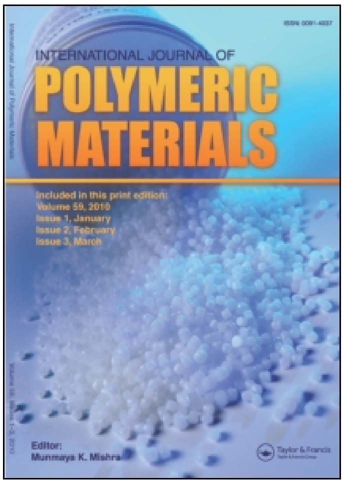

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Copolymerization of cashew nut shell liquid (CNSL) and phenol by condensation with hexamine

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COPOLYMERIZATION OF CASHEW NUT SHELL LIQUID (CNSL) AND PHENOL BY CONDENSATION WITH HEXAMINE

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Cashew Nut Shell Liquid (CNSL) is a naturally occurring phenolic material that has the advantages of low cost and renewable supply. It contains a variety of phenolic compounds with side chains of varying degrees of unsaturation at the meta position. This material can be condensed with formaldehyde to give phenol formaldehyde type resins. In this study copolymers of phenol and CNSL are prepared by condensation with hexamine. This overcomes some disadvantages of CNSL formaldehyde resins by improving mechanical properties and friability. Analytical attempts to characterize the product of condensation have not been satisfactory. A more fundamental approach based on separating the CNSL to its components and subsequent condensation is indicated.

Keywords: CNSL, phenol formaldehyde, hexamine, polycondensate, phenol

1. INTRODUCTION

CNSL is a naturally occurring phenolic substance that can replace phenol in many polymer synthesis reactions. As an agro byproduct it has the advantages of low cost and renewable supply [1–4]. It is a byproduct of the cashew nut processing industry, which is spread over many countries in Asia, Africa and South America. Large quantities of CNSL are available in these regions. With a need to conserve petrochemicals, increased utilization of this interesting substance assumes added importance. The most obvious and common method of obtaining polymeric material from CNSL is the polycondensation with formaldehyde or formaldehyde–containing materials. The reaction of CNSL with formaldehyde is slow compared to that of phenol with formaldehyde.

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Furthermore, pure CNSL-HCHO resin is a rubbery substance with somewhat inferior mechanical properties compared to phenol-HCHO resin [5]. For these reasons this study is based on a copolymer of CNSL and phenol obtained by condensation with hexamine.

2. CNSL STRUCTURE AND COMPOSITION

One of the earliest published works concerning the composition of cashew nut oil was authored by Staedeler [6]. Naturally occurring CNSL contains mainly four components, namely cardanol, cardol, anacardic acid and 2-methyl cardol. Figure 1 gives the chemical structure of these compounds. Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during the roasting process, which converts the anacardic acid to cardanol or 2 pentadecadiethylphenol [7,8]. The roasting process also leads to polymerization, which accounts for 20–25% polymeric substances in the oil. Crude CNSL is corrosive but becomes less so by decarboxylation and removal of H_2S during the refining process. The components of CNSL are themselves mixtures of four constituents differing in side chain unsaturation viz. saturated, monoene, diene and triene [9,10]. The structure of the side chains of varying degrees of unsaturation occurring in the four major components of CNSL are identical. Structure of these components are shown in Figure 2. Paul and Yeddnapalli [11] identified the components of anacardic acid as 1. 1-hydroxy-2-carboxy-3-pentadecylbenzene 2. 1-hydroxy-2-carboxy-3-(8′pentadecenyl)benzene 3. 1-hydroxy-2-carboxy-3-(8′,11′ pentadecadienyl)benzene and 4. 1-hydroxy-2-carboxy-3-(8′,11′,14′ pentadecatrienyl)benzene. Table 1 gives the constituents of anacardic acid as determined by various techniques. Symes, Dawson and Cornelius [12–14] identified the components of cardanol as 1. 3-pentadeca anisole 2. 3-(8′ pentadecenyl) anisole 3. 1-methoxy -3-(8′,11′ pentadeca dienyl) benzene and 4. 1-methoxy-3-(8′,11′,14′-pentadecatrienyl)benzene. Table 2 shows the composition of the constituents of cardanol. The same group of workers also identified the components of cardol as 1. 5-pentadecyl resorcinol 2. 5-(8′ pentadecyl) resorcinol 3. 5-(8′,11′ pentadecadienyl) resorcinol 4. 5-(8′,11′,14′-pentadecatrienyl) resorcinol. Composition of the constituents of cardol is shown in Table 3. Tyman [15] established the components of 2-methyl cardol as 1. 2-methyl-5-pentadecyl resorcinol 2. 2-methyl-5-(8′ penta decenyl) resorcinol 3. 2-methyl-5-(8′,11′ pentadeca dienyl) resorcinol 4. 2-methyl-5-(8′,11′,14′ pentadecatrienyl) resorcinol. The relative proportion of saturated and unsaturated constituents of 2-methyl cardol is shown in Table 4. It has been shown that cardanol, the main con-

