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Thermal Degradation and XRD studies of Diazotised-*p*-sulphanilic acid dye based resins synthesized from Renewable resource

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ABSTRACT

Recently, biobased polymers have received great interest due to their ecofriendly properties towards environment. As a substitute to the use of conventional reinforcing synthetic resins, biobased resins were synthesized from renewable resource cardanol, the meta- substituted phenolic compound isolated from Cashew nut shell liquid (CNSL), a byproduct of cashew industry. The resins have been synthesized by condensing diazotized-*p*-sulphanilic acid cardanol dye with formaldehyde, *o*-amino benzoic acid and thiourea. The resins have been characterized 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). Thermal stability of the resins has been compared by analyzing TG data which provided the kinetic parameter activation energy associated with the thermal decomposition. The DTA and XRD data indicated the percentage of crystallinity associated with the thermal stability of the resins.

Key words: Diazotised- *p*-sulphanilic acid, cardanol, thermal stability, crystallinity, activation energy.

INTRODUCTION

Resins are materials widely used in paint, varnishes, coating, adhesives and lacquers [1-3]. These resins are synthesized by the reaction of phenols with formaldehyde or other aldehyde [4-6]. There is a wide range of commercially available acrylates, isocyanates, phenols and crosslinking agents which has lead to many varied formulation possibilities for resins [7-9]. These starting monomers are derived from fossil feedstocks. Due to the high rate of depletion of petroleum resources and their escalating prices, polymer chemists have turned their attention to obtain monomers and polymers from renewable resource materials [10-12]. Cashew nut shell liquid (CNSL) an agricultural byproduct of cashew nut industry, represents the largest readily available bioresource of alkenyl phenolic compounds such as cardanol, cardol, anacardic acid and methyl cardol [13,14]. Phenolic resins derived from condensation of cardanol and formaldehyde has excellent adhesive properties and structural integrity. They can be used as high temperature resistant polymers [15, 16]. This paper presents a modified network of resins derived from cardanol. Cardanol is coupled with diazotised sulphanilic acid and resins are synthesized by condensing with formaldehyde, aromatic and aliphatic compounds in the presence of acid as catalyst. The structural confirmation of the resins is established by FT-IR and ¹H-NMR spectral studies. X- ray Diffraction studies and thermal behavior of the resins have also been studied.

MATERIALS AND METHODS

Cardanol was obtained from M/s Sathya Cashew Chemicals Ltd, Chennai. Formaldehyde (40%) solution and methanol were received from M/s BDH India Ltd. Sulphanilic acid, o-amino benzoic acid, thiourea, sodium nitrite and potassium hydroxide were obtained from SD Fine Chemicals Ltd, India. All the chemicals were used as received.

Ultraviolet spectral analysis was carried out in a UV-VIS double beam spectrophotometer 2201 Systronics. Infrared spectra of the resins were recorded with Shimadzu FT-IR spectrophotometer. The ¹H-NMR spectra of the resins in CDCl₃ were recorded with a Bruker Avance III 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. Percentage of crystallinity [17] and crystalline index [18, 19] were calculated using the following equation:

$$\text{Percentage of crystallinity (Xc)} = [I_c / (I_c + I_a)] \times 100$$

Crystallinity Index (CI) = $(I_c - I_a) / I_c$; where I_c and I_a are the intensity of crystalline and amorphous peaks.

TGA and DTA of all copolymer resins have been performed at a rate of 20°C/min in nitrogen using a Universal V4-3A TA instrument (model SDTQ 600). Thermograms were interpreted and analyzed to obtain information about the percentage weight loss at different temperatures. The kinetic parameters and the activation energy (E_a) have been calculated from the data obtained from the thermograms. It helps us to decide the thermal stability of copolymer resins.

