Formation, Characterisation and Curing of 4-Chlorobenzaldehyde and 2-Butanone-Furfuryl alcohol (Furan) resins

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Abstract

The 4-Chlorobenzaldehyde and 2-Butanone-Furfurylalcohol resins have been synthesized by condensation of 4-Chlorobenzaldehyde with Furfuryl alcohol and 2-Butanone with Furfuryl alcohol respectively with acid or base or metal salt as catalyst. These resin samples have been characterized by spectral studies viz. ^{13}C-NMR, ^{1}H-NMR and FTIR. The cross-linking of these resin samples are also accomplished by using various cross linking agents. These resins have immense application in removing metal ion, matrices for the Fabrication of laminates, in making spandex fibers etc.

Key words : Furan resin, cross-linking, curing.

Introduction

Polycondensation of bishphenol –C and Furfural[1] has been carried out in the presence of basic and acidic catalysts under various reaction conditions. Similarly polycondensation of bisphenol –F with furafural[2] has also been accomplished. Cross-linking of phenol-furfural (PFu) resin with hexamethylene tetramine (Hexa) have been studied by Differential Scanning Calorimetry technique both dynamically as well as isothermally[3]. Polycondensation of furfural, respectively with o-and p-chlorophenols has been carried out under various reaction conditions[4]. A number of resins were synthesized by reacting cardanol, a by product of the cashew industry, with furfural and substituted aromatic compounds in the presence of acid and basic catalysts[5]. The present Resol type resins were prepared in alkaline condition using furfurol[6]. The base or acid catalysed Resorcinol-formaldehyde (RF) reactions can form polymeric resins which are currently used as wood adhesive and composites[7,8] .

The present paper deals with synthesis, characterization and cross-linking of 4-chlorobenzaldehyde (4CB)-Furfuryl alcohol (FA) and 2-Butanone (2B)-Furfuryl alcohol

(FA) resin samples. The Cross-linking of these resin samples are also studied by using various cross-linking agents.

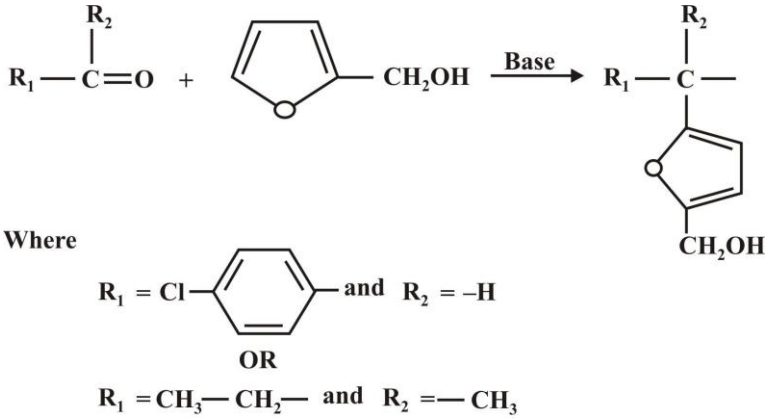
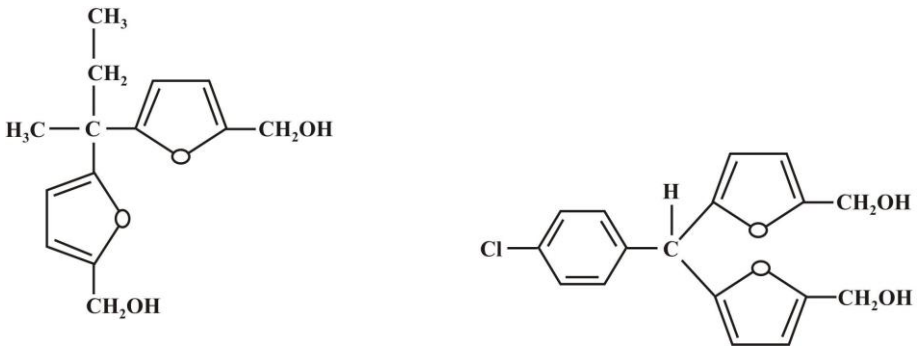


Fig. 1

This study is in continuation of work reported earlier for Synthesis, characterisation and curing of furan resins.

Results and Discussion

Both the 4CB-FA and 2B-FA resin samples present in Table-1 are dark solid. They are soluble in most of the common organic solvents such as chloroform, DMF, DMSO etc.



