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Synthesis of cardanol based phenolic resin with aid of microwaves.

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Abstract

Cardanol based novolac resin was prepared. Cardanol based novolac-type phenolic resin was prepared under microwave irradiation by the reaction of cardanol (*C*) and formaldehyde (*F*) with mole ratio 1:0.8 of *C*/*F* using tricarboxylic acid as catalyst. Analogical synthesize have been done using conventional heating for the comparison of the methods. The methylolation of cardanol was confirmed by Fourier-transform infra-red (FTIR) spectroscopic analysis and a reaction mechanism was proposed. The number-average molecular weight was found by gel permeation chromatographic (GPC) technique. On the basis of the calculated value of kinetic chain length, the structure of the novolac-type phenolic resin was proposed. The main advantage of the process is twofold reduction of reaction time of the process carried at microwave reactors in comparison to the conventional heating.

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Introduction

Cashew nut shell liquid (CNSL), an agricultural renewable resource material, produces natural phenolic distillates such as cardanol [1,2]. The cardanol has been the attraction for many researchers for the production of phenolic resins either novolac or resoles in the past [3-8, 17-18,]. In the Industry, These products are generally provided

under conventional heating in batch reactors for a couple of hours [13-16].

Recently there is growing interest in the new method of chemical synthesis using microwave to induce the reactions. Microwave irradiation can interact with the polar substance because of the inability to instant reorientation of dipole according to the changes in the electromagnetic field. Microwave energy can be converted into heat directly inside material. Therefore, it is possible to achieved rapid and uniform heating even in the materials showing low thermal conductivity (e.g. phenolic resin), because transfer of energy does not rely on heat diffusion. The advantage consists in much higher heating rates and shortening of the reaction time [9-12].

The aim of present work was to check the possibility of microwave irradiation using for cardanol based novolac resin synthesis using citric acid as catalyst.

Experimental

Materials

Cardanol (M/s Satya Cashsew Pvt. Ltd., Chennai), formaldehyde (40% solution), citric acid, and hydroxylamine hydrochloride were used during the investigation.

Analysis of cardanol

Cardanol, obtained from the distillation of commercial cashewnut shell liquid (CNSL) under reduced pressure (1 mm Hg) and was collected at 206-208°C, was subjected to extensive analysis, viz., for iodine value, viscosity, specific gravity, etc., as per the procedure mentioned in Indian Standards (IS 840-1964).

Synthesis of cardanol based novolac-type phenolic resin

Using microwave irradiation.

Novolac resin with mole ratio 1:0.8 of cardanol (*C*) to formaldehyde (*F*) was prepared using tricarboxylic acid, viz., citric acid, as catalyst. The mixture was irradiated and stirrded at temperature 120°C in a multi mode microwave reactor(Model LG MS 194 W) of microwave frequency 2.45 GHz. The reaction was continued until the free formaldehyde of the resin dropped to value 0.6.

Conventional method

Novolac resin with mole ratio 1:0.8 of cardanol (*C*) to formaldehyde (*F*) was prepared using tricarboxylic acid, viz., citric acid, as catalyst by a method similar to that adopted by Knop and Schieb [13]for phenol based novolac. Catalyst (1% based on cardanol) was, first, dissolved in methanol at 60°C. The methanolic solution of catalyst was added to the formaldehyde (40%) and this was added to the cardanol drop wise within one hour, once the temperature of the reaction kettle was maintained to 120°C. The initial pH of the reaction mixture was 6.0 which reduced to a value of 4.8 after 5 h of reaction at 120°C. Free-formaldehyde content were checked to see the completion of the methylolation reaction [14]. Purification was effected using the elutent mixture of ethyl acetate – benzene (60 : 40). The purified resin was analyzed by infra-red (IR) (Fig.1) and gel permeation chromatographic (GPC) analysis.

Fourier-transform infra-red (FTIR) spectroscopic analysis

Fourier-transform infra-red (FTIR) spectra of uncured and cured samples were recorded on a Perkin-Elmer (Model 843) infra-red spectrophotometer, using KBr pellet, in the wave length range of 500-4000 cm^{-1}.

