

Synthesis and characterization of cardanol- furan-2-aldehyde novolac resins

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ABSTRACT

Cardanol, an excellent monomer for polymer production, has been isolated from CNSL. Cardanol is a meta substituted phenol and is a renewable organic resource for polymer synthesis. Cardanol and phenol in various mole ratio are allowed to react with furan-2-aldehyde in the presence of hydrochloric acid catalyst to give novolac resins. The resins thus prepared are characterized. The physico- chemical and spectral properties of the synthesized resin have been studied.

Keywords: Cardanol, Phenol, Furan-2-aldehyde, Hydrochloric acid, Novolac resins.

1. INTRODUCTION

Naturally available cashew nut shell liquid (CNSL) is an abundant agricultural by-product whose main component, cardanol act as an excellent monomer for the production of polymeric materials [1-6]. Cashew nut shell liquid occurs as a reddish brown viscous liquid in the soft honey comb structure of the shell of cashew nut. Renewable organic resources continue to be in the common interest of both academic and industrial laboratories throughout the world at all times [7-10]. Among the renewable resources, cashew nut shell liquid (CNSL), unique in that it contains a natural phenolic distillate, cardanol [11]. The functional group in it can be activated for the preparation of many speciality materials, such as liquid crystalline polyesters [12], nanotubes, cross-linkable polyphenols, and polyurethanes [13].

2. EXPERIMENTAL

2.1. Materials

Cashew Nut Shell Liquid (CNSL) was obtained from M/S Kumaraswamy Chemicals, Cuddalore, Tamil Nadu State, India. Cardanol was separated from CNSL by vacuum distillation at 3 - 5 mm Hg. The fraction distilled at 230° - 240°C was collected. Phenol, furan-2-aldehyde, and toluene (E Merck) were used as received without purification.

2.2. Instruments

Ultraviolet spectral analyses were carried out based on ASTM E 169 - 69, using variants, CARY 100 BIO UV-Visible Spectrometer. Infra red

spectra were recorded as thin films using a SHIMADZU 8400S Spectrophotometer. ¹H-NMR spectra were recorded in CDCl₃ with tetramethylsilane as an internal standard using Burker DPX 300 FTNMR Spectrometer. Specific gravity, iodine value, hydroxyl value, acid value and intrinsic viscosity of the resin were determined according to the IS standard 840 - 1964. Molecular weight of the resins were determined by gel permeation chromatography, using Waters HPLC system, 600 pump, styragel - HR - 5E / 4E / 2 / 0.5 columns and 2414 Refractive index detector in series.

2.3. Synthesis of cardanol/phenol novolac resins (C1, C2, and C3)

Three novolac resins were synthesized using Cardanol, phenol, furan-2-aldehyde and hydrochloric acid as catalyst as per the formulation given in table 1.

For synthesizing novolac cardanol/phenol furan-2-aldehyde resin (C1), 5.4 moles of cardanol and 0.6 moles of phenol were weighed into a three necked flask, fitted with a Leibig's condenser, ground joint thermometer and a dropping funnel. 1 mole of furan-2-aldehyde was added to the reaction mixture through dropping funnel. The pH of the reaction mixture was noted using a pH meter, (pH=4) 1% by weight of hydrochloric acid was added as catalyst, and the pH drops to one. The mixture was heated in a nitrogen atmosphere using a rotamand at 150±5°C for three hours. The reaction mixture (1 ml) was withdrawn for the determination of

Table -1: Formulation of Cardanol / Phenol - furfuraldehyde resins

Resin	Mole ratio of cardanol	Mole ratio of phenol	Mole ratio of furan-2-aldehyde	Percentage of hydrochloric acid
C1	5.4	0.6	1	1
C2	4.8	1.2	1	1
C3	4.2	1.8	1	1

furan-2-aldehyde to check the completion of the formylation and subsequent condensation of formylated cardanol at definite intervals.

Cardanol/phenol furan-2-aldehyde resin (C2) was synthesized using 4.8 moles of cardanol and 1.2 moles of phenol and 1 mole of furan-2-aldehyde using 1% by weight of hydrochloric acid as catalyst. Similarly, the cardanol/phenol furan-2-aldehyde resin (C3) was synthesized using 4.2 moles of cardanol and 1.8 moles of phenol and 1 mole of furan-2-aldehyde using 1% by weight of hydrochloric acid as catalyst.

3. RESULT AND DISCUSSION

3.1 UV Spectroscopy of resins C1, C2 and C3

The UV analysis of cardanol novolac resin reveals a shift of peak from 281nm (absorbance 2.4536) for phenyl ring in cardanol which is due to the hyper chromic effect of the newly substituted methylene linkage. Such a shift towards higher wavelength is due to the para substitution at the benzene nuclei of the cardanol. The UV spectral data are given in table 2.

Table - 2: UV spectral data of cardanol based resins C1, C2 and C3

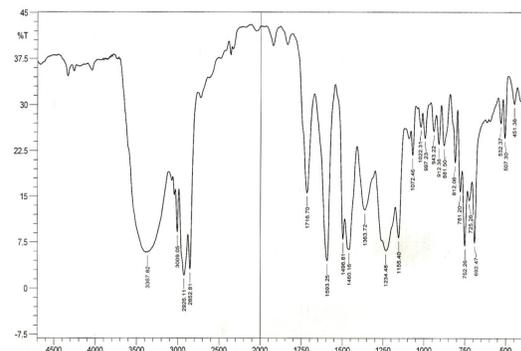
Resin	Wavelength (nm)	Absorbance
Cardanol	281	2.4536
C1	285	2.5443
C2	283	2.5274
C3	280	2.0268

3.2 IR Spectroscopy of resins C1, C2 and C3

The FT-IR spectra of resins C1, C2 and C3 are given in Table -3. The new peaks at 692cm⁻¹, 694cm⁻¹ and 695cm⁻¹ are due to the non conjugated CH=CH in side chain. IR spectra also exhibit a peak at 723cm⁻¹ and 725cm⁻¹ for the 1, 4 and 1, 2, 4 substitutions (ortho-para substitution) at benzene nuclei.

