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Synthesis and Characterization of Phenolic Resole Resins for Adhesive Applications

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In present studies, the phenol-formaldehyde resole resins have been synthesized in the presence of sodium hydroxide as catalysts. The activity of these catalysts was compared with the activity of barium hydroxide and ammonia. ^{1}H and ^{13}C NMR spectrometry and some physico-chemical methods were used to estimate the composition of the obtained resins and their properties. It was concluded from these studies that sodium hydroxide is active catalysts and the resins obtained in their presence show some interesting properties.

Key Words: Phenol-formaldehyde resins, Molding compounds, Thermosetting resins.

INTRODUCTION

Phenolic resole resins used for the manufacture of composites, plywood, *etc.* are thermosetting. Resoles are prepared by the reaction of phenol and formaldehyde under alkaline conditions, with an excess of formaldehyde, to produce water based polymer capable of cross-linking (condensation reaction) or curing merely with the addition of heat. Acid catalysts are used to increase the cure rate and lower the cure temperature. Various acid catalysts are available that provide a pot life ranging from 5 min to 5 h. Resins of varying viscosity and thixotropy are available, to accommodate the process[1-3].

Phenolic A-stage resins are well known to be prepared from a phenolic component and an aldehyde component which are catalytically reacted. A variety of ionizable catalytic agents are known for the preparation of resole resins, including various alkali metal compounds, alkaline earth metal compounds and amines. Residual ionizable catalyst permits subsequent heat cure of the resole resins, though at the expense of storage stability. One class of resole resins are benzylic ether resins formed by the reaction of a phenol and an aldehyde under substantially anhydrous conditions at temperatures generally below *ca.* 130 ºC, in the presence of a catalytic concentration of a metal ion dissolved in the reaction medium. Such metal ion catalytic agents include sodium and zinc acetate, lead acetate, lithium naphthanate, lead naphthanate, lead oxide, *etc.* Resole resins can be formed using alkaline catalysts, such as the alkali metal and the alkaline earth metal hydroxides in forming aqueous resoles, by the aqueous reaction of a phenol and formaldehyde at a moderate temperature, subsequently neutralizing the reaction medium to a pH of *ca.* 3.8-5.3 to form insoluble, non-ionizable salts, and then stripping water, to the extent desired, from the reaction medium under vacuum at temperatures ranging up to 130 ºC. The insoluble, non-ionizable salts may be removed by filtration or other common means prior to dehydration in order to lower the residual ionizability even more. The preparation and characterization of some of these resins are presented in detail of U.S. Patent No. 3,485,797.

The resole resins formed in this work are also known as high *ortho-ortho* resins in that the resins are characterized by *ortho-ortho* linkages, compared to conventional resole resins, whether formed under anhydrous conditions or not, wherein *ortho-para* linkages predominate. Phenolic resole resins can be converted to a cured network (C-stage) in the presence of hydrogen ion-type catalysts, such as typified by strong inorganic and organic acids. Though such resole resins can be cured readily in the presence of strong acid catalysts, the pot life of such acid catalyzed compositions (*i.e.*, the time until the composition is no longer useful in a particular application), suffers from the presence of such strong acid catalysts. Thus, there is a need in the phenolic resole art for improving their pot life or storage stability, while maintaining and even increasing the speed of cure of acid-catalyzed resole resins. In this way, the cure speed and pot life performance of phenolic resole resin compositions can match those now available from vinyl esters and polyesters, and phenolic resole resins may become a viable alternative in many applications[4]. Dent[5-7] in 1933 showed method of producing condensation products of formaldehyde and a phenolic 'body and is particularly aimed to provide an efficient method of making such products from so-called crude phenol, which is largely made up of the higher homologues of phenol and may contain only a small percentage of phenol.

EXPERIMENTAL

Reaction of phenol and formaldehyde in presence of alkali or alkaline earth metal hydroxide was done. In Fig. 1, the schematic of reaction was shown.

100 g of phenol and 2 g catalyst poured in reaction vessel and heated in 85 ºC bath with mixing. Then add 100 g formaldehyde dropwiseand finally sample was refluxed for 3 h.

In resole synthesis, three experiments were performed. First of all, kind of catalysts, second, addition of different mole parts of phenol to formaldehyde and third provides the use of different stabilizer and additives.

Kind of catalysts: Four types of catalysts NaOH, $Ba(OH)_2$, NH_3 and $Mg(OH)_2$ were tested. After testing resole (coming in analysis part), sodium hydroxide is the best catalyst.

