



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

*International Journal of Recent Scientific Research*  
Vol. 6, Issue, 5, pp.4050-4055, May, 2015

**International Journal  
of Recent Scientific  
Research**

## RESEARCH ARTICLE

# SYNTHESIS, CHARACTERIZATION AND XRD STUDIES OF DIAZOTISED RESINS FROM BIO RESOURCE

Mythili CV<sup>1</sup> and Kalyani V\*<sup>1</sup>

<sup>1</sup>Department of Chemistry, Rani Anna Govt College for Women, Tirunelveli, Tamil Nadu, India

<sup>1</sup>Department of Chemistry, Sardar Raja College of Engineering, Alangulam, Tirunelveli, Tamil Nadu, India

### ARTICLE INFO

#### Article History:

Received 2<sup>nd</sup>, April, 2015  
Received in revised form 10<sup>th</sup>,  
April, 2015  
Accepted 4<sup>th</sup>, May, 2015  
Published online 28<sup>th</sup>,  
May, 2015

#### Key words:

Diazotised p- ChloroAniline,  
cardanol, formaldehyde resins,  
physicochemical properties,  
crystallinity .

**Copyright** © Mythili CV and Kalyani V., This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

### INTRODUCTION

Renewable sources as a substitute to petrochemical derivatives have attracted the attention of many researchers for the synthesis of polymers. Cashew-nut shell liquid (CNSL) a byproduct of cashew industry is a unique natural source of unsaturated long chain phenol (Guo *et al.*, 2002; Petrovic *et al.*, 2005; Roloff *et al.*, 2005; Kong and Narine, 2007; Narine *et al.*, 2007). The phenolic nature of cardanol has promoted researchers to react with formaldehyde or with other aldehyde to produce numerous resinous materials (Phanikumar *et al.*, 2002; Oghome and Kehinde, 2004). In place of cardanol, many workers have synthesized and characterized a number of polymers from cardanol derivatives (Das *et al.*, 1998; Mohapatra *et al.*, 1994; Mishra D.K., Mishra *et al.*, 1996; Nayak *et al.*, 1999; Guru *et al.*, 1999). Cardanol based polymers have wide applications in composites (Tan, 1997; Sathiyalekshmi, 1993), polyurethanes (Sathiyalekshmi and Gopalakrishnan, 2000; Mythili *et al.*, 2004; Das and Lenka, 2011; Athawale and Shetty, 2010), surface coating (Santeusano *et al.*, 2013) and few others (Unikrishnan and Thachil, 2006; Unikrishnan and Thachil, 2008; Devi and Srivastava, 2006; Devi and Srivastava, 2007). This communication reports on the synthesis, characterization and XRD analysis of resins obtained by condensation of cardanol-

### 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. P-Chloroaniline has been diazotised and coupled with cardanol to prepare diazotised p- Chloroaniline cardanol dye (bio monomer). It was characterised by FT-IR, and <sup>1</sup>H-NMR studies. The obtained dye has been condensed with formaldehyde in presence of 3N.H<sub>2</sub>SO<sub>4</sub> to give diazotized p- ChloroAniline cardanol formaldehyde (homo polymer) resin. TLC and physicochemical properties of cardanol and homopolymer resins were studied. The condensed product has been allowed to react with organic compounds such as 4-hydroxy benzoic acid and ethylene glycol to form copolymer resins. The resins were characterized by FT-IR <sup>1</sup>H-NMR and XRD studies. XRD data indicated the percentage of crystallinity of the resins.

based dyes with formaldehyde in the presence of 3N.H<sub>2</sub>SO<sub>4</sub> as catalyst. The condensed product has been allowed to react with co monomer such as 4-hydroxy benzoic acid and ethylene glycol. The resin has been characterized by FT-IR, <sup>1</sup>H-NMR spectral studies. XRD analysis 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). 4-hydroxy benzoic acid & ethylene glycol were received from E. Merck, (Germany). The chemicals were used as received. Infrared spectra were taken in a Shimadzu-FT-IR spectrophotometer by KBr pellet method. <sup>1</sup>H-NMR spectra were recorded using Bruker avance 400 MHz FT <sup>1</sup>H-NMR spectrometer. XRD patterns of the resins were collected using a PANalytical X'Pert Pro MPD / goniometer with Cu-K 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 (Agarwal *et al.*, 2003) and crystalline index (Segal *et al.*, 1959 ; Reddy, 2005) were calculated using the following equation:

\*Corresponding author: **Kalyani V**

Department of Chemistry, Sardar Raja College of Engineering, Alangulam, Tirunelveli, Tamil Nadu, India

Percentage of crystallinity ( $X_c$ ) =  $[I_c / (I_c + I_a)] \times 100$   
 Crystallinity Index (CI) =  $(I_c - I_a) / I_c$ ; where  $I_c$  and  $I_a$  are the intensity of crystalline and amorphous peaks.

