



SYNTHESIS AND CHARACTERIZATION OF NATURAL FIBRE REINFORCED POLYURETHANE COMPOSITES BASED ON CARDANOL

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Abstract

In recent studies importance has been given to the use of natural products from renewable resources due to the decrease in the supply and price escalations of petroleum raw materials. Cardanol based resole type phenolic resin has been synthesized by condensing cardanol with furfural in a particular mole ratio using dicarboxylic acid catalyst such as phthalic acid. Polyurethane sheets were prepared by treating cardanol furfural resin with 4,41 – methylene bis(cyclohexyl isocyanate) and the catalyst dibutyltin dilaurate. Natural fibres are prospective reinforcing materials and their use until now has been more traditional than technical. Among the various fibres sisal is of particular interest in that its composites have high impact strength besides having moderate tensile and flexural properties compared to other fibres. Fibre reinforced polyurethane composites have been prepared by treating sisal fibre (10%) into polyurethane. The physico chemical, spectral and thermal properties of polyurethane and fibre reinforced polyurethane composites have been studied.

Keywords: Cardanol, furfural, sisal fibre, polyurethane, 4,41 – methylene bis (cyclohexyl isocyanate)

INTRODUCTION

In recent years, natural fibre reinforced composites have attracted the attention of the research community mainly because they are turning out to be an alternative solution to the ever depleting petroleum sources[1]. The interest in natural fibre reinforced composites is growing rapidly due to the high performance in mechanical properties. There are different types of natural fibres like coir fibre, sisal fibre, banana fibre, pineapple fibre etc. Fibres obtained from various parts of the plants are known as vegetable fibres[2].

Natural fibre composites are very cost effective materials, especially in building and construction, packaging, automobile and railway coach interiors and devices [3]. Cashewnut shell liquid an agricultural renewable resource and the byproduct of cashew industry. It is the source of unsaturated hydrocarbon, phenol and behaves an excellent monomer for polymer production[5]. Resins derived from cardanol are widely employed in the fields of surface coatings, adhesives, laminates and have several miscellaneous applications.

Furfural the heteroaryl aldehyde is obtained as an agricultural waste product which has an extensive application in the formation of resins[6]. Several resins have been prepared by using cardanyl acrylate and furfural in the presence of an acid catalyst and selective organic compound and their thermal properties were studied [7]. Novolac resins based on cardanol formaldehyde, phenol furfural have already been discussed by various workers [8-10].

Many research work has been done on petrochemical based polyurethane systems. Polyurethanes provide a versatile range of properties and find extensive applications as fibres, films, paints and lacquers, adhesives, foams and also have been extensively used and tested in different biomedical applications [11].

In the present study cardanol is made to react with furfural in the mole ratio 1:1.1 in the presence of phthalic acid catalyst and used for the production of polyurethane and polyurethane composite. The physico chemical characteristics, spectral properties of the resin and also the thermal properties of polyurethane and its composite have been evaluated.

EXPERIMENTAL

MATERIALS

Cardanol is procured from M/S Sathya Cashew Pvt. Ltd, Chennai. Furfural was obtained from Sisco Research Laboratory, Mumbai, was used for formylation. Phthalic acid were received from Sisco Research Laboratory, Mumbai. Methanol (BDH) from Nice Chemicals Pvt. Ltd, Kochi was used to dissolve the free catalyst. Catalyst dibutyltin dilaurate and 4, 4¹ methylene bis(cyclohexyl isocyanate) was received from Sigma – Aldrich chemicals, USA.

METHODS

Synthesis of Cardanol- furfural resole resin

Cardanol –furfural resole resin was synthesized from cardanol and furfural in the mole ratio 1:1.1, using phthalic acid as catalyst. The catalyst was dissolved in 10ml methanol. Cardanol was taken in a three necked round bottom flask and furfural was added drop wise to the cardanol through a dropping funnel along with the catalyst solution. The reaction mixture was heated under constant stirring at a temperature of 120⁰C. The reaction resulted in the formation of multinuclear cardanol furfural resin (CR₁).

