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SYNTHESIS AND CHARACTERISATION OF NOVEL CROSSLINKED BIOPOLYURETHANE FROM COTTON SEED OIL AS ECO-FRIENDLY BIO-DEGRADABLE MATERIAL

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ABSTRACT:
Novel cross linked Bio-polyurethane were synthesized from naturally occurring cottonseed oil. Polyurethane was prepared by Epoxidation followed by the formation of Polyol by thermal hydrolysis at high temperature for five hours. The formed polyol was converted into polyurethane by the addition of hexamethylenediisocyanate at different concentration. The cross linked novel biopolyurethane were evaluated by FTIR and NMR studies. The biodegradation of the formed polymer were evaluated by soil burial test. The Chemical resistance of the cross-linked polyurethane was analyzed by different solvents. As a result of these studies, it shows that the newly synthesized Polyurethane was potentially biodegradable and used for the manufacture of leather and automobile parts.
Keywords: Burial test, epoxidation, biodegradable.

INTRODUCTION

Cottonseed oil has been found to be more useful in the preparation of rigid, semi-rigid flexible urethane resistant to moisture. Polyurethanes prepared from cottonseed oil containing unsaturated linkages and contain poly-functional groups. Polyurethane possess high hydraulic stability and good electrical insulating properties.[i]

Polyurethane was a unique material with a wide range of physical and chemical properties. Polyurethanes were used as protective coatings, adhesives, fibers and thermoplastic elastomers. [ii]

The Polyurethane composed of aliphatic diisocyanates demonstrated a greater rate of biodegradation than the polyurethane composed of aromatic diisocyanates. When the polyol used was polyhexamethyleneadipatediol of polycaprolactonediol, the polyurethane obtained as a high rate of biodegradation in the composting condition.[iii]

Vegetable oils are triglycerides of fatty acids. In order to use these compounds as starting materials for polyurethane synthesis. The preparations of polymers from vegetable oils were receiving increasing attention because of economic and environmental concerns. The polymers were mainly manufactured by the addition of diisocyanate (NCO) with polydiol of various molecular weights. The properties of Polyurethane depend on certain factors as the content of reactive groups, the degree of cross linking and the enlargement of the reacting monomers. [iv] The renewable resources have proved to be useful for the synthesis of a variety of monomers as well as linear and cross linked polymers of different types. [v]

In the present study the potential utility of edible cottonseed oil used for the preparation of novel cross-linked biodegradable polyurethane as eco-friendly biodegradable material of various consumer applications such as manufacture of packaging materials etc.

Vegetable oils were the most widely used renewable resource for the chemical and polymer industries including high degradability easy availability and possess relatively low price. [vi]

Most of the worldwide market plastics derive from fossil fuels such as oil, coal and natural gas. The continuous depletion of fossil raw materials caused environmental problems. [vii]

Plant oils can be used as a starting compound for the production of advanced polymers at different concentration[viii]. Nowadays polymers absorb small amount of moisture content and Thermogravimetric analysis helped to determine the level of water content through degradation process [ix]. For Industrial applications cottonseed oil was the most important and cheaply available in common at all over the countries [x]. Most of these plant oils and their derivatives have been used due to their renewable nature, low cost and easy availability. A large amount of plant oils were used as alternative source for the production of polymers and they were used for making adhesives and nanocomposites [xi].

Recently Polymeric research enhances the various properties of polymers such as mechanical, optical and electrical which mainly depend upon the different advancements in science and technology. For example, Hybrid fillers are developed into polymer matrices [xiii].

Vegetable oils consist of mixture of isomers such as monoterpenoids, sesquiterpenes, aromatic and aliphatic compounds [xiv]. Plants consist of aromatic compounds have ecological functions which are used for the treatment of many infective diseases [xv]. Polyurethane plays a major role in case of polymers possessing different properties and applications. The selection of polyols determines the properties of the produced Polyurethane [xvi]. Cross linked biodegradable polymers have been prepared from edible oils and consist of unsaturated linkages and they were used for making roof tops [xvii].

Polyurethne has been developed as more versatile resin. The biodegradability depend upon the nature of vegetable oil used [xviii]. Oils are nonreactive raw material and certain agents were added to activate the double and ester linkages [xix]. Differential thermal analysis and thermogravimetric analysis allow determining thermal effects during physical and chemical changes [xx].

