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## Full Length Research Article

### SYNTHESIS AND CHARACTERIZATION OF CARDANOL/m-CRESOL RESIN BASED POLYURETHANES

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#### ABSTRACT

Cardanol an agricultural byproduct of cashew industry with m-cresol in various molar concentrations were condensed with formaldehyde. The resins R1, R2 and R3 thus prepared and characterized. The spectral studies confirm that the ortho substitution is favoured when the concentration of m-cresol is more. Polyurethanes PUR1, PUR2 and PUR3 were prepared using this resins and hexamethylene diisocyanate, an aliphatic diisocyanate. The polyurethanes were characterized by thermal, mechanical and x-ray diffraction studies. The polyurethanes have good thermal stability. The crystallinity of the polyurethanes were analyzed by XRD studies.

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#### INTRODUCTION

Many agricultural by-products from agricultural activities and agro-based processing litter the environments and constitute waste problems. The use of agricultural by-products to produce materials that are competitive with synthetic ones is gaining attention over the last decade, because of availability of materials and low cost (Gassan *et al.*, 2001). Cashew nut shell liquid (CNSL), an agricultural renewable resource and the by-product of the cashew industry, holds considerable promise in that direction, because it is the source of unsaturated hydrocarbon, phenol and behaves an excellent monomer for polymer production (Menon *et al.*, 1985 and Tyman, 1975). Cashew nut shell liquid occurs as a reddish brown viscous liquid in the soft honey comb structure of the shell of cashew nut. The literature on CNSL is replete with numerable patents and reports (Zadontsev *et al.*, 1981). However there exist substantial gaps between the technological consideration and scientific understanding. Mahindru (1977) reported the extraction process and uses of CNSL and tree. CNSL is obtained in India as a by-product by roasting the raw nuts (Menon *et al.*, 1985) or by hot oil process

(Compagine *et al.*, 1956). The principal components of CNSL are, cardanol, cardol, anacardic acid, and 2-methyl cardol (Kumar *et al.*, 2002). The chemical structures of these compounds are given in the (Figure-1).

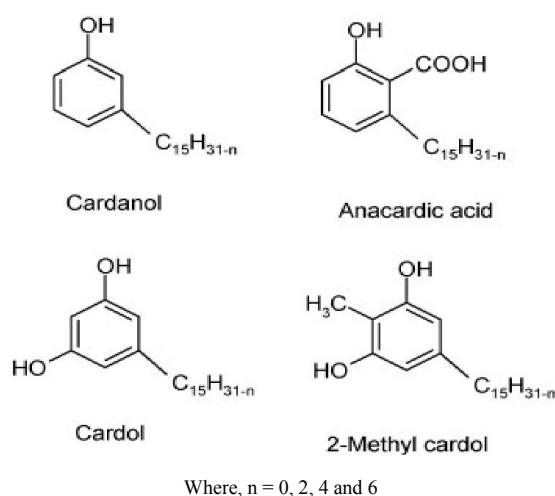


Figure 1. Components of CNSL

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Risfaheri *et al.* (2009) developed a method for isolation of cardanol from CNSL by vacuum distillation, whereby cardanol was obtained at 4-8 mm Hg, and the optimum

temperature was achieved at 280°C with 74.22% yield. Harvey (1937) distilled CNSL to obtain cardanol, technical CNSL was dissolved in a mixture of methanol and ammonium hydroxide (8:5) and extracted with hexane to obtain cardanol (Paramashirappa *et al.*, 2001). The meta substituted side chain of cardanol imparts hydrophobic nature to the polymer making the product water repellent and resistance to weathering. Therefore it is of particular interest to develop smart polyols that may be easily obtained from readily available and renewable resource materials, CNSL. It is aimed to evaluate the effect of this renewable phenolic compound with different proportions of m-cresol on the properties of the resulting polyurethanes and to develop a material for commercial uses that is quite inexpensive and somewhat eco-friendly.

## MATERIALS AND METHODS

Cashew Nut Shell Liquid (CNSL) was obtained from M/S Kumaraswamy chemicals, Cuddalur. Cardanol was separated from CNSL by vacuum distillation method. m-Cresol (BDH) and Formaldehyde (40% solution) (BDH) were used. Hexamethylene diisocyanate (HMDI), Dibutyl tin dilaurate, Toluene and silicone oil from Sigma-Aldrich were used as received without purification.