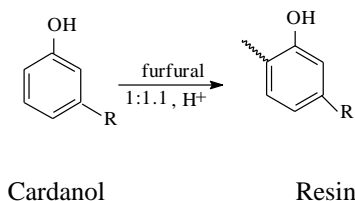


Figure 1: Formylation of cardanol

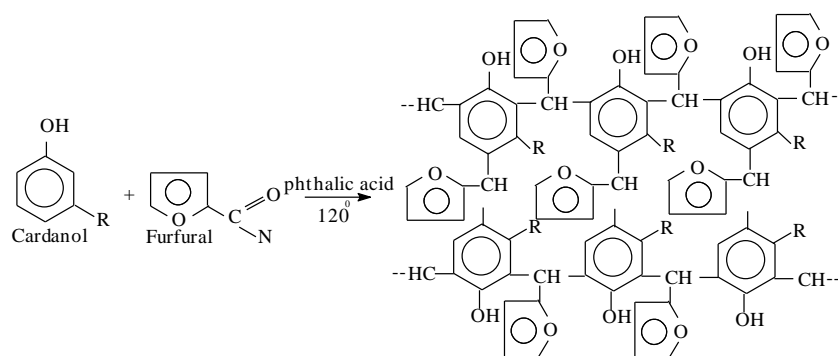


Figure 2: Structure of cardanol furfural resin

Synthesis of polyurethane and its composite

Polyurethane sheets (CR₁P) were prepared by treating cardanol furfural resin with 4, 4¹ – methylene bis(cyclohexyl isocyanate) and the catalyst dibutyltin dilaurate were mixed physically in a small plastic cup at room temperature. When the heat is liberated the solution mixture was poured into a silicone oil coated flat glass mould. The polyurethane sheets were allowed to stand at 24 hours without any disturbance. The sheets were again cured in a vacuum oven at 80⁰C for 48 hours. Polyurethane composite (CR₁PS) have been synthesized by incorporating sisal fibre (10%) into the polyurethane.

RESULTS AND DISCUSSION

Physico chemical characteristics of cardanol furfural resin

The synthesized resin is reddish brown colour. Thin layer chromatographic study of the resin in solvent system 100% Benzene, (1:1 Benzene) Showed a distinct single spot and R_f value for cardanol furfural resin was different from that of cardanol indicating the formation of the product. The decrease in Iodine value is observed which may be due to the steric effect in cardanol furfural resin during the addition of Iodine monochloride. The number of hydroxyl groups present in the resin is only the – OH groups in the benzene ring. The results are presented in Table 1.

Table 1: Physico Chemical characteristics of Cardanol furfural resin

Sl. No.	Properties	Cardanol	Cardanol – furfural resin (1:1.1)
1.	Colour	Dark brown	Reddish brown
2.	Odour	Phenolic	Phenolic
3.	Specific gravity (g/cc at 30 ⁰ C)	0.83	0.88
4.	Iodine Value	221	204
5.	Hydroxyl value	181	174
6.	Number of hydroxyl groups	1	5
7.	Moisture content (%)	0.296	0.173
8.	R _f (100% Benzene)	0.86	0.71

FT IR Spectroscopy of cardanol –furfural resin

Fig –3 depicted the FT IR spectrum of cardanol fufural resole type phenolic resin (CR₁). A broad peak centered at 3392 cm⁻¹ appeared in the spectrum (Fig-3) confirmed the presence of phenolic hydroxyl group in the resin .The peaks appeared at 3008 cm⁻¹ and 2854 cm⁻¹ might be due to the presence of aromatic C- H stretching and aliphatic C -H stretching respectively present in the side chain of cardanol .The stretching vibrations 2925.81 cm⁻¹ and 2854 cm⁻¹ and deformative vibrations near 1394.44 cm⁻¹ and 1458cm⁻¹ might be due to the presence of CH₂ and CH₃ groups. These above mentioned peaks due to stretching and deformative vibrations indicated that the polymerization has taken place through substitution of CH₂OH and not through the double bond in the side chain. The sharp peak at 2854cm⁻¹ might be due to the C-H stretching in a methylene bridge which might be due to the condensation reaction between cardanol and furfural. The sharp peaks near 723cm⁻¹ and 1271cm⁻¹ indicated ortho and para substitution in benzene nuclei. A peak around at 1271cm⁻¹ corresponding to phenol C-O stretching.

