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Der Chemica Sinica, 2011, 2 (3):138-146

ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis, characterization and thermal studies of some diazotised *p*-anisidine cardanol formaldehyde resins

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ABSTRACT

This research paper deals with the synthesis and characterization of resins from renewable source cardanol. p-Anisidine has been diazotised and coupled with cardanol to prepare diazotised p-anisidine cardanol dye. The dye obtained has been condensed with formaldehyde in presence of hydrochloric acid to give diazotized p-anisidine cardanol formaldehyde resin. The condensed product has been allowed to react with organic compounds such as o-amino benzoic acid, resorcinol and thiourea to form various resins. The resins were characterized by UV and FT-IR, ^{1}H-NMR spectroscopy. The thermal behavior of the resins has also been studied using thermo gravimetric analysis (TGA) and differential thermal analysis (DTA).

Key words: Diazotised p-anisidine, cardanol, formaldehyde resins, thermal studies.

INTRODUCTION

Renewable sources, as a substitute to the petrochemical derivatives have attracted the attention of many researchers for the synthesis of polymers. Cashewnut Shell Liquid (CNSL) a by-product of Cashew nut Industry is a unique natural source of unsaturated long chain phenol [1, 2]. Cashewnut shell liquid contains anacardic acid, cardol, 2- methyl cardol, and cardanol that differ in their side chain [3, 4]. It has found uses in areas as diverse as in the manufacture of adhesives, heat and waterproof paints, corrosion resistant varnishes and insulating enamels for the electrical industry[5 -7]. The anacardic acid present in CNSL is a derivative of o-carboxy phenol that readily decarboxylates on heating and converts to cardanol [8]. Cardanol, isolated from cashew nut shell liquid holds a place as bio-raw material for the manufacture of many Industrial products [9-11]. The phenolic nature of cardanol has prompted researchers to react it with formaldehyde or with other aldehydes to produce numerous resinous materials [12-14]. Synthesis and characterization of large number of resins using hydroxy aromatic compounds and formaldehyde have been reported by Lenka and co-workers [15, 16]. In place of cardanol Swain.J.R et al [17] have synthesized and characterized a number of resins from diazotised cardanol o-toluidine.

In the present study, p-anisidine is diazotised along with cardanol followed by condensing with formaldehyde and also with o-amino benzoic acid, resorcinol and thiourea in the presence of acid as catalyst. The resins have been characterized by UV and FT-IR, ^{1}H-NMR spectral studies. Thermal behaviour of the resins has also been studied.

MATERIALS AND METHODS

Cardanol was obtained from M/s Satya Cashew Chemicals Ltd, Chennai, Formaldehyde (40%) solution; sodium nitrite, potassium hydroxide and methanol were received from M/s BDH Ltd (India). p-anisidine, o-amino benzoic acid, resorcinol, thiourea were received from E.Merck,(Germany).The chemicals were used as received.

Ultraviolet spectral analysis was carried out in a UV- VIS double beam spectrophotometer 2201, Systronics. Infrared spectra were taken in a Shimadzu-FT-IR spectrophotometer by KBr pellet method. ^{1}H-NMR spectra were recorded using Bruker avance 400 MHz FT ^{1}H- NMR spectrometer. The resins were subjected to differential thermal analysis (DTA), Thermo gravimetric analysis at a rate of 20°C/min in nitrogen using a Universal V4-3A TA Instrument (model SDTQ 600). Specific gravity, Iodine value, Hydroxyl value and Acid value of the resins were determined according to the IS standard 840-1964.

