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Synthesis and characterization of bifunctional monomers for high performance polymers from renewable resource

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Abstract: Phenolic lipids from plant materials are new raw materials from renewable resources and are essential in the preparation of any polymer product. Cardanol, a meta- substituted alkyl phenol derived from Cashew Nut Shell Liquid (CNSL) a byproduct of cashew industry, holds a place as biomaterial for the manufacture of many industrial products. In the present study bifunctional monomers from cardanol has been synthesized by condensing diazotized p-anisidine / p-sulphanilic acid dye with formaldehyde and two organic compounds o-hydroxy benzoic acid and α-naphthol. The resins have been characterized by FT-IR and ^{1}H-NMR studies. Thermal behaviour of the resins has been studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Differntial thermal analysis shows two exotherms due to the decomposition reactions at higher temperature.

Key words: Cardanol,bifunctional monomer, diazotised p-anisidine, diazotised p-sulphanilic acid, thermo-gravimetric analysis.

Introduction

Natural vegetable oils, as a source of raw materials have been utilized in polymer synthesis via the attachment of functional groups such as hydroxyl, epoxy or carboxyl groups introduced on to the fatty acid chains of the vegetable oil [1]. Moreover polymers produced from vegetable oil and their derivatives have excellent hydrolytic stability and thermomechanical properties due to the presence of hydrophobic nature of the side chain [2]. Cashew Nut Shell Liquid (CNSL) obtained as a byproduct of cashew nut industry is invaluable raw material in many important industries such as polymers, plastics, lubricants, resins and antioxidants [3-5]. Cardanol isolated from the decarboxylated residue make a new family of phenolic resins and biocomposites [6, 7]. Polymers from CNSL and cardanol have been prepared either by condensation with electrophilic compounds such as formaldehyde, or by chain polymerization through unsaturation in the side chain using acid catalysts or functionalisation at the hydroxyl group and subsequent oligomerisation to get functionalized prepolymer [8, 9]. Ranjana Yadav and Deepak Srivatsava investigated the kinetics of the acid catalysed formaldehyde condensation of cardanol [10].

Cardanol was functionalized with both ortho-phosphoric acid and oligomerised, the resulting prepolymers act as multifunctional additives [11, 12]. Phenolic resins derived from condensation of cardanol and formaldehyde has excellent adhesive property and structural integrity [13]. They can be used as high temperature resistant polymers [14, 15]. This paper presents a modified network of bifunctional monomers derived from cardanol. Cardanol is coupled with diazotized p-anisidine / diazotised p-sulphanilic acid and the prepolymer resins have been synthesized by condensing with formaldehyde and two organic compounds o-hydroxy benzoic acid and α-naphthol in the presence of acid as catalyst. The resins have been characterized by FT-IR and ^{1}H-NMR spectral studies and the thermal behaviour of the resins have also been studied.

Experimental

Materials

Cardanol was obtained from M/s Sathya Cashew Chemicals Ltd, Chennai, Formaldehyde (40%) solution; sodium nitrite, potassium hydroxide and methanol were received from M/s BDH Ltd (India). p-Anisidine, p- sulphanilic acid, o-hydroxy benzoic acid, α- naphthol were received from E.Merck, (Germany). The chemicals were used as received.

Synthesis of diazotized p-anisidine cardanol bifunctional monomer resin

p-Anisidine (2.4 g) was diazotized using sodium nitrite (1.4 g) and dilute hydrochloric acid at 0°C with constant stirring. 3 g of cardanol, in a chilled solution of alcoholic potassium hydroxide was added dropwise to the diazonium salt solution at 0° -10°C. The red dye formed was stirred for a period of 6 h and poured in dil HCl with constant stirring. The red dye was separated, washed thoroughly with water and dried. The resin DCR-1 was prepared by refluxing a mixture of diazotised p- anisidine cardanol dye (2.15g), formaldehyde (2 ml), 6N hydrochloric acid (2 ml) and o- hydroxyl benzoic acid (0.35 g) at 100°C for 6 h. A black colored solid product (diazotised p-anisidine cardanol formaldehyde o-hydroxy benzoic acid resin- DCR-1) formed was washed well with 5N NaOH and then with hot distilled water and dried in vacuum. The resin DCR-2 was prepared by adding α- naphthol (0.30 g) along with diazotised p- anisidine cardanol dye (2.15 g), formaldehyde (2 ml) and 6N hydrochloric acid (2 ml).