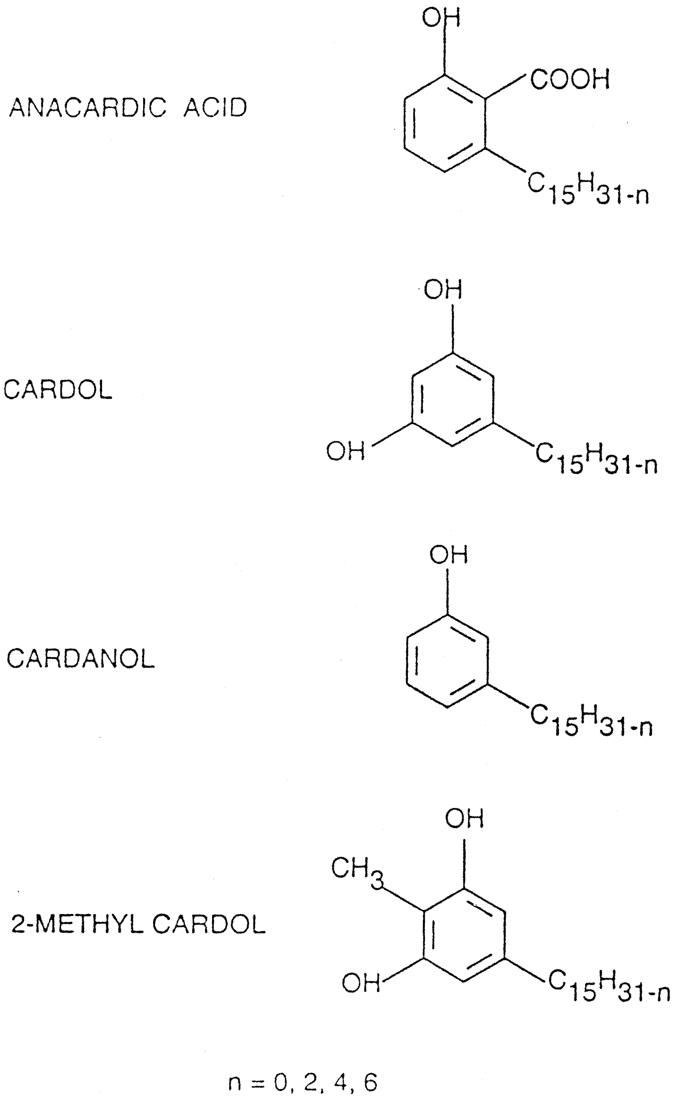

FIGURE 1 Chemical structure of the components of CNSL.

stituent, consists of species of varying degrees of unsaturation in the side chain. Table 5 gives typical compositions of natural and technical CNSL.

