Polymeric Resins from Renewable Resources. II. Synthesis and Characterization of Flame-Retardant Prepolymers from Cardanol

C. K. S. PILLAI,* V. S. PRASAD, J. D. SUDHA, S. C. BERA, and A. R. R. MENON, *Regional Research Laboratory (CSIR), Trivandrum 695019, India*

Synopsis

Phosphorylated cardanol preopolymers (PCP) are obtained by simultaneous phosphorylation and oligomerization of cardanol, an unsaturated pentadecylphenol extracted from the nuts of the plant *Anacardium occidentale* L. Although GPC showed the presence of only oligomeric species in the system, the high viscosity of 0.35–0.45 million cps was found to be due to involvement of hydrogen bonding. IR spectra of PCP gave bands at 1030 and 1240 cm^{-1}, indicating P$-$O$-$C linkages. The decrease in iodine value and the absence of vinyl IR bands at 895 and 907 cm^{-1} indicated oligomerization. NMR spectra of PCP showed partial loss of unsaturation. A carbonium ion initiated mechanism is indicated for the oligomerization. PCP was found to be highly reactive with aldehydes, amines, and isocyanates. Highly insoluble and infusible thermoset products could be obtained. TGA studies showed a two-stage decomposition with improved thermal stability above 500°C for PCP compared to cardanol-formaldehyde (novolac)-type resins. Completely cured PCP was highly resistant to hydrolysis by water. Studies on mechanical properties showed that the PCP cured with HMTA gave a tensile strength of 16.9–21.5 MN/m^2 and an impact strength of 1.63–2.04 J compared to 24–48 MN/m^2 and 1.35 J, respectively, for phenol formaldehyde (novolac) resin prepared under similar conditions. The lap shear strength of PCP-bonded wood pieces showed a value of 400 ± 10 N/cm^2 in comparison to 60 ± 10 N/cm^2 of cardanol formaldehyde (novolac) resin, indicating that phosphorylation improves the bonding characteristics. With a phosphorus content of 7.9%, PCP showed good fire-retardant properties. Vertical burning studies did not show any propagation of fire or any afterglow. PCP cured with HMTA gave a limiting oxygen index value of 35, which on bromination increased to 42.0. PCP could find application as polymeric fire-retardant additive for plastics and elastomers or as filled or unfilled fire-resistant plastics/composite products.

INTRODUCTION

In the search for alternate feedstocks for the production of polymers,[1-11] certain organic biomonomers possibly stand a good chance for potential utilization.[12] Among these biomonomers,[12] unsaturated hydrocarbon phenols[13] appear to possess very interesting structural features for the synthesis of speciality polymers.[14] According to Tyman,[13] there are a variety of such phenols present in a number of plant species available in many parts of the world. They are mostly mono and dihydric phenols or phenolic acids with a hydrocarbons side chain at the *meta* position, the number of carbon atoms in the side chain varying from C$_5$ to C$_{17}$.

* To whom correspondence should be addressed.

Though some of these phenols have certain applications,[15] it appears that use has not been made of the special structural features of these phenols.[14] These phenols could be polymerized either by step- or chain-reaction mechanism or a combination of these techniques.[13] They could also be suitably chemically modified to introduce specific functional groups and polymerized to make polymers with specific properties. Thus, speciality polymers could possibly be produced from a monohydric phenol with an unsaturated side chain R at the *meta* position through either (a) a prepolymer route or (b) a dimer route as shown below.