The presence of the peak at 912cm⁻¹ and 914cm⁻¹ support condensation and formation of methylene bridges between the two phenyl units. The bands around the region 3367 cm⁻¹ and 3394 cm⁻¹ indicate the presence of hydroxyl group. The peak at 1591 cm⁻¹ and 1593 cm⁻¹ is due to stretching of aromatic C=C stretching of side

chain. The shift of the peak due to -OH group to 3367 cm⁻¹, 3394 cm⁻¹ is due to the furfural moiety. IR spectra also reveal a fairly sharp peak at around 912 cm⁻¹ for 1, 4 substitutions at benzene nuclei for C1 and C2 resins; a shoulder at 914 appears for C3 resin. FT-IR spectrum of C2 in figure 1.

**Figure - 1: FT-IR Spectrum of C2**

3.4 NMR Spectroscopy of resins C1, C2 and C3

NMR spectral data of the resins are given in table 4. The peaks at 6.621 – 6.750δ is due to aryl protons of benzene nuclei, the peaks at 5.347-5.432δ are due to methylene proton of long alkyl side chain originally present in cardanol. The peaks between 0.859 and 2.562δ are due to the aliphatic long chain group of cardanol.

The presence of bulkier side chain in the aromatic nucleus in the case of cardanol could be expected to provide steric hindrance for the aromatic nucleus to come close together to condense with furfuraldehyde and its derivatives. The present mole ratio with cardanol and experiment pH conditions leads to higher para linkages with distorted branching structure as reported elsewhere [14].

3.5 Physico-chemical characterization of cardanol novolac resins

The physico-chemical properties of resin C1, C2 and C3 are presented in table 5.

Cardanol based C1, C2, C3 resins possess higher specific gravity and viscosity due to higher degree of condensation between cardanol and furan-2-aldehyde. In comparison with cardanol, the acid value is increased due to the increased acidic character due to the condensation of methylolated cardanols. The low iodine value in comparison

with that of cardanol may be due to steric hindrance of bulky groups on the olefinic addition of iodine monochloride during the estimation of

iodine value. Further as the molar concentration of cardanol increases the iodine value decreases.

Table- 3: IR spectral data of cardanol based novolacresins C1, C2 and C3

Wave number (cm ⁻¹)			Assignment
C1	C2	C3	
695	692	694	C-H of 1,3 bisubstituted phenyl ring
723	725	725	Para-ortho substitution
779	781	781	C=C in side chain
871, 912	881,912	873,914	adjacent H in benzene nuclei bend
993	997	997	Non- conjugated trans CH=CH inside chain
1155	1155	1153	-C-O stretch of -C(Ar)-OH
1265	1234	1242	-O-C=C- asym. stretch of the ring
1458	1460	1456	CH ₃ bend of side chain
1593	1593	1591	Aromatic C=C stretch of phenolic group
1716	1716	1718	C=C stretch of the side chain
2852	2852	2852	CH ₃ stretch of side chain
2926	2926	2926	CH asym. stretch of -CH ₂ of side chain
3007	3009	3009	CH stretch of aromatic ring
3394	3367	3367	-OH stretch of substituted benzene nuclei

Table - 4: NMR spectral data of cardanol resins C1, C2 and C3

Peaks (δ)			Assignment
C1	C2	C3	
0.859-0.931	0.860-0.931	0.859-0.930	Terminal methyl
1.260-1.578	1.259-1.581	1.299-1.574	Protons in the long chain -(CH ₂) _n -
2.022	2.023	2.023	Aliphatic side chain
2.557	2.562	2.562	CH in Ar-CH(furfuryl)-Ar linkage
4.295	4.319	--	Benzylic protons
5.347-5.364	5.347-5.431	5.348-5.432	Olefinic protons
6.621-6.747	6.628-6.752	6.628-6.750	Phenolic hydrogen
7.089-7.227	7.095-7.249	7.115-7.242	Aromatic protons

Table - 5: Physico-chemical characteristics of cardanol based resins C1, C2 and C3

Properties	C1	C2	C3
Specific gravity (g/cc) at 30°C	0.9315	0.9364	0.9413
Intrinsic viscosity (x10 ⁻²)	3.51	3.32	3.47
Acid value	92.5	93.8	138.5
Iodine value	222.1	232.7	243.2
Hydroxyl value (mg KOH/g)	135.55	156.35	107.56
Number of hydroxyl groups	3	3	3
Molecular weight (GPC) Mn/Mw	1383/1387	1346/1351	1332/1336

4. CONCLUSION

Development of valuable products from naturally available plant oils obtained as a byproduct in agro industries are highly relevant since the decline of the petroleum raw materials for the manufacture of several known engineering materials pose a major challenge. Using cardanol, one of the components of CNSL various resins were prepared along with furan-2-aldehyde and considerable quantity of phenol. Initially three types of cardanol novolac resins C1, C2 and C3 involving different mole ratio of cardanol, and furan-2-aldehyde were prepared using condensation reaction. Hydrochloric acid was used as catalyst for the formylation of cardanol. The spectral data indicate the formylation of cardanol has occurred under the present experimental conditions. The prepared novolac resins were characterized using UV, IR and NMR spectrum and found that, the para substitution was favoured for condensation reaction.

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