### Recovery of cardanol

Cardanol was obtained from cashew nut shell liquid by direct double vacuum distillation (5-10 mm Hg) in the temperature range 180 - 240°C. Initially, CNSL was heated to about 170 - 180°C and kept for 2h under vacuum so that anacardic acid was converted into cardanol. As soon as the evaporation of CO<sub>2</sub> stopped, the mother liquor was further heated under vacuum and the temperature was raised to 230 - 240°C. About 65% of the liquid distilled over as a light yellow oil, which was collected leaving behind a black viscous soild resinous mass in the flask. On analysis it was found that, cardanol has specific gravity (g/mm at 30°C) of 0.9165, Viscosity (centipoise) at 30°C of 130, Hydroxyl value of 18.8, Acid value of 22.82 and Iodine value of 221.3 which agree as per IS 840-1964 standard. UV spectrum of cardanol gives absorption peak at 287nm. The IR data are 694cm<sup>-1</sup>, 746 cm<sup>-1</sup>, 779 cm<sup>-1</sup>, 871 cm<sup>-1</sup>, 912 cm<sup>-1</sup>, 943 cm<sup>-1</sup>, 995 cm<sup>-1</sup>, 1074 cm<sup>-1</sup>, 1155 cm<sup>-1</sup>, 1265 cm<sup>-1</sup>, 1350 cm<sup>-1</sup>, 1458 cm<sup>-1</sup>, 1487 cm<sup>-1</sup>, 1591 cm<sup>-1</sup>, 2852 cm<sup>-1</sup>, 2925 cm<sup>-1</sup>, 3008 cm<sup>-1</sup>, 3076 cm<sup>-1</sup> and 3342 cm<sup>-1</sup>. The NMR data of cardanol was 0.93δ, 1.3 - 1.4 δ, 1.99 - 2.81 δ, 4.95-5.86δ and 6.6 - 7.2 δ.

### Formulation of cardanol/m-cresol - formaldehyde resin Synthesis of novolac resins R1, R2 and R3

Cardanol/m-cresol-formaldehyde resins R1, R2 and R3 were synthesized in the mole ratio as given in table-1, using hydrochloric acid as catalyst (Devi and Srivastava, 2006). Cardanol and m-cresol were taken in three-necked round bottomed flask and formaldehyde was added to the cardanol through a dropping funnel along with the catalyst. The reaction mixture was heated under constant stirring at a temperature of 150±5°C.

### Synthesis of polyurethanes

One of the key reactive material required to produce polyurethanes is diisocyanate. Hexamethylene diisocyanate

(HMDI) was used for the present study. Polyurethanes were synthesized using freshly prepared and vacuum dried Cardanol/m-cresol-formaldehyde resins, HMDI in toluene solvent, keeping the isocyanate index (NCO/OH) constant at 1.4 in a Nitrogen atmosphere in a three necked flask fitted with stirrer, Liebig condenser and a thermometer. The molar ratio of for the reactants for the three polyurethanes PUR1, PUR2 and PUR3 were given in table-2. Toluene solvent was added. The reaction mixture was heated in the presence of dibutyl tin dilaurate (0.25 wt %) at 150°C for 45 min, cooled and cast in a silicone oil coated glass plate. The polymer was cured in a vacuum oven at 80°C for 48h.

### Characterisation

The prepared novolac resins (R1, R2 and R3) were subjected to spectral analysis such as ultra violet, infra red and NMR and physic-chemical analysis such as specific gravity, viscosity, acid value and hydroxyl value, hydroxyl number and Iodine value were determined as per IS: 840-1964 standard procedure. Molecular weights were determined by GPC method. The prepared polyurethanes PUR1, PUR2 and PUR3n were characterized by thermal, mechanical and x-ray diffraction studies. The thermal analysis was carried out by using Perkin Elmer Diamond TG/DTA model, the micro hardness was studied by Vicker's hardness test using MH-6 model durometer. The X-ray diffraction studies were carried out by Bruker S D8 advance model diffractometer with angular range 10° to 80° in 2θ and a filtered Cu Kα radiation source (λ = 1.5406) was used.

**Table 1. Formulation of cardanol/m-cresol-Formaldehyde resins**

| Resin | Mole ratio of cardanol | Mole ratio of m - cresol | Mole ratio of formaldehyde | Percentage Hydrochloric acid |
|-------|------------------------|--------------------------|----------------------------|------------------------------|
| R1    | 4.5                    | 1.5                      | 1                          | 1                            |
| R2    | 5.1                    | 0.9                      | 1                          | 1                            |
| R3    | 5.7                    | 0.3                      | 1                          | 1                            |

**Table 2. Molar ratios of diisocyanate and Cardanol/m-cresol-formaldehyde resins**

| Polyurethane | Diisocyanate (HMDI) |                                     | Cardanol/m-cresol-formaldehyde |                                     |
|--------------|---------------------|-------------------------------------|--------------------------------|-------------------------------------|
|              | Mol                 | Concentration (mol x functionality) | Mol                            | Concentration (mol x functionality) |
| PUR1         | 2.6                 | 5.2                                 | 1.2                            | 3.6                                 |
| PUR2         | 3.9                 | 7.8                                 | 1.4                            | 5.6                                 |
| PUR3         | 2.5                 | 5.0                                 | 1.2                            | 3.6                                 |

## RESULTS AND DISCUSSION

### UV Spectroscopy of resins R1, R2 and R3

The UV spectral data are given in table-3. The spectra of the resins indicate a shift of peak towards the lower wavelength. The shift of peak from 287nm to 275nm in the case of R1 and to 270nm in the case of R2 and R3 is due to ortho substitution in cardanol (Knoop and Pilato, 2000). Such a shift was also observed in phenol with alkyl substituents in ortho position (Silverstein, 2000).