(a) Prepolymer route:
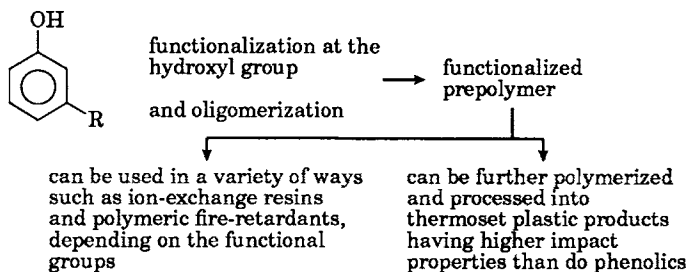
(b) Dimer route:
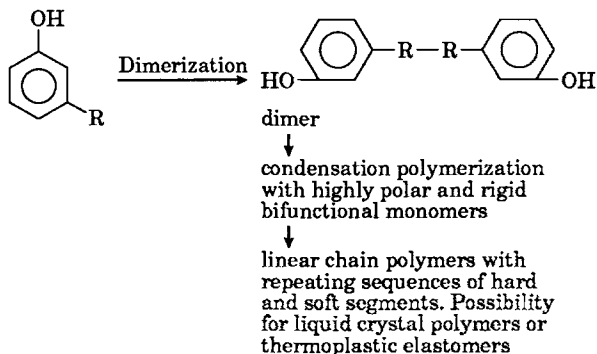
Unsaturated hydrocarbon phenols with a C_{15} side chain at the *meta* position are abundantly available in the plant species *Anacardium occidentale* L.,[15] the nuts of which are famous for their nutritious and high protein value. The liquid (commonly known as cashew nut shell liquid (CNSL; 8007-24-7) obtained from the outer shell of the nuts as a byproduct of the cashew industry consists mainly of mono and dihydric phenols.[16] Vacuum distillation of CNSL yields pure cardanol (37330-39-5) (**I**) alone in 90% yield:
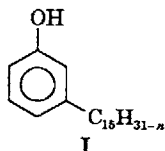
where $n = 0, 2, 4, 6$.[16] CNSL and cardanol are used in diverse applications such as friction materials, surface coatings, and laminating resins.[15-18] The literature

on CNSL is replete with innumerable patents[19,20] and reports,[21,22] but there exists substantial gaps between technology and scientific understanding of such systems.

In general, polymers from cardanol are prepared either by condensation with formaldehyde or by chain-reaction polymerization through the unsaturation in the side chain using acid catalysts. Recently, Misra and Pandey[23] reported the kinetics of formaldehyde condensation of cardanol. Oligomerization of cardanol using acid catalysts was studied by Manjula.[24] Though there are a few attempts on chemical modification[25,26] and functionalization[14] of cardanol and its polymers, studies on detailed investigations on the structure and properties and the characterization of the products are limited. Earlier attempts[27,28] to functionalize CNSL with orthophosphoric acid describe a tedious multistep process whereby the authors claim in their patents to have obtained a resin having improved adhesion with greater heat resistance. (However, they did not study cardanol alone.) The process requires the use of a solvent (xylene) and a catalyst system consisting of mercuric acetate and iodine. The maximum phosphorous content of the resin was 1.5% in the absence of the catalyst and 3%–6% in the presence of the catalyst. We have observed that CNSL[29] and cardanol[30] can be functionalized in a single-step reaction with orthophosphoric acid without using solvents and catalysts to obtain phosphorylated oligomeric products of phosphorous content of 7.9% having superior flame-retardant and bonding characteristics. The characterization of the phosphorylated cardanol prepolymer (PCP) is presented.

EXPERIMENTAL

Materials

Technical-grade CNSL of IS specification IS : 840 (1964)[31] was obtained from Kerala State Cashew Development Corporation, Quilon. Cardanol was obtained by vacuum distillation of CNSL at 3–4 mm Hg, and the fraction coming at 230–235°C gave a refractive index of 1.509 and Brookfield viscosity of 450–520 cps at 30°C as reported for pure cardanol.[32]

Orthophosphoric acid (AR grade) was a BDH product and gave an assay of 85% purity. Paraformaldehyde was a product of Sarabhai M. Chemicals, and hexamethylenetetraamine (HMTA) was from Arnold Otto Meyer, Hamburg, and used after recrystallization.

Phosphorylation and Oligomerization

Phosphorylation was carried out in a polymerization kettle fitted with stirrer, condenser, thermometer, and vacuum connection. In a typical experiment, orthophosphoric acid (390 g) calculated to fully esterify the phenolic hydroxyl function was added to cardanol (157.8 g) and the temperature raised to 175 ± 5°C under a vacuum of 10 mm Hg. These conditions were maintained for 4 h, when the unreacted orthophosphoric acid remaining in the vessel had been reduced to below 0.01% and the hydroxyl number of the resin exhibited a value below 10.0 mg KOH. The unreacted phosphoric acid content did not change much after 4 h of reaction. So unless otherwise mentioned, the products reported

here are for the reaction at $175 \pm 5°C$ for 4 h under a vacuum of 10 mm Hg. The reaction system was quenched, and the phosphorylated cardanol prepolymer (PCP) was washed with water and dried in a flash evaporator at 105°C for 2 h. Yield was 96.8%.

