

THERMAL DEGRADATION AND XRD STUDIES OF VEGETABLE OIL BASED NOVOLAC SCAFFOLDS FOR THE FORMULATION OF RESINS

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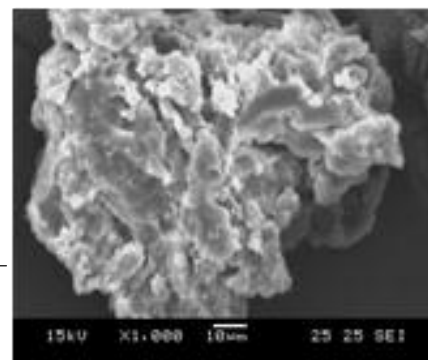
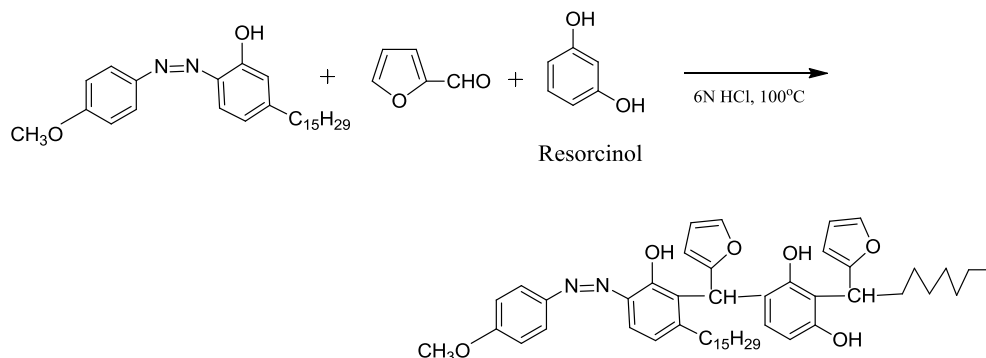
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Abstract

Biomaterials, chemicals and energy from renewable resources have been the object of considerable interest in recent years. Vegetable oils are one of the cheapest and most abundant biological sources available in large quantities and their use as starting materials has numerous advantages such as low toxicity, inherent biodegradability and high purity. They are considered to be one of the most important classes of renewable resources for the production of bio-based thermosets. As a substitute to the use of conventional reinforcing synthetic resins, biobased resins were synthesized from cardanol, renewable and low cost industrial grade oil obtained by vacuum distillation of Cashew Nut Shell Liquid (CNSL), an abundant agricultural byproduct of cashew industry. On the other hand to further expand the field of application, cardanol-based novolac scaffolds, used in the formulation of thermosetting resins by blending with a conventional epoxy resin, especially designed to be compatible with conventional bisphenol- A epoxy resins. In the present study resins have been synthesized by condensing diazotized p-anisidine cardanol dye with urea, resorcinol and furfural as condensing agent. The resins have been characterised by FT-IR, ¹H-NMR and XRD studies. Thermal behavior of the resins has been studied by Thermogravimetric Analysis (TGA) and Differential thermal analysis (DTA). The DTA, SEM and XRD data indicated the percentage of crystallinity associated with the thermal stability of the resins.

Keywords: Diazotized p-anisidine, cardanol, furfural, thermal stability, crystallinity.



INTRODUCTION

The petrochemicals that are used extensively in the worldwide chemical industry are limited resources that will be depleted within the foreseeable future, which has fueled efforts to find alternatives¹. Polymers produced from vegetable oils and their derivatives have excellent hydrolytic stability and thermochemical properties due to hydrophobic nature of side chains². Naturally occurring triacylglycerol oils are also significant starting material for the production of biodegradable polymers³. Cashewnut shell liquid (CNSL) an agricultural renewable resource material obtained as a byproduct of the cashew industry is one of the few major and economic sources of naturally occurring phenols and can be regenerated as a versatile and valuable raw material for polymer production⁴⁻⁷. Cardanol, a meta -substituted phenol from cashew nut shell liquid, a potential natural source for biomonomers, is used as the starting material for the synthesis of many industrial products⁸⁻¹⁰. Cardanol polymer has improved flexibility due to the internal plasticization effect of the long side chain and hence better processability. The side chain imparts hydrophobic nature to the polymer. Cardanol – formaldehyde resins have improved chemical resistance and mechanical properties than those of the pure phenol-formaldehyde resins¹¹. Cardanol- based epoxy resins are also used as binders for cathodic electrodepositions¹². Various copolymer resins can be synthesized by the condensation of a mixture of phenols, amines and formaldehyde¹³. Ion exchange copolymer resins have been synthesized from salicylic acid and formaldehyde¹⁴. Copolymer resins having good thermal stability have enhanced the scope for the development of polymeric materials. The study of the thermal degradation of copolymer resins have recently become a subject of interest. The present work deals with a modified network of resins derived from cardanol. Cardanol is coupled with diazotized p-anisidine and resins have been synthesized by condensing with furfural and aromatic and aliphatic compounds in the