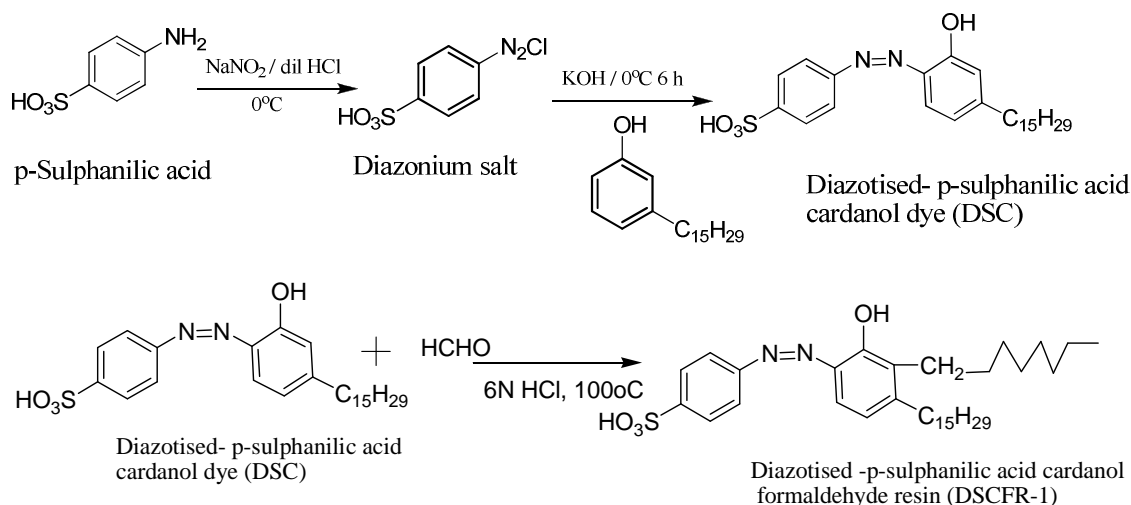
Synthesis of resins

p-Sulphanilic acid (1.73 g) was diazotised using sodium nitrite (0.70 g) and dilute Hydrochloric acid at 0°C with constant stirring. This diazonium salt solution was added drop wise to cardanol (3.0 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 recrystallized from methanol water mixture. The homopolymer resin, DSCFR-1 was prepared by refluxing a mixture of diazotised sulphanilic acid cardanol dye (1.94 g), formaldehyde (2 ml) and 2 ml of 6N hydrochloric acid at 100°C for 4-6 h. A reddish brown colored solid product was formed, washed with 5N NaOH and then with hot distilled water and dried in vacuum. The copolymer resin DSCFR-2 was prepared by condensing ortho amino benzoic acid (0.56 g) with diazotised sulphanilic acid cardanol dye (1.94 g), formaldehyde (2 ml) and 2 ml of 6N hydrochloric acid at 100°C for 4-6 h. The solid product formed was washed with 5N NaOH and then with hot distilled water and dried in vacuum. The copolymer resin DSCFR-3 was prepared by condensing thiourea (0.76 g) with diazotised sulphanilic acid cardanol dye (1.94 g), formaldehyde (2 ml) and 2 ml of 6N hydrochloric acid at 100°C for 4-6 h. The solid product formed was washed with 5N NaOH and then with hot distilled water and dried in vacuum.