### Synthesis of diazotised p-Chloro Aniline cardanol dye (DC)

To 2.2 g of p-Chloro Aniline dissolved in 10ml con.HCl and 10ml hot distilled water. 1.2 g of sodium nitrite solution was added at 0°C with constant stirring. 5 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°-10°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 (C) was recrystallized from methanol water mixture. The yield was 85 %.

### Synthesis of diazotised p-Chloro Aniline cardanol-formaldehyde resin (DCF)

2.2 g of diazotised p-Chloro Aniline cardanol dye was condensed with 2 ml of formaldehyde and 2 ml of 3N. H<sub>2</sub>SO<sub>4</sub>. The reaction was carried out at 100°C for 6 hours. A dark red brown colored solid diazotised p-Chloro Aniline cardanol formaldehyde resin (CH) obtained was washed well with dil NaOH and dried in vacuum.

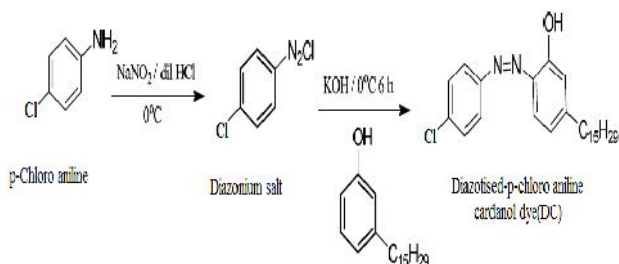
### Synthesis of diazotised p-Chloro Aniline cardanol-4-hydroxy benzoic acid organic compound resins (DCF-1)

2.15 g of diazotised p-Chloro Aniline cardanol dye, 2 ml formaldehyde, 0.52 g 4-hydroxy benzoic acid and 2 ml 3N. H<sub>2</sub>SO<sub>4</sub> were heated at 100°C in a round bottom flask fitted with condenser at constant stirring using mechanical stirrer for 6 hours. The resin (CC) was washed with dilute NaOH and then with hot distilled water and then dried in vacuum.

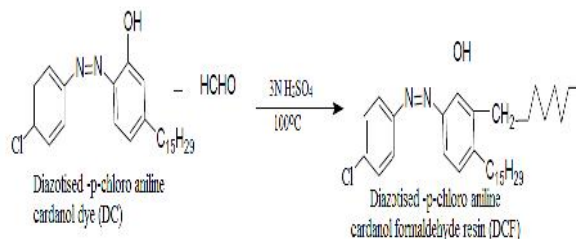
## RESULTS AND DISCUSSION

### Mechanism for the synthesis of resins

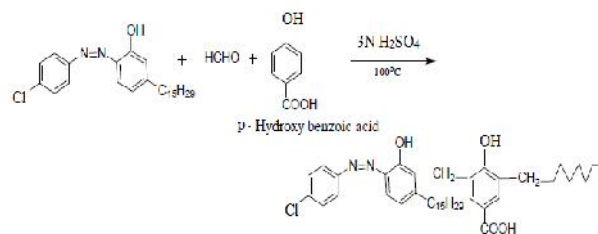
In the first step cardanol in alcoholic KOH is treated with diazotized p-Chloro Aniline (Scheme 1). The diazotised p-Chloro Aniline cardanol dye was condensed with formaldehyde in presence of 3N.H<sub>2</sub>SO<sub>4</sub> acid as catalyst to form CH<sub>2</sub> cross linkages (Scheme 2). The 4-hydroxy benzoic acid and ethylene glycol were also condensed with the dye and formaldehyde to form copolymer resins (Scheme 3 Scheme 4).