The phenolic nature of the constituents of CNSL along with varying degrees of unsaturation in the side chain makes it a highly

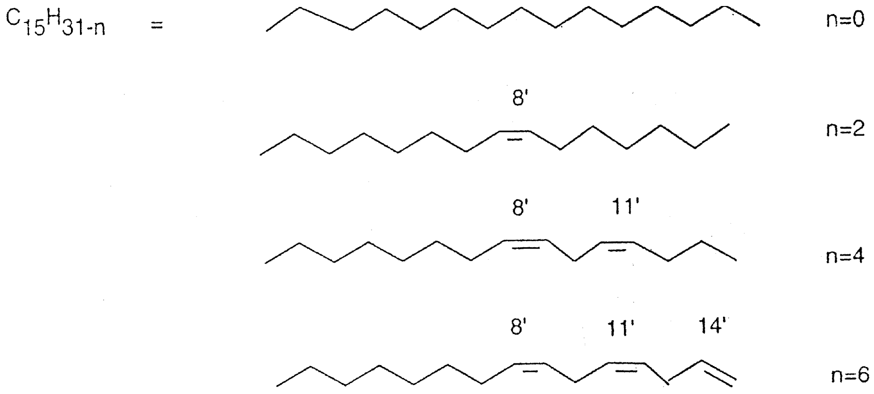

FIGURE 2 Components of side chain.

polymerizable substance amenable to a variety of polymerization reactions. Of overriding importance, however, is the condensation reaction with active methylenes that formaldehyde exemplifies. This leads to a phenol-formaldehyde type condensation.

3. QUALITY CONTROL TESTS FOR CNSL (16)

The following tests were conducted to estimate the quality of CNSL sample. The results so obtained are given in Table 6. The tests confirms to Indian Standards 840-1964.

A. Specific Gravity

The specific gravity of CNSL was determined using a specific gravity bottle.

TABLE 1 Composition of the constituents of anacardic acid as determined by various techniques

	Technique employed						
Constituents of anacardic acid	Low temp. crystallization	TLC-UV	TLC-grav	TLC-GLC	HPLC	TLC-mass spectrometry	
Saturated	4.00	–	–	4.00	4.30	3.65	2.2–3.0
Monoene	15.00	38.70	38.40	38.3	33.4	38.19	25.0–33.3
Diene	44.00	16.30	17.30	17.30	19.90	16.50	17.8–32.1
Triene	37.00	45.10	44.10	40.40	42.4	41.62	36.3–50.4

TABLE 2 Composition of the constituents of cardanol as determined by various techniques

	Technique employed					
Constituents of cardanol	Molecular distillation	Argentated column	TLC-GLC		TLC-mass spectrometry	
Saturated	–	5.40	2.68	3.11	1.98	3.94–4.35
Monoene	60.00	48.50	29.50	36.10	31.31	21.64–32.2
Diene	10.00	16.80	16.60	20.10	15.23	15.36–18.22
Triene	30.60	29.30	51.2	40.60	51.47	45.23–58.99

B. Insoluble Matter

About 50 g CNSL was dissolved in four times its volume of toluene by warming on a water bath. Then the solution was filtered and the weight of residue was found.

C. Volatile Matter

About 100 g CNSL were heated at 205°C for 30 minutes. The loss in weight was found.

D. Ash Content

About 2 g of CNSL was heated by means of a burner until the ash was free from carbanaeous matter.

E. Iodine Value

CNSL was treated in carbon tetrachloride medium with a known excess of iodine monochloride solution in glacial acetic acid. The excess

TABLE 3 Composition of the constituents of cardol as determined by various techniques

	Technique employed			
Constituents of cardol	TLC-GLC		TLC-mass spectrometry	
Saturated	0.30	–	0.24	0.19–2.70
Monoene	8.10	9.60	10.74	8.43–15.15
Diene	21.90	25.20	20.64	24.2–28.92
Triene	69.70	62.20	68.39	36.46–67.18

TABLE 4 Composition of 2-methyl cardol as determined by various techniques

Constituents of 2-methyl cardol	Technique employed			
	TLC-GLC		TLC-mass spectrometry	
Saturated	1.66	2.43	3.92	0.96–1.34
Monoene	13.90	15.30	18.43	16.27–25.28
Diene	18.50	20.40	20.15	20.56–24.36
Triene	65.90	61.50	57.50	49.82–62.20

iodine monochloride was treated with potassium iodide and the liberated iodine was estimated by titration with sodium thiosulphate solution.