Preparation of Cardanol-Formaldehyde (Novolac)

One hundred ten milligrams (0.825 mol) of cardanol, 24 mL (0.66 mol) of 37% aqueous formaldehyde, and 10 mL of $4N$ sodium hydroxide were taken in a reaction kettle fitted with a condenser, stirrer, and thermometer. The condensation was carried out at 100°C for 4 h. The product was washed with 10% hydrochloric acid, then with water and dried. The product was powered and mixed with 10% of HMTA and hot pressed at 130°C for 30 min. This was used for TGA measurement.

A similar procedure[33] was used to prepare phenol-formaldehyde (novolac) resin for TGA measurement.

Characterization

The iodine value was determined by following the Wijs method.[34,35] Hydroxyl number was determined by the acetylation method[34,35] and acid number by titration with alcoholic potash.[34] Unreacted phosphoric acid content was determined by direct titration with sodium hydroxide using thymolphthalene as indicator, after extracting 1 g of the resin with chilled water. The assay of orthophosphoric acid was carried out by direct titration with sodium hydroxide after proper dilution. The phosphomolybdate method[34] was used to determine the phosphorous content of the resin after digestion with a mixture of the sulphuric acid and nitric acid for 10 h to solubilize the phosphorous. Moisture content was determined by the infrared method.[35]

Instrumentation

Bulk viscosity was measured using a Brookfield viscometer of model HBTDV-1. Intrinsic viscosity was measured using a Ubbelohde viscometer at 30°C with methylethylketone or toluene as solvent. A digital pH meter (Elico) was used to measure the hydrogen ion concentrations.

IR spectra were recorded as thin films using a Perkin-Elmer IR spectrophotometer of model 2993B. ^{1}H-NMR spectra were recorded in CCl_4 with tetramethylsilane as standard using a JEOL FX-90Q spectrometer. Gel permeation chromatographs (GPC) were measured using a Waters 244 instrument fitted with 6000A lamp system and a column combination of 100 and 500 Å microstyrogel with tetrahydrofuran as solvent at a flow rate of 1 mL/min. A differential refractometer R40 with sensitivity 8× is used as detector.

TGA measurements were carried out using a Dupont 990 thermal analysis system with 951 TGA unit. All thermal measurements were carried out in nitrogen atmosphere at a flow rate of 50 cm^3/min; the heating rate was 10°C/min and the sample weight was 10 ± 2 mg.

Tensile strength was determined using a Universal Instron Testing Machine of Model 1195 at a cross-head speed of 20 mm/min. Impact tests were carried out as per ASTM D-256-56 using a Charpy impact tester. Lap shear tests were

made as per ASTM D-906-64 (reapproved 1976) between wood pieces. The values represented are an average mean of about 6–10 samples.

Hydrolytic stability was determined as per ASTM D-3137-75 by exposing tensile samples to water at 85°C for 96 h. The fully cured resin powder was also exposed to an excess of water at ambient temperature and also at 85°C, and the liberated (if any) orthophosphoric acid was titrated against standard sodium hydroxide periodically to determine the resistance to hydrolysis with water.

The liming oxygen index (LOI) was measured as per ASTM D-2863-77 using a Stanton Redcroft oxygen index equipment of model FTA-710. Specimens of size $3 \times 6 \times 100$ mm were hot pressed in a mold. The LOI value represented is the average of five to six samples reproducible within 0.025.

Preparation of Tensile Specimen

PCP was mixed with 8% HMTA or paraformaldehyde as curing agent and hot pressed in a mold of dimensions $130 \times 15 \times 3$ mm at 130–140°C for 30 min.

Curing Studies

PCP was mixed with various percentages of the curing agents such as HMTA and paraformaldehyde, and the curing temperature, curing time, and the optimum percentage of curing agent were determined by either measuring the insolubility of the cured material or by determining the hardness of the material.[33] Gel time[33] was determined by finding the time interval between the onset of gelation and the time of mixing the resin and HMTA in methylethylketone at 30°C.

RESULTS AND DISCUSSION

General Characteristics

The phosphorylated cardanol prepolymer (PCP) is a light brown liquid resin soluble in most of the common solvents, but insoluble and immiscible in water.