presence of acid as catalyst. The resins have been characterised by FT-IR, ¹H-NMR, XRD and SEM studies. The thermal behavior of the resins has also been studied.

EXPERIMENTAL

Materials and methods

Cardanol was obtained from M/s Sathya Cashew Chemicals Ltd, Chennai. Furfural and methanol were received from M/s BDH India Ltd. p-Anisidine, resorcinol and urea were received from E.Merck, Germany. Sodium nitrite and potassium hydroxide were obtained from SD Fine Chemicals Ltd, Mumbai, India. The chemicals were used as received.

Infrared spectra of the resins were recorded with shimadzu FT-IR spectrophotometer by KBr pellet method. The ¹H-NMR spectra of the resins in CDCl₃ were recorded with a Bruker Avance 400 MHz spectrometer. XRD patterns of the resins were collected using a PANalytical X'Pert Pro MPD θ/θ goniometer with Cu-K α radiation, and fixed slit incidence (0.5 deg. divergence, 1.0 deg. anti-scatter, specimen length 10 mm) and diffracted (0.5 deg anti-scatter, 0.02 mm nickel filter) optics. Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) were performed simultaneously at a rate of 20°C/min in nitrogen using a V4 - 3A TA instrument (model SDTQ 600). The Scanning electron micrograms was obtained using Philips EM-400 scanning electron microscope system (Model PW 6585).

Synthesis of resins

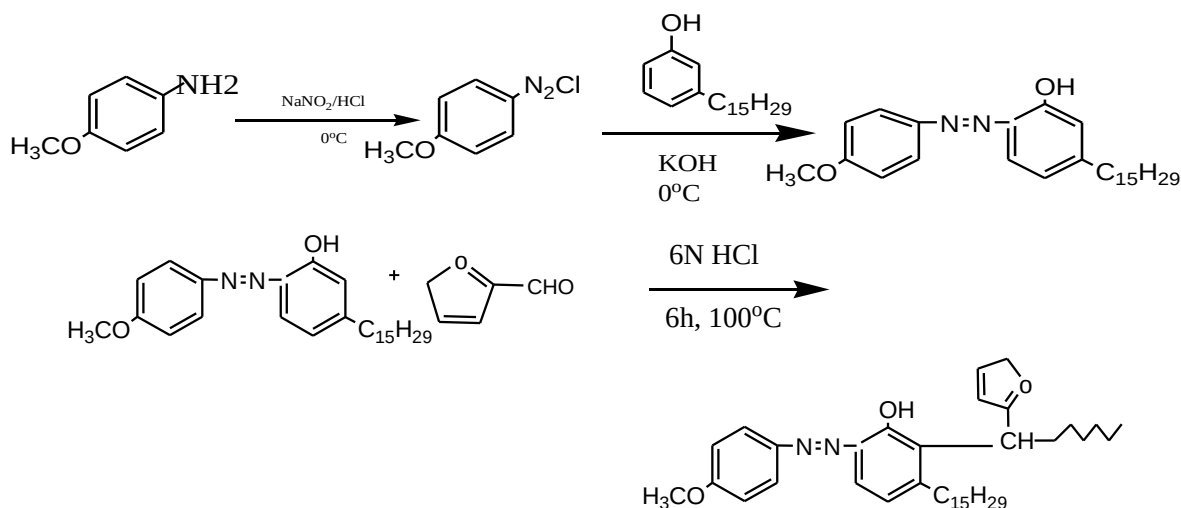
p-Anisidine (1.23 g) was diazotized using sodium nitrite (0.70 g) and dilute hydrochloric acid at 0°C with constant stirring. The diazonium salt solution was added drop wise to cardanol (3 g) dissolved in KOH (0.56 g) with constant stirring to give a reddish brown dye. The dye was stirred for a further period of 6 h and poured into dil HCl solution with constant stirring. The red dye was separated washed thoroughly with water and then dried. The dye was recrystallised from methanol water (1:1) mixture.

