

Synthesis and Spectral Studies on Cardanol Based Polyurethanes

Y. Jasmala Joy, A. Malar Retna, N.J. Sangeetha

Department of Chemistry and Research Centre, Scott Christian College (Autonomous), Nagercoil, Tamil Nadu, India

Abstract— Cardanol is a renewable organic resource obtained as a byproduct from the cashew industry. The present study has been carried out with an aim to manufacture rigid polyurethanes from natural and eco – friendly sources due to the rising prices of petrochemicals and also as an environmental concern. Vegetable oil based polyurethanes promising a new generation polymers which are low cost materials in the family of polyurethanes. Cardanol based phenolic resin has been synthesized by condensing cardanol with furfural in a particular mole ratio using phthalic acid as catalyst. The progress of the reaction was monitored by determining the free furfural and free phenol content. The resin was cured by using the curing agent 4, 4¹ - methylene bis(cyclohexyl isocyanate) and the catalyst dibutyltin dilaurate to produce polyurethane. Polyurethanes are an important class of polymers that have found place in many applications. The physico chemical and spectral properties of resin and polyurethane have also been studied.

Keywords— cardanol, dibutyltin dilaurate, furfural, polyurethane, resin.

I. INTRODUCTION

Cardanol is a meta substituted alkyl phenol derived from cashew nut shell liquid and can be regarded as a versatile and valuable raw material for polymer production and also it can be condensed with active hydrogen containing compounds to yield a series of phenolic resins, for instance base catalyzed resoles and acid catalyzed novolacs [1-5]. Considerable attention from polymer scientists is devoted to utilize their potential attributes as a substitute for petrochemical derivatives and had found use in cardanol based phenolic resins for brake linings, surface coatings, and other miscellaneous applications [6-8].

The synthesis of vegetable oil based polymeric materials is having an admirable physical and chemical property [9]. Raw materials based on vegetable oils are important in our life because they have a number of excellent properties for producing valuable polymers such as polyurethanes, amides, polyesters, and epoxy resins. There is a developing attentiveness in the improvement of vegetable oil based polyurethane. This interest is

economically guided due to vegetable oils are which cheap and renewable resources [10].

Polyurethanes are a unique class of polymers that have a wide range of applications because their properties can be readily tailored by the variations of their components [11]. Thus polyurethanes provide a versatile range of properties and find extensive applications especially in the biomedical field which include synthesis of catheters of wide range [12], pacemaker lead insulation [13], polyurethane vascular grafts and artificial heart valves [14].

II. EXPERIMENT

2.1 MATERIALS

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

2.2 METHODS

2.2.1 SYNTHESIS OF CARDANOL – FURFURAL RESIN

Cardanol – furfural resin was synthesized from cardanol and furfural by using phthalic acid as catalyst. The catalyst was dissolved in 10 ml methanol. Cardanol was taken in a three neck round bottom flask and furfural was added by drop wise to the cardanol through a dropping funnel along with the catalyst solution. The reaction mixture was heated under constant stirring at 120°C. The reaction resulted in the formation of cardanol - furfural resin [CFR].

2.2.2 SYNTHESIS OF POLYURETHANE

Polyurethane sheets (CFRPU) 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 80°C for 48 hours.

III. RESULTS AND DISCUSSION

3.1 PHYSICO CHEMICAL CHARACTERISTICS OF CARDANOL – FURFURAL RESIN

The physico chemical properties of the cardanol and the synthesized resins are presented in Table 1. From the table it is clear that the resin possess mild phenolic odour.

A slight decrease in the iodine value of the resin may be due to the steric hindrance of adjacent bulky groups to the addition of iodine mono chloride. The specific gravity of the resin found to be greater than cardanol. Thin layer chromatographic study of the resin in solvent system 100% benzene (1:1 benzene) should be a distinct single spot and the R_f value for cardanol- furfural resin was different from that of cardanol indicating the formation of the product.