Gel Permeation Chromatographic (GPC) analysis

Gel permeation chromatograph were recorded with a Shimadzu Europa GmbH, Duisburg, Germany high performance GPC (Model LC-6A).

3. Results and Discussions

3.1 Synthesis of cardanol-formaldehyde novolac type phenolic resin

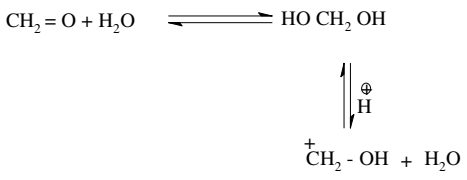
Reaction condition and results of all are given in Table 1. It is clear from the table that the microwave synthesizes product shows particularly its high

efficiency, leading to drastically reduced reaction times, higher yield and purer products. Shorting of reaction time for all process carried out in microwave reactor, in comparision to conventional heating, was observed.

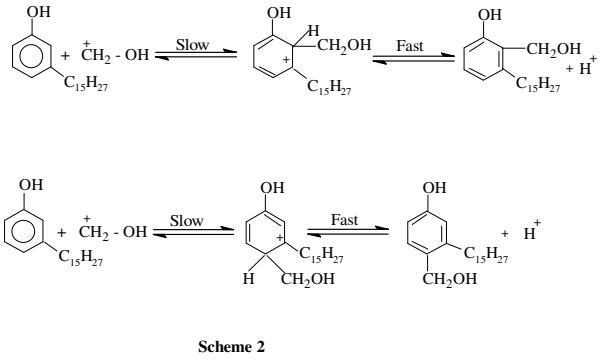
The methylolation of cardanol was carried out with formaldehyde in presence of tricarboxylic acid, viz., citric acid. The pH of the reaction mixture was 6.0 during initiation of the reaction. The methylolation reactions were carried out with 0.8 : 1 mole ratio of formaldehyde to cardanol. The completion of the methylolation reaction was checked by periodic withdrawal of reaction mixture to analyze formaldehyde using hydroxylamine hydrochloride [14]

3.2 FTIR analysis of cardanol-formaldehyde resin

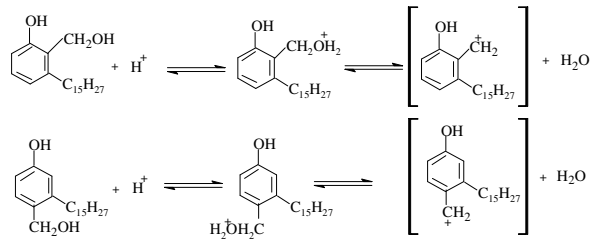
The IR-spectrum of cardanol-formaldehyde novolac resin is given in Fig. 1. A shift of a peak from 1076 to 1100 cm^{-1} and appearance of peak at 1720 cm^{-1} were observed in methylolated cardanol due to the CO stretching from CH_2OH. It has also been found that the intensity of peaks at 1594 cm^{-1} (C=C, str), 3010 cm^{-1} (C-H str of alkene) and 778 cm^{-1} (C-H out-of-plane deformation) remained almost unaffected which indicated that the polymerization has taken place through substitution of CH_2OH rather through the double bonds in the side chain. The preceding spectral data were found to identical with those given in the literature [15]. A reaction mechanism, based on the mechanism as proposed by Kuriakose and Manjooran [16], was also proposed. Based on this, the structure of the novolac resin may be proposed as in Scheme.



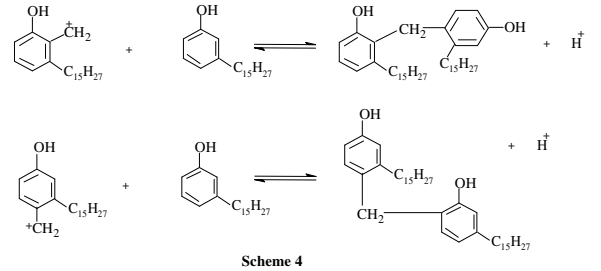
Scheme 1



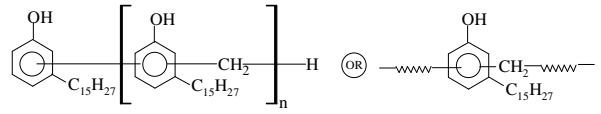
Scheme 2



Scheme 3



Scheme 4



where, n= 0, 1, 2, ... for dimer, trimer, etc.

