Polymers from Renewable Resources. XX. Synthesis, Structure, and Thermal Properties of Semi-Interpenetrating Polymer Networks Based on Cardanol–Formaldehyde-Substituted Aromatic Compounds Copolymerized Resins and Castor Oil Polyurethanes

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ABSTRACT: A large number of improved high-temperature stable semi-interpenetrating polymer networks (semi-IPNs) were synthesized by condensing copolymerized resins with castor oil-based polyurethane using ethylene glycol dimethacrylate (EGDM) as a crosslinker. The structures of these semi-IPNs were studied using various characterization techniques such as IR and nuclear magnetic resonance (NMR) spectra, and the thermal behavior of the semi-IPNs was also studied by thermogravimetric analysis (TGA). A plausible degradation mechanism was suggested in our previous communication. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **70:** 837–842, 1998

INTRODUCTION

Phenolic resins have been a workhorse as matrix resins in composites for structural and thermostructural applications in aerospace because of their thermal stability, ablative characteristics, and cost effectiveness.[1] An important phenolic compound from natural sources is cashew nut shell liquid (CNSL). CNSL, a byproduct of the cashew industry, is obtained from the shell of the cashew nut. Because of its phenolic character and long alkyl chain, which varies in its degree of unsaturation attached to the benzene nucleus of its molecules, the chief constituent of CNSL finds many applications in several fields.

In the twentieth century, high technology has fostered active participation of the phenolic resins based on CNSL in "high-tech" areas ranging from electronics, computers, communications, aerospace, biomaterials, biotechnology, and advanced composites.[2–9] Several polymeric systems based on cardanol have already been reported.[10,11]

This work was an attempt to synthesize modified thermally stable, semi-IPNs. It was achieved by condensing copolymerized resins with castor oil-based polyurethanes. This article deals with the synthesis of copolymerized resins from cardanol-substituted benzoic acid–formaldehyde/furfural by acid- and base-catalyzed reactions and the synthesis and characterization of semi-IPNs.
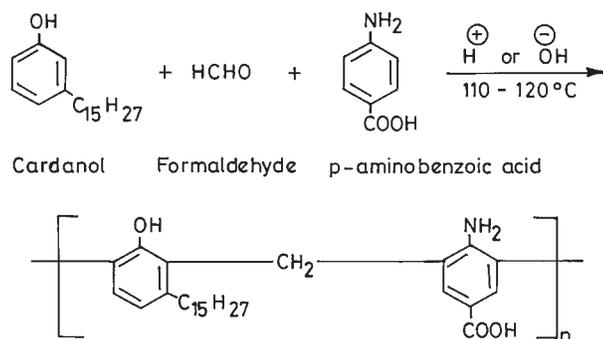
EXPERIMENTAL

Cardanol was obtained by double-vacuum distillation of CNSL (Kerala Cashewnut Development Corp., Quinol, India) at $4-5$ hp_a and the fraction distilled at 230–240°C was collected. The formaldehyde used (BDH) was a 36% (w/v) aqueous solution. THF (S.D. Fine Chemicals) was dried over sodium and distilled. Hexane (S.D. Fine Chemicals) was used as received.
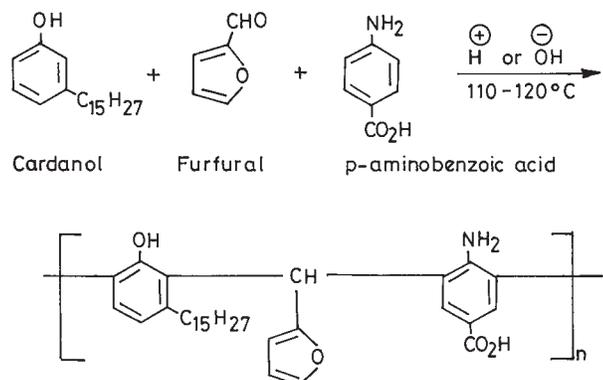
SCHEME-I

Cardanol   Formaldehyde   p-aminobenzoic acid

SCHEME-II

Cardanol   Furfural   p-aminobenzoic acid

Figure 1 Chemical structure of copolymerized resins.

INSTRUMENTATION

IR spectra were taken on a Nicolet DX-IR spectrophotometer. Thermal analysis were carried out using a thermal analyzer (DuPont) at a heating rate of 10°C/min in nitrogen. NMR was taken on a JEOL FX 90 MHz spectrometer.