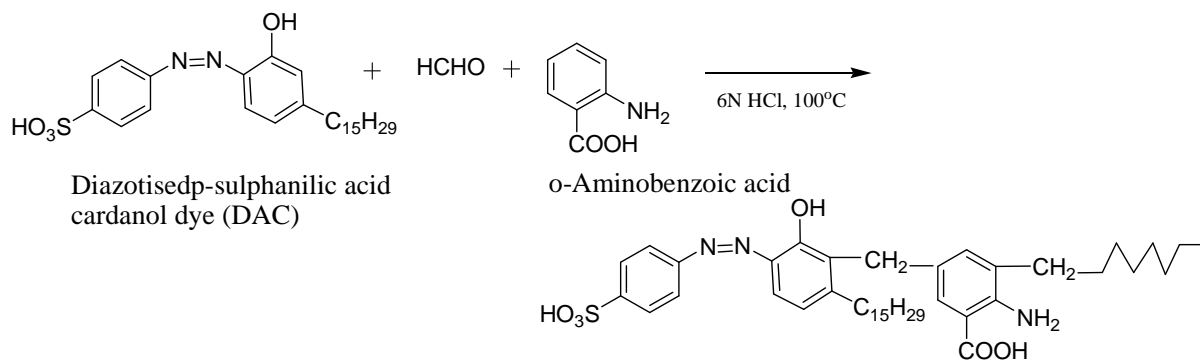
RESULTS AND DISCUSSION

Mechanism for the synthesis of resins

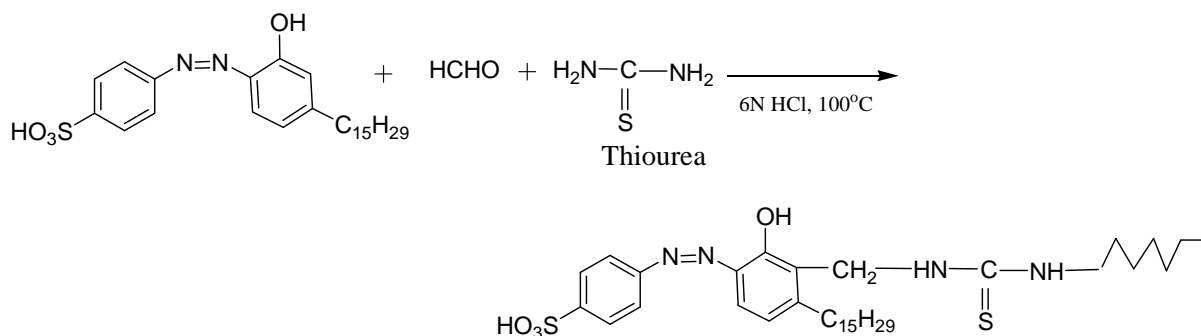
In the first step sulphanilic acid is diazotised in presence of sodium nitrite at 0°C and coupled with cardanol in presence of alcoholic KOH. In the second step the diazotised sulphanilic acid cardanol dye is condensed with formaldehyde in presence of HCl as catalyst to form CH₂ cross linkages. The o- amino benzoic acid and thiourea were also condensed with the dye and formaldehyde as cross linking agent to form copolymer resins. This has been illustrated in Scheme 1, Scheme 2 and Scheme 3.



Scheme 1. Synthesis of diazotised sulphanilic acid cardanol formaldehyde resin (DSCFR-1).



Scheme 2. Synthesis of diazotised sulphanilic acid cardanol formaldehyde o-aminobenzoic acid resin (DSCFR-2).



Scheme 3. Synthesis of diazotised sulphanilic acid cardanol formaldehyde thiourea resin (DSCFR-3).

Characterization

Characterization by UV-VIS and FT-IR Spectroscopy

The UV-VIS spectra of all the resins in CHCl₃ show two characteristic peaks at 238 nm and 244 nm which are due to $\pi \rightarrow \pi^*$ transition of aromatic nuclei and the absorption band at 358 nm is due to $n \rightarrow \pi^*$ transition of azo group. The FT-IR spectra of the three resins are shown in Fig. 1, Fig. 2 and Fig. 3 respectively. A broad absorption band at 3433 cm⁻¹ may be assigned to the stretching vibrations of hydrogen bonded phenolic hydroxyl group. A strong peak at 2924 cm⁻¹ is ascribed to O-H stretching of SO₃H group. The peak at 1438 cm⁻¹ shows the presence of azo group and the peak at 2852 cm⁻¹ shows the presence of methylene bridge. In Fig. 2 the peak at 1224 cm⁻¹ is due to the N-H

stretching frequency of ortho aminobenzoic acid and the peak at 1656 cm^{-1} is due to the C=O stretching frequency of COOH group. In Fig. 3 the peak at 1433 cm^{-1} is due to the C=S stretching frequency and the peak at 1030 cm^{-1} is due to the C-N stretching of $\text{—}\overset{\text{S}}{\parallel}{\text{C}}\text{—NH}_2$ group in thiourea.