The homopolymer resin DAR-1 was prepared by refluxing a mixture of diazotised p-anisidine cardanol dye (2.18 g), furfural (3 ml) and 2 ml of 6N hydrochloric acid at 100°C for 4-6 h. A black colored solid formed was washed with 5N NaOH and then with hot distilled water and dried in vacuum. The copolymer resin DAR-2 was prepared by condensing resorcinol (0.52 g) with diazotized p-anisidine cardanol dye (2.18 g), furfural (3 ml) and 2 ml of 6N hydrochloric acid at 100°C for 4-6 h. A black colored solid formed was washed with NaOH and then with hot distilled water and dried in vacuum. The copolymer resin DAR-3 was prepared by condensing urea (0.60 g) with diazotized p-anisidine cardanol dye (2.18 g), furfural (3 ml) and 2 ml of 6N hydrochloric acid at 100°C for 4-6 h. A black coloured solid formed was washed with 5N NaOH and then with hot distilled water and dried in vacuum.

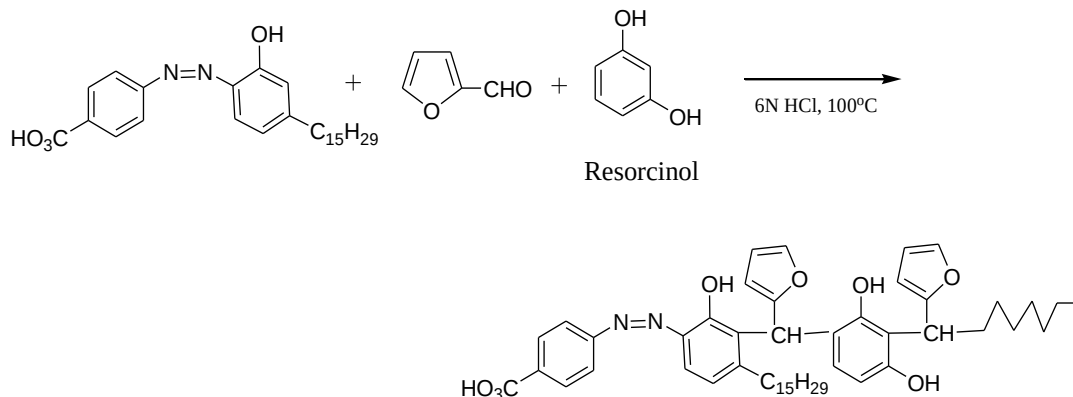
RESULTS AND DISCUSSION

Mechanism for the synthesis of resins

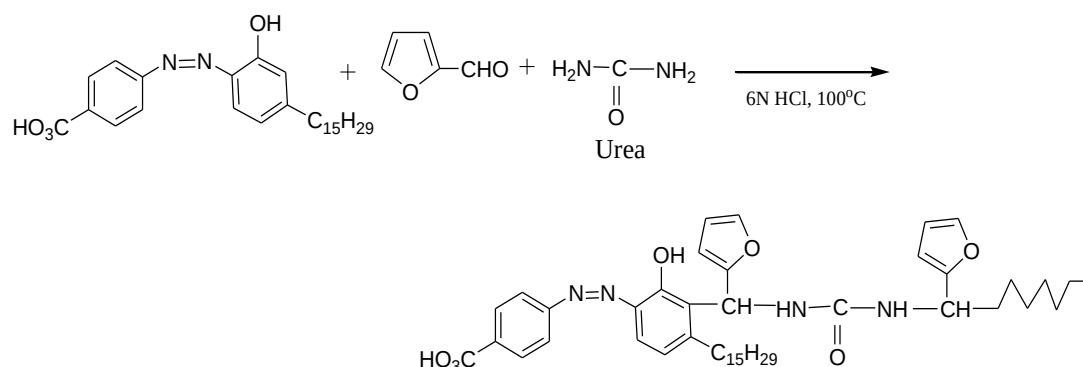
In the first step p-anisidine is diazotized in presence of sodium nitrite at 0°C and coupled with cardanol in presence of alcoholic KOH. In the second step the diazotized p-anisidine cardanol dye is condensed with furfural in presence of dilute hydrochloric acid as catalyst to form CH₂ cross linkages. The resorcinol and urea were also condensed with the dye and furfural as cross linking agent to form copolymer resins. This is illustrated in Scheme 1a, Scheme 1b and Scheme 1c.