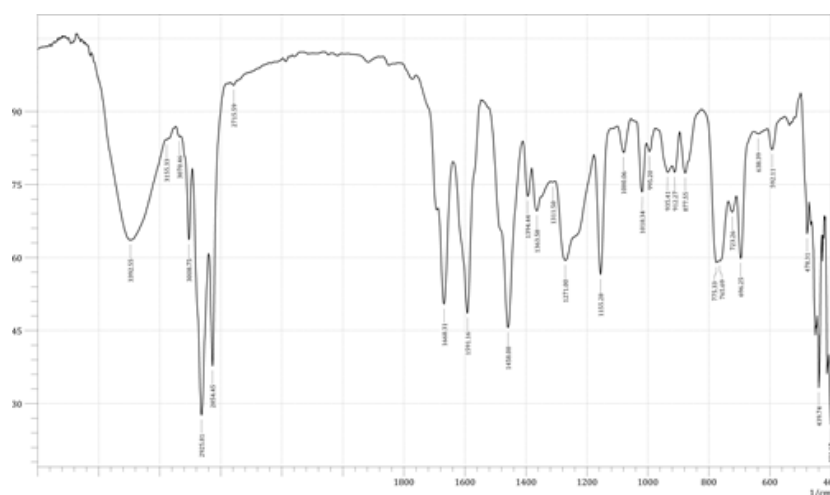


Figure 3: FT IR Spectrum of CR₁

¹H-NMR Spectroscopy of cardanol –furfural resin

In the ¹H-NMR spectra of cardanol - furfural resin samples, the peaks at 6.66 δ - 7.25 δ is due to aromatic protons of benzene and furan ring. The peaks around the region at 5 - 5.45 δ is due to the methylene (C=CH₃) protons of allyl side chain originally present in cardanol and the peaks at 0.8 - 2.83 δ as due to the long aliphatic chain. The peak at 0.805 δ is due to terminal methyl group of the

side chain. The strong peak at 1.30 δ is attributed to the long chain (more than five methylene groups) of the side chain. The peak at 2.82 δ is also indicates the methane proton of $C_6H_5-CH-C_4H_3O$ for the bridge between two phenyl rings and one furan ring. All these spectral data indicated that the condensation of methyloated cardanol with furfural has been completed under experimental conditions.

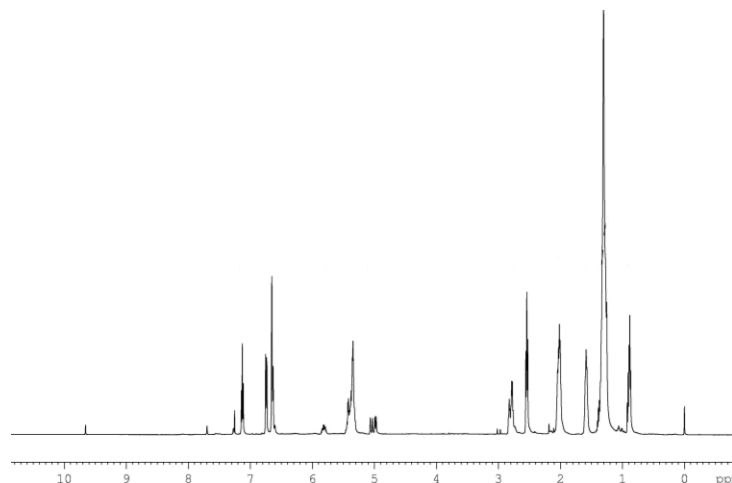


Figure 4: ¹H-NMR spectrum of CR₁

FT IR Spectra of polyurethane and its composite

The FT IR spectra of CR₁P and CR₁PS are shown in fig.5a and fig.5b. The characteristic absorption at 3341 cm^{-1} corresponding to urethane linkage (-NH stretching, bonded) which is broadened due to the formation of hydrogen bond and carbonyl group. There is a band at 1696 cm^{-1} which is attributable to free C=O urethane groups and the band at 1590 cm^{-1} corresponding to C=O stretching (bonded) in urethane and 1449 cm^{-1} corresponding to N-H bending in urethane.