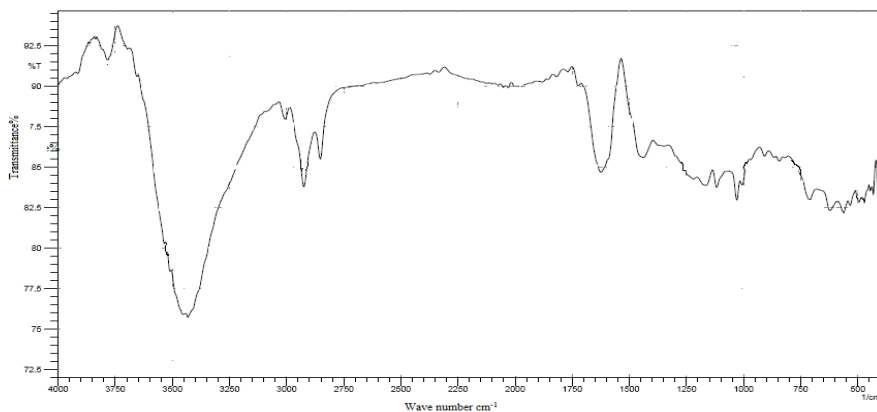


Fig. 1. FT-IR spectrum of DSCFR-1

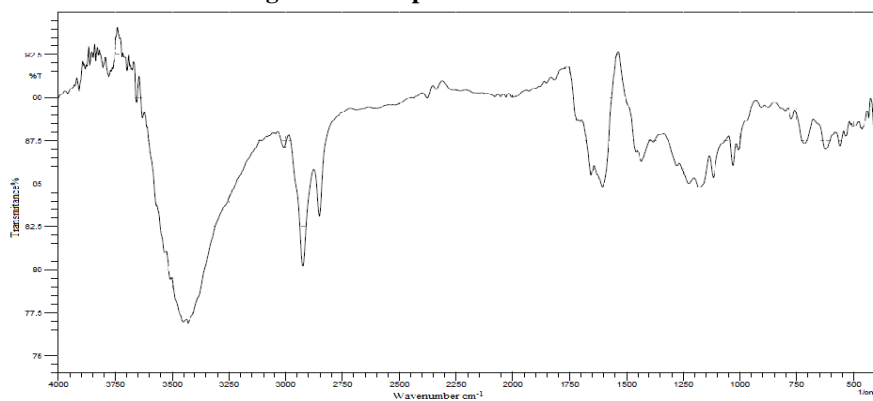


Fig. 2. FT- IR spectrum of DSCFR-2

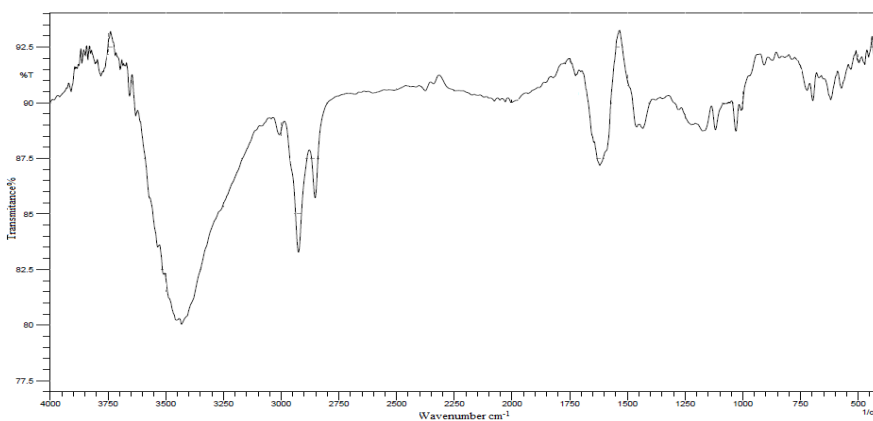


Fig. 3. FT- IR spectrum of DSCFR-3

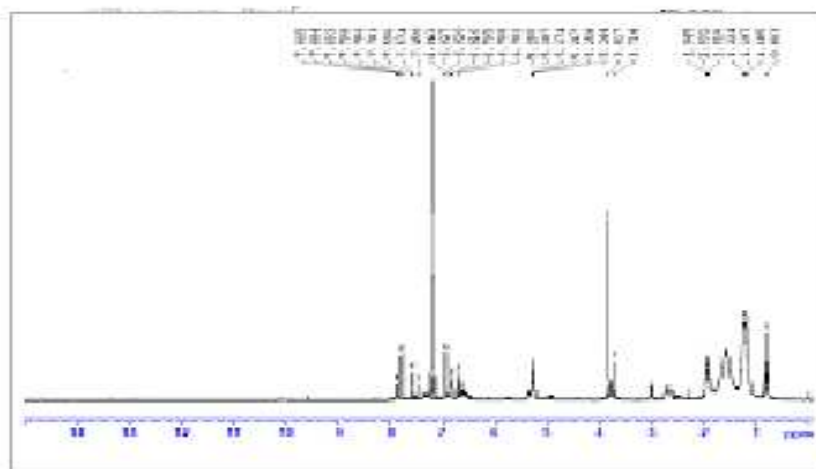


Fig. 4. ¹H- NMR spectrum of DSCFR-1

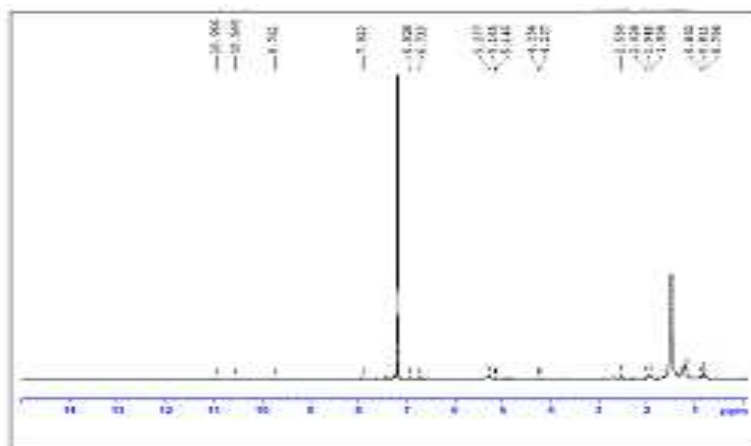


Fig. 5. ¹H-NMR spectrum of DSCFR-2

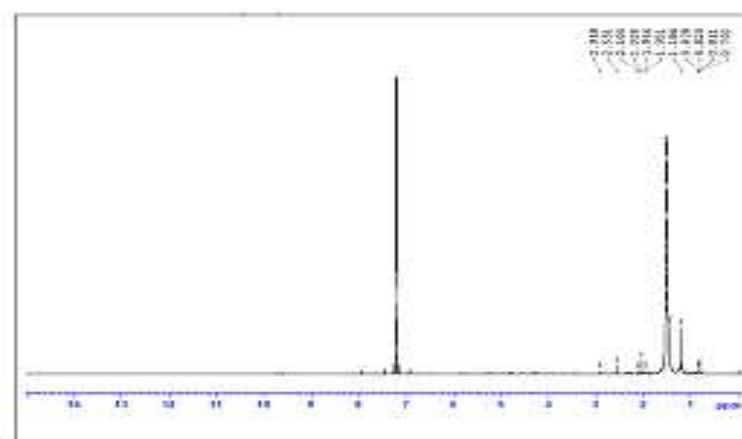


Fig. 6. ¹H-NMR spectrum of DSCFR-3

Characterization by $^1\text{H-NMR}$ Spectroscopy

The $^1\text{H-NMR}$ spectra of the three resins are presented in Fig.4, Fig. 5 and Fig. 6 respectively. The peaks at 7.5 – 7.9 ppm and 6.6 – 6.9 ppm are due to the presence of aromatic protons. The singlet at 2.0 ppm is attributed to the OH proton of SO_3H group. The singlet at 5.0 ppm is due to the O-H proton of aromatic hydroxyl group. The multiplets at 2.9 – 3.4 ppm are due to the presence of methylene protons and the peak at 1.8 ppm is assigned to the presence of methyl protons.

X-ray Diffraction studies

The calculation of percentage of crystallinity of polymeric materials by X-ray diffraction may be rendered difficult by the number of overlapping crystalline phases and amorphous halos that contribute to the diffraction pattern. Phenol formaldehyde resins are