Synthesis of diazotised-p-anisidine cardanol dye (DCA)

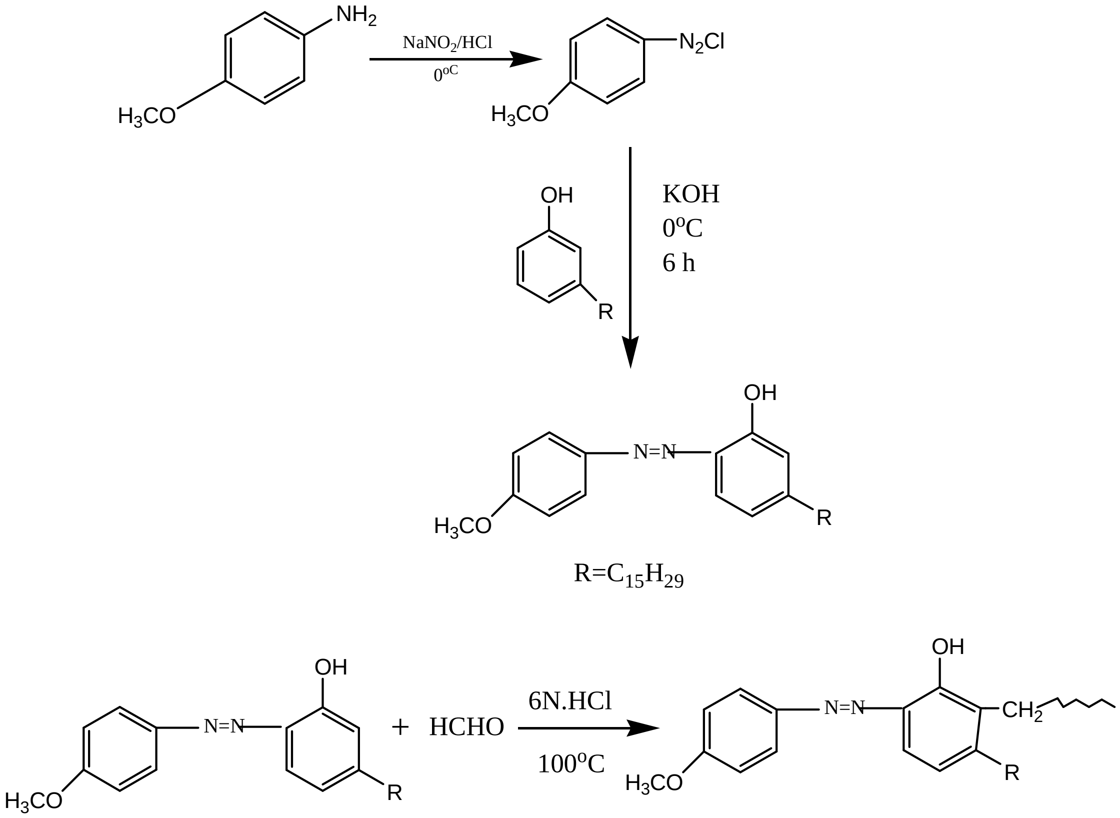
To 2.4 g of p-anisidine dissolved in dilute HCl 1.4 g of sodium nitrite was added at 0^{o}C with constant stirring. 6 g of cardanol was dissolved in a chilled solution of alcoholic potassium hydroxide and was added dropwise to the diazonium salt solution. The whole system was kept in ice bath within the temperature range of 0^o-10^{o}C. The red dye formed was stirred for a period of 6 hours and poured in dil HCl with constant stirring. The red dye was separated, washed thoroughly with water and dried. The dye (DCA) was recrystallized from methanol water mixture. The yield was 80 %.

Synthesis of diazotised p- anisidine cardanol- formaldehyde resin (DCAR 1)