4CB-FA resin 2B-FA resin

Fig. 2

The infra-red spectrophotometric measurements showed bond formation processes occurring in the resin samples. Position of characteristic absorption in IR spectra of both the resin samples are :

Table 1 : FTIR data of uncured 4CB-FA and 2B-FA resins

Resin Sample	Band (cm^{-1})	FTIR characteristics
4 CB-FA resin	1629.4 and 1591.3	C═C stretching of aromatic rings
	1109.4 and 1014.4	C─O stretching of ─CH2OH group
	775.8 and 669.9	represents the C─Cl stretching
2B-FA resin	2928.1 and 2832.0	C─H stretching vibration of C─H group
	1591.4	C═C stretching of aromatic rings
	1362.8	C─H def. vibration
	1151.6 and 1013.4	C─O stretching of ─CH_2OH group

Table 2 : ^{1}H-NMR spectral data of the resin sample

Resin Sample	δ ppm in ($CDCl_3$)
4CB─FA	3.953-3.992, 2.255, 1.874, 7.316, 6.350-6.308, 6.210
2B-FA	3.621, 7.278-7.433, 5.811-5.907, 6.229-6.363, 3.969-4.010, 0.865-0.892

Table 3 : ^{13}C-NMR spectral data of 4CB-FA resin sample

Resin sample	δ ppm (in $CDCl_3$)
4CB-FA	56.3, 142.4, 109.4, 110.0, 141.0

The above spectroscopic analysis reveals that the 4CB-FA and 2B-FA resin samples have the structure as depicted in Fig. 2.

Cross-linking 4CB and 2B-FA resin samples:

Cross-linking of 4CB-FA and 2B-FA resin samples with cross-linking agents are summarized below in Table-2 along with certain details.

Table 4 : Cross-linking features of 4CB and 2B-FA resin samples.

Resin sample	Quantity of resin (g)	Curing agent	Amt. of curing agent (g)	Curing temp. (ºC)	Curing time (min)	Colour	% of curing
4CB-FA	0.1	Hexamine	0.01	~200	25	Yellowish	57.14
	0.1	Zinc Chloride	0.01	~200	10	Chocolate	75.00
2B-FA	0.1	Hexamine	0.01	~150	35	Yellowish	88.09
	0.1	Zinc Chloride	0.01	~150	2.0	Chocolate	80.00

Table 5 : FTIR data of 4CB and 2B-FA cross-linked resin samples :

Resin Sample	Band (cm^{-1})	FTIR characteristics
4 CB-FA resin	1598.5	C═C stretching of aromatic rings
	1363.9	C─O stretching of ─CH_2OH group
	1089.0	Due to ethereal group
	775.1 and 669.7	represents C─Cl stretching
2B-FA resin	2929.1	C─H stretching vibration of C─H group
	1366.7	C─H def. of C─H group
	1149.5 and 1072.3	represents C─O stretching of ─CH_2OH group
	1013.6 and 884.2	C─C stretching of C─C group

The IR spectra of both the cross-linked resin samples reveal tremendous change in terms of shape and peak portion in comparion with the resin samples (Not cross-linked as evident from FTIR band). This is indicative of strong interaction between resin and metal salt.

Experimental

The catalysts, monomers, and solvents employed for the resin synthesis were purified as and when thought necessary. Furfuryl alcohol was purified by distillation.

A mixture of Furfuryl alcohol (0.02 mol, 1.96 g) 4-Chlorobenzaldehyde (0.01 mol, 1.41 g), sodium hydroxide and water (each 5% of the weight of Furfuryl alcohol) was

heated at 100ºC for 5h. The thick red reaction mixture was poured into water with stirring. The solid was filtered, suspended in water and steam distilled for 2h to remove unreacted Furfuryl alcohol. Finally the resin was washed repeatedly with hot water to remove unreacted 4-Chlorobenzaldehyde.

Other resin samples listed in Table-1 were synthesized following the method described above under the reaction conditions mentioned in the same table.

Table 6 : Base catalysed 4CB and 2B-FA condensation.

Resin sample	Molar ratio	Catalyst and medium	Colour change	Reaction Temp. (ºC)	Reaction time (h)
4CB-FA	1:2	5% each (NaOH and H2O of the wt. of FA)	Light red to dark	~100	5
2B-FA	1:2	5% each (NaOH and H2O of the wt. of FA)	Red to Black	~100	6

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