SYNTHESIS OF SEMI-IPNs

For synthesis of copolymerized resins (Polymer-I), cardanol (1.192 g, 0.004 mol) and a substituted aromatic compound (0.004 mol) were mixed in a three-necked flask to which 2 mL hydrochloric acid (6N) was added as the catalyst. The reaction mixture was stirred with the help of a mechanical stirrer and heated to 120°C. Formaldehyde (1.66 cm^3, 0.06 mol) was added dropwise to it. Stirring and heating were continued for 7–9 h. The impurities were removed by washing the novolac first with ice-cold water and then hot water. The unreacted cardanol was removed by adding the novolac in THF to hexane. The novolac was then dried in a vacuum at 60°C until completely dry. Similarly, the copolymerized resin was synthesized by using furfural in place of formaldehyde and the base as the catalyst.
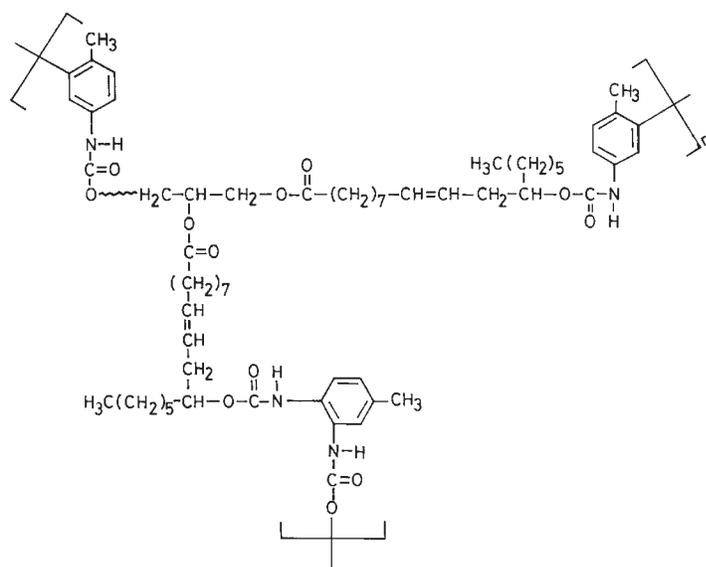
Figure 2 Probable structure of the castor oil urethane equivalent linear polymer (repeating unit).
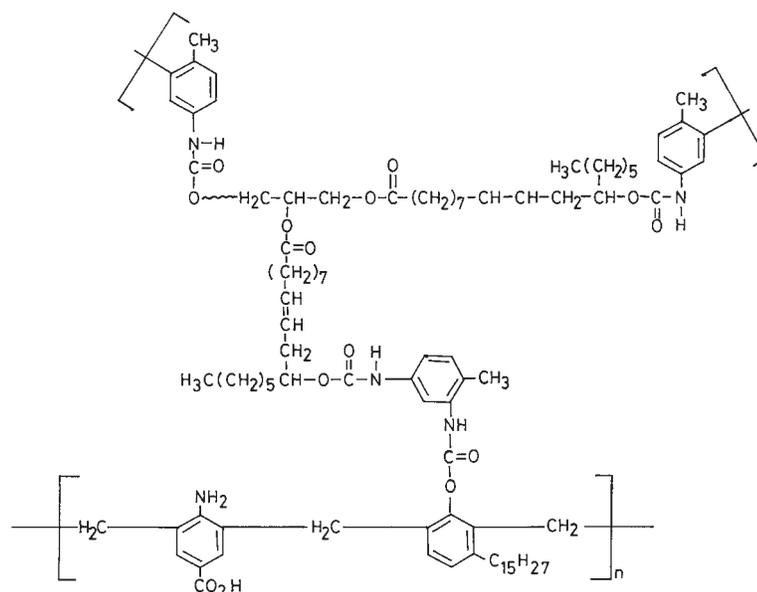
Figure 3 Probable structure of the semi-IPN.

