength when the medium is rendered basic. For example, UV spectrum of the OCLPFu-2 resin sample exhibits bands at 230 nm ($\log \epsilon = 4.15$) and 294 nm ($\log \epsilon = 2.61$) in the neutral medium and at 233 nm ($\log \epsilon = 4.09$) and 290 nm ($\log \epsilon = 2.12$) in the acidic medium. In the basic medium, the spectrum of OCLPFu-2 comprises bands at 235 nm ($\log \epsilon = 4.07$) and 303 nm ($\log \epsilon = 3.57$).

Examination of the TG thermograms of PCLPFu-2 and PCLPFu-10 and OCLPFu-2 and OCLPFu-10 resin samples measured in air at a heating rate $10^{\circ}/\text{min}$ (see Fig. 2), revealed that each resin started to degrade at $\sim 200^{\circ}\text{C}$, suffered 50% degradation between 520° to 530°C , and complete degradation between 650° and 700°C . The actual values depend upon the nature of the resin. The Broido method¹⁷ was applied to the TG data to estimate the value of the energy of activation of the degradation reaction. The value of E was found to be 33 and 28 kcal/mol for the degradation of PCLPFu-2 and PCLPFu-10 and 22 and 18 kcal/mol for the degradation of OCLPFu-2 and OCLPFu-10 resin samples, respectively.

Examination of the DSC thermograms of the curing of OCLPFu-2 and PCLPFu-2 samples by hexamine (12% by the weight of resin) was studied at three scan rates in static air. The DSC data are presented in Table II. The DSC thermograms, shown in Figure 3, reveal that the OCLPFu-2 and PCLPFu-2 resin samples are cured in the range of 165 – 240°C and 145 – 177°C , respectively when the heating rate was $10^{\circ}\text{C}/\text{min}$. The peak exotherm (T_p) is shifted to higher temperature and curing time decreases with increase in the scan rate, β , ($^{\circ}\text{C}/\text{min}$). Such a trend is observed by many authors during the study of curing of epoxy and phenolic resins.¹⁸⁻²⁰ The $T_p - \beta$ data are analyzed by the treatments suggested by Ozawa,²¹ Kissinger,²² and Crane

TABLE II
Curing Characteristics of *o*- and *p*-Chlorophenol-Furfural
Resin Hexamine^a Mixture at Different Heating Rates

Resin sample	Heating rate β °C/min	Initiation of curing °C	Completion of curing °C	Peak temperature °C	Cure range °C	Cure time min	$\frac{\Delta H}{\text{m.cal}} / \text{mg}$
OCLPFu-2	10	165	240	205	75	7.5	—
	20	165	265	225	100	5.0	6.2
	40	180	280	245	100	2.2	8.0
PCLPFu-2	10	145	200	177	55	5.5	1.6
	20	165	225	187	60	3.0	1.7
	40	165	245	202	80	1.8	1.4

^a12% by weight of resin.

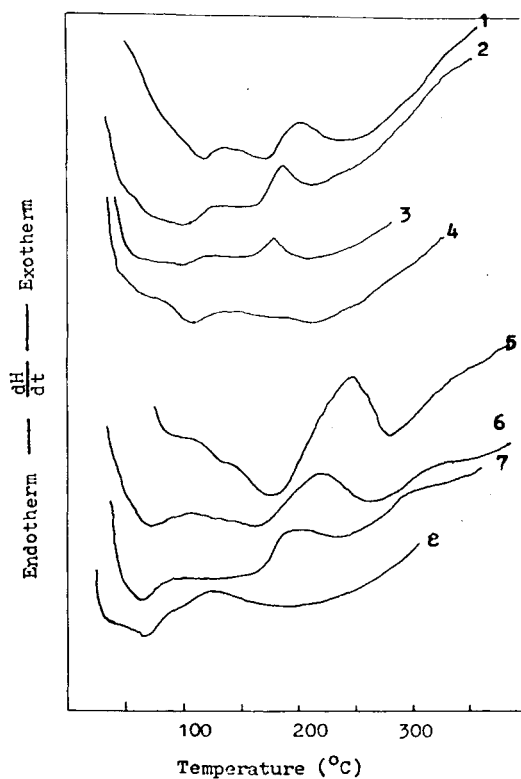


Fig. 3. DSC scans. Sample (1) PCLPFU-2 + hexa, HR: 40°C/min. (2) PCLPFu-10 + hexa, HR: 20°C/min. (3) PCLPFu-2 + hexa, HR: 10°C/min. (4) PCLPFu-2 HR: 20°C/min. (5) OCLPFu-2 + hexa, HR: 40°C/min. (6) OCLPFu-2 + hexa, HR: 20°C/min. (7) OCLPFu-2 + hexa, HR: 10°C/min. (8) OCLPFu-2 HR: 20°C/min.