TABLE I
Chemical and Physical Characteristics of PCP

Sample no.	Property	Cardanol	PCP
1	Color	Pale yellow	Light brown
2	Moisture content (%)	0.001	0.05–0.065
3	Specific gravity at 29°C	0.9320	1.0590
4	Viscosity at 30°C cps	450–520	350,000–450,000
5	Hydroxyl number, mg of KOH	185–200	4–10
6	Iodine value g/100 g of resin (Wijs method)	212 minimum	90–100.0
7	Unreacted phosphoric acid content (%)	—	0.01–0.009
8	Phosphorous content (%)	-	7.9

Table I gives the chemical and physical characteristics of the resin. Since phosphorylation involves esterification at the phenolic hydroxyl of cardanol, the hydroxyl number has decreased as expected from 197 mg of KOH to below 10.0 mg of KOH. The large difference in the pK value[36] of the ionization of the first hydrogen ion (7.52×10^{-3}) from the second (6.23 ± 10^{-8}) and third (2.23×10^{-13}) hydrogen ions of phosphoric acid has favored the formation of the monoester with a phosphorous content of 7.9%. But Table I also shows that the iodine value has undergone a decrease from 210 to 90–100, and the bulk viscosity at 30°C has shown a steep increase from 450 cps to 0.35–0.45 million cps. The introduction of a phosphate group at the hydroxyl of cardanol alone cannot account for the decrease in iodine value and the increase in the bulk viscosity. Complete phosphorylation of the hydroxyl was not achieved, but the present results were repeatable.

Spectral Analysis

Figure 1 gives the IR spectra of cardanol and PCP, and Table II provides the important peaks and their assignments. The formation of the phosphate is indicated by the appearance of the P—O—C bands at 1030 and 1240 cm^{-1}.[37] The shift in the P—O—Ar peak expected at 1240–1190 to 1030 cm^{-1} might possibly be due to the existence of hydrogen bonding in the system.[38] The phenolic hydroxyl band at 3390 cm^{-1} has clearly diminished, but not completely vanished, as can be expected from the hydroxyl number of 4.0–10.0 mg of KOH.

Figure 1 and Table II also show that a number of vinyl vibrations has either vanished or diminished in intensity. Thus, the terminal vinyl vibrations of 907 cm^{-1} has completely vanished as has also the 630 cm^{-1} vinyl peak.[37]

The decrease in the iodine value and the disappearance of the vinyl functions coupled with the increase in viscosity probably indicate polymerization through the side chain simultaneously taking place during the phosphorylation reaction. The GPC profile of PCP (Fig. 2) shows that the resin contains oligomeric species such as dimer, trimer, and tetramer as major components and a small percentage of higher oligomers. Cardanol is known to polymerize/oligomerize through the side chain unsaturation in the presence of acid catalysts such as sulphuric acid, phosphoric acid, and borontrifluoride etherate.[24]
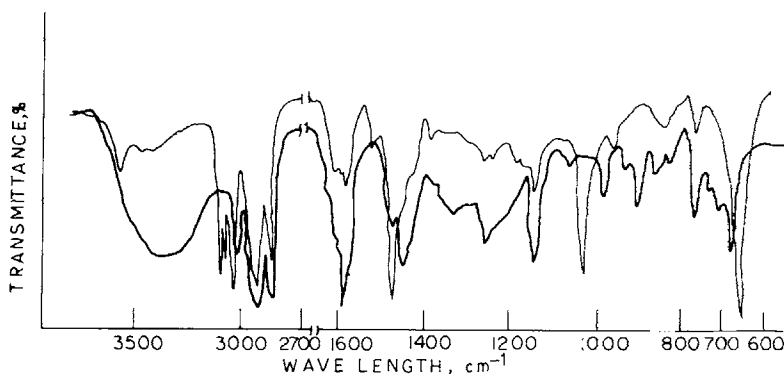

Fig. 1.   Infrared spectra of cardanol (– – –) and phosphorylated cardanol prepolymer (– · – · –).

TABLE II
Infrared Spectral Data of Cardanol and Phosphorylated Cardanol Prepolymer (PCP)

Peak (cm^{-1})	Assignment	Intensity[a]	Change in PCP
630	Vinyl	w	Vanished
690	—CH$_2$—CH$_2$CH$_2$CH—	m	Increased intensity and shifted to 665 cm^{-1}
765	C = C	w	Intensity reduced
770	C = C	m	
895	Terminal vinyl	w	Vanished
907			
995	Vinyl	w	Intensity decreased
1030	C—O—P	s	New band
1170	C—O—P	s	New band
1240	C—O—P	m	New band
1600	Vinyl	w	Intensity decreased
1635	Vinyl	w	Intensity decreased
1685	Vinyl	w	Intensity decreased
3015	Vinyl	w	Intensity decreased
3300	Phenolic OH	s	Decreased greatly

[a] w = weak, m = medium, s = strong.