Synthesis of Castor Oil-based Polyurethanes (Polymer-II)
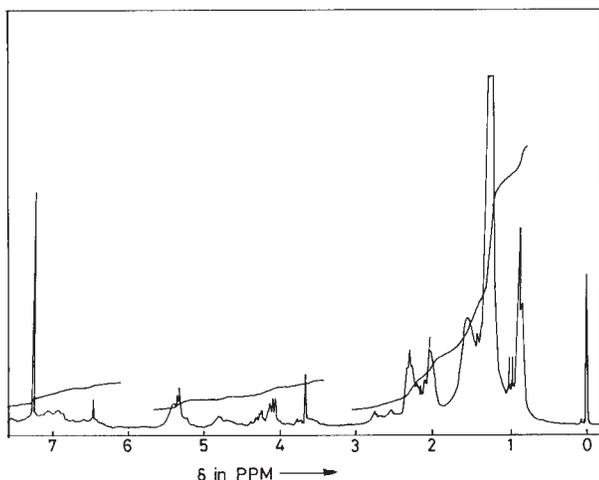
Castor oil (55 g, 0.555 mol) was allowed to react with toluene-2,4-diisocyanate (TDI) (17.8 g, 0.099 mol) to maintain the NCO/OH ratio at 1.6. The reaction was carried out at 45°C with continuous stirring for 2 h. The prepolymer was isolated as a viscous liquid.

Polyurethanes with different NCO/OH ratios such as 1.8, 2, and 2.2 were prepared in a similar manner. Similarly, a number of polyurethanes were also prepared with different NCO/OH ratios using diphenylmethane diisocyanate (DPMDI),

Figure 4 Proton NMR of C–PABA–F semi-IPN.

hexamethylene diisocyanate (HMDI), and isophorone diisocyanate (IPDI).

Synthesis of Semi-IPNs

Semi-IPNs were prepared from various polyurethanes and copolymerized resins. The resin (Polymer-I) and polyurethane (Polymer-II) were taken in various proportions in benzene. Then, 5 cm^3 of 1% ethylene glycol dimethacrylate (EGDM) was added and stirred well by a mechanical stirrer. The stirring was continued until the reactants were intimately mixed. The entire process was carried out at ambient.

RESULTS AND DISCUSSION

Cardanol-substituted benzoic acid–formaldehyde/furfural novolac with different proportions of cardanol were synthesized by copolymerizing cardanol with substituted benzoic acid, formaldehyde, and furfural under acidic and basic conditions as shown in Figure 1. Characterizations of these resins were done by elemental analysis, NMR, IR, and TG, and the results were reported in a previous communication[12] (see also Fig. 2).

Characterizations of these semi-IPNs were done by elemental analysis, IR, NMR, and thermal analysis (Fig. 3). A typical NMR spectra is given in Figure 4, which shows the absence of OH
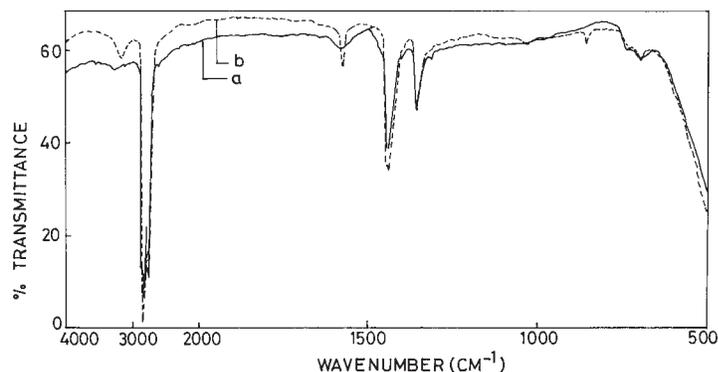
Figure 5 FTIR spectrum of (a) cardanol-*p*-aminobenzoic acid–formaldehyde resin (HCl-catalyzed) and (b) cardanol-*p*-hydroxy benzoic acid–formaldehyde (HCl-catalyzed) resin.

proton. This indicates that almost all the isocyanate was reacted with —OH groups of cardanol and castor oil.

IR Characteristics of the Semi-IPNs

The semi-IPNs were characterized by IR spectroscopy, which indicates the absence of free OH groups and, hence, complete conversion of both —OH groups of cardanol and castor oil to the urethane moiety

$$(-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O-)$$
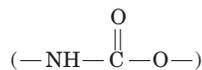
Typical IR spectra of semi-IPNs are shown in Figure 6. The characteristic —NH stretching vibration was located at 3405 cm^{-1} apart from other

peaks as a broad band. Bands at 2932 and 2894 cm^{-1} are the synchronous reflection of OH stretching (asymmetric and symmetric) of CH$_2$ bridges. A strong peak was shown in the spectrum near 1724 cm^{-1} which corresponds to the $\diagdown$C$=$O$\diagup$ stretching absorption band of the repeating unit. Its constant position, high intensity, and relative freedom from interfering bands make this one of the easiest bands to recognize in the IR spectrum (Fig. 6).