Determination of mole fraction of phenol to formaldehyde (F/P): Because of importance of mole fraction of phenol to formaldehyde in structure of resole, we

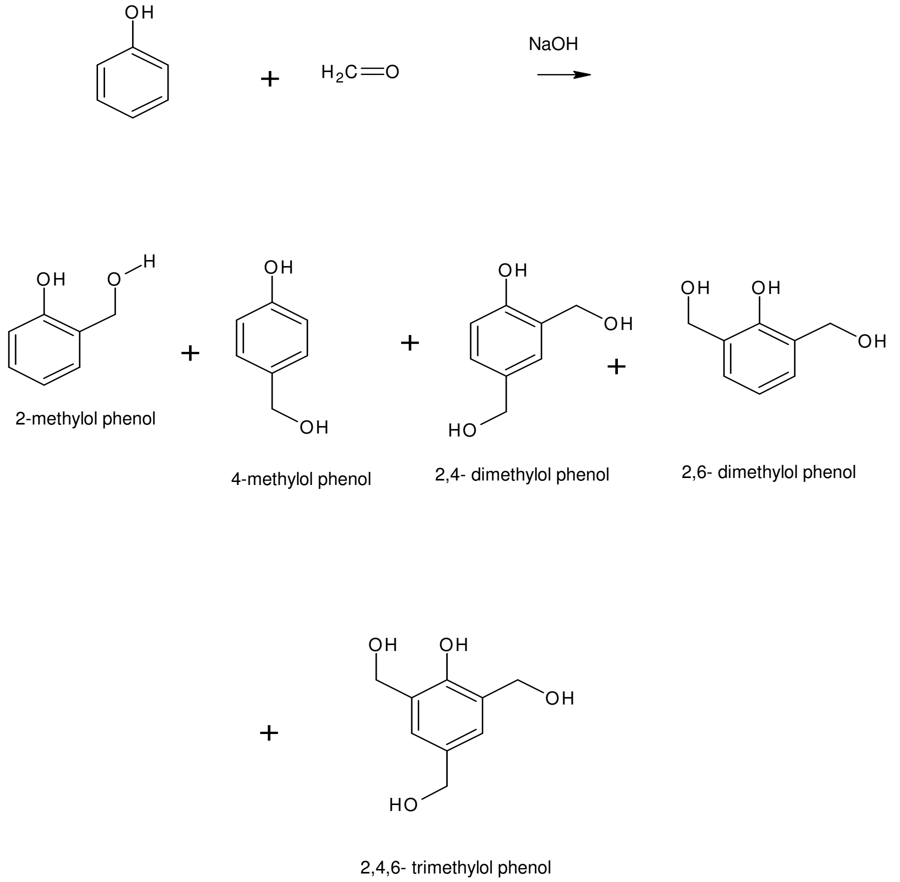


Fig. 1. Reactants and products of reaction of phenol and formaldehyde

make decision to put mole fractions as below: 1.15, 1.16, 1.30, 1.45, 1.50, 1.80, 1.85, 2.00 and 3.00. But temperature and content of catalyst is constant. The results show for every use of resole, for example adhesive, one fraction of F/P is used. In preparing of pressure-sensitive adhesive from resole, the mole fraction (F/P) must be 1/5.

Determination of temperature and time of reaction and relation of them with viscosity: Time of reaction is important in viscosity of resole, because the reactants have effect on the resole. When time of reaction increases, the active groups on phenolic ring is increased and cause to resole will be more viscose. In Table-1 different time and temperatures are shown.

The prepared resole showed that 70 ºC is the temperature for reaction and 2 h is the time for better yield.

Additives and stabilizers: Because of resole hardening in short time, the life of resole is short and can't be able to preserve as a liquid. In most industries, the prepared resole is consumed as soon as possible. But for a few industries the additives

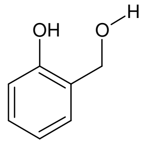
TABLE-1
TEMPERATURES AND TIMES OF REACTION AND NUMBER OF REPEATING

No. of repeating	Time (min)	Temperature (°C)
1	200	70
1	600	70
1	80	210
3	85	180
1	600	85
9	60	70
3	90	70
9	120	70
1	180	70

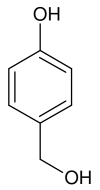
are best choices, because additives stabilize the resole viscosity and add the solid per cent of polymer. Reducing of temperature and keep in refrigerator cause resole to more life period, but adding some materials as below can help industries to keep resole as a liquid: *p*-toluene sulfonic acid, sodium sulfite, sulfuric acid, sodium bisulfate, aromatic amines (as aniline), benzaldehyde, benzyl alcohol, cooling.