Synthesis of diazotized p-sulphanilic acid cardanol bifunctional monomer resin

p- Sulphanilic acid (2.45 g) was diazotized using sodium nitrite (1.4 g) and dilute hydrochloric acid at 0°C with constant stirring. 3 g of cardanol, in a chilled solution of alcoholic potassium hydroxide was added dropwise to the diazonium salt solution at 0°-10°C. The red dye formed was stirred for a period of 6 h and poured in dil HCl with constant stirring. The red dye was separated, washed thoroughly with water and dried. The resin DCR-3 was prepared by refluxing a mixture of diazotised p - sulphanilic acid cardanol dye (2.15 g), formaldehyde (2 ml), 6N hydrochloric acid (2 ml) and o-hydroxy benzoic acid (0.35 g) at 100°C for 6 h. A black colored solid product (diazotised p-sulphanilic acid cardanol formaldehyde o-hydroxy benzoic acid resin DCR-3) formed was washed well with 5N NaOH and then with hot distilled water and dried in vacuum. The resin DCR-4 was prepared by adding α- naphthol (0.30 g) along with diazotised p-sulphanilic acid cardanol dye (2.15 g), formaldehyde (2 ml) and 6N hydrochloric acid (2 ml).

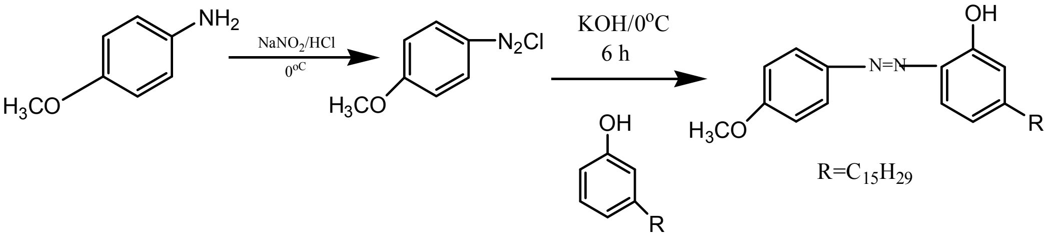
Characterization

Solubility of the prepared resins was tested with various organic solvents such as petroleum ether (40°-60°C), acetone, benzene, dimethyl sulphoxide, ethanol, methyl ethyl ketone and water. Infrared spectra were taken in a Shimadzu-FT-IR spectrophotometer by KBr pellet method. The resins were subjected to differential thermal analysis (DTA) and Thermo gravimetric analysis (TGA) at a rate of 20°C/min in nitrogen using a Universal V4-3A TA Instrument (model SDTQ 600).