### IR Spectroscopy of resins R1, R2 and R3

The IR spectral data of the resins R1, R2 and R3 are given in table-4. IR spectral data of cardanol formaldehyde resin reveal

not only the condensation of methylolated cardanol, but also the degree of ortho and para substitution (Sathiyalakshimi and Gopalakrishnan, 2000). The peak at  $967\text{cm}^{-1}$ ,  $964\text{cm}^{-1}$ ,  $966\text{cm}^{-1}$  corresponding to R1, R2 and R3 are due to substitution in benzene nuclei. The peak at  $695\text{cm}^{-1}$ ,  $695\text{cm}^{-1}$ ,  $694\text{cm}^{-1}$  corresponding to R1, R2 and R3 are due to three adjacent hydrogen atoms in benzene nuclei. The more intense peak for R1 in this region support that higher mole ratio of m – cresol has favoured ortho substitution. The sharp peak at  $778\text{cm}^{-1}$  for R1 and R2,  $779\text{cm}^{-1}$  for R3 indicates the ortho substitution at benzene nuclei. The peak at  $869\text{cm}^{-1}$  for R1 and R2 and  $870\text{cm}^{-1}$  for R3 indicates the para substitution at benzene nuclei. The appearance of peak at  $1718\text{cm}^{-1}$  due to -C-O stretching from -CH<sub>2</sub>-OH of formylated cardanol. The band at  $3410\text{cm}^{-1}$  is due to the presence of hydroxyl groups in the formylated cardanol.

**Table 3. UV spectral data of cardanol and resins R1, R2 and R3**

|                | Wave length (nm) | Adsorbance |
|----------------|------------------|------------|
| Cardanol       | 287              | 2.44       |
| R <sub>1</sub> | 275              | 0.155      |
| R <sub>2</sub> | 270              | 0.161      |
| R <sub>3</sub> | 270              | 0.125      |

**Table 4. IR spectral data of cardanol based resins R1, R2, R3**

| Resin1        | Resin2        | Resin3        | Assignment                                      |
|---------------|---------------|---------------|-------------------------------------------------|
| 695           | 695           | 694           | three adjacent hydrogen atoms in benzene nuclei |
| 778           | 778           | 779           | ortho substitution                              |
| 869           | 869           | 870           | Para substitution                               |
| 967           | 964           | 966           | Substitution at benzene nuclei                  |
| 1155 and 1260 | 1154 and 1231 | 1153 and 1231 | C – O stretching                                |
| 1455          | 1454          | 1456          | Alcoholic OH deformation                        |
| 1593          | 1593          | 1591          | Aromatic C = C                                  |
| 1718          | 1727          | 1728          | C – O str. from CH <sub>2</sub> OH              |
| 2854, 2922    | 2854, 2922    | 2853, 2922    | - CH stretching from CH <sub>2</sub>            |
| 3410          | 3396          | 3405          | Hydroxyl group                                  |

### NMR Spectroscopy of resins R1, R2 and R3

NMR spectral data of the resins are given in table-5. In the <sup>1</sup>H NMR spectra, appearance of small peak at  $2.8\delta$  due to benzylic protons of the CH<sub>2</sub>OH group formed by methylation. The peaks at  $6.60 - 7.20\delta$  is due to aryl protons of benzene nuclei, the peak at  $5.3\delta$  is due to methylene proton of long alkyl side chain originally present in cardanol. The peaks between  $0.8$  and  $2.4\delta$  are due to the aliphatic long chain group of cardanol.

**Table 5. NMR spectral data of cardanol and resins R1, R2, R3**

| R1 ( $\delta$ ) | R2 ( $\delta$ ) | R3 ( $\delta$ ) | Assignment                             |
|-----------------|-----------------|-----------------|----------------------------------------|
| 0.865 – 0.906   | 0.865 – 0.891   | 0.865 – 0.891   | Terminal methyl group                  |
| 1.252 – 1.584   | 1.256 – 1.634   | 1.256 – 1.746   | long chain (>5 members)                |
| 1.990 – 2.556   | 1.965 – 2.590   | 1.965 – 2.590   | Aliphatic side chain                   |
| 2.8             | --              | --              | Benzylic protons of CH <sub>2</sub> OH |
| 5.345 – 5.373   | 5.346 – 5.380   | 5.346 – 5.380   | Methylene proton of alkyl side chain   |
| 6.630 – 6.749   | 6.630 – 6.885   | 6.629 – 6.884   | Phenolic hydrogen                      |
| 7.109 – 7.247   | 7.021 – 7.254   | 7.020 – 7.252   | Aromatic protons                       |

The small peak at  $0.8\delta$  represents the terminal methyl group of the chain. The strong peak at  $1.3\delta$  is attributed to the long chain (>5 member) of the side chain. The doublet at  $5.3\delta$  for R2 and R3 support higher percentage of ortho substitution. Spectral studies indicate the initial formylation of cardanol leads to methylation under the present experimental conditions ranging from single to triple substitution.