IIMATERIALS AND METHODS

Materials:

Cottonseed Oil (Sigma Aldrich), 30% Hydrogen peroxide (Rankem), Glacial acetic acid (Sigma Aldrich), Para toluene sulphonic acid (Sigma Aldrich), 1,6-hexylene glycol (Sigma Aldrich), N,N^1 Diphenylamine (Sigma Aldrich), Hexamethylenediisocyanate. (Sigma Aldrich).

Experimental Procedure:

The technique adopted for the synthesis of Polyurethane was Stepwise polycondensation. In this method, the reaction started with the preparation of epoxy resin followed by the ring opening of epoxide linkage to polyol in the presence of an acidic medium such as, para toluene sulphonic acid. Finally, the polyol was converted to polyurethane, by the addition of a monomer such as, hexamethylenediisocyanate.

About 100g of the Cottonseed oil was taken in a three necked flask and 18g of glacial acetic acid was added in to it. About 120ml of 30% hydrogen peroxide was added dropwise for about two hours. The setup was heated for about 60 to 70^0 C for about ten hours. At last the epoxidised cottonseed oil was formed and washed it again with light warm water and keep it for about 110 ^{0} C for half an hour.

The next step was the conversion of epoxidised cottonseed oil to polyol. To a small amount of epoxy resin add 1,6-hexamethylene glycol in the ratio of 1:2. Then to the mixture add paratoluene sulphonic acid and it was kept at 250^0 C for 6 hours. At last a dark brown viscous liquid was formed and it indicated the polyol synthesis.

The final step was the addition of a monomer to the polyol in the ratio of 1:2. After the addition of hexamethylene diisocyanate to the polyol and add two drops of diphenyl amine as a catalyst. Finally, the product was transferred to a preheated mould at 110◦ C for about one week. At last a thin film of Polyurethane was formed and its thermal stability was analyzed by TG-DTA analysis

III. RESULT AND DISCUSSION

The Polyurethane cross-linked polymer was analyzed by FTIR, NMR and TG-DTA analysis. The thermal properties and the extent of degradation were also analyzed by thermogravimetric analysis. The biodegradability was studied by SEM Analysis. The Surface phenomena explained briefly about the particle degradation before and after soil burial test. The chemical resistance of the polymer against different solvents was analyzed.

FTIR (Fourier transform Infrared) Spectral studies:

FTIR spectrum showed the presence of polymeric products. The presence or absence of absorptions at certain wavelengths in the infrared spectrum can be interpreted in terms of certain features in the compound. In the FTIR Spectrum of cottonseed oil, the absorption band at 1750-1690 cm −1showed the presence of carbonyl group. The absorption band in the range of 3000-3370 cm $^{-1,}$ which indicates the presence of OH stretching frequencies. The spectral region at 1230 cm -1 and 1159 cm -1 showed the presence of the stretching vibrations of C-O bond in esters.

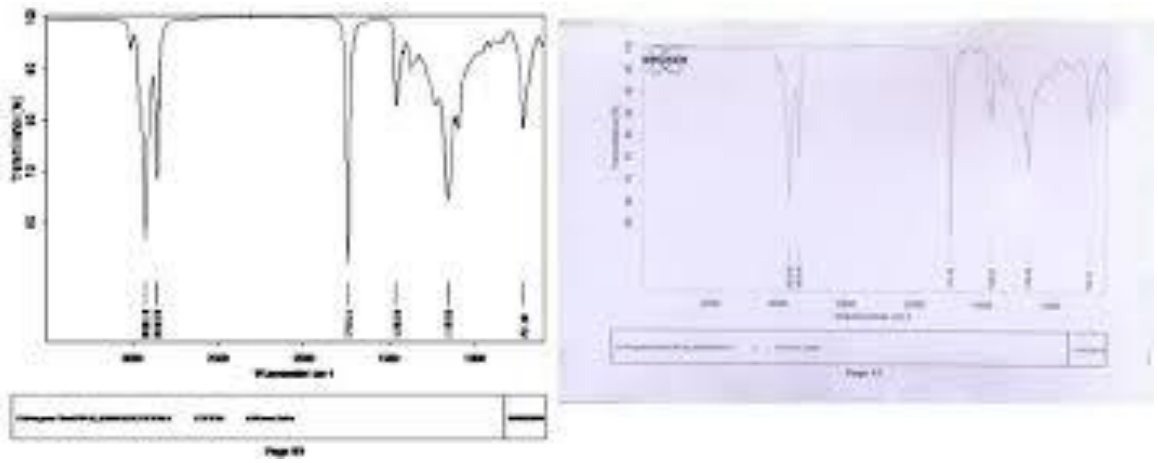


Fig.1:FTIR Spectrum of Cotton seed oil.