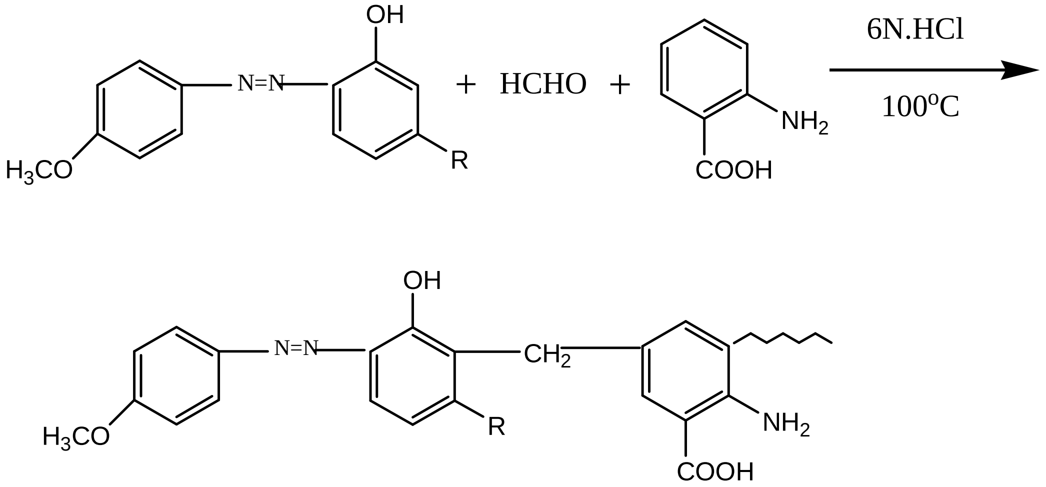
2.15 g of diazotised p- anisidine dye was condensed with 2 ml of formaldehyde and 2 ml of 6N HCl. The reaction was carried out at 100°C for 6 hours. A dark red brown colored solid (diazotised p-anisidine cardanol formaldehyde resin) (DCAR 1) obtained was washed well with dil Na OH and dried in vacuum.

Synthesis of diazotised p- anisidine cardanol - formaldehyde organic compound resins

2.15 g of diazotised p- anisidine cardanol dye, 2 ml formaldehyde, 0.54 g o-amino benzoic acid and 2 ml 6N. HCl were heated at 100^{o}C in a round bottom flask fitted with condenser at constant stirring using mechanical stirrer for 6 hours. The resin (DCAR 2) was washed with dilute NaOH and then with hot distilled water and then dried in vacuum. Similarly two more resins were prepared by adding of 0.75 g of resorcinol (DCAR 3) and, 0.76 g thiourea (DCAR 4).



Scheme 1a Formation of diazotised p-anisidine cardanol formaldehyde resin



Scheme 1b Formation of diazotised p-anisidine cardanol formaldehyde organic compound resin

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 dye was condensed with formaldehyde in presence of HCl acid as catalyst to form CH_2 cross linkages. The o-amino benzoic acid, resorcinol and thiourea were also condensed with the dye and formaldehyde to form various resins Scheml a & 1b.

UV, FT IR and ^{1}H-NMR Spectrum of diazotised p- anisidine cardanol dye

Diazotised p-anisidine cardanol dye shows sharp peak at 364 nm, which is related to the n-π* transition of azo unit of the dye and a sharp peak at 285 nm which is attributed to aromatic phenyl ring. IR Spectral data of diazotised p-anisidine cardanol dye reveal that the diazotization of p-anisidine with.cardanol. The peak at 1458 cm^{-1} shows the presence of azo group (Fig. 1a). In the ^{1}H-NMR spectra (Fig.1b) of diazotized p-anisidine cardanol dye, the peak at 6.6- 7.1 ppm shows the aryl protons of benzene nuclei and the peak at 5.3 ppm shows the phenolic hydroxyl group. The peak at 7.6-7.8 ppm shows the aryl protons of p- anisidine. The peak at 1.3- 2.5 ppm shows the methylene group of the long alkyl side chain of cardanol. The peak at 0.8 ppm shows the terminal methyl group of side chain of cardanol.