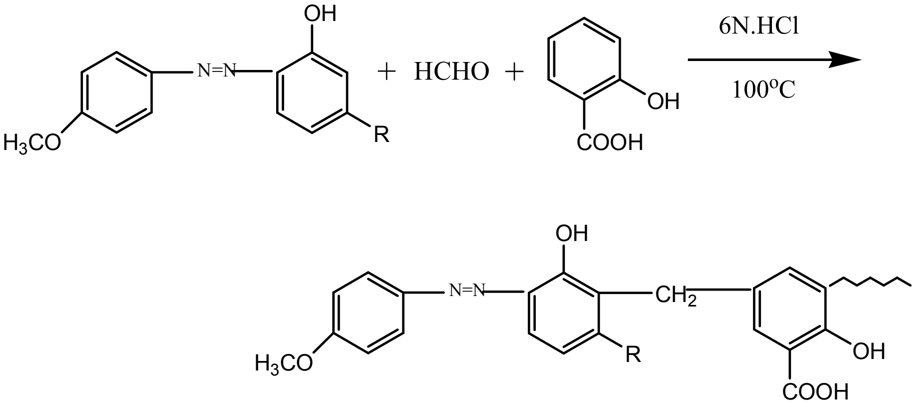
Results and Discussion

Mechanism for the synthesis of resins

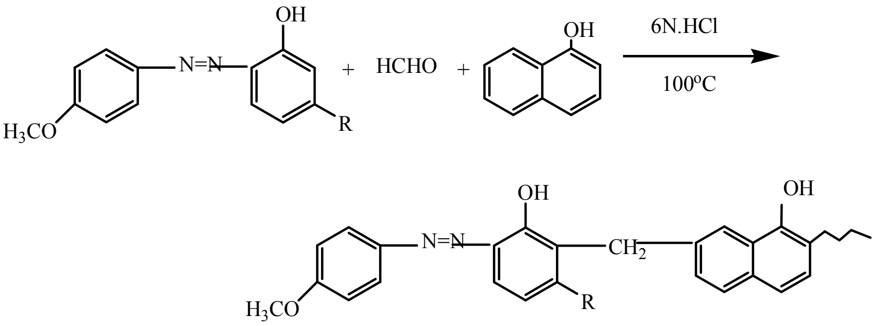
In the first step cardanol in alcoholic KOH is treated with diazotized p-anisidine.The diazotised p-anisidine cardanol dyeis condensed with formaldehyde in presence of hydrochloric acid as catalyst to form CH_2 cross linkages. The o-hydroxy benzoic acid, α-naphthol also condensed with the dye and formaldehyde to form various resins. This has been illustrated in Scheme 1a represents the formation of diazotized p-anisidine cardanol dye, Scheme 1b represents the formation of diazotized p-anisidine cardanol o-hydroxy benzoic acid resin and Scheme 1c represents the formation of diazotized p-anisidine cardanol α-naphthol resin.



Scheme 1a. Formation of diazotised p-anisidine cardanol dye



Scheme 1b. Formation of diazotised p-anisidine cardanol formaldehyde o-hydroxy benzoic acid resin



Scheme 1c. Formation of diazotised p-anisidine cardanol formaldehyde α- naphthol resin

Solubility

The powdered resin (5 mg) was suspended over 3 ml of the chosen solvent and the solubility was checked after 24 h at room temperature. All the resins were found to be insoluble in water, partially soluble in ethanol, acetone, petroleum ether (40°-60°C). The resin is soluble in dimethyl sulphoxide, methyl ethyl ketone and benzene. Hence a wide range of solvents can be applied for the processing of the polymer resins. The solubility properties of the resins are presented in Table 1.

Table 1. Solubility behavior of the resins

Resins	Solubility in different solvents						
	Petroleum ether	Acetone	Benzene	Dimethyl Sulphoxide	Ethanol	Methyl ethyl ketone	Water
DCR-1	±	±	+	+	±	+	_
DCR-2	±	±	±	+	±	+	_
DCR-3	±	±	+	+	±	+	_
DCR-4	±	±	+	+	±	+	_

(+) Soluble, (±) partially soluble, (-) insoluble

FT- IR analysis

The FT-IR spectra of the four resins are presented in Figures 1a to 1d. A broad absorption band at 3446 cm^{-1} shows the O-H stretching frequency of hydrogen bonded phenolic OH group. The peak at 2924 cm^{-1} shows the symmetrical CH_2 stretching of the side chain of cardanol and 2853 cm^{-1} shows the CH_2 group in formaldehyde. The peak at 1458 cm^{-1} shows the presence of azo group. In Figure 1a and Figure 1c the peaks at 1281 cm^{-1} and 1660 cm^{-1} are due to the intermolecular hydrogen bonding of o-hydroxy benzoic acid. In Figure 1b and Figure 1c the peaks at 831 cm^{-1} and 717 cm^{-1} show the presence of C-H out of plane bending of 3-adjacent H atoms showing the presence of fused aromatic ring α- naphthol.

