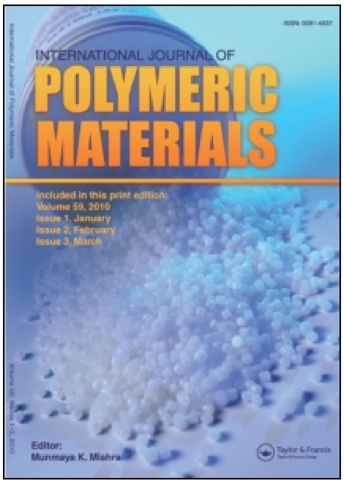

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Patel, A. U. , Soni, S. S. and Patel, H. S.(2009) 'Synthesis, Characterization and Curing of *o*-Cresol - Furfural Resins', International Journal of Polymeric Materials, 58: 10, 509 — 516

To link to this Article: DOI: 10.1080/00914030903035436

URL: http://dx.doi.org/10.1080/00914030903035436

International Journal of Polymeric Materials, 58:509–516, 2009

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030903035436

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Synthesis, Characterization and Curing of *o*-Cresol – Furfural Resins

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Polycondensation of o-*cresol (OC) with furfural (F) was carried out under various reaction conditions. The resultant resin samples designated as OCFs were characterized by elemental analysis, spectral studies, viscometric measurement of solution in 1,4-dioxane and by the estimation of the number – average molecular weight. Thermogravimetric analysis (TGA) of selected resin samples has been carried out. The curing kinetic reaction of selected OCF resin samples was studied by differential scanning calorimetry (DSC). Hexamethylenetetramine (Hexamine) has been used as curing reagent.*

Keywords: cresols, differential scanning calorimetry (DSC), number average molecular weight, phenol-furfural resins, phenolics, thermogravimetric study, viscometric study

INTRODUCTION

Due to ease of formation and good thermal and mechanical properties, phenolics (i.e., phenol-formaldehyde resins) are well-known commercial resins for various applications [1–3]. Instead of formaldehyde, other aldehydes like acetaldehyde, propionaldehyde, and benzaldehyde are also used for phenolic resin formation [1–3], but they have very little practical value. The heteroaryl aldehyde furfural is an agricultural waste product which is also used extensively for resin formation [4]. Its resinification with phenol derivatives has been reported and most of the reports are confined to patent literature [5,6]. Only few reports indicate the detailed studies [4,7]. Phenolic derivatives

Received 23 February 2009; in final form 20 April 2009.

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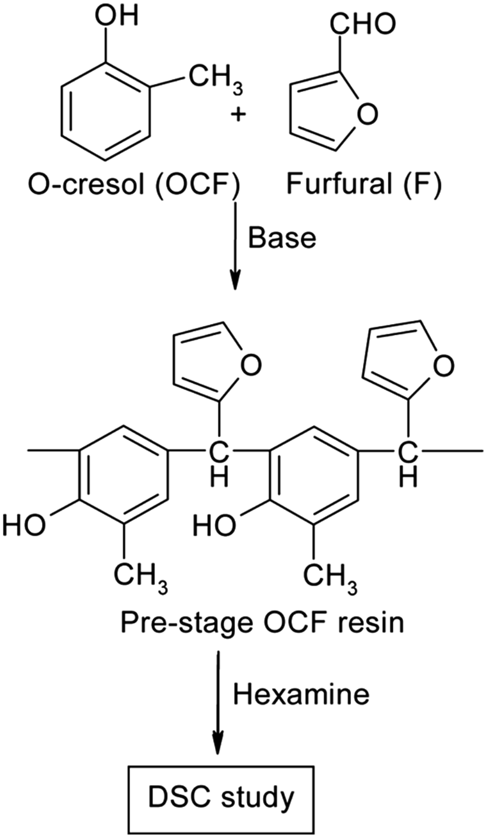


SCHEME 1 Synthesis of resins.

like cresols have also been reported for resin formation with furfural, but systematic studies [8,9] are not provided. Hence the present communication deals with synthesis and characterization of *o*-cresol-furfural (OCF) resins. The work is drawn schematically in Scheme 1.

EXPERIMENTAL

MATERIALS

All the chemicals used were of pure grade.