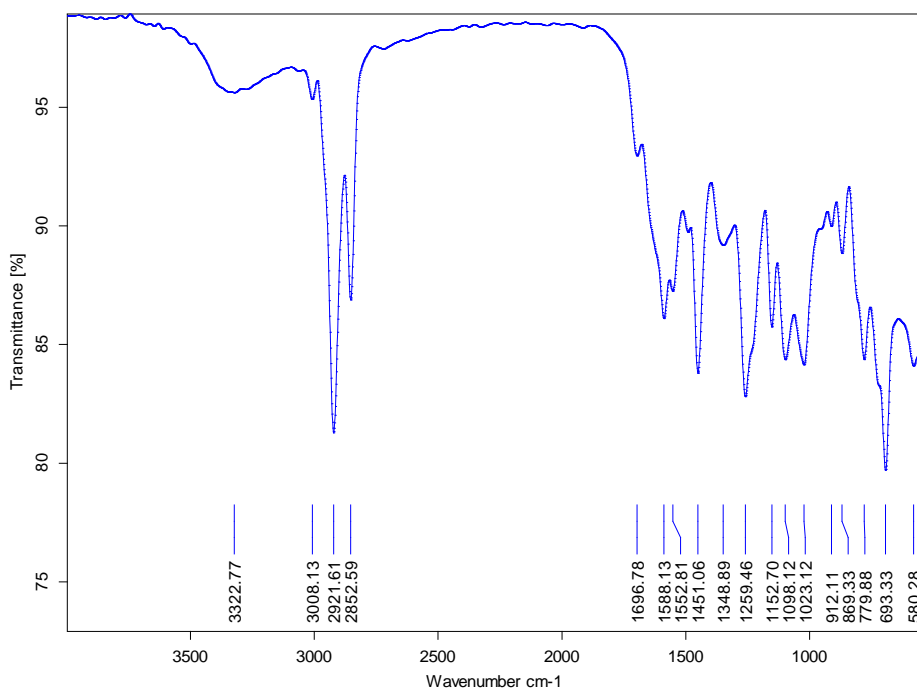


Figure 5a: FT IR spectra of CR₁P

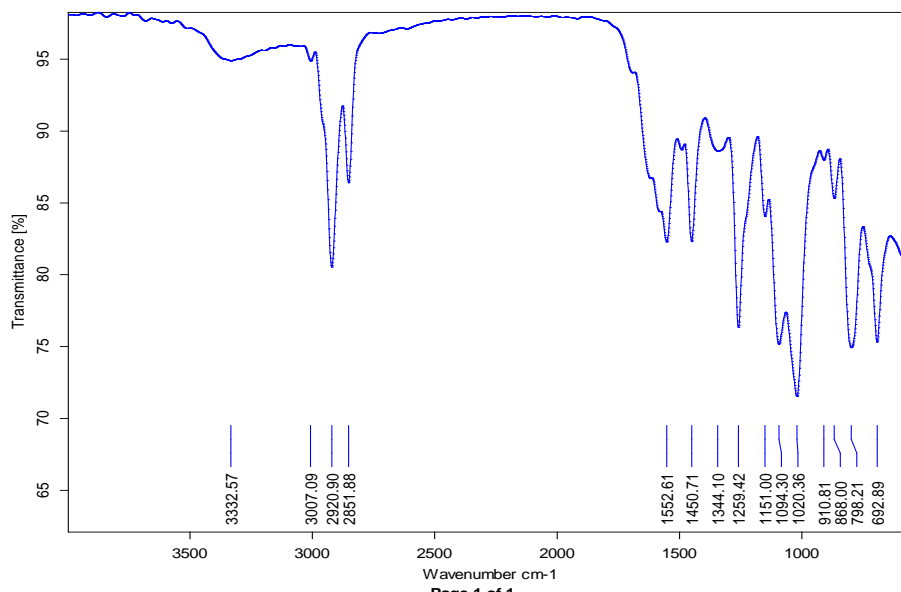


Figure 5b: FT IR spectra of CR₁PS

Thermal properties of polyurethane and its composite

TG/DTA thermograms of polyurethanes (CR₁P) and its composite (CR₁PS) are presented in Fig 6a and 6b respectively. The polyurethane sheet shows three exotherms, a very weak one below 200⁰C and two strong exotherms around at 380⁰C and 520⁰C. The weak exotherm is due to the cleavage of meta substituted alkyl side of the phenyl ring. The polyurethane composite shows three exotherms a very weak one is at 200⁰C and two strong exotherms around at 500⁰C and 635⁰C. The polyurethane composite thermally degraded successively after the cleavage of meta substituted alkyl side chain due to higher crosslink density.

The TGA curves of polyurethanes and polyurethane composite decompose in three distinct stages. The initial decomposition at 200⁰C is attributed to the moisture retained in the sample. The polyurethane