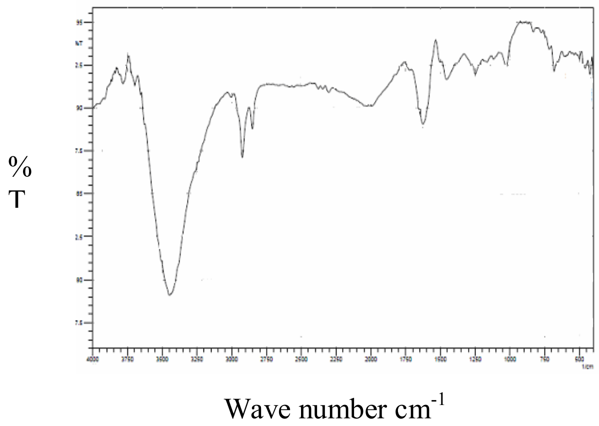


Fig. 1a. FT- IR spectrum of DCR- 1

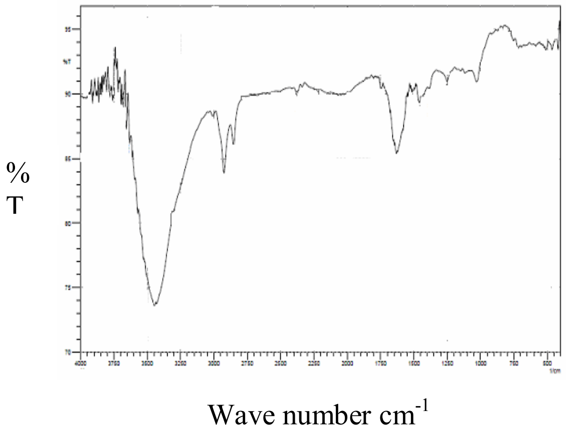


Fig. 1b. FT- IR spectrum of DCR- 2

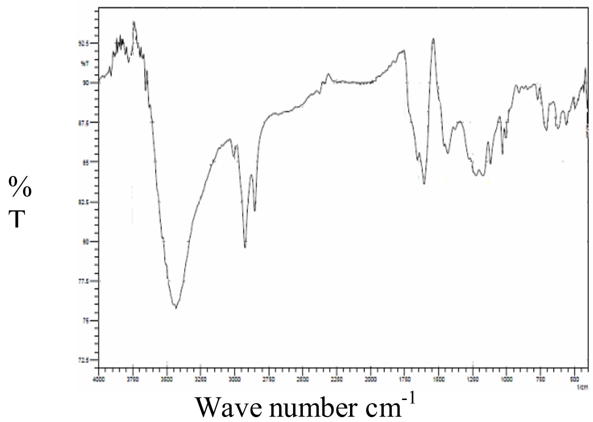


Fig. 1c. FT- IR spectrum of DCR- 3

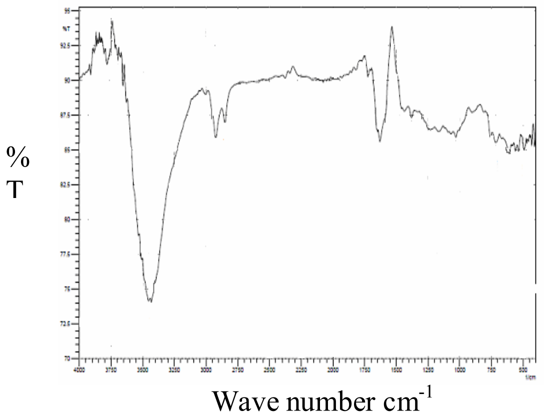


Fig. 1d. FT- IR spectrum of DCR- 4

^{1}H-NMR analysis

The ^{1}H-NMR spectra of the resins are presented in Figures. 2a to 2d. The peaks at 7.5 – 7.9 δ and 6.6 - 6.9 δ are due to the presence of aromatic protons. The singlet at 2.0 δ is attributed to the OH proton of the SO_3H group. The singlet appearing at 5.0 δ is due to the O-H proton of aromatic hydroxyl group. The multiplets at 2.9 – 3.4 δ are due to the presence of methylene protons and the peak at 1.2 δ is assigned to the presence of methyl protons.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of the resins reveals that the resins decomposed in two distinct steps in the temperature range 100°C -600°C after the loss of water molecule (3%- 7%). Table 2 shows percentage weight loss at different temperatures. The Initial decomposition temperature (IDT) of DCR-1, DCR-2, DCR-3 and DCR-4 are 273°C, 238°C, 202°C and 196°C respectively. In the first step of thermal degradation 200°C-460°C weight loss upto 27% is observed in DCR-1, DCR-2, DCR-3 and DCR- 4. This may be caused by thermal degradation of the small fragments like CH_3, OH and the side chain. The resins DCR-1, DCR-2, DCR-3 and DCR-4 are thermally more stable up to 430°C.The weight loss around 80% in the second stage of thermal degradation (470°C-600°C) may be due to the depolymerisation and the cleavage of the aromatic ring in an oxydegradative manner.