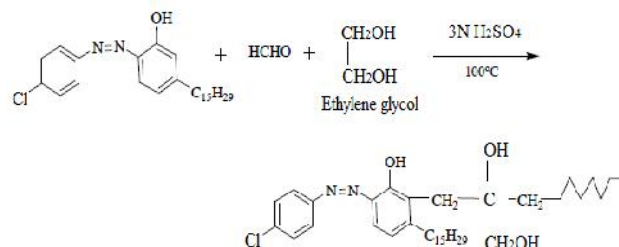
Scheme 1 Synthesis of diazotised p-Chloro Aniline cardanol dye (DC)



Scheme 2 Synthesis of Homopolymer resin (DCF)



Scheme 3 Synthesis of copolymer resin (DCF-1)



Scheme 4 Synthesis of copolymer resin (DCF-2)

### FT IR and <sup>1</sup>H-NMR Spectrum of Cardanol(C)

In the IR spectra of cardanol, (Fig. 1). The spectrum shows broad peak at 3381 cm<sup>-1</sup> for O-H stretching frequency of hydrogen bonded phenolic OH group. The peak at 3007 cm<sup>-1</sup> shows the aromatic C-H stretching. The peaks at 2924-2854 cm<sup>-1</sup> show the asymmetric C-H stretching of the side chain of cardanol. The peaks at 995-869 cm<sup>-1</sup> confirm that the substituent is at the meta position of phenol. The peak at 779-694 cm<sup>-1</sup> shows -C=C- stretching in the side chain of cardanol. The strong peak at 1591cm<sup>-1</sup> shows the unsaturated long chain of cardanol. The multiplet at 6.6-6.9 is due to the aromatic protons of benzene nuclei of cardanol. The peak at 5.3 is due to phenolic hydroxyl proton. The peak at 1.3-2.5 ppm shows the methylene group of the long alkyl side chain of cardanol.

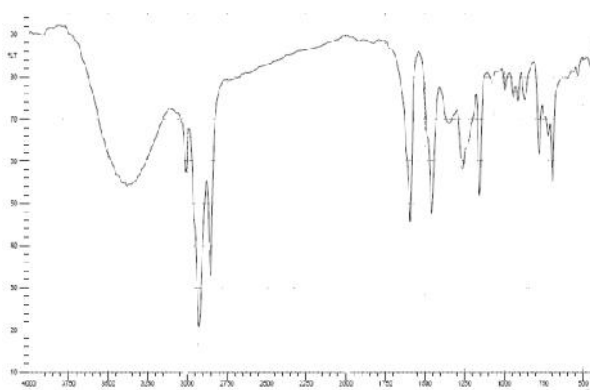


Figure 1 FT-IR spectrum of C

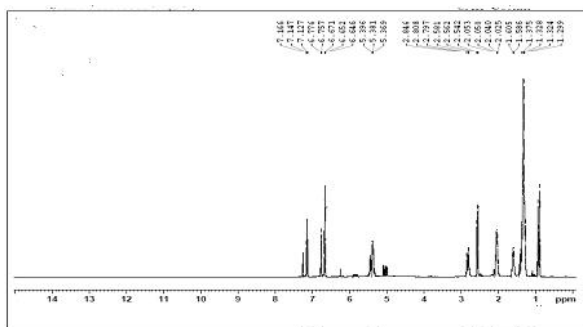


Figure 2 <sup>1</sup>H-NMR spectrum of C

**FT IR and <sup>1</sup>H-NMR Spectrum of diazotised p- Chloroaniline cardanol dye (DC)**

IR Spectral data (Fig. 3) of diazotised p- Chloroaniline cardanol dye (DC) reveal that the diazotization of p- Chloroaniline with cardanol. The peak at 1458 cm<sup>-1</sup> shows the presence of azo group. phenolic hydroxyl group stretching appears at 3404 cm<sup>-1</sup>. The peak at 2926 cm<sup>-1</sup> shows the symmetrical CH<sub>2</sub> stretching of the side chain of cardanol. The peak at 750cm<sup>-1</sup> shows the C-Cl stretching of p-chloro aniline. In the <sup>1</sup>H-NMR spectra (Fig. 4) of diazotized p- Chloroaniline cardanol dye, the peak at 6.7- 6.8 ppm shows the aryl protons of benzene nuclei and the peak at 5.0 ppm shows the phenolic hydroxyl group. The peak at 7.4-7.8 ppm shows the aryl protons of p- Chloroaniline. The peak at 1.3- 2.5 ppm shows the methylene group of the long alkyl side chain of cardanol. The peak at 0.9 ppm shows the terminal methyl group of side chain of cardanol.