Resin Synthesis

The condensation of *o*-cresol with furfural was carried out by varying parameters like using different molar proportions of the monomers, concentration of basic catalysts, reaction time and temperature. All the resin samples were prepared under the reaction conditions mentioned in Table 1. A typical resin synthesis is described here.

Polycondensation of o-Cresol with Furfural in the Presence of Base as a Catalyst

Formation of OCF – 5 Resin Sample: A mixture of *o*-cresol (5.4 g, 0.05 mol), potassium carbonate (0.108 g, 2% by weight of *o*-cresol),

TABLE 1 Base-Catalyzed *o*-Cresol – Furfural Polycondensation: Reaction Conditions and Preliminary Characteristics

Resin sample	Molar ratio *o*-cresol:Furfural	Yield (%)	Softening range (°C)	Number average molecular weight, $\overline{M_n} \pm 100$
OCF – 1	1:0.75	59	125–130	930
OCF – 2	1:1	63	135–140	1160
OCF – 3	1:1.25	64	150–160	1160
OCF – 4[a]	1:0.75	68	135–140	1160
OCF – 5[b]	1:1	74	145–150	1270
OCF – 6[c]	1:1.25	75	160–170	1330
OCF – 7[d]	1:0.75	71	160–170	1250
OCF – 8[e]	1:1	75	165–172	1330
OCF – 9[f]	1:1.25	77	168–175	1420
OCF – 10[g]	1:1	61	120–130	930
OCF – 11[h]	1:1	79	170–180	1420
OCF – 12[i]	1:1	64	138–149	1160
OCF – 13[j]	1:1	78	175–180	1430
OCF – 14[k]	1:0.75	71	165–170	1330
OCF – 15[l]	1:1	73	170–180	1380
OCF – 16[m]	1:1.25	76	185–190	1480

Medium: Water (5% by weight of OC).
Reaction temperature: 135°C.
Reaction time: 4 h.
Catalyst: K_2CO_3 (2% by weight of OC).
[a,b,c,g,h,i,j,k,l,m] Reaction time 5 h.
[d,e,f] Reaction time 6 h.
[g] Catalyst 1%.
[h] Catalyst 3%.
[i] Reaction temp. 120°C.
[j] Reaction temp. 150°C.
[k,l,m] Catalyst 2% NaOH.

water (0.27 g, 5% by weight of *o*-cresol), and furfural (4.8 g, 0.05 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) containing 10 mL of concentrated HCl. The solid was filtered and washed with water until the filtrate was free from acid. It was air-dried. The dark-colored solid, softening in the range 145–150°C, had a yield of 74%. This resin sample was designated as OCF – 5. It was soluble in common organic solvents.

Characterization of Resins

Carbon and hydrogen contents of the resin samples were estimated by Coleman C and H analyzer. The infrared (IR) spectra were scanned on UR – 10 spectrophotometer in KBr. NMR spectra of resins were taken by Bruker NMR spectrophotometer. The number – average molecular weight was estimated by nonaqueous conductometric titration in pyridine against standard sodium methanolate in pyridine [10]. The dilute solution viscosities were measured in 1,4-dioxane at 35°C ± 0.1°C using Ubbelohde-type viscometer. The curing of OCF resin samples by hexamethylenetetramine was monitored by differential scanning calorimetry (DSC) following the procedure described earlier [11,12].

RESULTS AND DISCUSSION

All the OCF resin samples presented in Table 1 were brown-colored solids. The CH contents of all the resins are consistent with the predicted structure. They were soluble in most common organic solvents. The OCF resin samples soften over a range somewhere between 120 and 190°C. The softening range, percentage yield and the value of $\overline{M_n}$ of the resin samples of each series were found to increase with the increase in the ratio of furfural to *o*-cresol, the reaction temperature, the percentage of the catalyst (K_2CO_3), 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 potassium carbonate as a catalyst. Brown has also made similar observations during the study of phenol-furfural resin synthesis [4].

It was found that the softening range and yield of a OCF resin is higher as the *o*-cresol:furfural ratio is increased under similar experimental conditions. The same trend was observed when K_2CO_3 was replaced by NaOH. The intrinsic viscosity of the dioxane solution of the resin samples was found to lie between 0.02 and 0.04 $dL \cdot g^{-1}$. The value of intrinsic viscosity estimated by the application of

Huggins and Kraemer's [13,14] relations agree very well. The Mark-Houwink relation between intrinsic viscosity and $\overline{M_n}$ of the resin samples worked out as:

$$[\eta] = 2.102 \times 10^{-4}\,\mathrm{M}^{0.95} \tag{1}$$

It was reported that for the solution of novolak in methanol [15], the value of constant K and α are 10^{-4} and 0.7 and for solution of *o*-cresol – furfural resins in 1,4-dioxane, [16] these constants are reported to be 10^{-4} and 0.79, respectively.