### Physico – chemical characterization of cardanol novolac resins

The Physico – chemical properties are presented in table-6

**Table 6. Physico – chemical characteristics of cardanol and cardanol based resins R1, R2, R3**

| Properties                      | R <sub>1</sub> | R <sub>2</sub> | R <sub>3</sub> |
|---------------------------------|----------------|----------------|----------------|
| Colour                          | Dark brown     | Dark brown     | Dark brown     |
| Odour                           | Phenolic       | Phenolic       | Phenolic       |
| Specific gravity (g/cc at 30°C) | 1.008          | 1.006          | 0.996          |
| Viscosity (centipoise) at 30°C  | 223            | 244            | 250            |
| Hydroxyl value                  | 157.08         | 168.3          | 179.52         |
| Number of hydroxyl groups       | 3              | 4              | 3              |
| Acid value                      | 21.879         | 23.001         | 23.562         |
| Iodine value                    | 221.1          | 220.2          | 218.4          |
| Mol.wt (GPC) Mn/Mw              | 930/970        | 1240/1294      | 1060/1090      |

Cardanol based R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> resins possess higher specific gravity and viscosity due to higher degree of condensation between cardanol and formaldehyde. In comparing with cardanol, the acid value is increased due to the increased acidic character of more aromatic –OH groups by the condensation of methylolated cardanols. The low iodine value in comparison with that of cardanol may be due to steric hindrance of adjacent bulky groups to the olefinic addition of iodine monochloride during the estimation of iodine value. Further as the molar concentration of cardanol increases the iodine value decreases.

### Thermal Properties of Polyurethanes

TGA is most favoured technique for evaluation the thermal stability of polymers. Polyurethanes have relatively low thermal stability, mainly due to the presence of urethane bonds. The thermal stability of obtained polyurethanes, PUR1, PUR2, PUR3 were studied with TGA at a heating rate of  $10^\circ\text{C}/\text{min}$  in a nitrogen atmosphere and the obtained data are shown in table -7. It can be seen that the decomposition of the polyurethanes in a nitrogen atmosphere do not takes place below  $295^\circ\text{C}$ .

**Table 7. Thermal and mechanical properties of Polyurethanes**

| Polyurethanes | TGA                        |                             | Hardness (HV) |
|---------------|----------------------------|-----------------------------|---------------|
|               | T <sub>20%</sub> loss (°C) | T <sub>max%</sub> loss (°C) |               |
| PUR1          | 365                        | 455                         | 30.1          |
| PUR2          | 349                        | 452                         | 33.3          |
| PUR3          | 296                        | 450                         | 38.7          |

The thermal decomposition of the polyurethanes, PUR1, PUR2, PUR3 involves at least two overlapping steps, a small drop below  $300^\circ\text{C}$  is followed by the main loss weight above  $450^\circ\text{C}$  (see figure-2a, 2b & 2c). The first stage degradation

