

# Effect of Cashew Nut Shell Liquid (CNSL) on Properties of Phenolic Resins

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## SYNOPSIS

Cashew nut shell liquid (CNSL) is a natural product, and because of its phenolic nature it undergoes reactions similar to those of phenol. The cost of CNSL is much less than phenol. The effect of replacement of phenol by CNSL on the properties of novolak and resol resins was experimentally investigated. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Cashew nut shell liquid (CNSL) is a natural product obtained from the shells of the cashew nut. In its natural form, crude CNSL is a mixture of different phenolic compounds. The main constituents are, however, anacardic acid, cardol, and cardanol.<sup>1,2</sup> The structures of these components are shown in Figure 1.

Because of the phenolic nature and unsaturation in the side chain, CNSL offers reaction sites on the aromatic ring and also on the side chain, which makes it a suitable raw material for variety of reactions. CNSL reacts with active methylenes like formaldehyde or hexamethylene tetramine via the hydroxyl group and can undergo addition polymerization through unsaturation present in the side chain.

Therefore, different type of resins can be synthesized from CNSL, its isolated constituents, or from chemically modified CNSL. Synthesis and properties of resins from CNSL and different aldehydes,<sup>3-7</sup> styrenated CNSL-formaldehyde resins,<sup>8</sup> polyurethanes, acetal resins, acrylic resins, and a variety of resins have been reported in the literature.<sup>9-20</sup>

Phenol is a synthetic raw material. CNSL is naturally available in many parts of the world, such as India, Brazil, Bangladesh, Tanzania, Kenya, Moz-

ambique, and in the tropical regions of Africa, southeast and far east Asia.

The cost of phenol in India varies between 40 and 50 rupees/kg while cost of CNSL is around 6-8 rupees/kg, depending upon the season. Cost of these two materials, respectively, are \$0.80/kg and \$0.30/kg in the United States. In Europe the cost of phenol is 1.1-1.3 DM/kg while the cost of CNSL is comparable to that in the United States.

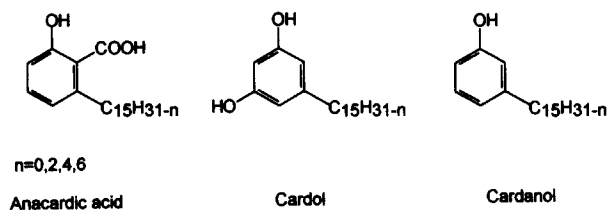
Thus use of CNSL in phenolic resins as a partial or full replacement may be of immense interest in the days of dwindling petroleum deposits. There is very little published information on the preparation and properties of novolak and resol type resins prepared from the mixture of CNSL and phenol. Therefore, the effect of process conditions and characteristics of CNSL on the properties of resins prepared from a mixture of (CNSL + phenol) with formaldehyde is pragmatically interesting.

## EXPERIMENTAL

### Materials

Commercial grade CNSL, technical grade phenol, and aqueous formaldehyde (37% w/w) were used in resin preparation. Specifications of CNSL used were reddish brown color, 5-7 mg of KOH/g of sample acid value, 304 mg of iodine absorbed/100 g of sample iodine value, 0.9632 specific gravity at 32°C, 263 s polymerization time, and no moisture content. Analytical grade chemicals were used for characterizing the resins and raw CNSL.

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**Figure 1** Constituents of crude CNSL.

### Resin Preparation

(CNSL + phenol) : formaldehyde resins were prepared using acid catalyst and alkaline catalyst. Average molecular weight of CNSL was considered as 300 on the basis of iodine and acid value of CNSL, for deciding the amount of CNSL (by weight) to be used. Phenol was replaced up to 90% by weight in the preparation of different resins.

### Acid Catalyzed (Novolak) Resins

In novolak preparation, initially CNSL was charged and reacted with aqueous formaldehyde. The mole ratio of CNSL to formaldehyde was maintained at 1 : 1.15. A small quantity of concentrated sulfuric acid (98%) was added as a catalyst, the amount being 1% (w/w) of the total charge of CNSL. After about 3 h of reaction time, a mixture of phenol and aqueous formaldehyde containing sulfuric acid as

catalyst (1% by weight on the basis of phenol charged) was added to the reacting mass. The amount of phenol, CNSL, and total formaldehyde were so adjusted that the ratio of total phenol (i.e., phenol + CNSL) to formaldehyde in the final reaction mass was maintained at 1 : 0.95. Thus by adjusting the amount of CNSL and phenol, the desired replacement of phenol could be achieved.