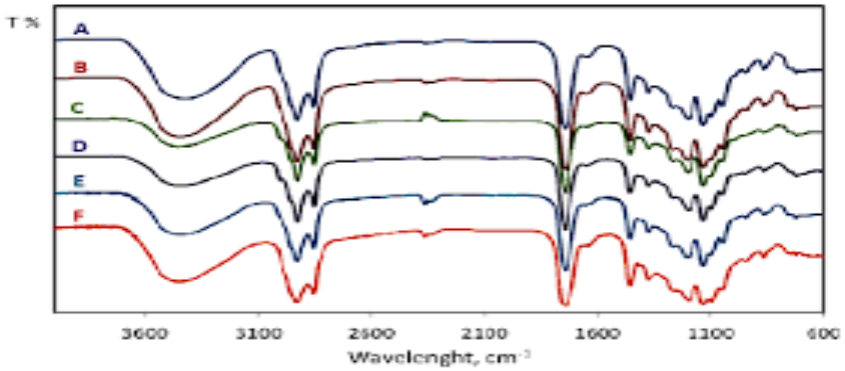


Fig.2:FTIR Spectrum of Cotton seedpolyol

The epoxidised cottonseed oil showed an absorption band at 900 cm -1due to the presence of epoxy group. Then the epoxy group disappears in the polyol spectrum due to the oxirane ring opening. The spectra of polyol showed the broad stretching peak around 1049-1269 cm -1.

H ^{1} NMR (Nuclear Magnetic Resonance) Analysis:

The H ^{1}NMR spectra recorded for cottonseed oil, epoxidised cottonseed oil and cottonseed polyol. The region ∂ between 5 to 5.4 ppm indicate the presence of olephinic proton. This peak disappeared for the epoxidised cottonseed oil. The peak ranges from 5-5.4 ppm was disappeared in the spectrum of cottonseed polyol and the peaks appear at 3.4-4.3 ppm corresponds to methylinic proton associated with–OH groups.