The involvement of the unsaturated protons in polymerization can be studied by the NMR spectra. Figures 3 and 4 give the ^{1}H NMR of cardanol and PCP, respectively. The unsaturated proton integral at 5.5 δ showed considerable changes. The ratios of the unsaturated proton integrals to the saturated protons (0.98 δ to 2.50 δ) integrals of cardanol and PCP are 1 : 6.75 and 1 : 24.54, respectively, showing a large increase in the saturated protons. Manjula[24] reported a similar trend in the ratio of unsaturated to saturated protons on oligomerization of cardanol with orthophosphoric acid as acidic initiator. Tyman[13] has proposed that the polymerization of cardanol under acidic conditions might involve the formation of an allylic carbonium ion. Manjula[24] also proposed a carbocationic mechanism[39] with the addition of a hydrogen ion to one of the double bonds of the side chain of cardanol. Since cardanol exists as a mixture
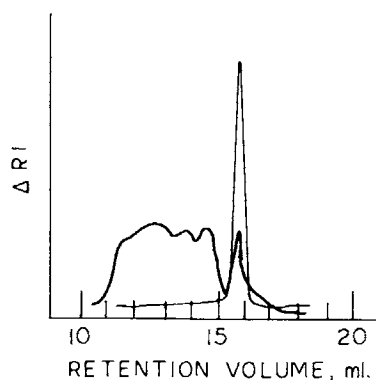

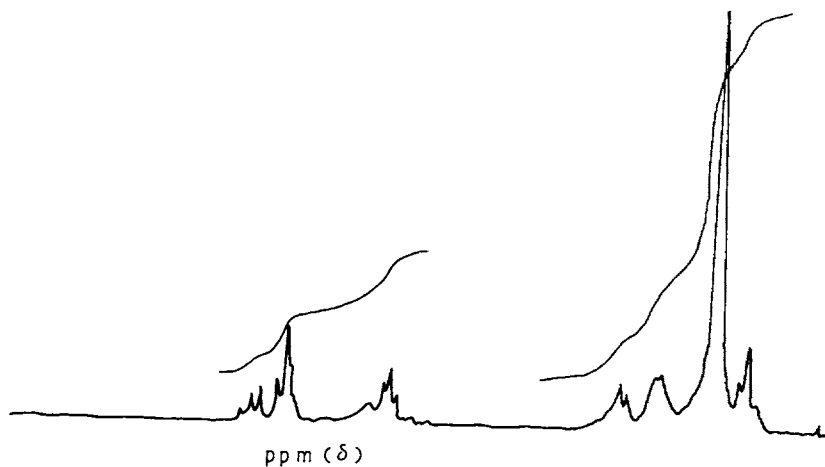Fig. 2. GPC of cardanol and phosphorylated cardanol prepolymer.

Fig. 3. ^{1}H-NMR spectra of cardanol in CCl$_4$.