A sample of resin was withdrawn at regular intervals and tested for free formaldehyde. Reaction was stopped when the free formaldehyde content (limiting reactant) was reduced to less than 1%. A reaction temperature of  $92 \pm 2^\circ\text{C}$  was maintained.

Free phenol content was analyzed for information related to unused phenol but has no relevance to the final properties of the resin. The resin was made free from moisture by vacuum distillation before further testing of mechanical properties.

### Alkali Catalyzed (Resole) Resins

The required quantities of phenol, CNSL, and aqueous formaldehyde were mixed by keeping the mole ratio of total phenol (i.e., phenol + CNSL) to formaldehyde at 1 : 1.85. An aqueous solution of 2.5N sodium hydroxide (1%, w/w, on the basis of total charge of phenol and CNSL) was employed as the catalyst. A reaction temperature of  $65 \pm 2^\circ\text{C}$  was maintained.

**Table I** Composition Reaction Conditions and Other Properties of CNSL Based Novolak Resins

Phenol : CNSL		Reaction Time (h)	Nature of Resin	Solubility in Methanol	Free Phenol (%)	Free Formaline (%)	Norton Flow (mm)
Wt %	Mol %						
100 : 00	100 : 00	4	Solid	Soluble	0.97	Nil	85
90 : 10	97 : 03	4	Solid	Soluble	0.91	Nil	83
85 : 15	95 : 05	4	Solid	Soluble	0.76	Nil	72
83 : 17	94 : 06	5	Solid	Soluble	0.57	Nil	61
80 : 20	93 : 07	6	Solid	Soluble	0.40	Nil	65
75 : 25	90 : 10	6	Sticky solid	Partially soluble	0.87	Nil	—
55 : 45	80 : 20	7	Sticky thick viscous mass	Insoluble	0.61	Nil	—
50 : 50	70 : 30	7	Sticky thick viscous mass	Insoluble	0.45	Nil	—
30 : 70	60 : 40	7	Sticky thick viscous mass	Insoluble	0.50	Nil	—
25 : 75	50 : 50	7	Sticky thick viscous mass	Insoluble	0.48	Nil	—
20 : 80	40 : 60	7	Sticky thick viscous mass	Insoluble	0.85	Nil	—
10 : 90	30 : 70	7	Sticky thick viscous mass	Insoluble	0.37	Nil	—

Reaction temperature,  $92 \pm 2^\circ\text{C}$ .

**Table II Properties of CNSL Based Novolak Molding Powder**

Phenol : CNSL (w : w)	Curing Time at 160°C (s)	Flow Time of Molding Powder at 160°C (s)	Tensile Strength (kg/cm <sup>2</sup> )	Impact Strength (kg/m)	Breakdown Voltage (V/mm)	Hardness (Shore D)
100 : 00	68	29	484	0.036	2498	75
90 : 10	70	20	463	0.037	2531	80
85 : 15	73	20	451	0.038	2553	80
80 : 20	80	19	403	0.039	2681	85
75 : 25	85	23	405	0.038	2685	80
55 : 45	97	14	298	0.038	2662	—
50 : 50	103	13	285	0.043	2649	85
30 : 70	107	11	281	0.040	2689	85
25 : 75	107	12	279	0.039	2496	85
20 : 80	110	10	265	0.039	2025	85
10 : 90	110	11	205	0.038	2060	85

A sample of resin was withdrawn at regular intervals and tested for free phenol (limiting reactant). The reaction was stopped when the free phenol content was reduced to less than 1%. Moisture in the resin was eliminated by vacuum distillation before testing for mechanical properties.

### Resin Characterization

Resins were characterized for free phenol, free formaldehyde, and gel time. Molding powder was prepared from novolak resins using 55 phr (per hundred parts rating) wood flour, 8–13 phr hexamethylene tetramine as a curing catalyst, and calcium oxide and zinc stearate as other additives.

The mixture of novolak resin, filler, catalyst, and additives was mixed to a stage B on a two roll mill at temperatures between 100 and 120°C for 10 min. It was then ground into fine powder. The test specimens were molded under pressure of 480 kg/cm<sup>2</sup> and cured at 160°C. Tensile strength, impact

strength, flow time, shore hardness, and breakdown voltage (BDV) were determined for molded samples.

The solid content of the resole resins was determined and laminates with jute mats were prepared and tested for mechanical properties. A 150 × 150 mm jute mat was dried by warming it for 20 min at 80°C. Resole resin (50% solids in acetone) was applied over it by the hand lay-up method and by maintaining the ratio of resin to jute at 40 : 60 (w/w). The solvent was evaporated at 70°C and samples were then cured at 160°C with a pressure of 480 kg/cm<sup>2</sup> for 15 min. Tensile strength, impact strength, shore hardness, and BDV of these laminates were determined.