F. Polymerization Time

CNSL was heated at 205°C with continuous stirring till foaming ceases. Took 5 g of this dehydrated CNSL and 0.5 ml 25% solution of con.H_2SO_4 in diethyl sulphate in a test tube. Kept the tube immersed in an oil bath at 176°C. The time taken for the material to gel was taken as the polymerization time.

G. Viscosity

Viscosity of the sample was determined using Brookefield Viscometer [17].

H. Molecular Weight

Both number average and weight average molecular weights were determined by Gel Permeation Chromatography (GPC) using Hewlett

TABLE 5 Phenolic composition of natural and technical CNSL

Component	Natural CNSL	Technical CNSL
Cardanol	1.2	62.86
Cardol	11.31	11.25
2-methyl cardol	2.04	2.08
Polymer	20.3	23.8
Anacardic acid	64.93	–

TABLE 6 Characteristics of CNSL

Characteristics	
Specific gravity	0.954
Matter insoluble in toluene, % by wt.	0.042
Loss in weight on heating, % by wt.	1.89
Iodine value (Wijs)	249
Brookfield Viscosity, cp	104
Ash, % by wt.	1.023
Polymerization time, min	10

Packard (1081B) equipment. Tetrahydrofuran was used as the solvent. A flow rate of 1ml/min was employed and refractive type detector was used.

4. COPOLYMERIZATION

The best known reaction for synthesizing polymeric products from CNSL is the reaction with formaldehyde or formaldehyde–containing materials leading to phenol formaldehyde type condensation polymers. Resoles and novolaks [18], the two well known classes of polymers belonging to the PF category, can be synthesized from CNSL also. Resoles are produced by reacting phenol with molar excess of formaldehyde under basic conditions. Novolaks are produced by reacting molar excess of phenol with formaldehyde under acidic conditions.

Initial studies conducted on CNSL with hexamine yielded a highly plastic mass. This condensation was found to require a much longer synthesis time than phenol with hexamine. The product was rubbery with very little friability. Hence it was decided to investigate the effect of copolymerizing CNSL with phenol by condensation with hexamine in various proportions. Earlier attempts to synthesis this copolymer [5] yielded a resin that was employed for molding directly. In this case, the aim was to arrive at a powder molding composition based on this product. This is part of a larger research project for identifying and developing value–added product from CNSL.

5. EXPERIMENTAL

5.1 Raw Materials

A. Hexamine

Hexamine used for the experiment was supplied by Laboratory and Industrial Chemicals, Cochin, and was of industrial grade. Purity of the sample was estimated by titration against perchloric acid [19]. Structure of hexamine is shown in Figure 3.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6\,CH_2O + 4NH_3$$

B. Phenol

Necessary quantities of phenol of commercial grade were supplied by Laboratory and Industrial Chemicals, Ernakulam. In this case too, purity was estimated by well known procedure for estimation of phenol [20].

C. CNSL

Refined CNSL of export quality was supplied by Pierse Leslie Limited, Cochin in 200 L barrels.