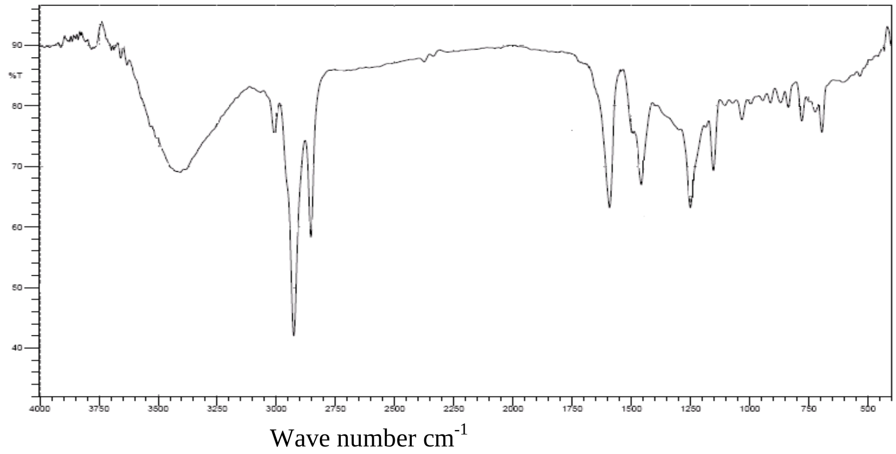


Fig 1a: FTIR Spectrum of diazotized p- anisidine cardanol dye

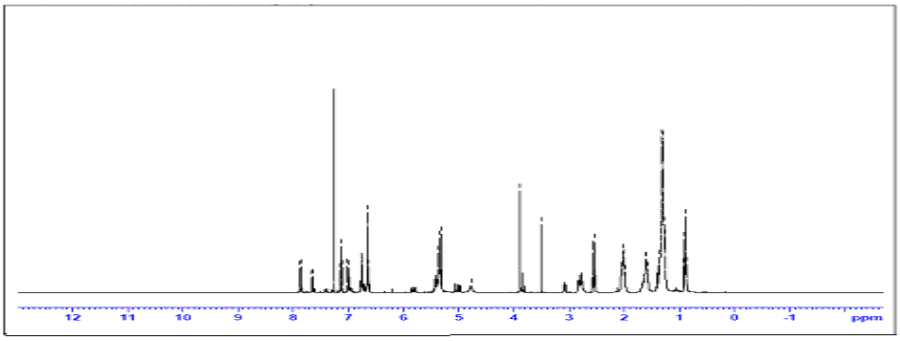
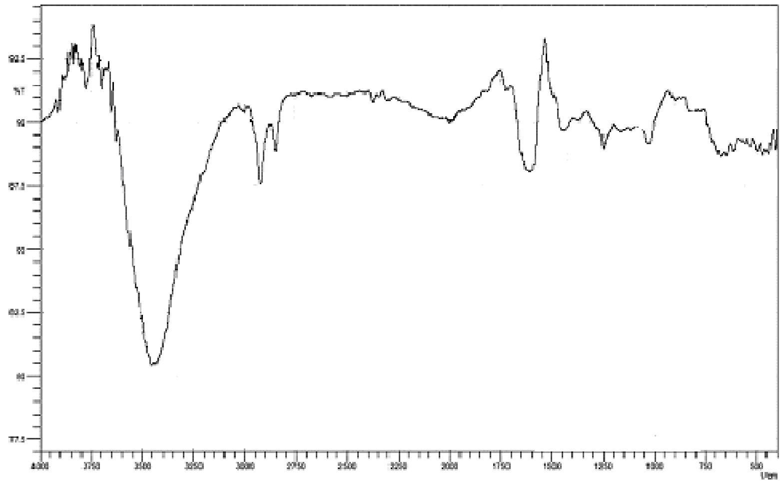


Fig 1b: ^{1}H-NMR spectrum of diazotised p- anisidine cardanol dye

FTIR and ^{1}H-NMR Spectrum of diazotised p- anisidine cardanol formaldehyde resin

In the IR Spectra of resins DCAR 1 (Fig. 2a) the peak at 3426 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 the (Fig. 2b) the peak at 6.6-6.9 ppm shows the aryl protons of cardanol and the peak at 3.0 ppm shows the methylene group of formaldehyde. The peak at 7.6- 7.8 ppm shows the aryl protons of p-anisidine and the peak at 1.2-1.9 ppm shows the methylene group of the side chain of cardanol.