sheet decomposed around at 370⁰C, but polyurethane composite decomposed around at 380⁰C. This is due to the decomposition of polyurethane moiety. The third decomposition of polyurethane is at 520⁰C and the decomposition of polyurethane composite is at 545⁰C. This is due to the disintegration of the resin moiety into simpler molecules.

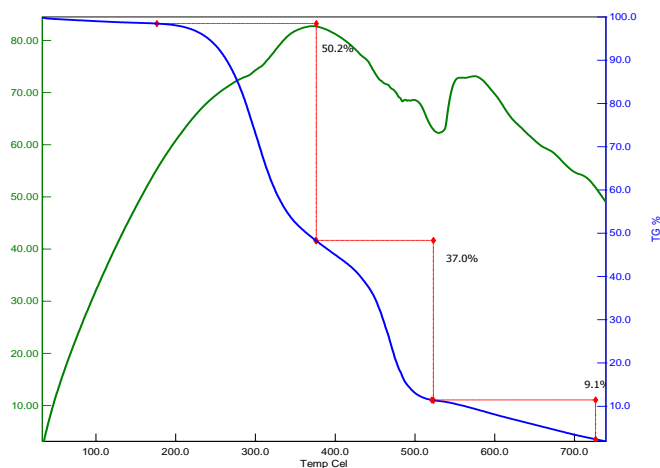


Figure 6a: TG/DTA curves of CR₁P

When compared to the TG/DTA curves of CR₁P and CR₁PS, the polyurethane composite has got more withstanding capacity. The degradation temperature of CR₁PS is more than the CR₁P sheets. So it is more stable when compared to CR₁P sheets.

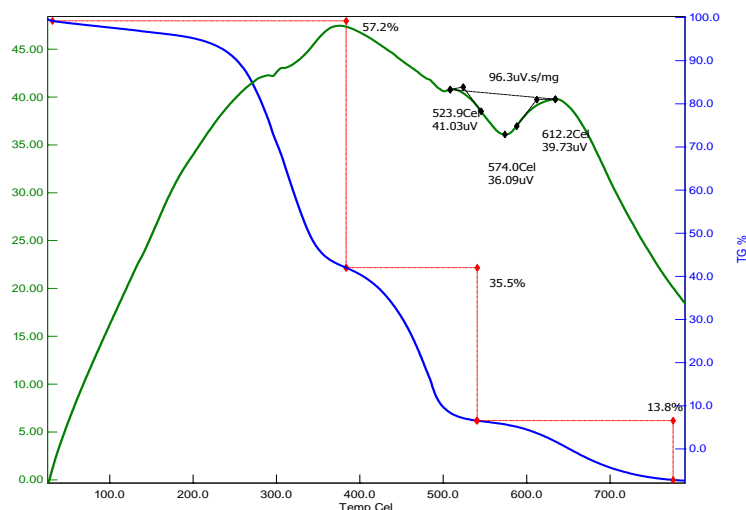


Figure 6b: TG/DTA spectra of CR₁PS

CONCLUSION

From the results it can be concluded that the fibre reinforced polyurethane composite sheets were better thermal stability than polyurethane sheets. The polyurethane composites are used in biomedical applications.

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