NMR Studies

Few NMR spectra of semi-IPNs have been studied. The spectrum of the semi-IPN prepared by condensing cardanol-based copolymerized resin
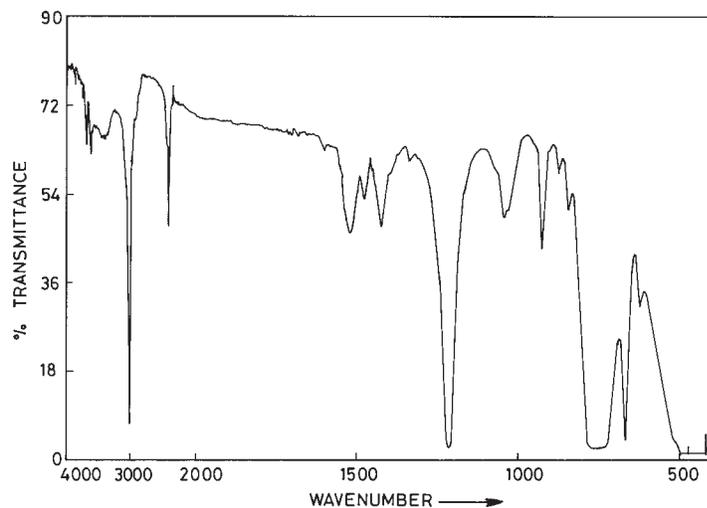
Figure 6 IR spectra of semi-IPN (C–PABA–F + COPU).

Table I **¹H-NMR Data of Semi-IPN**

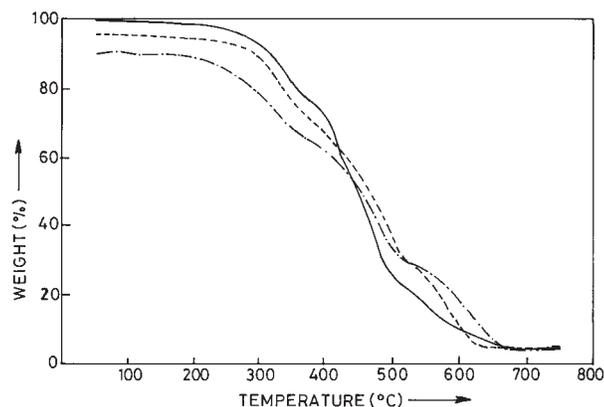| Types of Protons	N—H	Aromatic	Olefinic	—CH₂— Bridge	—CH₂—CH=CH— CH₂—CH=CH	—CH₂Ar	Terminal —CH₃ Group
Chemical shifts (ppm)	7.26	6.5–7.7	5.42	4.1	2.78	2.32	0.9

with castor oil-based polyurethane is represented in Figure 4. The spectrum of CNSL in CDCl₃ shows the presence of peaks corresponding to aromatic protons, olefinic protons, methylenic protons, and methyl protons and is in agreement with the work reported earlier[13] (Table I).

Aromatic protons appeared as a multiplet in the range of 6.5–7.72 ppm (Fig. 4). Olefinic protons appeared as a multiplet in the range 4.93–5.45 ppm. The CH₂ groups sandwiched by two double bonds, i.e., —CH=CH—CH₂—CH=CH—, appeared at 2.78 ppm. The peak at 4.1 ppm could be attributed to the —CH₂— and that at 2.04 ppm could be due to the (—CH₂—CH=CH—) component of cardanol. —CH₂— groups appeared as a singlet of sharp intensity at 1.28 ppm. The terminal —CH₃ group in the side chain gave a triplet at 0.89 ppm.

The hydroxy group protons of cardanol should have appeared as a singlet at 5.7 ppm but in Figure 4, the absence of a peak at the said chemical shift indicates that there is no free —OH group.

Thermal Characteristics of the Semi-IPNs

The thermograms of six typical semi-IPNs derived from cardanol-substituted benzoic acids–formaldehyde and castor oil-based polyurethane were studied and the thermograms are represented in Figures 7 and 8. A comparative picture of the thermal data characteristics, including the oxygen index value (O.I.), are furnished in Table II. Van Krevlin[14] showed that the oxygen index of a material can be taken as a measure of its nonflammability. The oxygen index values were calculated based on carbonaceous char as related by the empirical equation

$$O.I. \times 100 = 17.5 + 0.4 \times C.R. \qquad (1)$$

From Figures 7 and 8, it is evident that all the semi-IPNs prepared decompose in two to three distinct stages. The initial weight loss of about 3–10%, which occurs for all the semi-IPNs up to 200°C, is attributed to moisture and unreacted formaldehyde retained in the sample. Around 300–400°C, decrosslinking starts, which is a slow process initially. Above 400°C, all the semi-IPNs start to decompose at a faster rate and the weight loss occurs, up to 60% in the temperature range of 500°C. In between 500 and 700°C, a sharp weight loss of up to 90% occurs due to depolymerization and unzipping of polymeric chains.