Scheme 1a. Synthesis of diazotized p-anisidine cardanol furfural resin DAR-1



Scheme 1b. Synthesis of copolymer resin DAR-2



Scheme 1c. Synthesis of copolymer resin DAR-3

CHARACTERISATION

FT-IR Spectroscopy

The FT-IR spectra of the three resins are presented in Figure 1a to Figure 1c. A broad absorption band at 3433 cm⁻¹ is assigned to the stretching vibrations of hydrogen bonded phenolic hydroxyl group. A strong peak at 2924 cm⁻¹ shows the symmetrical CH₂ stretching of the side chain of cardanol and the peak at 2852 cm⁻¹ shows the presence of methylene bridge. The peak at 1438 cm⁻¹ shows the presence of azo group. In Figure 1b the peak at 1250 cm⁻¹ is due to the free O-H inplane bending of resorcinol. In Figure 1c the peak at 1600 cm⁻¹ is due to the C=O stretching frequency of acyclic urea group and the peak at 1030 cm⁻¹ is due to the C-N stretching present in urea.

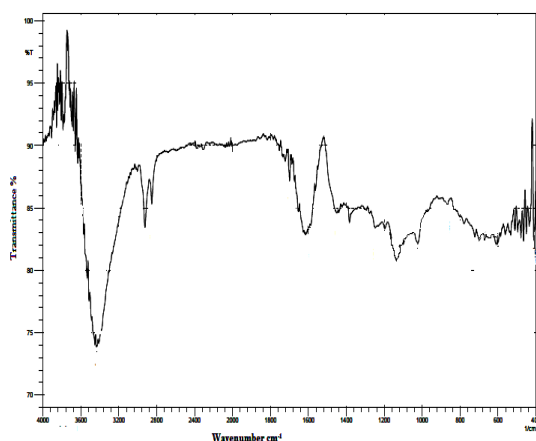


Figure 1a. FT-IR Spectrum of DAR- 1

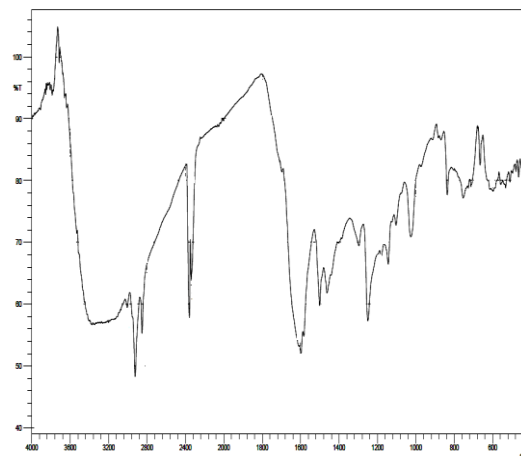


Figure 1b. FT-IR Spectrum of DAR- 2

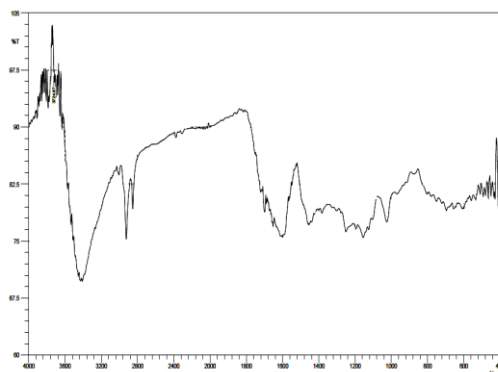


Figure 1c. FT IR Spectrum of DAR- 3

¹H-NMR Spectroscopy

The ¹H-NMR spectra of the three resins are presented in Figure 2a to Figure 2c. The peaks at 7.5 – 7.9 δ and 6.6 -6.9 δ are due to the presence of aromatic protons. The peak appears at 5.0 δ is due to the O-H proton of aromatic hydroxyl group. The multiplets at 1.9 – 2.7 δ are due to the presence of methylene protons and the peak at 0.8 δ is assigned to the presence of methyl protons. In Figure 2b the peaks at 5.2 δ-5.3 δ are due to the presence of aromatic hydroxyl protons of copolymer resin containing resorcinol. In Figure 2c the peak at 2.5δ to 2.7 δ are attributed to the presence of NH protons of amine group present in copolymer resin containing urea.