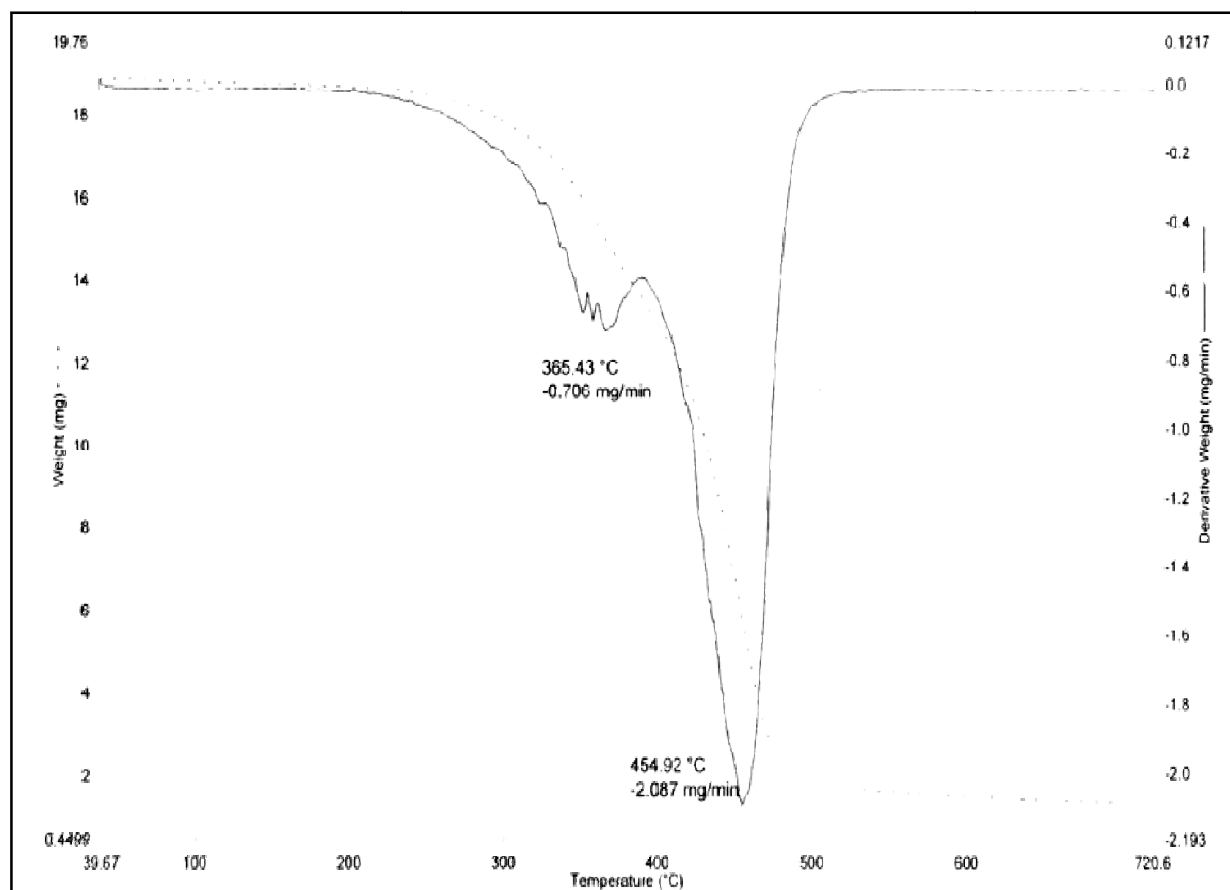


Figure 2a. TGA for PUR1

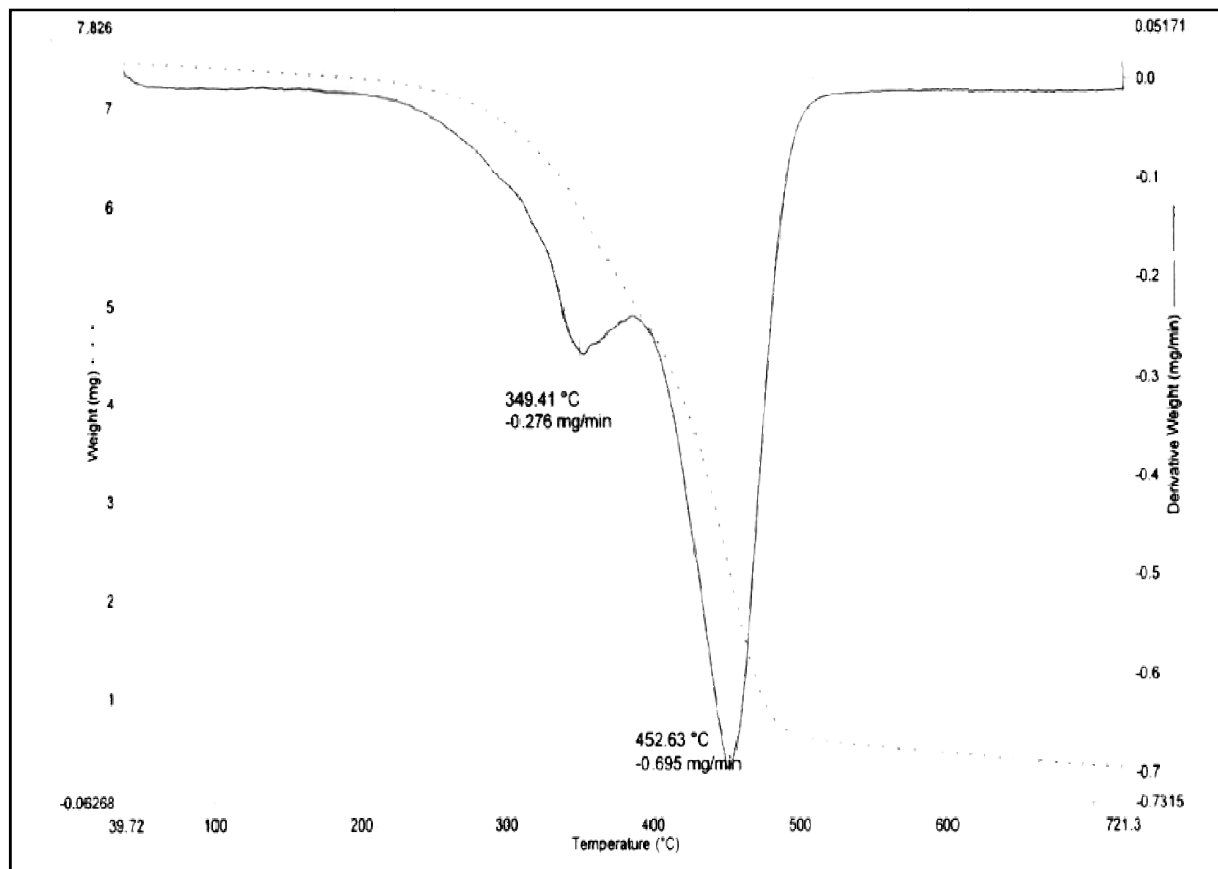


Figure 2b. TGA for PUR2

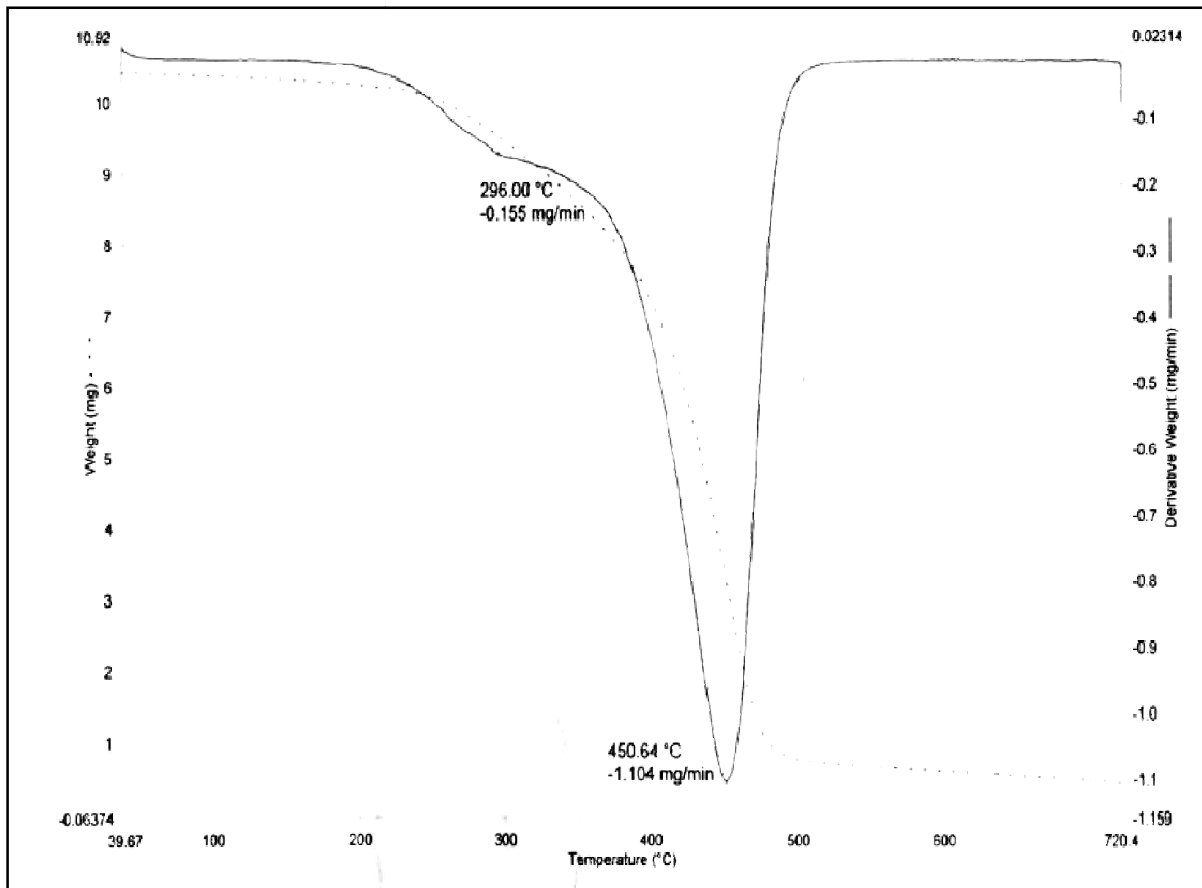


Figure 2c. TGA for PUR3

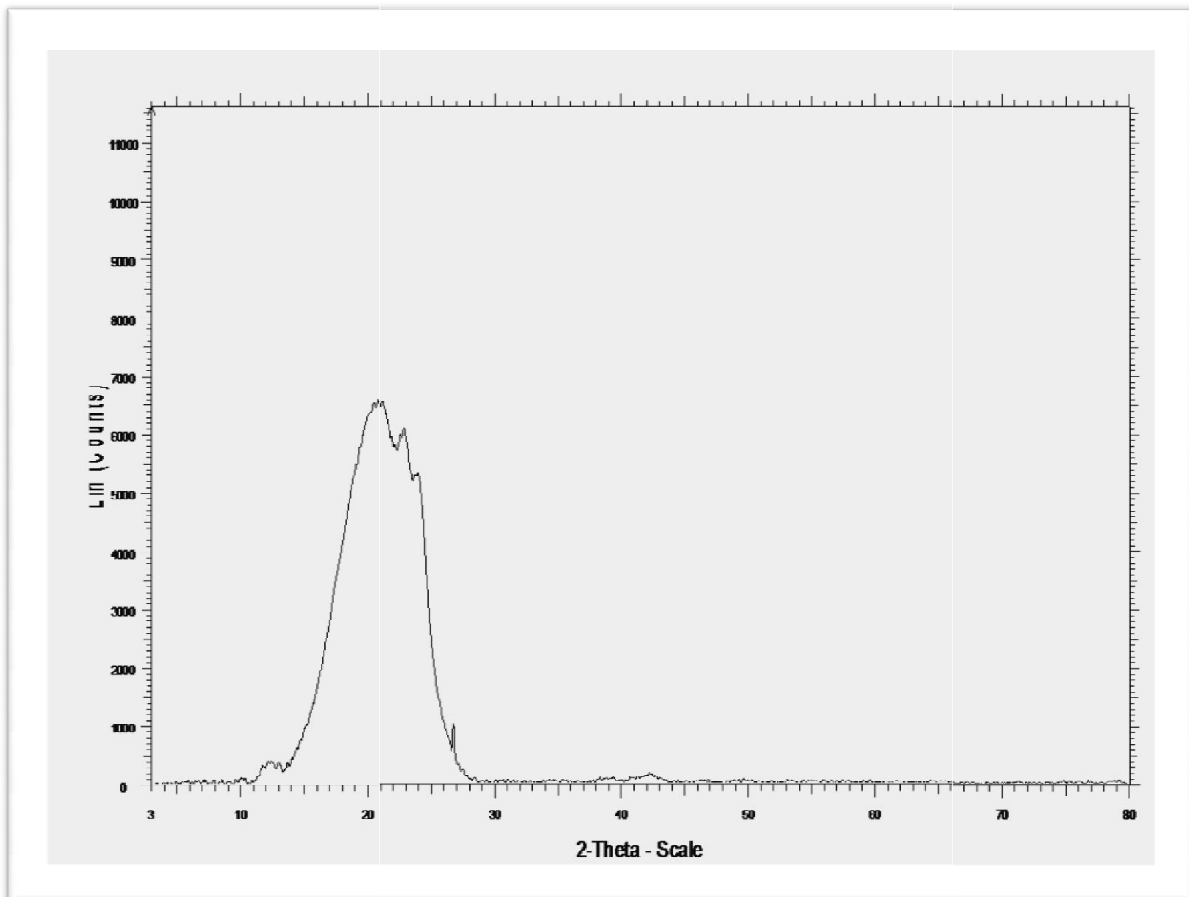


Figure 3a. XRD for PU

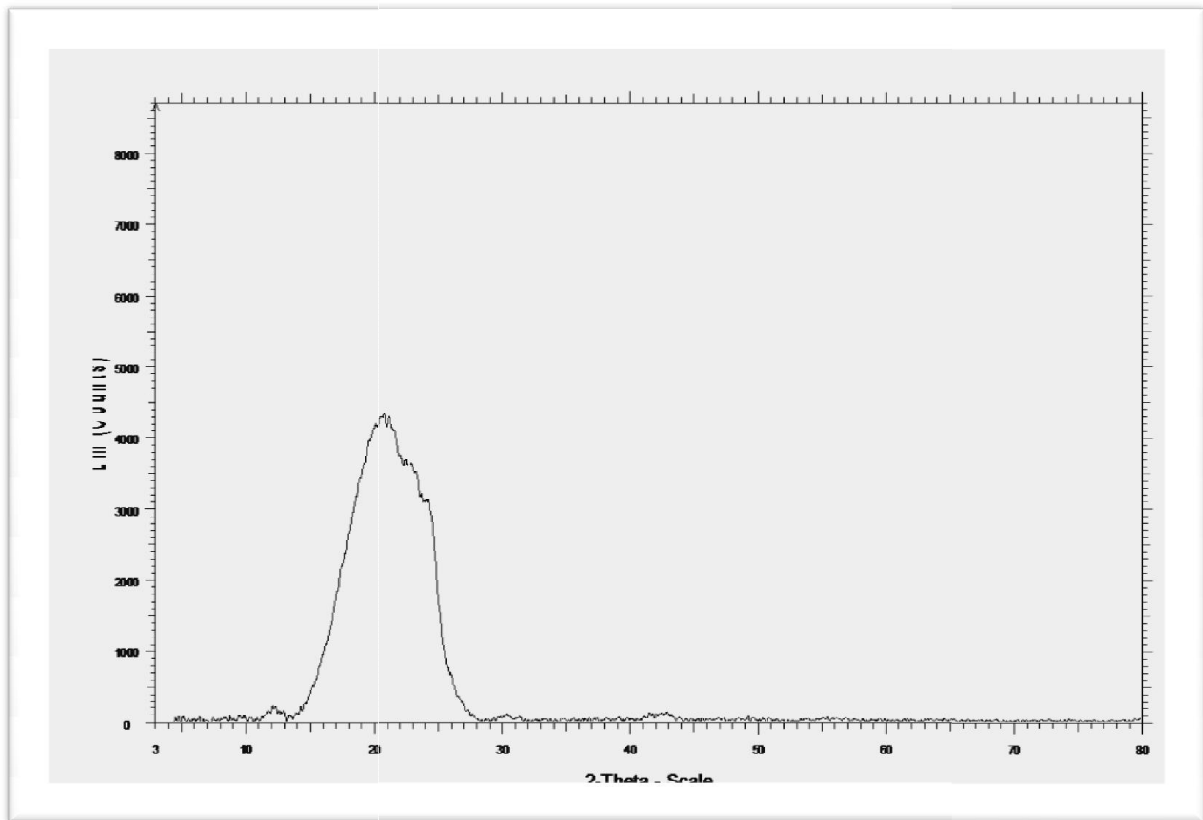


Figure 3b. XRD for PUR2

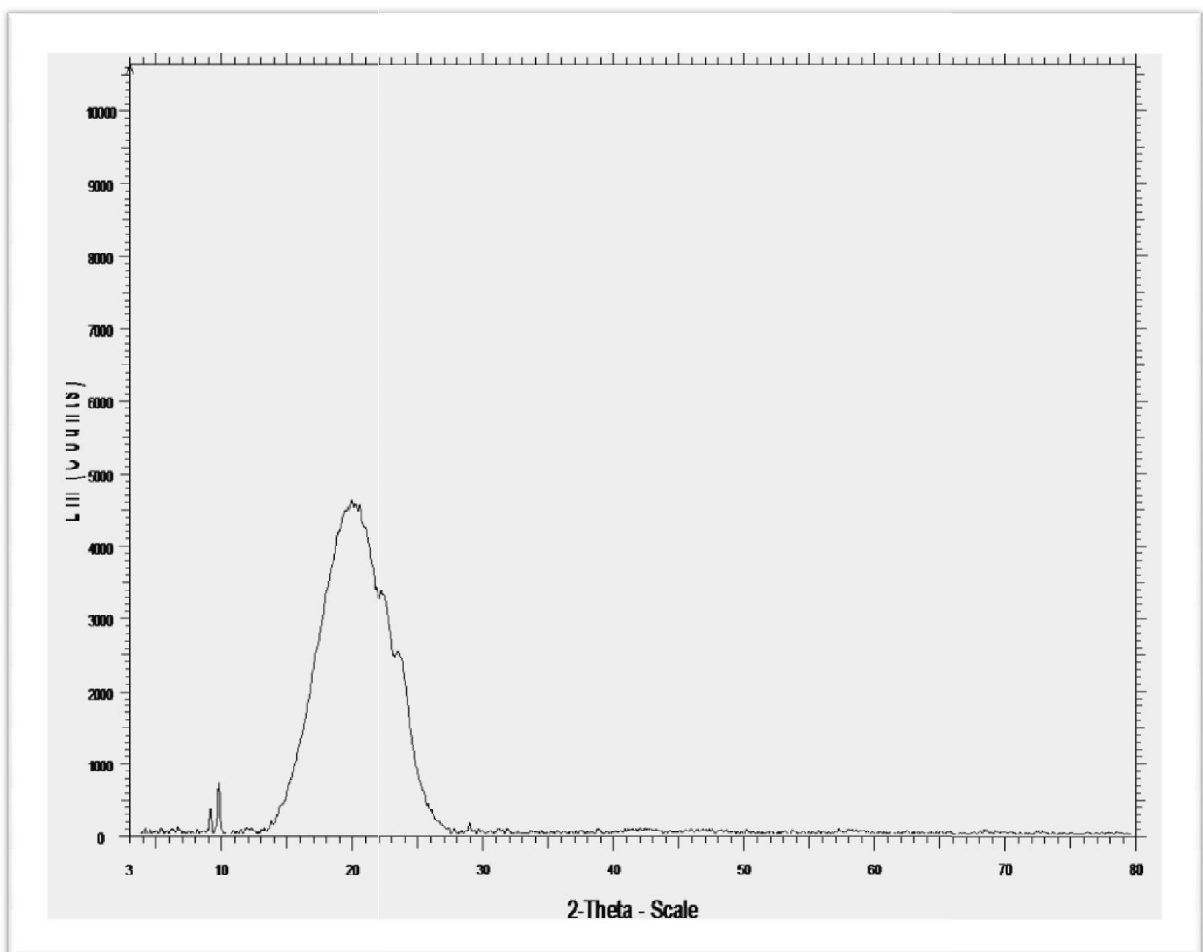


Figure 3c. XRD for PUR3

confirms the PU linkage (Hepburn, 1982). The first weight loss is related to the decomposition of urethane bonds, which takes place through the dissociation to isocyanate and alcohol (Levchik and Weil, 2004). The weight loss in the first step increases as the percentage of m-cresol increases, which is in accordance to the existence of a higher amount of weaker urethane bonds.