The IR spectra of all the OCF samples are almost identical in all respects. All the spectra comprise the bands due to tolyl and α-furyl system. The band due to bridge – CH – appeared at 1340 cm^{-1}. The NMR spectra of all the resin samples comprise a multiplicity due to aromatic protons and hydroxyl and enolic protons (5.2–5.3 ppm). A singlet at δ : 2.8 ppm confirm the bridge – CH – .

Examination of the TG thermograms of OCF – 5 and OCF – 15 resin samples measured in air at a heating rate 10°C/min (Figure 1), reveals that each resin starts to degrade at ~200°C, suffers 50% degradation between 500 to 530°C, and complete degradation between 620 and 650°C. The Broido method [17] was applied to the TG data

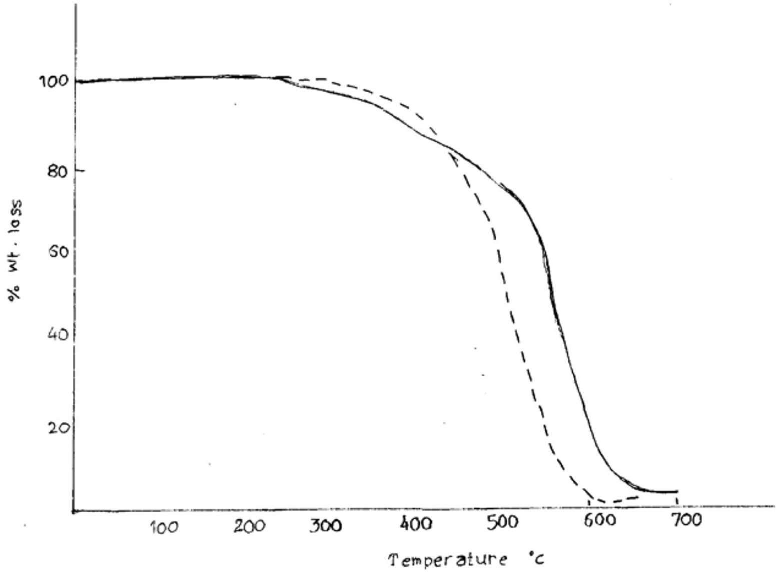


FIGURE 1 TGA curve for OCF – 5 (solid line) and OCF – 15 (dotted line) resins.

TABLE 2 Curing Characteristics of *o*-Cresol – Furfural Resin Hexamine[a] Mixture at Different Heating Rates

Resin sample	Heating rate β (°C/min)	Initiation of curing (°C)	Peak temperature (°C)	Completion of curing (°C)	Cure range (°C)	ΔH (m · cal/mg)
OCF – 5	10	100	140	200	100	1.6
	20	105	145	210	95	1.7
	40	125	150	245	120	1.4

[a] 12% by weight of resin.

to estimate the value of the energy of activation of the degradation reaction. The value of E was found to be 37 and 15 kcal/mol for the degradation of OCF – 5 and OCF – 15 resin samples, respectively.

Examination of the DSC thermogram of the curing of OCF – 5 sample by hexamethylene tetramine (12% by the weight of resin) was studied at three scan rates in static air. The DSC data are presented in Table 2. The typical DSC thermograms, shown in Figure 2, reveal that the OCF – 5 resin sample is cured in the range of 100–200°C, when the heating rate was 10°C/min. The peak exotherm (T_p) is shifted to a higher temperature and curing time decreases with an increase in the scan rate, β (°C/min). Such a trend was observed by many authors during studies of the curing of epoxy and phenolic resins [18–20]. The $Tp - \beta$ data are analyzed by the treatment suggested by Ozawa [21], Kissinger [22] and Crane et al. [23] through