Wave number cm^{-1}

Fig 2a: FTIR spectrum of DCAR 1

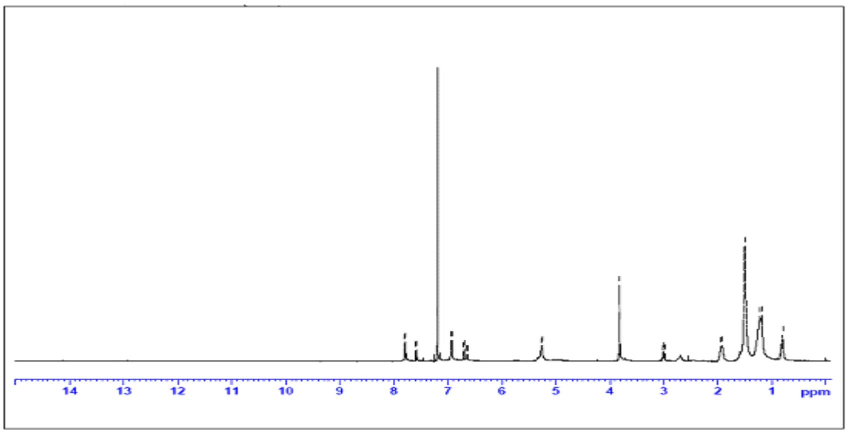
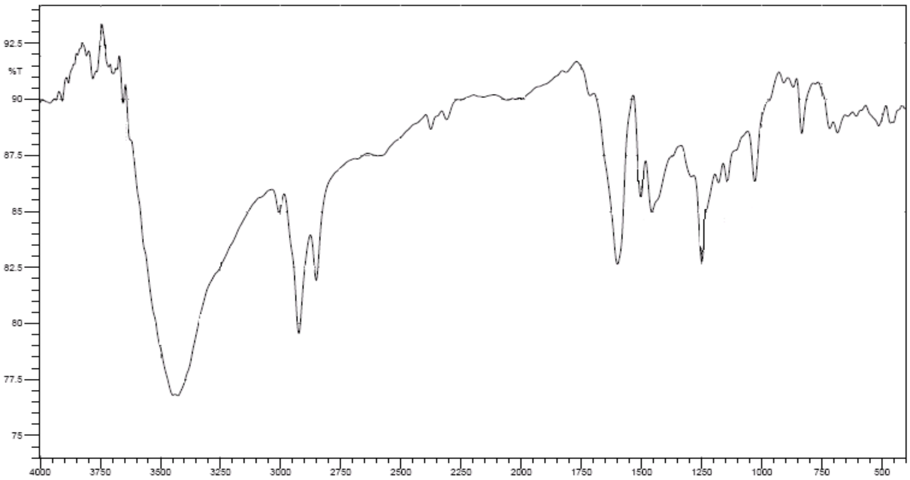
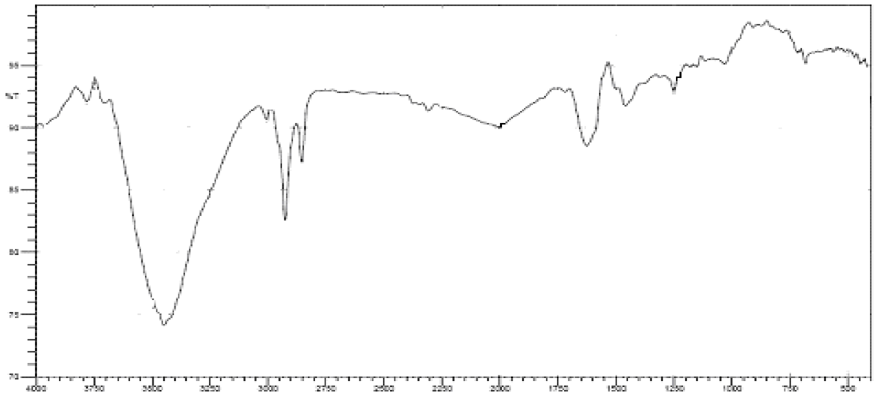


