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Research Article

ENHANCED COATING PROPERTIES OF POLYURETHANES DERIVED FROM *GOSSYPIUMHIRSUTUM L. SEED* OIL

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ABSTRACT

Polyurethanes (PUs), are measured as one of the mainly used synthetic polymer families in the world. At the industrial scale, PUs were obtained through a polycondensation reaction of polyisocyanate with polyol. Nowadays bio-based polyurethanes have been occurred a large attention. These biobased PUs could replace petroleum-based polyurethanes in industry and particularly as coatings, binders or compounds for automotive and aircraft industries. This large application can be described due to their good mechanical and thermal properties, including abrasion resistance, high toughness as well as chemical resistance. *Gossypiumhirsutum L.* (cotton) seed oil is one of the dominant vegetable oils and one of the earliest seeds used to produce oil because of its ample supply, lower price than competing oils and biodegradability. This present work succeeded with the improved properties PUs using, the bio-resource, *Gossypiumhirsutum L.* (cotton) seed oil. Through in-situ epoxidation and hydroxylation, the cottonseed oil was transformed into a polymerizablepolyol. This hydroxylated cottonseed oil was polymerized with hexamethylenediisocyanate at pre-studied NCO-to-OH ratio to furnish enhanced propertied polyurethanes. Analytical methods such as FT-IR and 1H-NMR, and physical properties of viscoelastic behaviours, tensile strength, modulus, % elongation, specific gravity and mechanical ability were employed. The individual characterisations of FT-IR and ^{1}H-NMR characterizations strongly supports the presence of hydrolysed cottonseed oil and polyurethane formations. In addition to that the higher acid value and hydroxyl values such as 9.86 and 166.2 respectively reflects the excellent formation of hydroxylated cottonseed oil. The static mechanical properties of synthesised polyurethane at optimum NCO-to-OH ratio obtained as: tensile strength (σ)-15.29 MPa, modulus (E)-4.49 MPa and %elongation as 93.47 ($\%E$). These properties reinforced the polyurethane matrix and make it more compact and stiffer.

Keywords: *Gossypiumhirsutum L.*,Cotton Seed, Polyurethanes, Coating.

1. INTRODUCTION

Polyurethanes (PUs), having a relatively short history, of slightly more than 70 years, became one of the most dynamic groups of polymers, demonstrating flexible properties suitable for use in nearly all the fields of polymer applications-foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibers and so on. With a worldwide production of 14Mt in 2006, PUs are the 6th most widely used polymer [1]. Additionally, they are used in some specialty applications such as biomedical surgery. PUs are obtained by the reaction of an oligomericpolyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate). All these resources come from petroleum but recently, chemical industry has paid rigorous interest to the production of biobasedpolyols, mostly synthesized from vegetable oils [2-4].

Among many approach from different resources, the main attentive approach is to obtain biobasedpolyols consists in the use of natural oils (vegetable or animal) i.e. the most rich and cheapest renewable organic resources [5]. Vegetable oils are coming from various plants (soybean, palm, rapeseed…) and contain mainly triglycerides molecules where the three hydroxyl functions of glycerine are esterified with fatty acids (Figs. 1 and 2). These fatty acids could be saturated - with non-reactive aliphatic chains (stearic or palmitic acids…) or unsaturated - with aliphatic chains bearing double bonds (oleic, linoleic, linolenic, ricinoleic acids…). These natural oils, and particularly unsaturated ones, are very interesting because several reactions could be performed from their different clusters in order to obtain biobased polyols, enabling reactions with diisocyanates to get polyurethanes.

Gossypiumhirsutum L. (cotton) seed oil has just been used as initial material in the synthesis of midway macromolecules and for succeeding development of polymers for coating applications [6-10]. For the reason that of the availability of cotton seed oil in India and its capability to offer the required functionality, for example double bonds and ester linkages, it may be a potential, vital, and low-priced raw material for making of plant oil based resin for coating applications. In cotton seed oil, the ratio of unsaturated (65-75%) to saturated (26-35%) fatty acids is almost 2:1; of its unsaturated fatty acids 18-24% are monounsaturated and 42-52% are polyunsaturated [11-13]. This current research aimed to improve the properties PUs using, the bio-resource, *Gossypiumhirsutum L.* (cotton) seed oil.