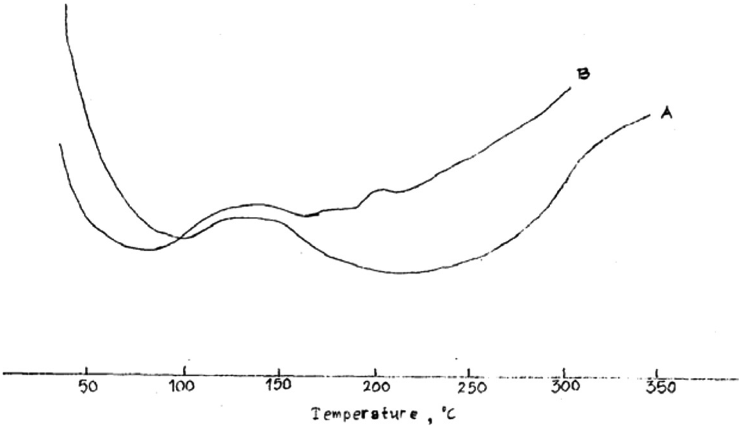


FIGURE 2 DSC curve of (A) OCF – 5 resins, (B) OCF – 5 + hexamine.

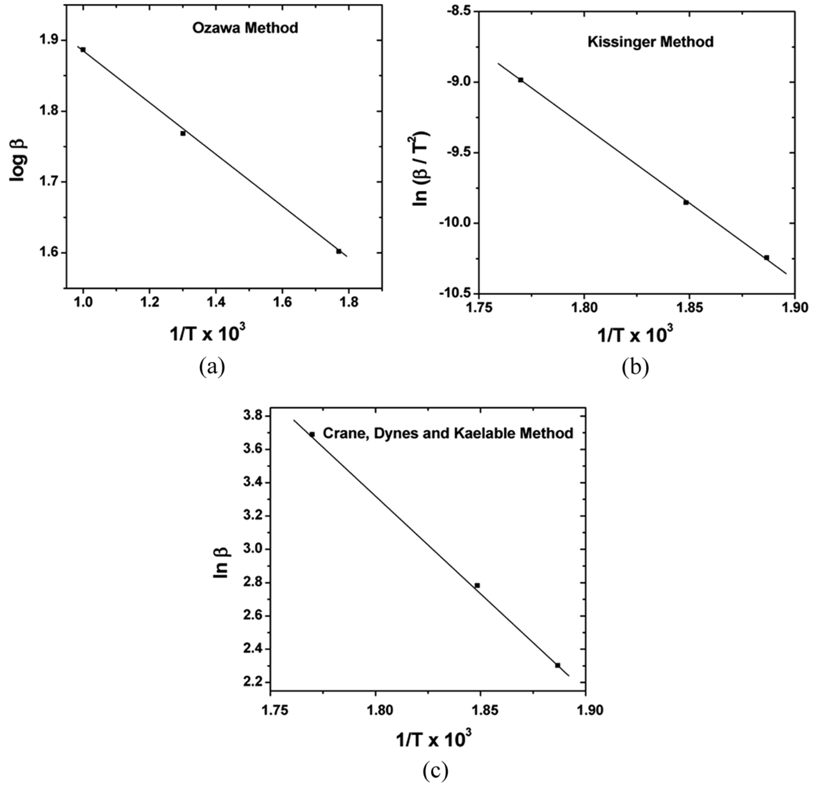
the originally proposed relation 2, 3 and 4, respectively, to estimate the kinetic parameters.

$$E = -2.19R\frac{d\log\beta}{d(1/T_p)} \tag{2}$$

$$\ln\left(\beta/T_p^2\right) = \frac{E}{R}(1/T_p) \tag{3}$$

$$\frac{d\ln\beta}{d(1/T_p)} = -\left[\frac{1}{n}\cdot\frac{E}{R}\right] \tag{4}$$

The relevant plots of $\log\beta$ vs. $1/\mathrm{T_p}$, $\ln(\beta/\mathrm{T}_2^{\mathrm{p}})$ vs. $1/\mathrm{T_p}$ and $\ln\beta$ versus $1/\mathrm{T_p}$ for OCF – 5 resin sample are shown in Figure 3. From



(a) (b) (c)

FIGURE 3 Plots using different equations for OCF resins.

the estimated value of the slope of the linear plot, based on appropriate relation 2, 3 or 4 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 and found to be practically the same (22 kcal/mol). 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 an excess of hexamine is very nearly equal to one.

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