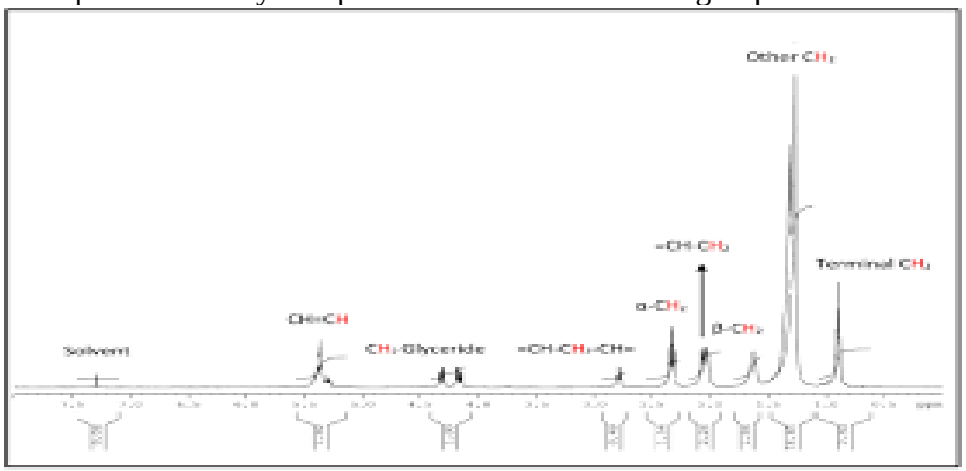


Fig.3: H1 NMR spectrum of cottonseed oil

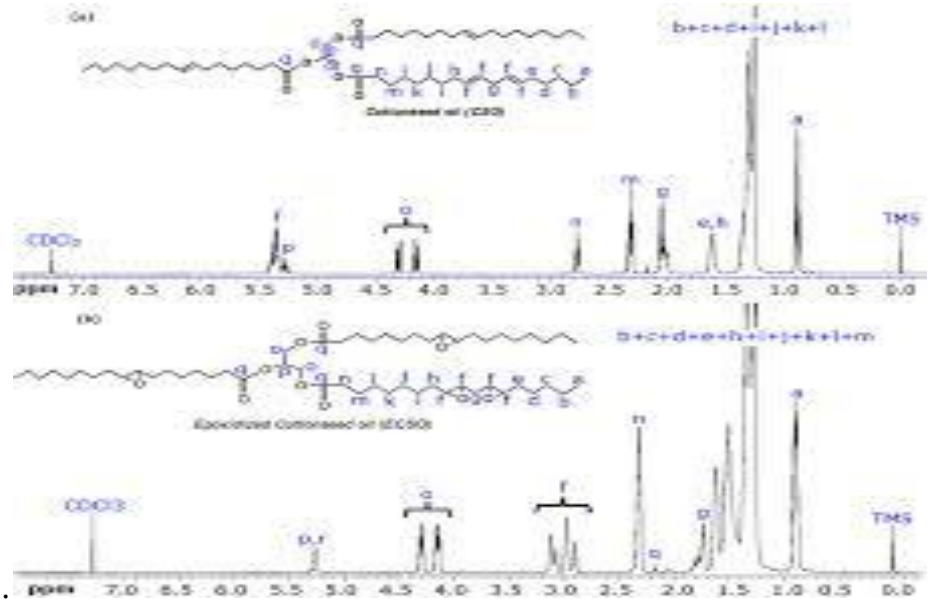


Fig.4: H1 NMR spectrum of cottonseed Polyol

Thermal Analysis:

The thermal studies showed that the prepared cottonseed oil was thermally stable. In the TG-DTA analysis of cottonseed polymer, the degradation started from 206.66^{0}C and gradually the polymer weight decreases and finally reached to 445.64^{o}C. The polymer formed was thermally stable upto 450^{o}C. The degradation of water molecule also studied at different time intervals with increase in temperature. From this study, the thermal stability of the thin film of Polyurethane was analyzed systematically.

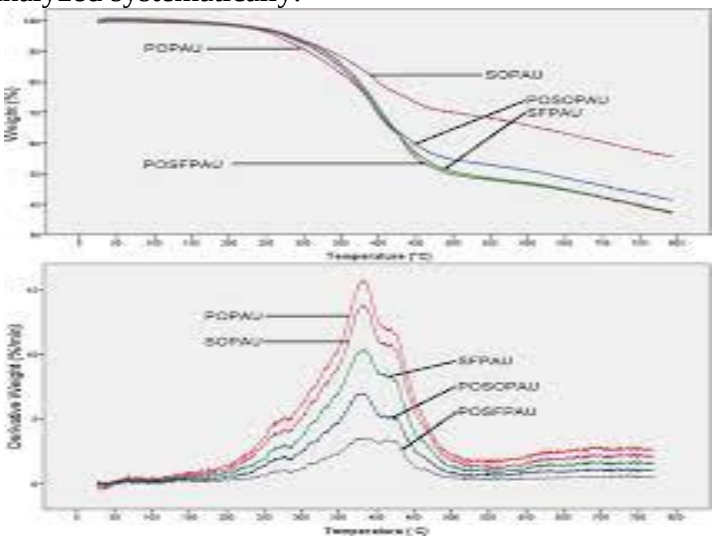


Fig. 5: TG-DTA Curve of polyurethane

Scanning Electron Microscope (SEM) Analysis:

SEM Analysis was clearly studied by soil burial test. In Soil burial test around 1.5 cm to 2 cm thin film was cut into square shape and buried into the soil. Before the soil burial test, the SEM image was taken. Daily spread water over the surface of the soil, subsequently after 72 days, the polymer was taken from the soil and washed with distilled water and dried over oven at 110 ^{0} C. Then, after soil burial again the SEM image was taken in order to compare the two images. From these, it was concluded that the prepared polymer was biodegradable in nature. SEM analysis helped to find out the distribution of particles in the polymer synthesized from

natural oils. The Scanning micrograph of SPU at 100 µm to 2 µm magnification represented in the following figure:

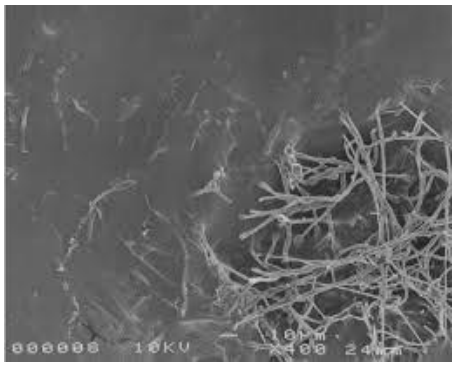


Fig. 6: SEM images of cottonseed polyurethane before soil burial test.