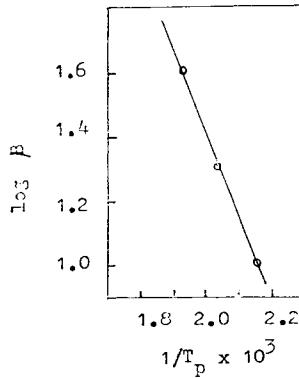


Fig. 4. Plot of $\log \beta$ vs. $1/T_p$ sample OCLPFu-2.

et al.²³ through the originally proposed relations 1, 2, and 3, respectively, to estimate the kinetic parameters.

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

$$\ln(\beta/T_p^2) = \frac{E}{R} (1/T_p) \tag{2}$$

$$\frac{d \ln \beta}{d(1/T_p)} = - \left[\frac{1}{n} \cdot \frac{E}{R} \right] \tag{3}$$

The relevant plots of $\log \beta$ versus $1/T_p$, $\ln(\beta/T_p^2)$ versus $1/T_p$ and $\ln \beta$ versus $1/T_p$ for OCLPFu-2 resin sample are shown in Figures 4, 5, and 6. From the estimated value of the slope of the linear plot based on appropriate

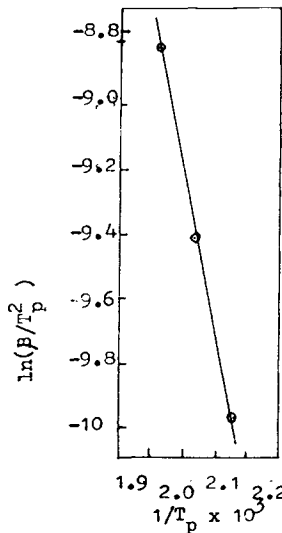


Fig. 5. Plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ sample OCLPFu-2.

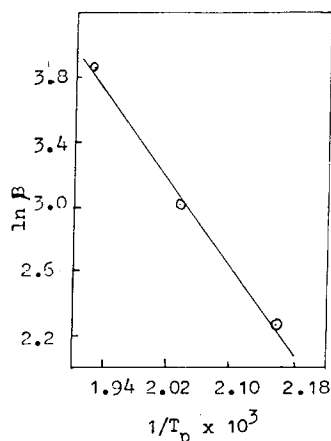


Fig. 6. Plot of $\ln \beta$ vs. $1/T_p$ sample OCLPFU-2.

TABLE III
Energy of Activation of Curing Estimated by Method Based on Peak Temperature Program Rate Relationship

Resin sample	Energy of activation of curing E kcal/mol		Crane ^a et al.
	Ozawa	Kissinger	
OCLPFu-2	16.0	16.0	17.0
PCLPFu-2	22.0	22.0	23.0

^aActually it is E/n .

relation 1, 2, or 3, as the case may be, the value of the energy of activation of the curing reaction (E) was estimated by the three methods for each resin sample (shown in Table III) and found to be practically the same. The agreement between the values of E estimated by the methods of Ozawa and Kissinger and that of E/n estimated by Crane's method suggested that the value of the order of the curing reaction of the resin with excess of hexamine is very nearly equal to one. It is observed that the value of E for curing of PCLPFu-2 resin is higher than that of the curing of OCLPFu-2 resin.

The resin content of the glass laminates prepared from OCLPFu-2 and PCLPFu-2 resins is estimated to be $30 \pm 2\%$. Their thickness was found to be 2.9 ± 0.1 mm. The flexural strengths of the laminate prepared using OCLPFu-2 and PCLPFu-2 as resin matrix are found to be 1300 ± 100 and 1350 ± 100 kg/cm², respectively. These values are much lower than those of the glass laminate prepared using phenol-furfural as resin matrix. Glass laminates prepared using OCLPFu-2 and PCLPFu-2 as resin matrices did not delaminate when left in boiling water for 2 h or when left in cold water (30°C) for 7 days, but the flexural strength of the laminates was reduced by about 20% on such treatments. These laminates delaminated when left in contact with 10% aqueous alkali for 7 days. These properties of the laminates suggest that the *o*- and *p*-chlorophenol-furfural resins cannot be employed as effective resin

matrices for fabrication of glass composites and that these resins do not possess the characteristic alkali resistance of phenol-furfural resin.

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