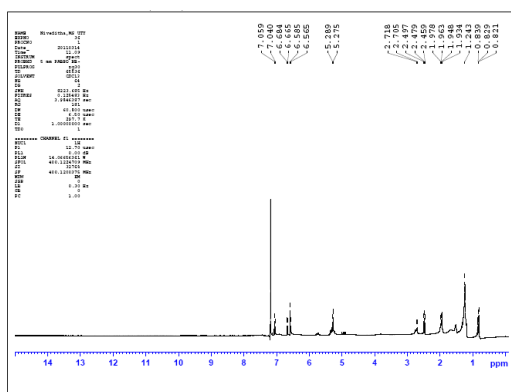


Figure. 2a. 1H-NMR Spectrum of DAR -1

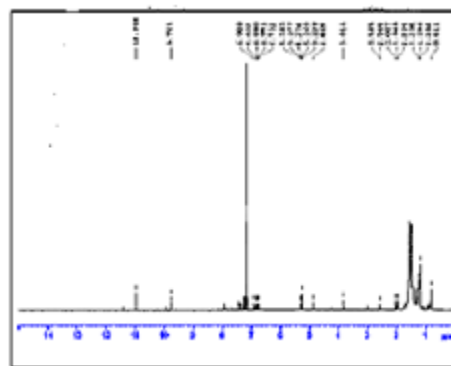


Figure 2b. 1H-NMR Spectrum of DAR -2

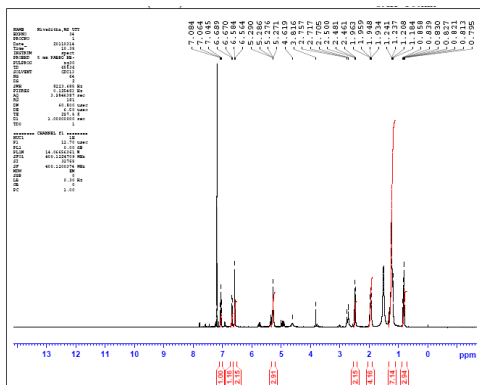


Figure 2c. 1H-NMR Spectrum of DAR- 3

X-ray diffraction studies

X-ray diffraction results of the three synthesized resins are presented in Table 1. Most of the polymers possess both crystalline and amorphous regions. The occurrence of both types of features in the polymer indicates that ordered and disordered regions coexist in crystalline polymers. The incorporation of additional monomer to the backbone disturbed its crystalline lattice and caused a marked change in the crystallinity¹⁵. Since crystallinity index gives a quantitative measure of the orientation of the cardanol furfural crystals in the polymer and the counter reading of highest peak intensity near 21° represents crystalline material and peak near 15° in the halo-pattern corresponds to the amorphous material in the polymer^{16,17}. It is evident from the Table 1 that the three resins DAR- 1, DAR- 2 and DAR-3 show 72 % crystallinity, 74 % crystallinity and 70 % crystallinity respectively. The crystallinity index of the resins DAR- 1, DAR- 2 and DAR- 3 are found to be 0.57, 0.66 and 0.57 respectively. The XRD patterns of the three resins are presented in Figures 3a to 3c. The intensity of the peak increases from DAR- 1 to DAR- 2 This may be due to the addition of aromatic compound resorcinol. The intensity of the peak decreases from DAR- 1 to DAR- 3 may be due to the addition of aliphatic compound urea.