Fig 2b: ^{1}H-NMR spectrum of DCAR 1



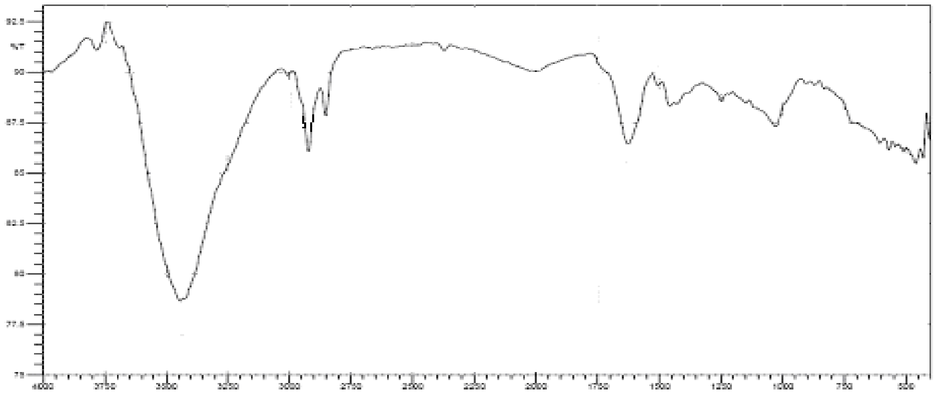
Wave number cm^{-1}

Fig. 2c: FT IR spectrum of DCAR 2



Wave number cm^{-1}

Fig. 2d: FT IR spectrum of DCAR 3



Wave number cm^{-1}

Fig. 2e: FT IR spectrum of DCAR 4

FTIR Spectrum of diazotised p- anisidine cardanol formaldehyde organic compound resins

In the IR Spectra of resins DCAR 2, DCAR 3 and DCAR 4 (Figs. 2c- 2e) the peak at 3426 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. The peak at 2595 cm^{-1} shows the N-H stretching frequency (Fig. 2c), The peak at 1251cm^{-1} shows the free O-H in plane bending (Fig. 2d) and the peak at 1250 cm^{-1} shows the presence of C=S stretching in thiourea (Fig. 2e).

Physico chemical characteristics of diazotised cardanol -p- anisidine – formaldehyde resin

The physico chemical properties are presented in table 1. The diazotised cardanol-p-anisidine resin has higher specific gravity due to higher degree of condensation between diazotized cardanol and formaldehyde. The low iodine value in comparison with that of cardanol may be due to the steric hindrance of adjacent bulky groups to the olefinic addition of iodine monochloride during the estimation of iodine value.

Table 1 Physico-chemical characteristics of cardanol and diazotised p-anisidine cardanol formaldehyde resin.

Properties	**Cardanol**	**Diazotized-p-anisidine cardanol formaldehyde resin**
Colour	Dark brown	Brownish red
Odour	Phenolic	Mild phenolic
Specificgravity(g/cc at 30°C)	0.9284	0.9326
Hydroxyl value	193.2	187
Iodine value	262.64	256
Acid value	2.24	3.2
Saponification value	31.78	45.6

Thermo gravimetric analysis of the resins

The thermo gravimetric analysis table 2. reveals that the resins decomposed in two distinct steps. In the first step of thermal degradation 100°-200°C weight loss upto 5% is observed in DCAR 1, DCAR 2, DCAR 3 and 18 % in DCAR 4 (Figs. 3a – 3d). This may be attributed to the removal of moisture retained in the resin. A gradual weight loss occur in the temperature ranges 200°-400°C may be caused by thermal degradation of the small fragments like CH_3, OH and the side chain. The resins DCAR 1, DCAR 2 and DCAR 3 are thermally more stable up to 400°C.The weight loss around 80% in the last stage of thermal degradation may be due to the depolymerisation and the cleavage of the aromatic ring in an oxydegradative manner.