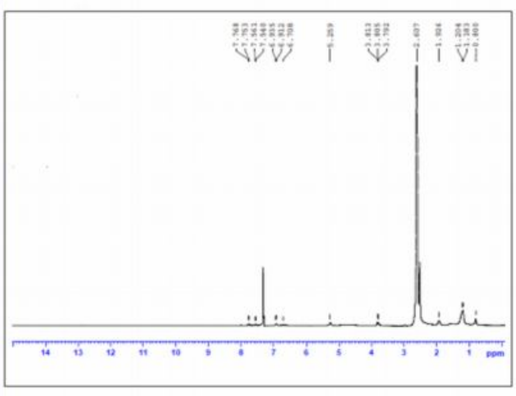


Fig. 2a. ^{1}H-NMR spectrum of DCR- 1

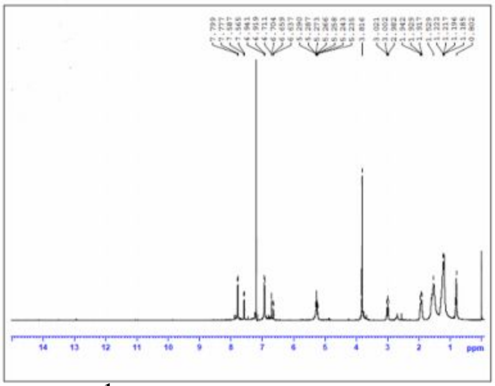


Fig. 2b. ^{1}H-NMR spectrum of DCR- 2

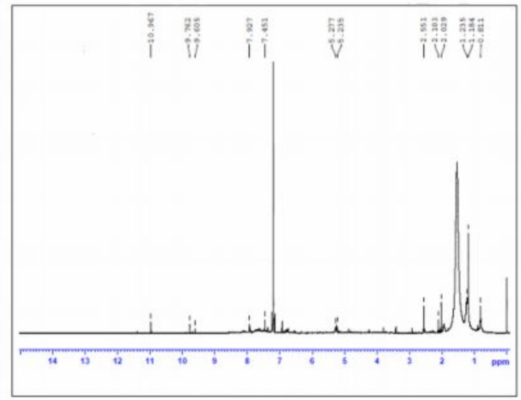


Fig. 2c. ^{1}H-NMR spectrum of DCR- 3

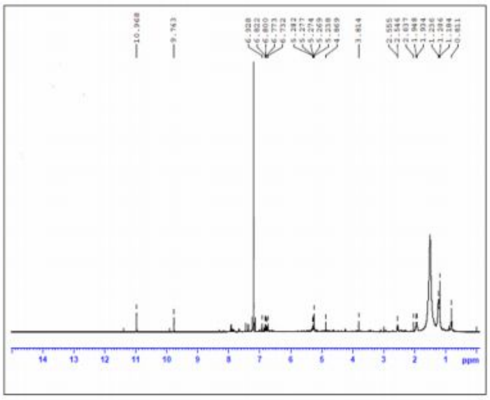


Fig. 2d. ^{1}H-NMR spectrum of DCR- 4

Table 2. Thermogravimetric analysis of the resins

Resins	Initial decompo-sition temperature (°C)	percentage of weight loss at different temperature (°C)					
		100	200	300	400	500	600
DCR-1	273	2	3	17	27	68	77
DCR-2	238	0	3	7	15	72	90
DCR-3	202	2	5	12	19	75	83
DCR-4	196	3	7	13	22	68	78