Other details of the experimental procedure are reported by Mahanwar.<sup>21</sup>

### RESULTS AND DISCUSSIONS

Table I shows the effect of replacing part of the phenol by CNSL on the properties of resins. Up to 20%

**Table III Composition and Other Properties of CNSL Based Resole Resins**

Phenol : CNSL		Reaction Time (h)	Free Phenol (%)	Free Formaline (%)	Gel Time at 150°C (s)	Solids (%)	Solubility in Methanol
Wt %	Mol %						
100 : 00	100 : 00	4	0.31	1.97	250	81.5	Soluble
85 : 15	95 : 05	6	0.82	1.98	262	74.5	Soluble
80 : 20	92 : 08	6	0.52	1.99	269	77.2	Soluble
75 : 25	90 : 10	6	0.33	3.01	275	71.9	Soluble
55 : 45	80 : 20	6	0.44	1.09	347	79.8	Soluble
40 : 60	70 : 30	6	0.65	2.07	389	75.9	Soluble

Reaction temperature, 65 ± 2°C.

**Table IV Properties of CNSL Based Resole Laminates**

Phenol : CNSL Weight Ratio	Tensile Strength (kg/cm <sup>2</sup> )	Charpy Impact (J/mm <sup>2</sup> )	Breakdown Voltage (V/mm)	Hardness (Shore D)
100 : 00	319.49	0.969	1674	85
85 : 15	298.69	1.256	2110	90
80 : 20	238.69	1.799	2083	90
75 : 25	216.69	2.430	2283	90
55 : 45	160.90	2.435	2666	90
40 : 60	64.20	2.376	2390	90

The filler used was jute fiber mats; the resin : filler ratio was 40 : 60; and curing conditions were curing time, 10 min, curing temperature, 160°C, and pressure 180 kg/cm<sup>2</sup>.

(by weight) replacement of phenol, the resulting resins were solid at room temperature (30°C). With further replacement of phenol, the resins became sticky and their solubility in methanol was also reduced. The flow time reduced steadily as the amount of CNSL increased, indicating higher viscosities.

The reaction times also increased and became almost double as more and more of the phenol was replaced by CNSL. The increase in reaction time could be because of the low reactivity of the CNSL, arising from the stearic hindrance caused by the side chain.

#### Molding of Novolak Resins

The molding powders from these resins were prepared by blending catalyst, filler, calcium oxide, and zinc stearate. A typical formulation was 45 g resin, 55 g wood flour, 0.45 g zinc stearate, 0.45 g zinc oxide, and 5.5 g hexamethylene tetramine. The test specimens were compression molded at a temperature of 160 ± 2°C and under a pressure of 480 kg/cm<sup>2</sup>. Table II shows the effect of CNSL on the mechanical and electrical properties of molded specimens. It was observed that the gel times increased, while tensile strength and flow times decreased progressively with increasing CNSL. Impact strength remained almost unaltered. The shore hardness also remained relatively unaltered. The electrical insulating properties initially increased and later deteriorated. Because CNSL has a long side chain, it induced a plasticizing action and changed the properties of the resin accordingly.

#### Resole Resins

The resole resins were prepared using aqueous sodium hydroxide as a catalyst. Table III shows the effect of replacement of phenol by CNSL on the properties of the resins. It seems that properties

other than gel time remained unaltered as compared to phenol based resoles. Gel time increased with increasing CNSL. However, unlike novolak resins all the resole resins were soluble in methanol.

The laminates were prepared and properties of these laminates are given in Table IV. Similar to novolak resin powders, the tensile strength decreased considerably, but there was a distinct improvement in impact strength and BDV. The increase in impact strength can perhaps be attributed to the long side chain in the CNSL. Hardness remained almost unaffected.

#### Effect of CNSL Characteristics

When CNSL with acid value more than 10 was used, no satisfactory resin could be formed. The resulting mass was only a viscous fluid with very low resin contents. This suggests that only CNSL with acid value less than 10 was suitable for resin preparation.

## CONCLUSIONS

Addition of CNSL into phenol seems to increase reaction times for the preparation of novolak as well as resole type resins. Addition of CNSL leads to a decrease in tensile strength but an improvement in impact strength and electrical properties of the resole resins. CNSL with acid value above 10 is unsuitable for making resins.

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