crystalline in nature. The incorporation of additional monomers to phenol formaldehyde backbone disturbed its crystallinity [21]. It is evident from the Table 1 the resin DSCFR-1 shows 70 % crystallinity, DSCFR-2 shows 72 % crystallinity and DSCFR-3 shows 63.6 % crystallinity. The crystallinity index of the resins DSCFR-1, DSCFR-2 and DSCFR-3 are found to be 0.57, 0.61 and 0.43 respectively. The XRD pattern of all the resins was shown in Fig.7, Fig. 8 and Fig. 9 respectively. The resins DSCFR-1, DSCFR-2 and DSCFR-3 exhibited a peak at (2θ) 20.5°C, 20°C and 19.8°C respectively. The percentage of crystallinity of the resins decreases on copolymerization. The percentage of crystallinity decreases by adding thiourea as comonomer. This is due to dis-orientation of the diazotised-p-sulphanilic acid cardanol formaldehyde crystals at the backbone. Therefore on copolymerization crystallinity decreases rapidly, with reduction in stiffness and hardness. Such morphological transformations are due to the addition of the amorphous content, increase in molecular weight and cross linking network. In case of DSCFR-2, the percentage of crystallinity increases by adding *o*-amino benzoic acid as comonomer. This may be due to the presence of aromatic compound as comonomer in the copolymer resin²².