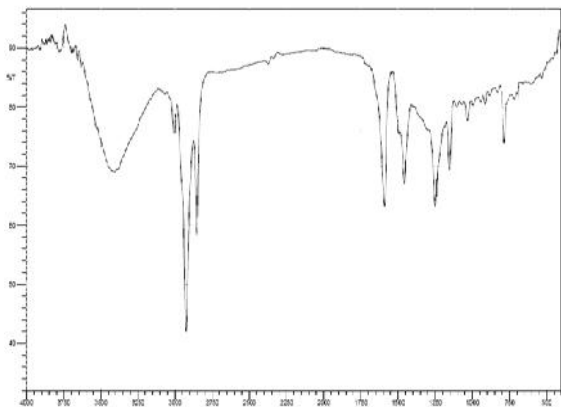


Figure 3 FT-IR spectrum of DC

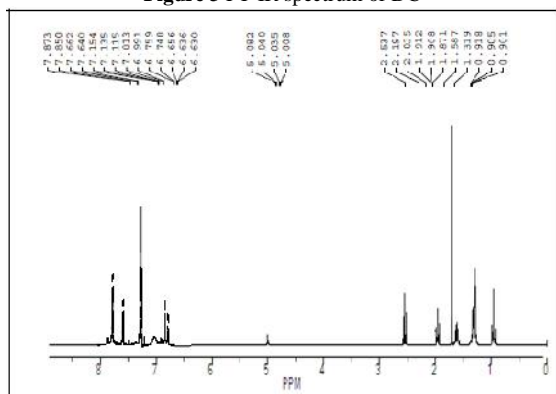


Figure 4 <sup>1</sup>H-NMR spectrum of DC

**FTIR and <sup>1</sup>H-NMR Spectrum of diazotised p- Chloroaniline cardanol formaldehyde resin (DCF)**

In the IR Spectra of resin DCF (Fig. 5) the peak at 3426 cm<sup>-1</sup> shows the O-H stretching frequency of hydrogen bonded phenolic OH group. The peak at 2924 cm<sup>-1</sup> shows the symmetrical CH<sub>2</sub> stretching of the side chain of cardanol and 2853 cm<sup>-1</sup> shows the CH<sub>2</sub> group in formaldehyde. The peak at 1458 cm<sup>-1</sup> shows the presence of azo group. In the <sup>1</sup>H-NMR spectra of resin DCF (Fig. 6) the peak at 7.5-6.8 ppm shows the aryl protons of cardanol and the peak at 7.8-7.4 ppm shows the aryl protons of p- Chloroaniline. The peak at 1.2-2.5 ppm show the methylene group of the side chain of cardanol and the peak at 5.0 ppm shows the phenolic hydroxyl group.

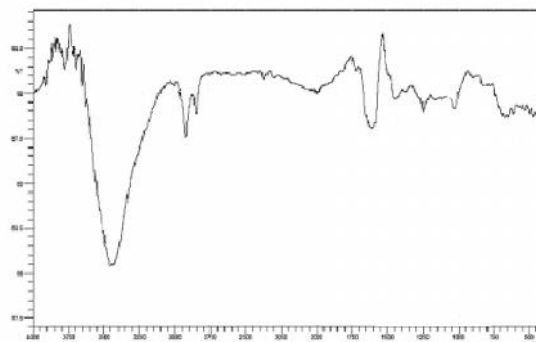


Figure 5 FT-IR spectrum of DCF

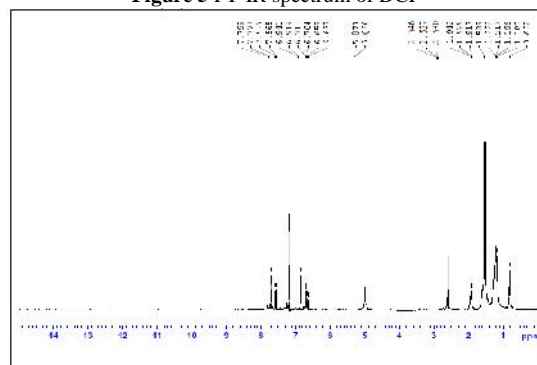


Figure 6 <sup>1</sup>H-NMR spectrum of DCF

**FTIR and <sup>1</sup>H-NMR Spectrum of Copolymer resin (DCF-1)**

In the IR Spectra of resin DCF-1 (Figs. 7) the peak at 3427 cm<sup>-1</sup> shows the O-H stretching frequency of hydrogen bonded phenolic OH group. The peak at 2924 cm<sup>-1</sup> shows the symmetrical CH<sub>2</sub> stretching of the side chain of cardanol and 2852 cm<sup>-1</sup> shows the CH<sub>2</sub> group in formaldehyde. The peak at 1449 cm<sup>-1</sup> shows the presence of azo group.