It is observed from Table II that the semi-IPN-5 prepared by reacting castor oil-based polyurethane from IPDI and the cardanol–formaldehyde–PHBA resin copolymer in the ratio 30 : 70 and semi IPN-6 prepared by reacting castor oil-based polyurethane from DPMDI and cardanol–

Figure 7 TG curve of (----), semi-IPN 1, (---) semi-IPN 2, and (-----) semi-IPN 3.
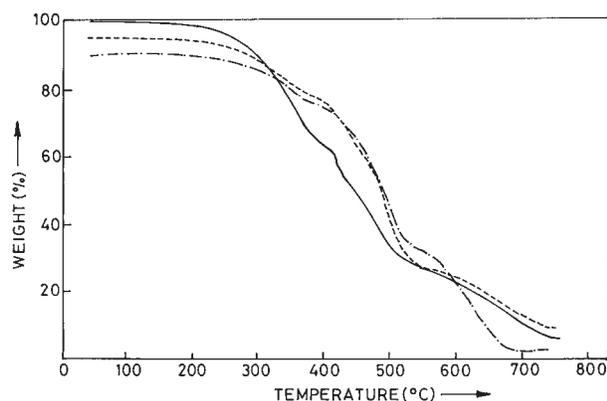
Figure 8 TG curve of (——), semi-IPN 4, (---) semi-IPN 5, and (– · – · – · –) semi-IPN 6.

Table II   Thermal Data Characteristics

| Sample No. | Chemical Composition | Percentage of Weight Loss at Various Temperatures (°C) | | | | | | | OI |
		100	200	300	400	500	600	700	
1	CARD−FA−PHA (R) + TDI−CO (PU) (1.6)	0	1.59	6.78	26.55	73.34	89.83	95.48	.1765
2	CARD−FA−PHBA (R) + TDI−CO (PU) (1.8)	0	0.64	5.99	27.41	61.33	86.91	94.65	.1775
3	CARD−FA−PABA (R) + TDI−CO (PU) (2.0)	0	1.88	12.5	31.25	60.63	77.50	93.63	.1759
4	CARD−FA−PHA (R) (CU) + TDI−CO (PU) (1.6)	0	3.00	9.6	35.60	56.1	76.3	88.7	.1758
5	CARD−FA−PHBA (R) (CU) + IPDI−CO (PU) (1.6)	0	2.5	5.99	17.89	51.21	73.88	85.72	.1785
6	CARD−FA−PABA (R) (CU) + DPMDI−CO (PU) (1.6)	0	1.09	5.50	15.58	45.82	72.91	90.22	.1770

CARD: cardanol; TDI: toluene-2,4-diisocyanate; FA: formaldehyde; IPDI: isophorone diisocyanate; PABA: *p*-aminobenzoic acid; DPMDI: diphenyl methane diisocyanate; PHA: *p*-hydroxyacetophenone; CO: castor oil; PHBA: *p*-hydroxybenzoic acid; PU: polyurethane; CU: curing; O.I.: oxygen index.

formaldehyde−PABA copolymerized resin, can withstand very high temperatures before decomposition. This is attributed to the strong network formed between polyurethane prepared from IPDI, DPMDI, and copolymerized resin. From Table II, it is observed that the stability of semi-IPNs increases with the increase of the resin content. Although both the polymers are step-growth polymers, the resin backbone is plastic in nature whereas the polyurethane network is rigid in nature.

Hence, with increase in the resin content, the flexibility of semi-IPNs increases, enhancing the thermal stability. This has been clearly observed in the case of compounds 3 and 5, where the resin content is 70% and the polyurethane content is 30%.

CONCLUSION

The results clearly indicate that the stability of the synthesized semi-IPNs increases with increase of the resin content. In this type of semi-IPNs, the resin backbone is plastic in nature, whereas the polyurethane network is rigid in nature. Hence, with increase in resin content, the flexibility of the semi-IPN increases, enhancing the thermal stability. Further studies on such semi-IPNs can give useful information regarding the potential commercial application of products.

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