(chromatographic[16] separation did not yield quantities enough for a polymerization reaction) of monoene, diene, and triene components, the complex nature of the system cautions conjectures on the nature of the mechanism of polymerization. However, it appears that the reactions could be said to be carbocationic in nature and might involve protonation of the phosphorylated cardanol as the initiation step followed by addition of other monomer molecules as given below:
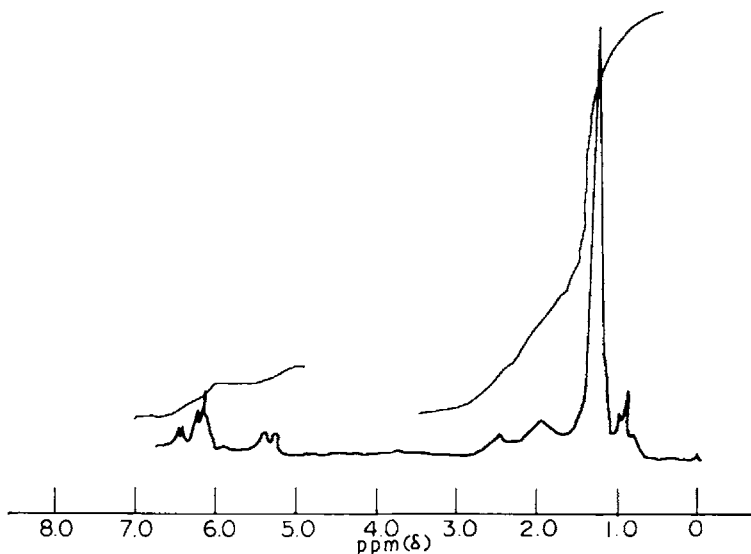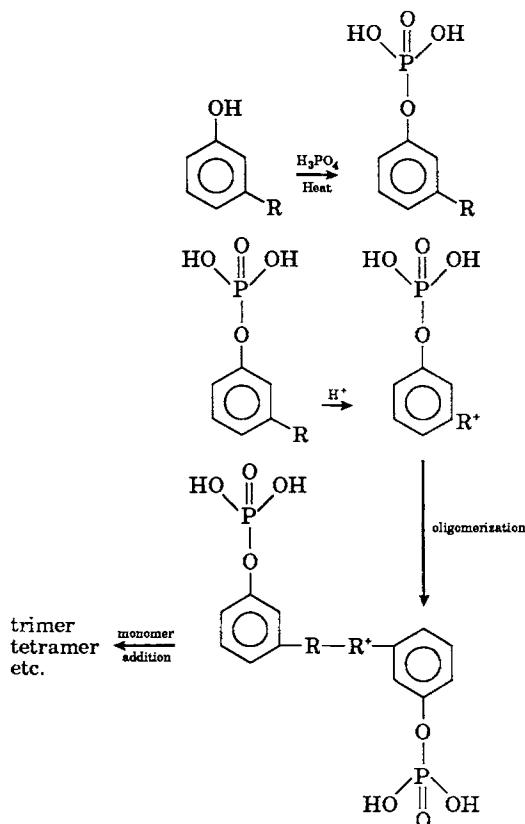

Fig. 4. ^{1}H-NMR spectra of phosphorylated cardanol prepolymer in CCl$_4$.

The bulky nature of the side chain and steric hindrances restrict the molecular weight attainable in this oligomerization.

In a kinetic study,[24] Manjula has shown that the oligomerization of cardanol with sulphuric acid involves a first-order reaction and that the termination possibly takes place through transfer to monomer. A more detailed study is required to throw more light on the mechanism. It is, however, possible that under the highly acidic conditions the transfer reactions might also involve a Friedel–Crafts-like attack of the protonated side chain on the aromatic ring. Such carbonium ion-involved substitution reactions are possible with phenols.[33]

Viscosity

The bulk (Brookfield) viscosity at 29°C showed a steep increase from 450 cps to 0.35–0.45 million cps. However, the viscosity of PCP in dimethyl formamide solution was only 70–90 cps. The intrinsic viscosity was only 0.05 dL/ mg, indicating that the bulk viscosity at ambient temperature is abnormal since there are no contributions from chain length. It is reported[40] that oligomeric polypropyleneglycol shows an abnormal behavior in viscosity that has been attributed to entanglements of the transient hydrogen-bonded structures. It is well known[41-43] that polymers containing polar groups such as amide (polyamides, polypeptides, proteins), urethane (polyurethane), hydroxyl (cellulose, polyvinyl alcohol), carboxyl (polyacrylic acid), etc. exist in hydrogen-bonded forms and their properties such as melting point, viscosity, solubility,

TABLE III
Curing Behavior of Phosphorylated Cardanol Prepolymer

Curing agent	Amount of curing agent needed	Time of curing (min)	Temperature (°C)	Remarks
Formaldehyde	10	30	80	Gels
Paraformaldehyde	8	30	120	Hard insoluble product
HMTA	8	30	130	Hard insoluble product
Furfural	10	40	140	Gels
Desmodur	2	30	Room temperature	Solid product
Sulfur	10	50	150	Solid rubbery product
Hydrogen peroxide	16		Room temperature	Viscosity increased
Melamine	2	30	140	Hard infusible product

crystallinity, etc. are greatly affected by hydrogen bonding. Biopolymers such as proteins and nucleic acids undergo denaturation involving disruption of their hydrogen bonds on heating followed by a drastic reduction in viscosity.[44,45] PCP on heating to 150°C showed a drastic reduction in viscosity to 150 cps. It is therefore probable that the abnormal viscosity of PCP could be due to contributions from secondary forces such as hydrogen bonding.