The peak at 1123 cm<sup>-1</sup> shows the C-O stretching frequency of carboxylic acid. In the <sup>1</sup>H-NMR spectra of resin DCF-1 (Fig. 8) the peak at 7.5-6.8 ppm shows the aryl protons of cardanol and the peak at 3.0 ppm shows the methylene group of formaldehyde. The peak at 7.8- 7.4 ppm shows the aryl protons of p- Chloroaniline and the peak at 1.2-2.5 ppm show the methylene group of the side chain of cardanol.

The peak at 5.2 ppm shows the phenolic hydroxyl group and the peak at 11.0 ppm shows the OH group of the carboxylic acid.

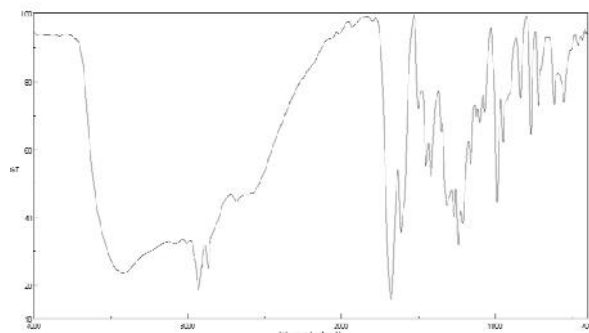


Figure 7 FT-IR spectrum of DCF-1

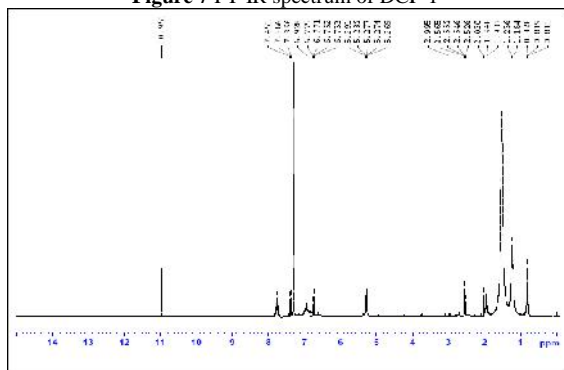


Figure 8 <sup>1</sup>H-NMR spectrum of DCF-1

**FTIR and <sup>1</sup>H-NMR Spectrum of Copolymer resin (DCF-2)**

In the IR Spectra of resin DCF-2 (Figs. 9) the peak at 3436 cm<sup>-1</sup> shows the O-H stretching frequency of hydrogen bonded phenolic OH group. The peak at 2926 cm<sup>-1</sup> shows the symmetrical CH<sub>2</sub> stretching of the side chain of cardanol and 2854 cm<sup>-1</sup> shows the CH<sub>2</sub> group in formaldehyde. The peak at 1464 cm<sup>-1</sup> shows the presence of azo group.