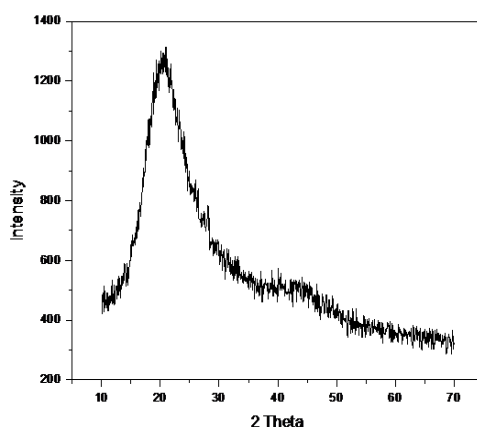


Fig.7. XRD pattern of DSCFR-1

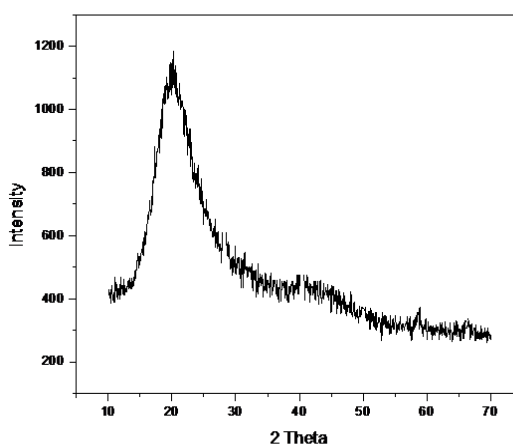


Fig. 8. XRD pattern of DSCFR-2

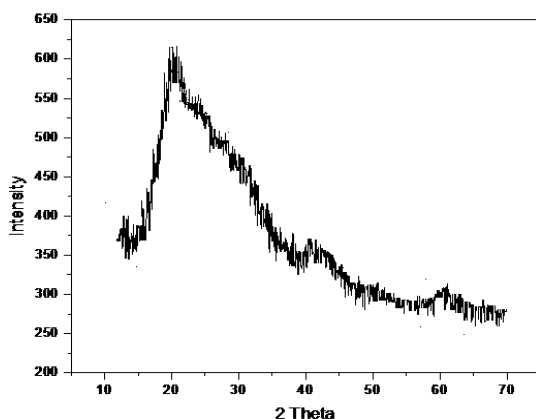


Fig. 9. XRD pattern of DSCFR- 3

Table 1. Percentage of crystallinity and crystalline index of the resins

Resin	Intensity of		Percentage of crystallinity (Xc)	Crystalline index (CI)
	Crystalline peak	Amorphous peak		
DSCFR- 1	1315	560	70.0	0.57
DSCFR- 2	1197	465	72.0	0.61
DSCFR- 3	613	350	63.6	0.43

Thermogravimetric analysis

Thermogravimetric analysis of the resins was 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.

TGA of DSCFR-1 homopolymer resin

Thermogram of the resin DSCFR-1 is shown in Fig.10 which depicts two steps decomposition in the temperature range 100°C - 600°C, after loss of water molecule (2%). First step decomposition starts from 200°C - 400°C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group which is found to be 7.5% -19%. Second step decomposition starts from 400 °C - 600 °C, which corresponds to the removal of side chain as well as ring stripping which is found to be 78%.

Table 2 . Thermogravimetric analysis of the resins

Resins	Percentage weight loss at various temperature					
	100°C	200°C	300°C	400°C	500°C	600°C
DSCFR- 1	1	2	7.5	19	74	78
DSCFR- 2	1.5	3	7	14	70	76
DSCFR- 3	0	2	9	20	79	84

TGA of DSCFR- 2 copolymer resin

Thermogram of the resin DSCFR-2 is shown in Fig.11 which depicts two steps decomposition in the temperature range 100°C - 600°C, after loss of water molecule (2%). First step decomposition starts from 200°C - 400°C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group which is found to be 14%. Second step decomposition starts from 400°C - 600 °C, corresponds to the removal of side chain as well as ring stripping and is found to be 76%.