5.2 Procedure

A three–necked 1 L RB flask equipped with a stirrer passing through a mercury seal, a water condenser and a thermometer were employed for the reaction. Heating was done by an electric mantle with temperature control. 100 g each of phenol and CNSL were weighed out and charged into the flask. Hexamine was added in varying amounts corresponding to a molar ratio varying from 1:1.1 to 1:2.9. (Total phenol:formaldehyde). The resins synthesized were of the resol type

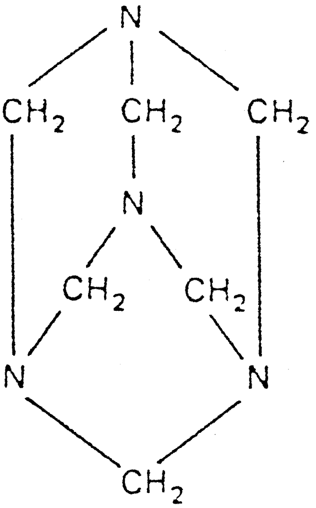

FIGURE 3 Structure of hexamine.

where there is a molar excess of formaldehyde generated from the decomposition of hexamine.

The reaction was done at 100°C for 1.5 hours with continuous stirring. The semisolid product was removed from the flask and cooled to room temperature. It was consequently ground to a powder and vacuum dried for 6 hours.

As a variation to this procedure the resin after synthesis was discharged from the RB flask into a glass dish and subsequently dried in an air oven for 2 hours at 100°C . This additional step was aimed at completing the unfinished reaction between hexamine and phenolic materials. The resin directly tested after synthesis is designated as A and after the oven heating as B.

5.3 Characterization

The following characterization studies were conducted on the synthesized resin.

A. Gel Time

Gel time of 0.5 g resin at 150°C was determined by a hot plate method [21]. An electrically heated plate was maintained at 150°C. 0.5 g resin was stroked with a spatula until the sol-gel transition occurs. Sol-gel transition was indicated by rapid increase in rubberiness or gel character of the resin. The gel time of the resin was found directly after synthesis and drying and also after extraction with water for 96 hours.

B. Residual Hexamine Content

0.05 g resin was dissolved in 50 ml glacial acetic acid and was titrated with standardized 0.1 N perchloric acid using 0.25% methyl violet as indicator until the color changed from violet to green.

C. Flow Temperature

Flow temperature of the different samples was determined using a heated capillary tube.

D. Water Insolubles

Water insolubles of the samples after extracting with water were determined.

E. Molecular Weight

Molecular weight of the resin was determined in one particular case as a sample. The number average and weight average molecular weights were measured using GPC. Values obtained were:

Number average molecular weight-878
Weight average molecular weight-3345
Z-average molecular weight-67166.

A Hewlett Packard instrument employing a RI detector and tetrahydrofuran as solvent (flow rate 1ml/min) was employed.

6. RESULTS AND DISCUSSION

The CNSL sample tested for quality was found to be similar to standard material prescribed in the specification [16] as is evident from Table 7.

The gel times obtained for cases A and B are plotted in Figure 4. It was found that case B leads to longer gel times than case A. This may look surprising as case B corresponds to the product obtained after a longer processing time. It is likely that a portion of unreacted hexamine decomposes during oven heating. Formaldehyde liberated presumably does not combine with the phenol groups because of the ventilated atmosphere. Moreover, reduction in the amount of hexamine slows down the final crosslinking. This explains the longer gel times for case B. The effect of the ratio of phenol and formaldehyde on the gel time is not very disernible. But the gel time appears to reach a minimum around molar ratio of 1:1.9.

Figure 5 shows the effect of composition on gel time after extracting the powdered resin with water. In both cases A and B one can safely assume that there is no free hexamine or formaldehyde. In the absence

TABLE 7 IS specifications for CNSL

Characteristic	Requirement
Specific gravity	0.95–0.97
Viscosity at 30°C, cp(max)	550
Moisture, % by wt.(max)	1.0
Matter insoluble in toluene, % by wt. (max)	1.0
Loss in wt. on heating, % by wt.(max)	1.0
Ash, % by wt. (max)	1.0
Iodine value (max)	
(a) Wijs method	250
(b) Catalytic method	375
Polymerization	
(a)Time, min (max)	4
(b)viscosity at 30°C, cp (min)	30
(c)viscosity after acid washing at 30°C, cp (min)	200