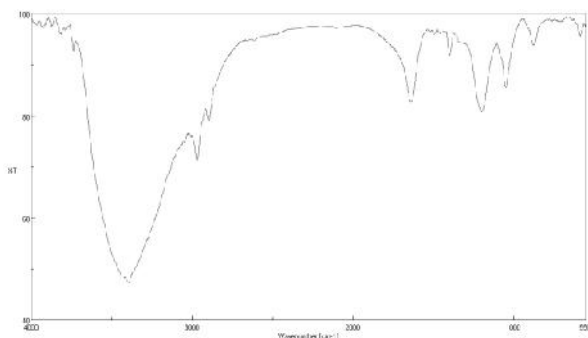


Figure 9 FT-IR spectrum of DCF-2

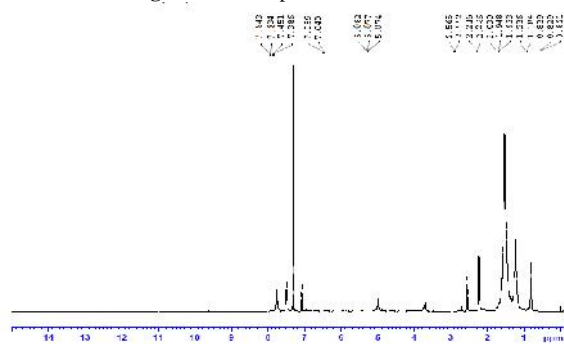


Figure 10 <sup>1</sup>H-NMR spectrum of DCF-2

The peak at 1049&1198 cm<sup>-1</sup> shows the C-O stretching frequency of aliphatic alcohol. In the <sup>1</sup>H-NMR spectra of resin DCF-2 (Fig. 10) the peak at 7.5-7.0 ppm shows the aryl protons of cardanol and the peak at 7.8- 7.4 ppm shows the aryl protons of p- Chloroaniline and the peak at 1.2-2.5 ppm show the methylene group of the side chain of cardanol. The peak at 2.2 ppm shows the OH group of the aliphatic alcohol.

**Physico chemical characteristics of cardanol and homopolymer resin(C & DCF)**

The physico chemical properties are presented in Table 1. The diazotised cardanol-p- chloro Aniline 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 resins

S.No	Properties	C	DCF
1	Colour	Pale brown	Reddish brown
2	Odour	Mild phenolic	Mild phenolic
3	Specific gravity (g/cc) at 30°c	0.9285	0.9296
4	Iodine value	262.6	258
5	Hydroxyl value (mg KOH/g)	191.5	182
6	Molecular weight	302	1751
7	Acid value	2.4	3.2
8	Saponification value	21.03	16.83
9	Number of hydroxyl group	1	6

**Thin layer chromatography**

The R<sub>f</sub> values of cardanol, synthesized biomonomers and the homopolymer resins are presented in Table 2. Thin layer chromatographic study in three different solvent systems Petroleum ether (40°-60°C) : Diethyl ether (7:3), 100% Benzene, Benzene: Chloroform 1:1) shows a single spot indicating the purity of the sample. R<sub>f</sub> values of biomonomers and homopolymer resins are different from that of cardanol indicating the formation of condensation product.

Table 2 Thin layer chromatographic behaviour of cardanol, synthesised bi monomer and homopolymer resin.

Resins Resin	R <sub>f</sub> values		Benzene : Chloroform (1:1)
	Petroleum ether : Diethyl ether (7:3)	Benzene 100 %	
C	0.85	0.75	0.80
DC	0.67	0.71	0.72
DCF	0.65	0.68	0.76

**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 (Kalia *et al.*, 2009). It is evident from the Table 3 the resin DCF shows 68.6 % crystallinity, DCF-1 shows 70.6 % crystallinity and DCF- 2 shows 62.5 % crystallinity .The crystallinity index of the resins DCF, DCF-1 and DCF-2 are found to be 0.54, 0.59 and 0.40 respectively. The XRD pattern



of all the resins were shown in Fig.11, Fig. 12 and Fig. 13 respectively. The resins DCF, DCF-1 and DCF-2 exhibited a peak at (2  $\theta$ ) 20°C, 20.5°C and 19.7°C respectively. The percentage of crystallinity of the resins decreases on copolymerization. The percentage of crystallinity decreases by adding ethylene glycol as comonomer. This is due to disorientation of the diazotised-p-chloro aniline cardanol formaldehyde crystals at the back bone. 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 DCF-1, the percentage of crystallinity increases by adding p-hydroxy benzoic acid as comonomer. This may be due to the presence of aromatic compound as comonomer in the copolymer resin22.