### X-ray Diffraction study

X-ray Diffraction study of the prepared polyurethanes PUR1, PUR2 and PUR3 were carried out using Cu K $\alpha$  target in the angular range 10° to 80° in 2 $\theta$ . For PUR1 and PUR2, the diffractogram shows a broad band from 13° to 29° in 2 $\theta$  and 14° to 28° in 2 $\theta$  respectively. In these two polyurethanes no traces of crystalline region were found. It shows the polyurethanes, PUR1 and PUR2 are amorphous in character. For PUR3, the diffractogram shows two sharp bands at 9° in 2 $\theta$  and 10° in 2 $\theta$  with low intensity (see figure-3a, 3b & 3c). This shows that, there is a trace of crystalline region. This implies that, some order in the PU samples may be in the hard phase but the addition of m-cresol to cardanol resists molecular orientation, hence resulting in a lower the degree of crystallinity (Allegrezze *et al.*, 1974).

### Hardness

The hardness of the polyurethanes were measured and presented in table-7. The hardness decreased as the proportion of m-cresol increases. This is attributed to installation of low molecular weight between the cross links. It has been reported that, hardness is primarily governed by the hard segment concentration (Patravac *et al*, 1991).

### Conclusion

Usage of agricultural waste materials for the synthesis of polymeric products is considerable interest. CNSL is one of the agricultural waste material. Using this cardanol, one of the components of CNSL various resins were prepared along with considerable quantity of m-cresol and formaldehyde. The prepared novolac resins R1, R2 and R3 were characterized using UV, IR and NMR spectrum and found that, the ortho substitution will favoured for condensation reaction. The prepared polyurethanes from these resins and hexamethylene diisocyanate have higher thermal stability. From X-ray diffraction studies, it was confirmed that, the addition of

m-cresol decreases the crystallinity. Due to installation of low molecular weight m-cresol to cardanol, the hardness also decreases

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