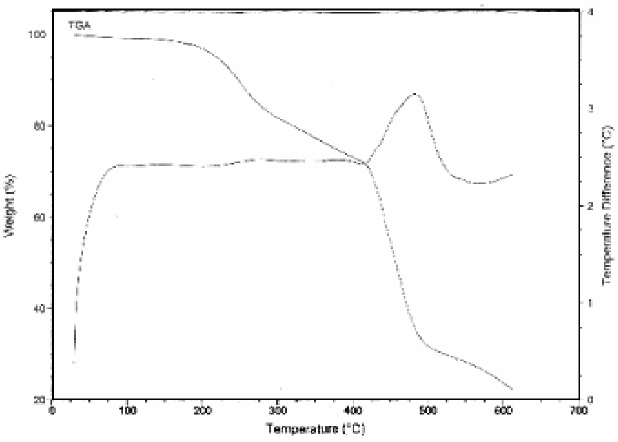


Fig. 3a. TGA & DTA curve of DCR- 1

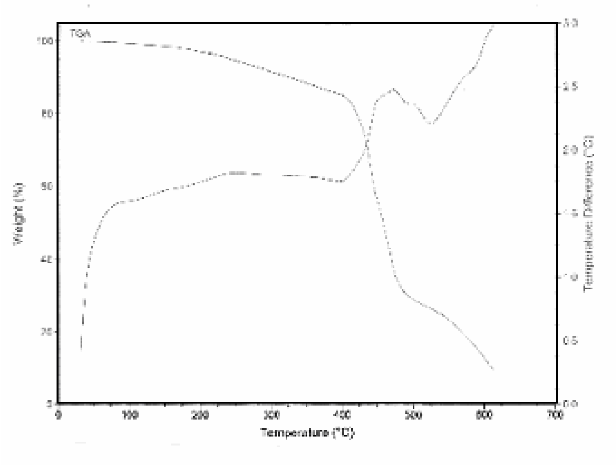


Fig. 3b. TGA & DTA curve of DCR- 2

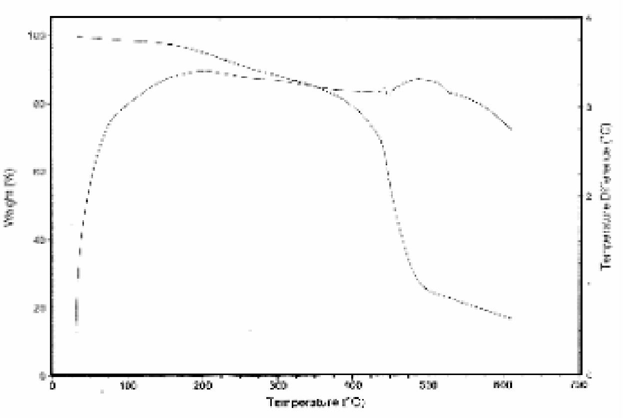


Fig. 3c. TGA & DTA curve of DCR- 3

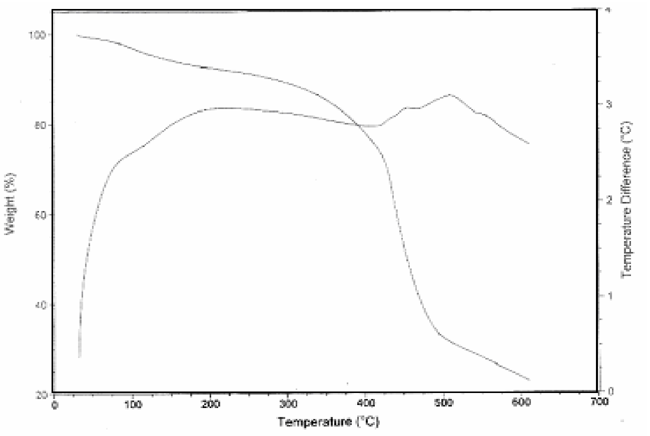


Fig. 3d. TGA & DTA curve of DCR- 4.

Differential thermal analysis (DTA)

DTA curves are recorded simultaneously with TGA curves (Figures 3a to 3d). DTA curves shows first order transition namely crystallization and melting appears as peaks in the exothermic and endothermic directions respectively. After melting the material may undergo decomposition reactions at higher temperature which give broad peaks; these may be generally exothermic but are sometimes more complex in nature.

Table 3. Differential thermal analysis of the resins.

Resins	1st exotherm (°C)	2nd exotherm (°C)
DCR-1	430	478
DCR-2	454	472
DCR-3	436	490
DCR-4	454	511

DTA analysis (Table 3) shows two isotherms, a weak one around ranging from 430° - 455°C and a strong one above 470°C ranging from 472°-511°C. The weak exotherm may be due to the cleavage of meta-substituted alkyl side chain in the phenyl ring of the cardanol moiety. The differential thermal analysis clearly indicates the thermal stability of the resins at higher temperature.

Conclusions

Diazotised p-anisidine cardanol and diazotized p-sulphanilic acid have been functionalized with o-hydroxy benzoic acid and α- naphthol. The resulting prepolymer act as multifunctional additives. The initial decomposition of resins containing o- hydroxyl benzoic acid (DCR-1 and DCR-3) is higher when compared to that of resins containing α- naphthol (DCR-2 and DCR-4). This indicates that DCR-1 and DCR-3 possess higher thermal stability than DCR-2 and DCR-4.

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