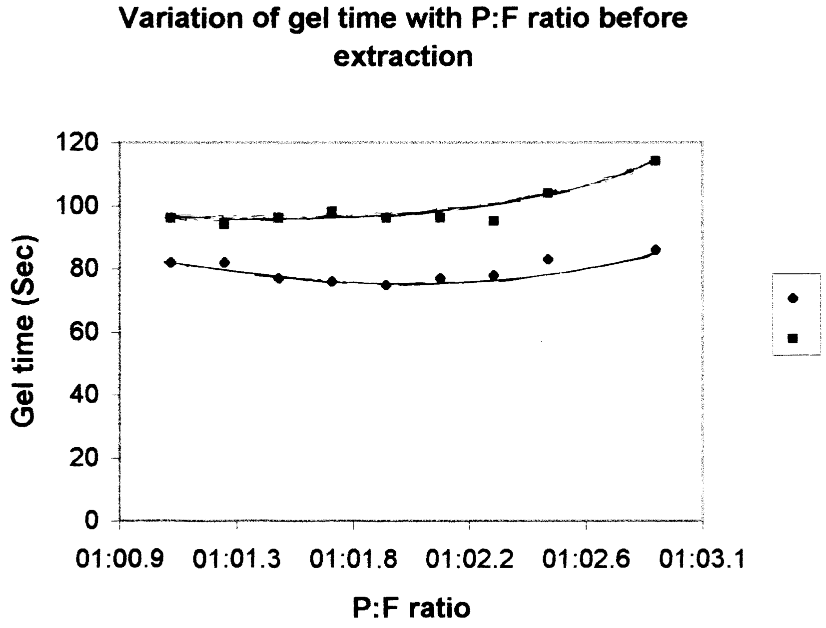

FIGURE 4 Gel time of the resin before extraction as a function of composition.

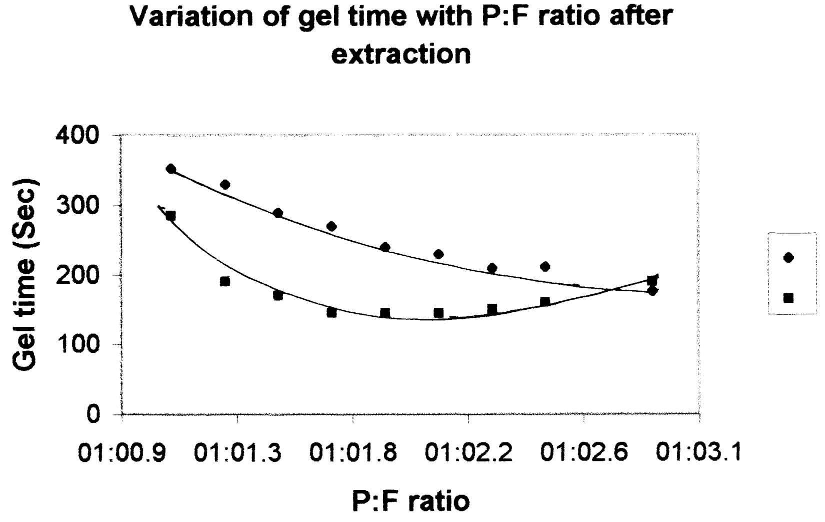

FIGURE 5 Gel time of the resin after extraction as a function of composition.

of hexamine gel times for case A are found to be longer than for case B. Crosslinking under these conditions is achieved by means of methylol groups alone. Case B, which has been processed for a longer time, contains a larger amount of methylol groups. This accounts for shorter gel times exhibited by case B.