Scheme 1

GPC chromatogram of novolac prepolymer made by polycondensation of cardanol and formaldehyde. The GPC curve gave the values of number-average (M_n) and weight-average (M_w) molecular weights as 498(conventional sample) and 500 (microwave sample)

Considering the linear structure of polymeric species, the average chain length of cardanol based novolac-type phenolic resin was calculated using the following equation based on the equation given by Podzimek and Hroch [18] for phenol based novolac resin.

$$\nu = 1 + \frac{\overline{M}_n - (299+1)}{312}$$

$$\text{or } \nu = \frac{\overline{M}_n + 12}{312}$$

With the value of M_n (= 498,& 500 from GPC the average kinetic chain length was calculated to be 1.44. and 1.64.

The characterizations of the final product shows that the resins prepared by the microwave and conventional method have comparable properties. Particularly, GPC analyses showed that the entire sample prepared have a similar number average molecular weight.

Conclusions

It was demonstrated that it is possible to obtain cardanol based novolac resin with desired free formaldehyde content irradiation (2.45GHz) to heat up the reaction mixtures of cardanol and formaldehyde in presences of citric acid as catalyst. The main advantage of such a process carried out in the microwave reactor is reaction time reduction.

Table 1. Synthesis and properties of the cardanol based novolac product obtained

Catalyst concentration	Conventional method					Microwave method				
	Temperature °C	Free formaldehyde %	Yield %	Solid content %	Time (hour)	Temperature °C	Free formaldehyde %	Yield %	Solid content %	Time (min)
1%	120	0.6	74.75	44.32	4.15	120	0.17	78.28	58.95	40.11
1%	120	0.56	74.62	44.24	4.25	120	0.13	79.61	57.48	40..20
1%	120	0.55	75.63	44.84	4.23	120	0.12	80.12	57.9	40.13
1%	120	0.58	74.55	44.20	4.13	120	0.15	82.58	59.62	40.19

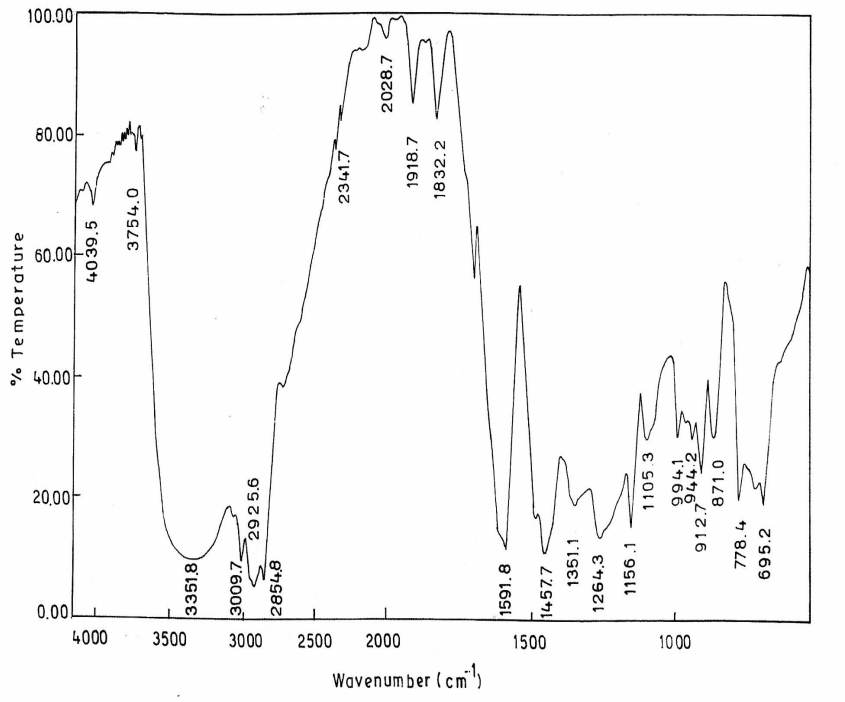


Fig. 1. : FTIR spectrum of cardanol-based novolac resin.

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