TGA of DSCFR-3 copolymer resin

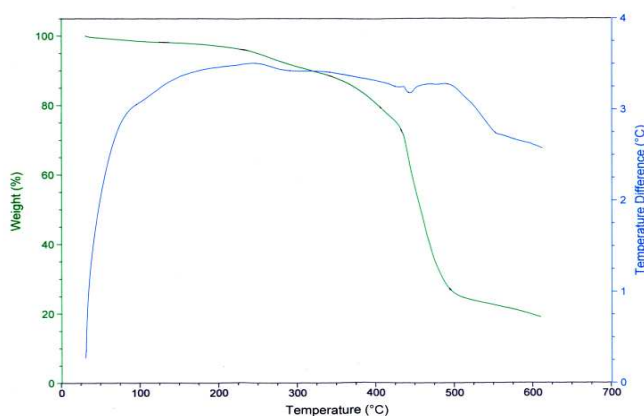
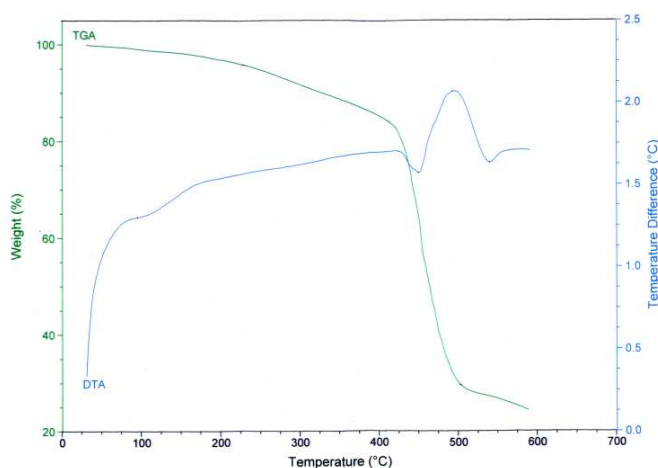
Thermo gram of the resin DSCFR-3 is shown in Fig.12 which shows two steps decomposition in the temperature range 100°C - 600°C, after loss of water molecule (2%). First step decomposition starts from 200°C - 400°C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group which is found to be 20 %. Second step decomposition starts from 400°C - 600°C, found to be 84% which corresponds to the removal of side chain as well as ring stripping.

Differential thermal analysis

DTA curves are recorded simultaneously with TGA curves. In the DTA trace the base line remains unchanged as long as there is no thermal transition in the sample. First order transition namely crystallization and melting appear 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 shape. DTA curves presented in Fig.10, Fig.11 and Fig.12 respectively of the three resins show two exotherms around 425°C and 494°C, which is due to the cleavage of meta-substituted alkyl side chain in the phenyl ring of the cardanol moiety.

Table 3. Differential thermal analysis of the resins

Resin	1 st exotherm (°C)	2 nd exotherm (°C)
DSCFR-1	442	492
DSCFR-2	425	494
DSCFR-3	420	493

**Fig. 10. TGA & DTA curve of DSCFR-1****Fig.11. TGA & DTA curve of DSCFR-2**

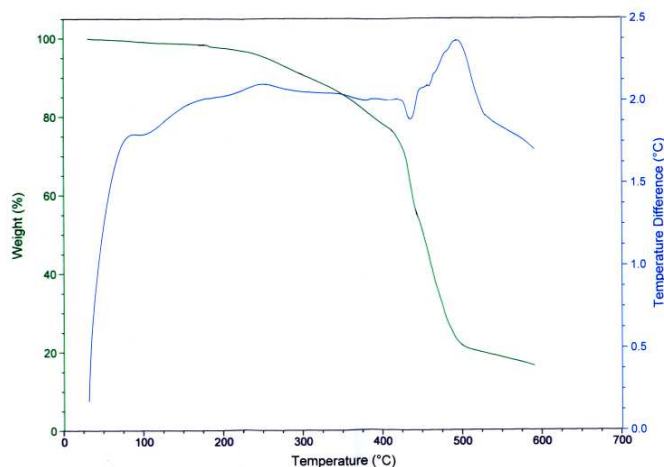


Fig. 12. TGA & DTA curve of DSCFR-3

CONCLUSION

X-ray diffraction studies show that the percentage of crystallinity decreases by adding thiourea as comonomer and the percentage of crystallinity increases by adding o-amino benzoic acid as comonomer. Thermogravimetric analysis of the resins shows two steps decomposition. First step decomposition represents the degradation of side chain attached to aromatic nucleus and hydroxyl group. Second step decomposition corresponds to the removal of side chain as well as ring stripping. The three resins show good thermal stability up to 420°C.

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