Figure 6 is the plot of phenol:formaldehyde against volume of perchloric acid. $HClO_4$ Titration is done in molding powders for estimating hexamine content. In the case of CNSL, which contains a variety of compounds, the presence of other substances reactive towards $HClO_4$ cannot be ruled out. Case B gives values that are almost 100% greater than those given by case A. As resin from Case B cannot contain more hexamine than that from case A, the volume of $HClO_4$ consumed is not due to hexamine alone. It is likely that the complex nature of the constituents of CNSL and possible side reactions cause this anomaly. Figure 7 shows the volume of $HClO_4$ consumed after the samples were extracted with water as a function of formaldehyde:phenol ratio. Both cases A and B are found to give practically the same titer values. It is to be concluded that volume of $HClO_4$ consumed cannot be taken as a basis for estimating hexamine content.

Figure 8 shows the loss in weight on extracting with water. In cases A and B, case B shows a higher loss in weight compared to case A. Side reactions or the presence of substantial amount of water–soluble

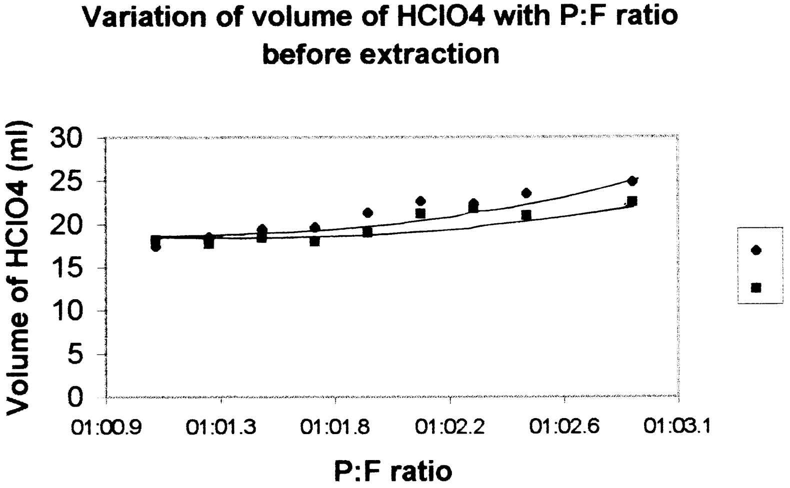

FIGURE 6 Volume of $HClO_4$ against composition of the resin before extraction.

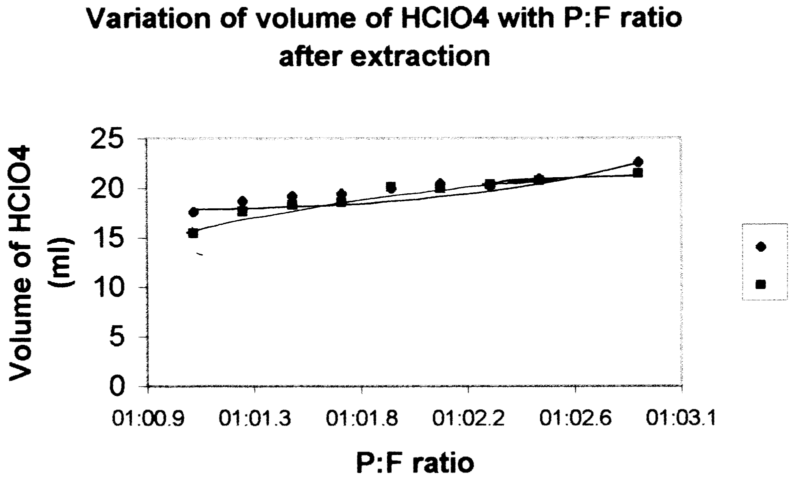

FIGURE 7 Volume of $HClO_4$ against composition of the resin after extraction.

oligomers only can explain this behavior. In view of the large variety of compounds contained in CNSL, one can conclude that characterization of resin in this case requires a more fundamental approach.