Table.1: Physico chemical characteristics of cardanol- furfural resin

Sl.	Properties	Cardanol	Cardanol - furfural
1.	Colour	Dark brown	Reddish brown
2.	Odour	Phenolic	Phenolic
3.	Specific gravity(g/cc at 30°C)	0.83	0.961
4.	Iodine Value	221	203.6
5.	Hydroxyl value	181	198
6.	Molecular weight	302	1950
7.	Moisture content	0.296	0.789
8.	Thin layer chromatography, R _f value, 1: 1 benzene	0.98	0.71

3.2 FT - IR SPECTROSCOPY OF CARDANOL – FURFURAL RESIN

The FT - IR spectrum of cardanol- furfural resin is presented in Fig:1. The phenolic hydroxyl band is observed at 3396 cm⁻¹. The peaks at 3008 cm⁻¹ and 2925 cm⁻¹ are aromatic C-H stretching and aliphatic C-H stretching respectively. CH₂ peaks are found at 2713cm⁻¹

while CH₃ peaks are seen at 2854 cm⁻¹ and are confirmed by the presence of their deformative peaks at 1460 cm⁻¹ and 1392cm⁻¹ respectively. The sharp peak at 759 cm⁻¹ indicates the ortho substitution of benzene nuclei and the sharp peak at 879cm⁻¹ indicates the para substitution of benzene nuclei.

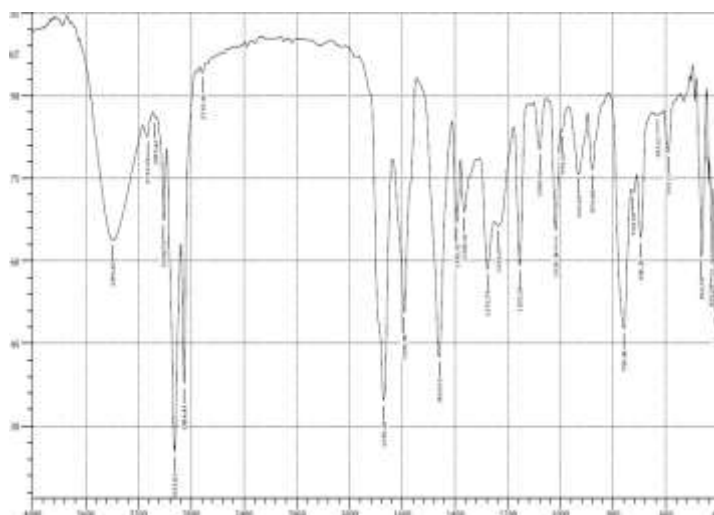


Fig: 1: FT - IR spectrum of CFR

3.3 ¹H - NMR SPECTROSCOPY OF CARDANOL – FURFURAL RESIN

In the ¹H - NMR spectra of cardanol - furfural resin samples, the peak is formed at to 6.6 - 7.25δ due to aromatic protons of benzene and furan ring. The peak around the region 5-5.85 δ is due to the methylene

(C=CH₂) protons of alkyl side chain originally present in cardanol and the peak at 0.9 δ is due to the long aliphatic chain. The peak at 0.82 δ is due to the terminal methyl group of a side chain. The strong peak at 1.31 δ is attributed to the long chain of the side chain. The peak at 2.82 δ also indicates the methine proton of (C₆H₅)₂ - CH

– C₄H₃O for the bridge between two phenyl rings and one furan ring. All these spectral data indicated that the

condensation of methylolated cardanol with furfural has been completed under experimental conditions.