RESULTS AND DISCUSSION

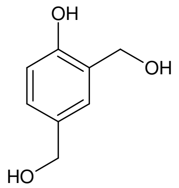
Analysis of resole was done by ^{1}H and ^{13}C NMR and IR spectroscopy. In ^{1}H and ^{13}C NMR spectra, because of complexity of structure of resole, the interpretation of spectra is difficult, but it can be interpreted by structure of constituent's compounds. Resole is a mixture of phenol derivatives for example:



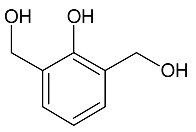
2-methylol phenol



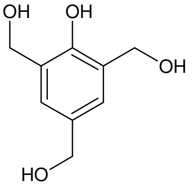
4-methylol phenol



2,4- dimethylol phenol



2,6- dimethylol phenol

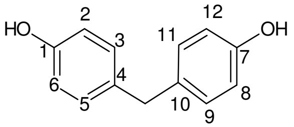


2,4,6- trimethylol phenol

The chemical shift of them was calculated and was compared with experimental data in NMR of resole. The resole has complex structure and for interpretation the spectrum, calendar must be used.

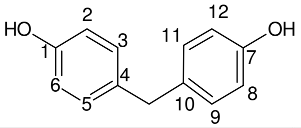
For interpretation of ^{1}H NMR of resole, the chemical shifts of some materials that may be existed in resole structure (Tables 2 and 3). In these tables, only one benzene ring exists. But there can be have two or more benzene rings, so we must tell about them and interpret them also. In Table-3 the other possible molecule is predicted.

TABLE-2
CHEMICAL SHIFTS OF ^{13}C-AND ^{1}H-NMR OF PHENOL



Carbon number		Carbon chemical shifts		Hydrogen chemical shifts	
		Aromatic carbon	-CH_2OH	Aromatic proton	-CH_2OH
1	Without substitute	157.4,129.3,118.8,115.3	-	7.165,6.77	-
2	-CH_2OH at carbon no. 2	154,128.5,127.2,118.6,114.5	58.2	7.25,7.038,6.75	4.485
3	-CH_2OH at carbon no. 4	156.2,132.7,128.1,114.8	62.8	7.139,6.747	4.396
4	-CH_2OH at carbon no. 2,6	151.8,128,125.9,118.8	59.3	7.143,6.80	4.561
5	-CH_2OH at carbon no. 2,4	152.9,132.5,127.9,126.2	58.3,63	7.252,6.989,6.696	4.472, 4.37
6	-CH_2OH at carbon no. 2,4,6	150.5,132.6,128.1,124.4	59.3,63	7.099	4.574, 4.38

TABLE-3
CHEMICAL SHIFTS OF ^{13}C AND ^{1}H NMR OF THE FOLLOWING MOLECULES:



Carbon number		Carbon chemical shifts			Hydrogen chemical shifts		
		Aromatic carbon	-CH_2	-CH_2O	Aromatic proton	-CH_2	-CH_2O
7	Without substitute	155.3, 132, 129.4, 115	39.4	-	6.97, 6.672	3.687	-
8	-CH_2OH at carbon no.2	155.3, 152.31, 132.1, 131.8, 129.3, 128.2, 127.5, 127.3, 115, 114.4	39.8	58.3	7.113, 6.975, 6.861, 6.675, 6.672	3.699	4.454
9	-CH_2OH at carbon no.2, 6	155.3, 149.9, 132.1, 129.4, 127.9, 126.1, 115.1	40	59.4	6.975, 6.967, 6.658	3.7	4.51
10	-CH_2OH at carbon no.2, 8	152.2, 132, 128.2, 127.5 127.3 114.4	40.1	58.3	7.1, 6.86, 6.67	3.704	4.44
11	-CH_2OH at carbon no.2, 6, 8	131.8, 128.1, 127.9, 127.5, 127.3, 126, 114.4	40.3	58.3, 59.4	7.133, 7.003, 6.902, 6.705	3.708	4.43, 4.405
12	-CH_2OH at carbon no.2, 6, 8, 12	149.9, 132.1, 127.9, 126.1	40.4	59.4	6.966	3.74	4.502

Analysis result (such as gel time and hydroxyl number) of resole confirms the resole product. In investigation of resole structure in alkaline DMSO solution, structure with substitutions and low molecular weight is dominant. So, First resole acetylated with acetyl reagents, then separated by column chromatography and take NMR spectra. In study of catalyst effect on products amount and quality, the result of analysis showed the NaOH catalyst is better and the result resole has better quality (such as colour, flammability, water content and the less, the phenol and formaldehyde content). The stabilized phenolic resole resin composition prepared by reacting an aldehyde with a phenol such that the molar ratio of aldehyde to phenol is from 1.1: 1 to 3: 1 in the presence of NaOH catalyst.

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