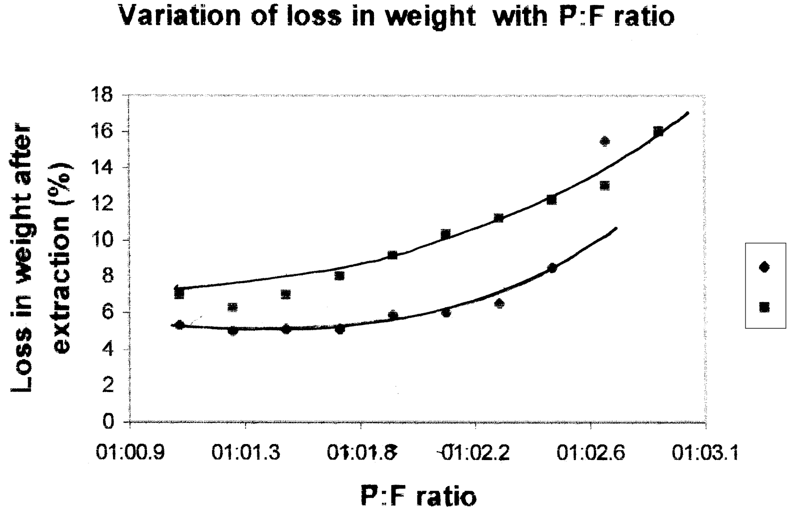

FIGURE 8 Loss in weight of the resin on extracting with water as a function of composition.

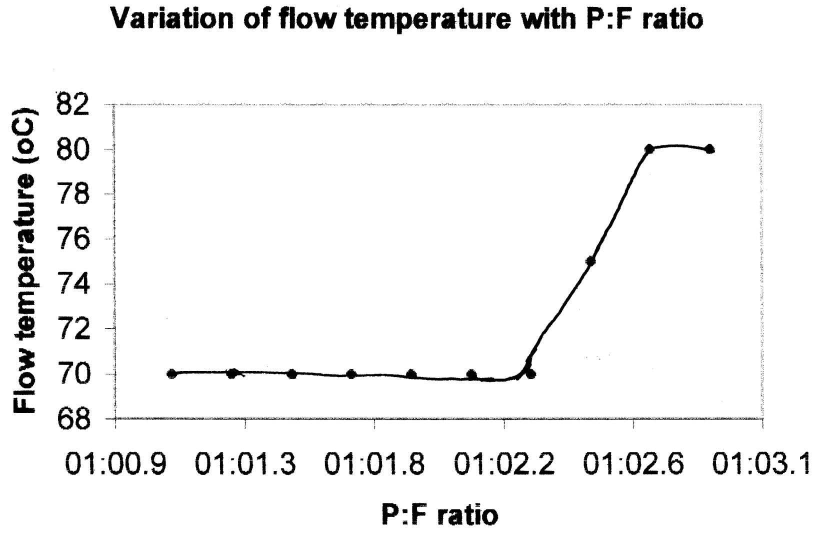

FIGURE 9 Variation of flow temperature with P:F ratio.

Figure 9 is a plot of the flow temperature against phenol:formaldehyde ratio. Flow temperature remains constant at 70°C until a stochiometric ratio of 1:2.5 is reached. There is a steady increase in flow temperature at 1:2.5 reaching 80°C finally at 1:2.9.

7. CONCLUSIONS

Phenol CNSL copolymers can be synthesized by condensation with formaldehyde.

While quality tests like cure time on a hot plate can be conducted on this polymer it is difficult to correlate such properties with the stochiometric ratio of phenol:formaldehyde. The method of estimating unreacted hexamine by titration against perchloric acid is not very helpful in this case because of the presence of a wide variety of known and unknown compounds in CNSL. The effect of stochiometric ratio on the flow temperature of the resin is not noticeable until about 1:2.5. It is to be concluded that analytical studies on the resin synthesized will yield better results when the individual components are separated. The copolymer obtained by condensation of phenol and CNSL with hexamine is found to be harder and less flexible than the product of CNSL-hexamine condensation alone. Such a product requires shorter reaction times and can be the basis for formulating a powder molding composition.

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