Curing Studies and Reactivity

PCP is found to be highly reactive with aldehydes, amines, and isocyanates. The reactivity was much higher than that of cardanol or phenol. For example, addition of formaldehyde to PCP in toluene at 60°C forms a gel in a few minutes, whereas similar gelling for phenolics takes place near 150°C.[33] PCP can be directly crosslinked with paraformaldehyde or hexamine, and the product is a highly insoluble and infusible thermoset plastic. The curing behavior of the resin with a number of curing agents is given in Table III. The optimum curing agent needed to cure PCP into a thermoset product was found to be 6%–8%.

Mechanical Properties

Table IV gives the mechanical properties of PCP in comparison with those of the unmodified cardanol formaldehyde (CF) novolac resin. The tensile strength showed a threefold increase after phosphorylation. The conventional phenol–formaldehyde (PF) resin (asbestos short fiber-filled) gave a value of

TABLE IV
Effect of Phosphorylation on the Mechanical Properties of Cardanol-based Polymer

Property	Cardanol formaldehyde (novolac)	PCP	Phenolics
1. Tensile strength (MN/m²)	5.3	16.9–21.5	24–48
2. Impact strength (J)	—	1.63–2.04	1.35
3. Lap shear strength (N/cm²)	60 ± 10	400 ± 10	230 ± 10

24–48 MN/m^2 compared to 16.9–21.5 MN/m^2 of PCP. Though the tensile modulus was lower for PCP, the impact properties were superior to that of PF. Table IV also shows that PCP exhibits good adhesion strength between wood pieces. Although PCP-based adhesive cured with paraformaldehyde gave a lap shear strength of 400 ± 10 N/cm^2, the CF resin gave only 80 ± 10 N/cm^2. The superior bonding characteristics of the phosphate group is indicated.

Thermal Stability

The thermal behavior of the fully cured PCP is shown in Figure 5 in comparison to conventional CF (novolac) and PF (novolac) resins. Though an overall thermal stability was expected for the PCP resin over that of CF resin, Figure 5 shows that the improvement in thermal stability is only above 500°C. This could be understood from the structure of the two resins. Crosslinked CF can be represented as
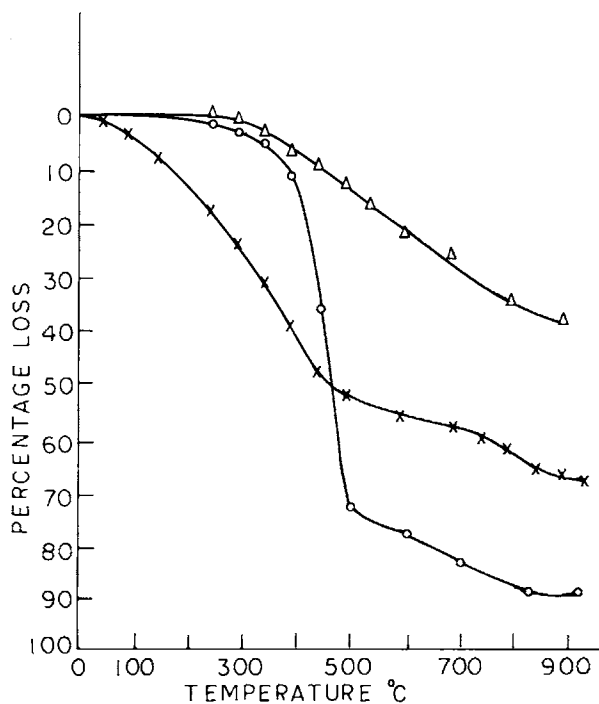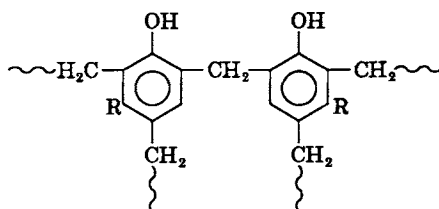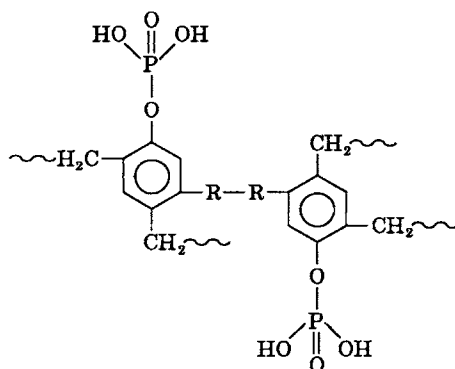

Fig. 5.   TGA of phosphorylated cardanol prepolymer cured with HMTA (×–×–×), cardanol-formaldehyde (Novolac, –O–O–O) and phenol–formaldehyde (Novolac, ———).

where R stands for the side chain. In comparison, the crosslinked PCP will have the following structure (tentative):

where instead of the methylene bridges,[33] the long aliphatic segment between the aromatic nuclei deteriorates the stability drastically. So it appears that the thermal stability of PCP could be further improved if phosphorylation is carried out after introducing methylene bridges by formaldehyde condensation.