The surface SEM images of CPU were uniformly distributed before soil burial test. The SEM images of CPU after burial under the magnification from 100 µm to 2 µm showed that they were not uniformly distributed and the polymer synthesized were biologically degradable.

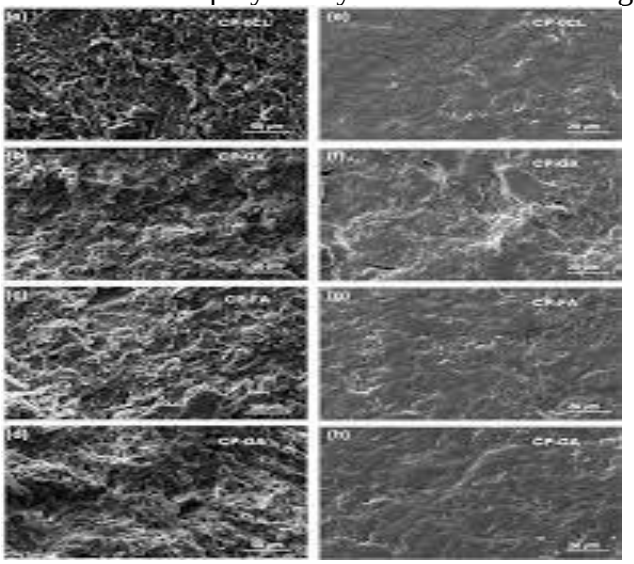


Fig. 7: SEM images of CPU after Soil burial test.

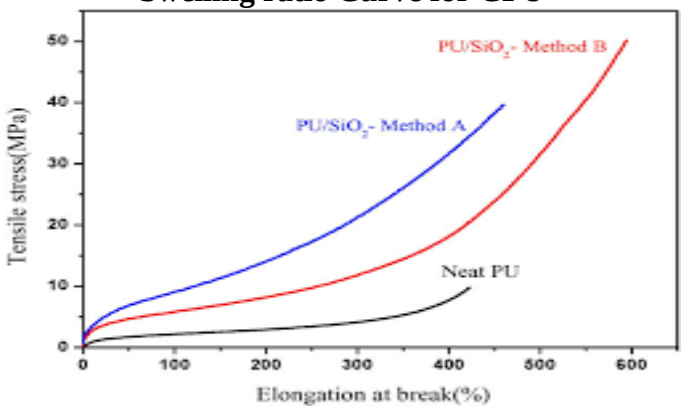
Swelling Analysis:

The percentage of swelling in Polyurethane was studied systematically. The samples for swelling analysis suspended in alkaline and acidic medium. All the polymeric samples show minimum swelling in basic medium. But the polymeric sample shows swelling in case of acidic solvents, such as sulphuric and sodium chloride. The polymeric samples were allowed to immerse in different solvents for 72 hours at room temperature. Then the samples were weighed after 2,4,6,8,12,24,48 and 72 hours.

Degree of Swelling and Swelling Ratio:

Squares of 1.5 cm to 2 cm of thin film of cotton polyurethane were finely cut into pieces and dried at 60^{o} C and initially the weight of the polymer (w1) was taken. Then the sample was immersed in distilled water at 30^{0} C for a minute. The samples were taken out from the water and moisture was removed by using filter paper. They were weighed again and it was noted as (w2). The samples were weighed again drying at 60^{0} C and noted as (w3). The degree of swelling is calculated by using the equation Degree of Swelling= (w2-w3)/w3.

Swelling ratio Curve for CPU



IV. CONCLUSION

The biodegradable cotton seed polyurethane was prepared by stepwise polymerization technique. The method used for the preparation was simple and easily carried out. The presence of epoxy, alcoholic group was analyzed by FTIR spectrum. The nature of protons in the product was clearly explained by NMR analysis. The thermal stability of the polymer was studied by TG-DTA analysis. The removal of moisture content at different stages was analyzed by thermo gravimetric analysis. The SEM images obtained after soil burial test, which was explained the biodegradability of the polymer. The difference in swelling phenomena indicated that the difference in weight of the polymer was due to the nature of the solvent taken for swelling analysis, which influenced the physical properties of the cotton seed polyurethane polymer.

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