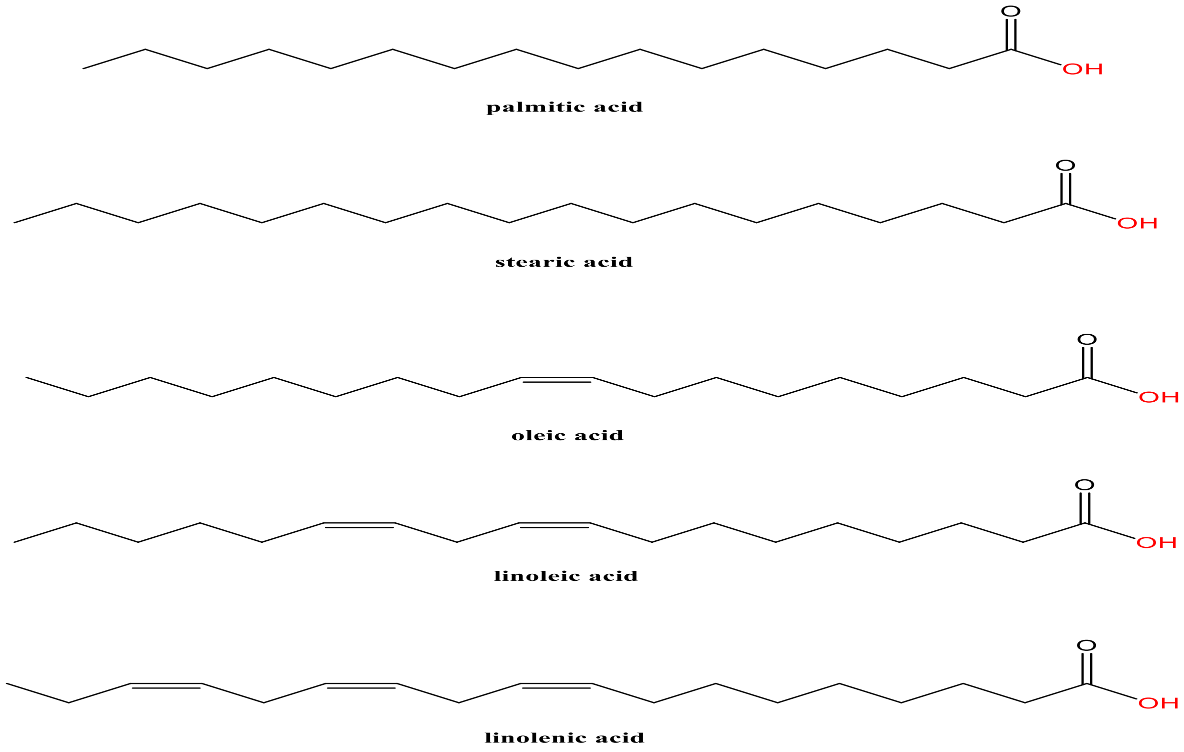


Fig. 1: Chemical structures of basic constituents mostly presented in cotton seed oil