Table 1: Percentage of crystallinity and crystallinity index of the three resins

Resin	Intensity of peak (cps)		Percentage of crystallinity	Crystallinity index
	Crystalline	Amorphous		
DAR-1	1315	560	70	0.57
DAR-2	1853	630	74	0.66
DAR-3	703	300	70	0.57

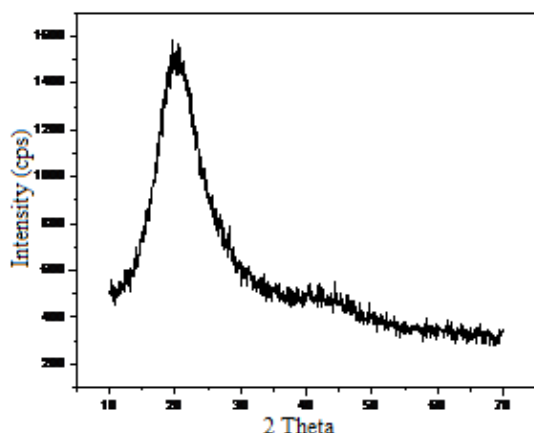


Figure 3a. XRD pattern of DAR-1

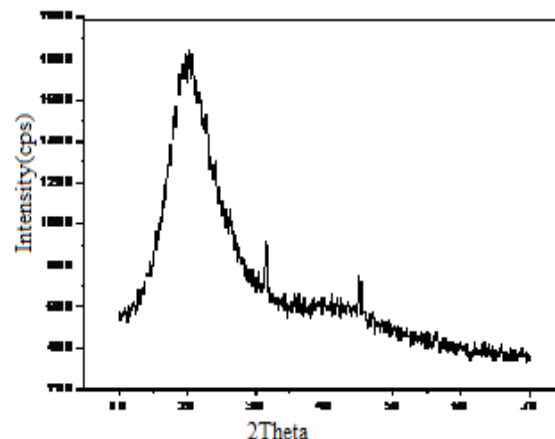


Figure 3b. XRD pattern of DAR- 2

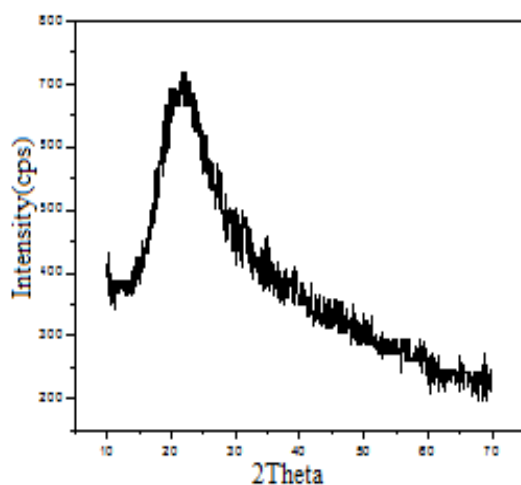


Figure 3c. XRD pattern of DAR- 3

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis of the resins is carried as a function of weight loss versus temperature (Table 2). The degradation occurred in various forms as dehydration, demethylation, decarboxylation, decrosslinking and chain scissions. The thermo gravimetric analysis (Figure 4a to Figure 4c) revealed that the resins decomposed in two distinct steps. In the first step of thermal degradation (100°-192°C) weight loss is upto 7%. This is due to the removal of moisture retained in the resin. A gradual weight loss occur in the temperature range 200°-400°C may be caused by thermal degradation of the small fragments like CH₃, OH and the side chain. The thermal degradation at 400o-600oC may be due to the depolymerisation and the cleavage of the aromatic ring in an oxydegradative manner.

Table 2: Thermogravimetric analysis of the synthesized resins.

Resin	% Weight loss at different temperature					
	100°C	200°C	300°C	400°C	500°C	600°C
DAR-1	0	3	20	28	65	72
DAR-2	2	7	26	33	52	58
DAR-3	2	7	26	53	56	68