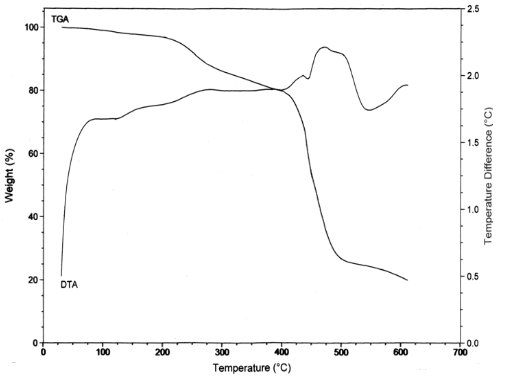


Fig. 3a: TGA & DTA curve of DCAR 1

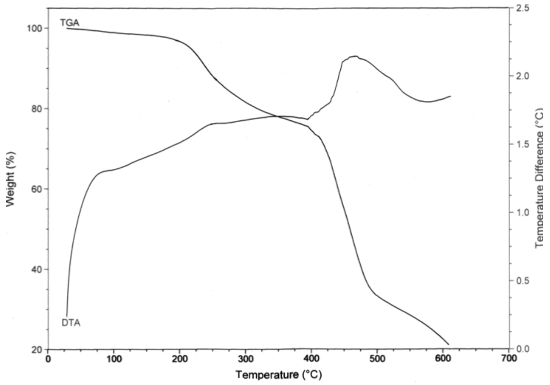


Fig. 3b:TGA & DTA curve of DCAR 2

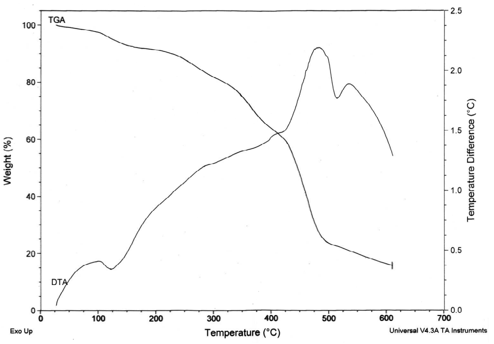


Fig. 3c: TGA & DTA curve of DCAR 3

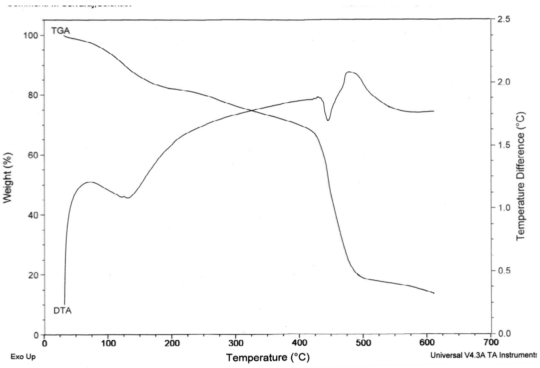


Fig. 3d: TGA & DTA curve of DCAR 4.

Table 2 Thermo gravimetric analysis of the resins

Resins	**% of weight loss at different temperature (°C)**					
	100	**200**	**300**	**400**	**500**	**600**
DCAR 1	0	2	10	19	74	80
DCAR 2	1	4	19	25	66	76
DCAR 3	2	5	17	36	78	86
DCAR 4	6	18	25	33	82	86

Differential thermal analysis of resins

DTA analysis table 3. shows two isotherms, a weak one around 400°C and a strong one above 450°C ranging from 400°-600°C. The weak exotherm is 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.

Table 3 Differential thermal analysis of the resins

Resins	1st exotherm (°C)	2nd exotherm (°C)
DCAR 1	434	488
DCAR 2	395	465
DCAR 3	421	480
DCAR 4	430	476

CONCLUSION

All the resins showed good thermal stability up to 400°C. The percentage of weight loss of the resin DCAR 2 at higher temperature is low and it showed more thermal stability when compared to that of the other resins. The exothermic temperature of the resins decreases by the addition of organic compounds.

Acknowledgement

One of the authors N.T.Nevaditha thanks the University Grants Commission, New Delhi,the Principal, Nesamony Memorial Christian College, Marthandam for selecting her under FDP programme.

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