Hydrolytic Stability

The presence of the hydrolyzable phosphate ester linkage may pose problems to end product utilization. So the effect of water on hydrolysis of the resin was studied. The hexamine cured PCP was powdered and exposed to water under stirring. The phosphoric acid liberated was titrated against alkali. Only a few milligrams of NaOH were utilized for 1 g of the resin over a period of 7 days. Tensile samples prepared from fully cured PCP and exposed to water at 85°C for 96 h as per ASTM D 3137-75 showed only negligible decay in the stress-strain diagram, indicating excellent resistance to hydrolysis by water.

Fire-retardant Behavior

One of the significant characteristics of PCP is its fire-retardant behavior. Phosphorous-containing compounds are generally known to exhibit fire-retardant properties.[46-50] When fully cured (HMTA) samples of PCP were tested as per UL-94 vertical burning tests, there was no propagation of fire and no afterglow. Table V gives the limiting oxygen index (LOI) values of the fully cured (HMTA) samples measured as per ASTM D3863-77. The LOI is also

TABLE V
Limiting Oxygen Index Value of Cured PCP Resins

Resin	LOI
PCP (HMTA cured)	35.0
PCP (paraformaldehyde cured)	33.0
Brominated PCP	42.0
Cardanol–formaldehyde (novolac)	21.0
Polyethylene	16.9

found to vary with the nature of the curing agent. For example, the hexamine cured product gave a value of 35.0, whereas paraformaldehyde cured product was 2 units less. This shows the effect of nitrogen introduced through hexamine.

Bromination of PCP improved the LOI value from 33 to 42.0. Yang and Chen[51] have shown that brominated phenolic compounds containing aliphatic allyl groups show improved stability and fire-retardant activity. The effect of the aliphatic side chain of the brominated PCP is yet to be studied. However, addition of antimonytrioxide showed synergism with bromine.[50]

Fire-retardant Applications

The phosphorylated cardanol with both hydrophilic and hydrophobic moieties within the same molecule is expected to show compatibility with a wide spectrum of polymers. Preliminary blending studies showed that PCP is compatible with plastics and elastomers. Adequate fire retardancy was achieved at the 20% level addition of PCP to polyethylene. Nonbloomability and improvement in mechanical properties were observed when blended with natural rubber.[52]

Other Applications

PCP was also found to be useful as a filled or unfilled thermoset product or as a two-component adhesive.[53] Asbestos short fiber (chrysotile)-filled PCP showed a value of fade as low as 19%, a factor that enhances the lifetime of brake linings.[54] It could also form matrices for fire-retardant composites.[55] Another interesting finding is that the brominated PCP showed ablative behavior in asbestos/carbon fiber-reinforced panels under oxyacetylene flame.[50,56]

CONCLUSIONS

The phosphorylation of cardanol with orthophosphoric acid gave an oligomeric resinous product having abnormally high viscosity. The phosphorylated cardanol prepolymer (PCP) thus obtained contains a mixture of oligomers. Infrared spectra gave bands at 1030 and 1250 cm^{-1}, indicating P—O—C linkage. Absence of vinyl bond at 895 and 907 cm^{-1} indicated oligomerization through the side chain. ^{1}H-NMR spectra of PCP indicated partial loss of unsaturation.

PCP was found to be highly reactive with aldehydes, amine, and isocyanates. Highly insoluble and infusible thermoset products were obtained. TGA showed a two-stage decomposition compared to cardanol-formaldehyde resin. PCP showed higher thermal stability above 500°C. Crosslinked PCP was highly resistant to water. Completely cured PCP did not propagate fire and did not show any afterglow and had an LOI of 35. The PCP could find application as a polymeric fire-retardant additive for plastics and elastomers and also as filled or unfilled fire-retardant plastic/composite products.

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