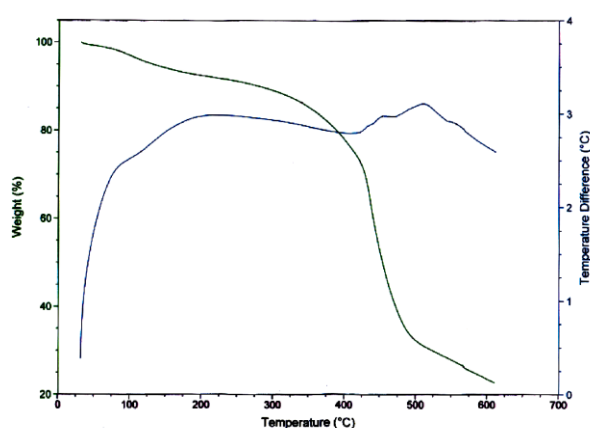


Figure 4a.TGA and DTA curves of DAR- 1

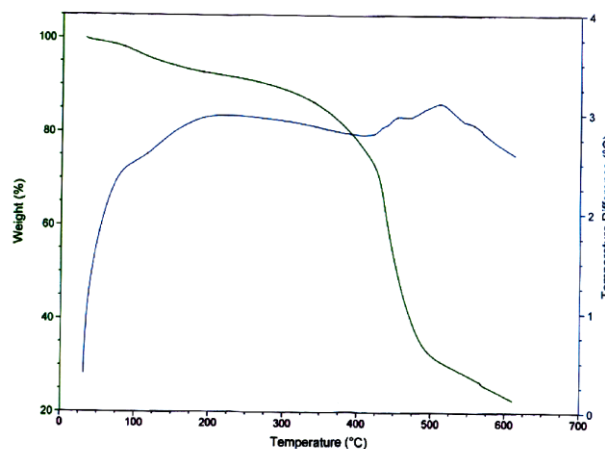


Figure 4b.TGA and DTA curves of DAR- 2

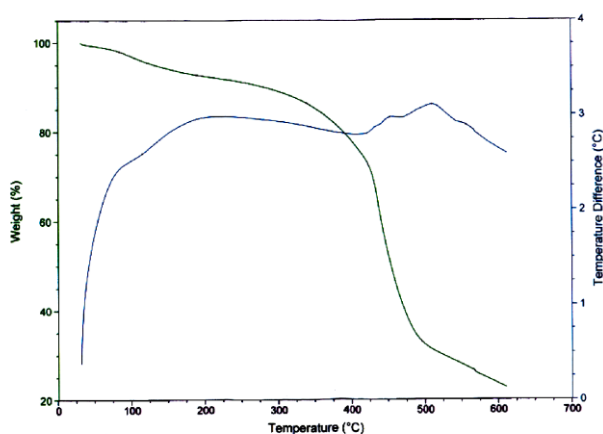


Figure 4c.TGA and DTA curves of DAR- 3

DIFFERENTIAL THERMAL ANALYSIS

TGA studies have been supported by the DTA evaluation pattern (Table 3). The DTA curve of DAR-1 shows two exotherms at 352°C and 450°C. The weak exotherm at 352°C is due to the cleavage of meta- substituted alkyl side chain of the phenyl ring. Similarly the resins DAR-2 and DAR-3 shows two exothermic peaks and the final combustion of the resins have been found to be at higher temperature than that of the DAR-1. The first transition peak reveals the dehydration, adsorption and oxidation from the semicrystalline host and the second major peak signified the irreversible dissociation of the crystallites followed by fusion.

Table 3: Differential thermal analysis of the resins

Resin	1 st exotherm (°C)	2 nd exotherm (°C)
DAR-1	352	450
DAR-2	420	478
DAR-3	407	475

SEM ANALYSIS OF THE HOMOPOLYMER RESIN

The SEM photograph of the resin DAR-2 is presented in the Figure 6(a). The SEM of DAR-2 shows the distorted geometry containing crystalline and amorphous region. This may be due to the disorientation of the crystals at the backbone.

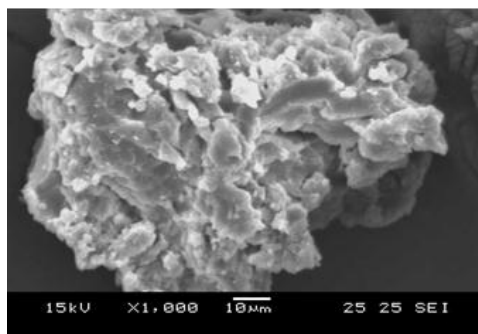


Figure 6a: SEM of the copolymer resin DAR-2

CONCLUSIONS

The degradation process for all the three resins DAR-1, DAR-2 and DAR-3, depends on the percentage of crystallinity. The percentage of crystallinity varied in copolymer resins is due to disorientation of diazotized p-anisidine cardanol furfural crystals to the backbone during copolymerization. Thermal study of the resins shows the thermal stability of the resins at high temperature. Copolymer resin containing aromatic compound is thermally more stable than aliphatic compound.

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