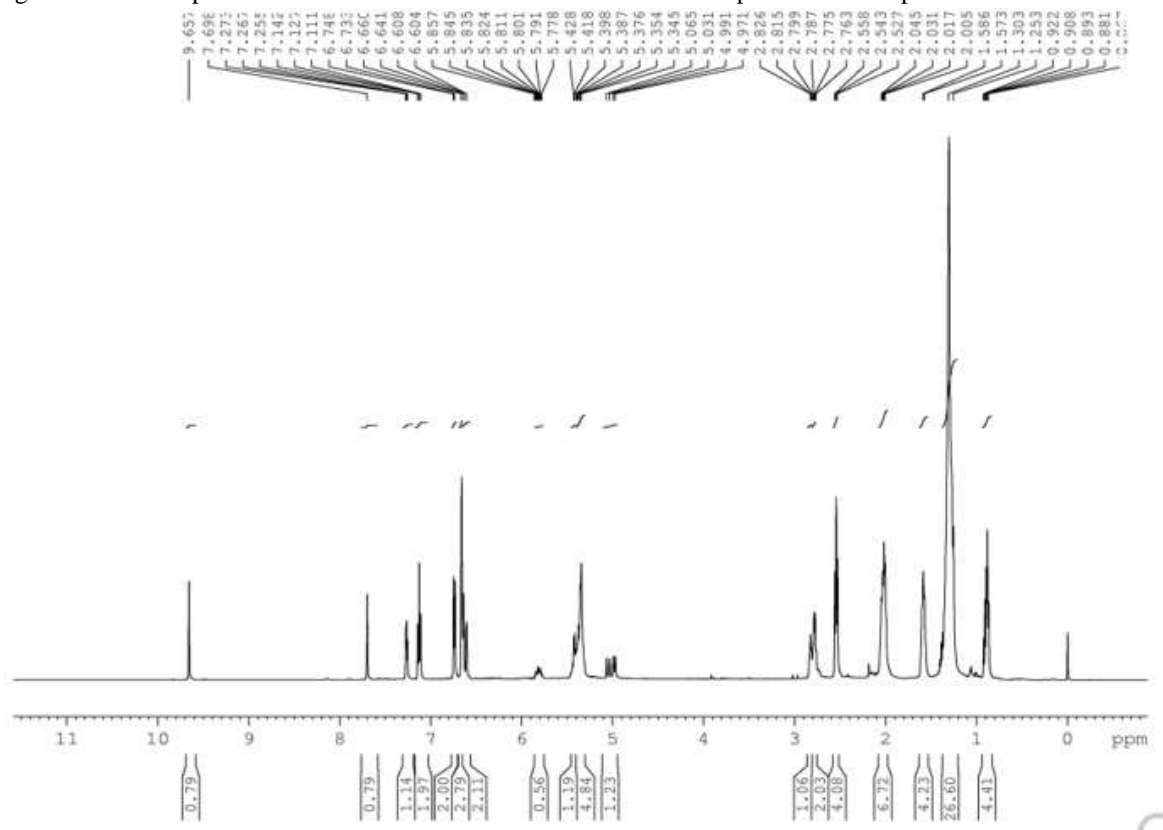


Fig.2: ¹H – NMR spectrum of CFR

3.4 FT- IR SPECTRUM OF POLYURETHANE

The FT-IR spectra of the synthesized polyurethanes are shown in Fig: 3. The characteristic absorption at 3335 cm⁻¹ corresponding to urethane linkage (-NH stretching,

bonded) which is broadened due to the formation of hydrogen bond with a carbonyl group. There is a band at 1647 cm⁻¹ which is attributed to free C = O urethane groups.

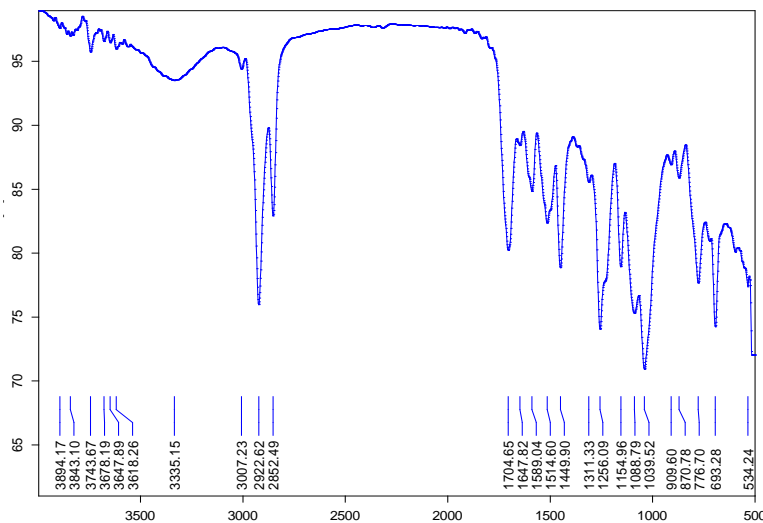


Fig.3: FT-IR spectrum of CFRPU

IV. CONCLUSION

The cardanol – furfural resin system finds numerous applications such as surface coatings, composite matrix, lamination industry, brake linings, azodyes, pesticides etc.

The modified resin has possible to diminish the use of phenolic resin based petrochemical derivatives.

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