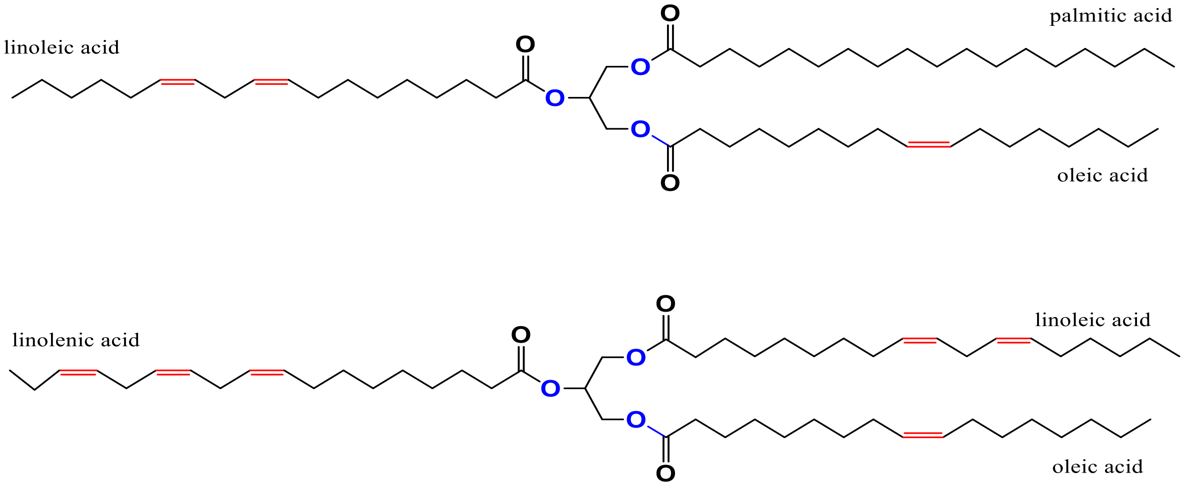


Fig. 2: Chemical structures of triglycerides established in cotton seed oil

2. EXPERIMENTAL METHODS

2.1. Chemicals

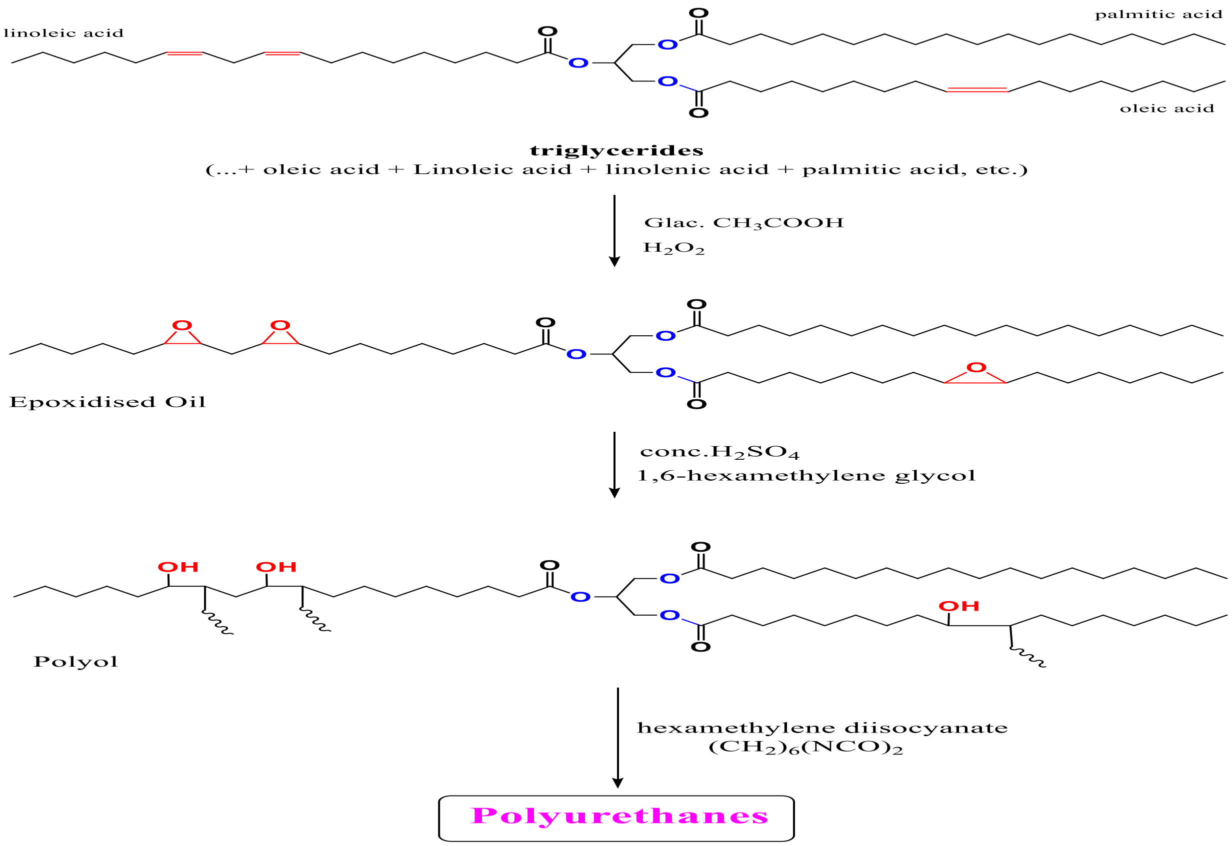
Commercial cottonseed oil was procured from local market at Tirunelveli, Tamilnadu, India. The chemicals glacial acetic acid, hexamethylenediisocyanateand 1,6-hexamethylene glycol were supplied from Sigma-Aldrich and the remains hydrogen peroxide (30% w/v), conc. sulfuric acid, sodium sulfate, sodium bicarbonate, hydrochloric acid, sodium chloride, sodium hydroxide, toluene, etc., were purchased from S.D. Fine Chemicals, Mumbai, India. All the reagents were used without further purification and double distilled water was used throughout the study wherever required.