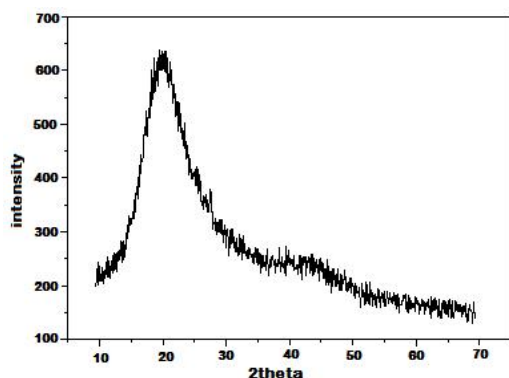


Figure 11 XRD pattern of DCF

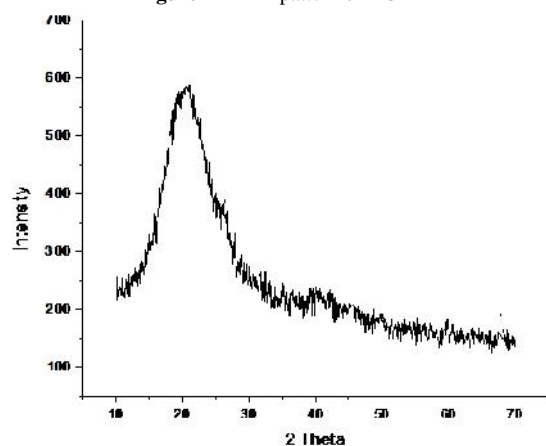


Figure 12 XRD pattern of DCF-1

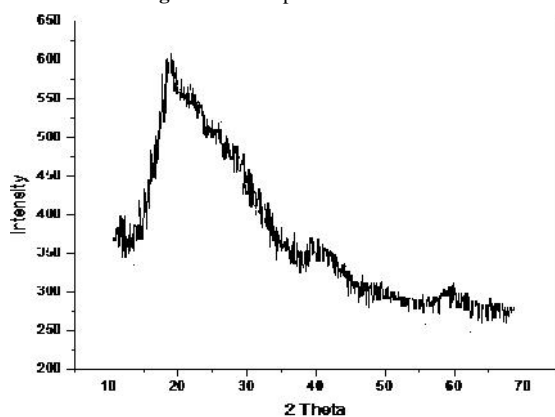


Figure 13 XRD pattern of DCF-2

Table 3 Percentage of crystallinity and crystalline index of the resins

Resin	Intensity of peak		Percentage of crystallinity (Xc)	Crystallinity Index (CI)
	Crystalline (Ic)	Amorphous (Ia)		
DCF	636	291	68.6	0.54
DCF-1	591	245	70.6	0.59
DCF-2	600	360	62.5	0.40

## CONCLUSION

Homopolymer resin was synthesised from the bio monomer. Copolymer resin was further synthesised from the homopolymer resin. All the resins were characterised by IR and NMR studies. X-ray diffraction studies show that the percentage of crystallinity decreases by adding ethylene glycol as comonomer and the percentage of crystallinity increases by adding p-hydroxy benzoic acid as comonomer.

## References

- Agarwal, A.M., Manek, R.V., Kolling, W. M. Neau, S. H. (2003) *AAPS Pharma sci Tech* 4:E60. Athawale, V., and Shetty, N. (2000) *Surface Coatings International*, 4, 168-172.
- Athawale, V., and Shetty, N. (2010) *Synthesis and characterization of low cost cardanol polyurethanes. Pigment and Resin Technology*, 3, 9-14
- Das D, Nayak, P.L., and Lenka, S. 1998. Interpenetrating polymer networks derived from castor oil isophorone diisocyanate cardanyl acrylate/cardanyl methacrylate-Thermal and XRD studies, *Polym. Plast. Tech. Eng.* 37, 419-426.
- Das TK, Das D, Guru BN, Das BN and Lenka S (1998) Synthesis, characterization and thermal studies of semiinter penetrating polymer networks derived from castor oil based polyurethane and cardanol derivatives. *Polym. Plast. Tech. Eng.* 37: 427-435.
- Das, T.K., and Lenka, S. (2011). Thermal and X-ray diffraction studies on interpenetrating polymer networks of castor oil-based polyurethane and cardanol based dyes. *Polym. Plast. Tech. Eng.* 5, 481-484.
- Devi A and Srivastava D (2006) Cardanol-based novolac-type phenolic resins. I. A kinetic approach. *J. Appl. Polym. Sci.* 102, 2730-2737.
- Devi A and Srivastava D (2007) Studies on the blends of cardanol based epoxidized novolac type phenolic resin and carboxyl-terminated polybutadiene (CTPB). *Matter Sci.Eng.* 458, 336-341
- Guo A, Demydov D, Zhang W and Petrovic ZS (2002) Polyols and polyurethanes from hydroformylation of soybean oil. *J. Polym. Environ.* 10, 49-52.
- Guru BN, Das TK and Lenka S (1999) Studies on synthesis, characterization and thermal properties of resins derived from cardanyl acrylate-furfural-organic compounds. *Polym. Plast. Tech. Eng.* 38, 179 – 187.
- Kalia, Kumar S and Kaith, B. S (2009) *Malaysian Polymer Journal*, 4, 46-51.
- Kong X and Narine SS (2007) Physical Properties of Polyurethanes Plastic Sheets Produced from Polyols from Canola Oil. *Biomacromolecules.* 8, 2203-2209.

- Lu Y and Zhang L (2002) Morphology and mechanical properties of semi-interpenetrating polymernetworks from polyurethane and benzyl konjac glucomannan. *Polymers*, 43, 3979 – 3986.
- Mishra DK, Mishra BK, Lenka S and Nayak PL (1996) Thermal properties of the semi-interpenetrating polymer networks composed of castor oil polyurethanes and cardanol-furfuralresin. *J. of Polymer Engineering and Science*. 36, 1047-1051.
- Mohapatra NK, Lenka S and Nayak PL (1994) Thermal properties of copolymers derived from semicarbazone of 4-hydroxyacetophenone-furfural-substituted benzoic acids. *Thermochim.Acta*. 241, 51-56.
- Mythili CV, Malar Retna A and Gopalkrishnan S (2004) Synthesis, mechanical, thermal and chemical properties of polyurethanes based on cardanol. *Bull matter Sci*. 2, 235-241.
- Narine SS, Kong X, Bouzidi L and Sporns P (2007) Physical properties of polyurethanes produced from polyols from seed oils. *J. Am. Oil Chem. Soc.* 84, 65–72.
- Nayak SS, Das SK and Lenka S (1999) Synthesis and characterization of copolymers from cardanyl acrylate and vinyl monomers. *React. Funct. Polym.* 40, 249-254.
- Oghome P and Kehinde AJ (2004) Separation of cashew nut shell liquid by column chromatography. *African journal of science and technology (AJST)*. 5, 92-95.
- Petrovic ZS, Zhang W and Javni I (2005) Structure and properties of polyurethane. *Biomacromolecules*, 6, 713-719.
- Phanikumar P, Paramashivappa R, Vithayathil PJ, SubbaRao PV and SrinivasaRao A (2002) Process for Isolation of Cardanol from Technical Cashew Nut Shell Liquid. *J.Agric. Food. Chem.* 50, 4705-4708.
- Reddy N, YanG Y *Polymer*, (2005) 46, 5494-5500.
- Roloff T, Erkens U and Höfer R (2005) Polyols based on renewable feedstocks: A significant alternative, *Urethanes Technology*, 22, 29-33.
- Santeusanio S, Attanasi OA, Majer R, Cangiotti M, Fattori A and Ottaviani MF (2013) Effect of hydrogenated cardanol on the structure of model membranes studied by EPR and NMR. *Langmuir*, 29, 11118-11126.
- Sathiyalekshmi K (1993) Studies on structure and properties of CNSL novolac resins prepared with succinic acid catalyst. *Bull matter Sci*. 16, 137-150.
- Sathiyalekshmi K and Gopalakrishnan S (2000) Synthesis and characterisation of rigid polyurethanes based on hydroxyalkylated cardanolformaldehyde resin. *Plast Rubber compos.* 29: 63-69.
- Segal LC, Martin AE Conrad.(1959) *Textile Res.J*, 29, 786- 794.
- Tan TTM (1997) Thermoplastic composite based on jute fiber treated with cardanol formaldehyde. *Polym. Compos.* 5, 273-279.
- Unikrishnan KP and Thachil ET (2006) The modification of commercial epoxy resin using cardanol-formaldehyde copolymers. *Int. J. Polym, Matter.* 55, 323-338
- Unikrishnan KP and Thachil ET (2008) Studies on the Modification of Commercial Epoxy Resin using Cardanolbased Phenolic Resins. *J. Elast. Plast.* 40, 271-286.

**How to cite this article:**

Mythili CV and Kalyani V., Synthesis, Characterization and Xrd Studies of Diazotised Resins From Bio Resource. *International Journal of Recent Scientific Research Vol. 6, Issue, 5, pp.4050-4055, May, 2015*

\*\*\*\*\*