2.2. Synthesis of Polyurethanes (Epoxidation-RingOpen-Polymerization)

Vegetable oils can be epoxidized leading to interesting building blocks for biobased chemistry [14]. The most currently used method to epoxidize vegetable oil is based on peracetic acid formed in situ from reaction between acetic acid and hydrogen peroxide, with ion-exchange resin catalyst, at 60°C in toluene, during 12 h (Scheme 1). Double bond conversion into epoxide functions can be quantitative [15] and estimated as well.

About 100g of the cottonseed oil was taken in a three necked flask and 18g of glacial acetic acid was added into it. About 120 mL of 30% (v/v) hydrogen peroxide was added dropwise for about two hours. The setup was heated for about 60 to 70°C for about ten hours. At last the epoxidized cottonseed oil was formed and washed it again with light warm water and kept it for about 110°C for half an hour.

The next step is the conversion of epoxidized cottonseed oil into polyol. About 1:2 ratio of epoxidized cottonseed oil and 1,6-hexamethylene glycol were mixed together. Then, the mixture was added with paratoluenesulphonic acid and then kept at 250°C for six hours. Finally a dark brown viscous liquid was formed which indicated the completion and formation of polyol synthesis. The hydroxyl numbers in all formulations were determined as per MGA 0491. The hydroxyl number is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid produced by the hydrolysis of one gram of acetylated fat.



Scheme 1: Schematic representation of synthesis of polyurethanes from the triglycerides found in cotton seed oil

The final step i.e., the synthesis of polyurethanes was the addition of a monomer to the polyol in the ratio of 1:2. Next to the polyol synthesis, the prestudied quantity of hexamethylenediisocyanate was added to the polyol and few drops of diphenyl amine was added as a catalyst. Finally, the whole mixture was transferred to a preheated mould at 110°C and kept for about one week. At last a thin film of polyurethane was formed and then characterized to study its mechanical and other physical properties.

2.3. Characterizations

Fourier-transform infrared (FTIR) spectra of the cottonseed oil, epoxidized cottonseed oil, hydrolysed cottonseed oil (polyol) and synthesised polyurethanes were recorded by use of a Perkin-Elmer Spectrum 100 (USA) within the range 450-4000 cm^{-1} with resolution of 4 cm^{-1}. ^{1}H NMR spectra of epoxidized cottonseed oil and polyols were recorded, at ambient temperature, by use of a Bruker 500 MHz spectrometer; CDCl$_3$ was used as solvent and tetramethylsilane (TMS) as standard. The viscoelastic behavior of PU films was analysed by use of a dynamic mechanical thermal analyser (DMTA; DMA-Q-800; TA Instruments, USA) in tensile mode at a frequency of 1 Hz and a heating rate of 5°C min^{-1}. The tensile strength and percentage elongation of free PU films were determined by use of a Shimadzu (Japan) model AGS-10k NG universal testing machine (UTM) at room temperature. Other physical properties such as modulus, %elongation and specific gravity were studied as per standard recommended procedures.

3. RESULTS AND DISCUSSION

3.1. Physical Properties of Cottonseed Oil and Hydroxylated Cottonseed Oil

The proposed synthetic routes were carefully carried out at each stages of polyurethane synthesis from *Gossypiumhirsutum L.* cottonseed oil. Specific gravity and viscosity of the cotton seed oil and hydroxylated cotton seed oil were found to be as 0.926; 53 cps; and 1.0073; 5526 cps respectively at room temperature. In addition to that acid value and hydroxyl values of hydroxylated cottonseed oil are observed as higher such as 9.86 and 166.2 respectively reflects the excellent formation of hydroxylated cottonseed oil.

3.2. FTIR Characterization

Fig. 3 shows the FTIR spectra of synthesised polyurethanes from cottonseed oil. The missing of apeak at 2230 cm^{-1}corresponds to N=C=Oconfirms that all the isocyanate groups reacted during the polymerization. Characteristic top at 1742 cm^{-1} (-C=O stretch of amide-I), 1461 cm^{-1} (amide-II stretch consisting of a mixture of top mN-H, mC-N, and mC-C), and 721 cm^{-1} (amide-IVCO-NH out-of-plane vibration) are symptomatic of urethane formation. The amalgamation band at 1655 cm^{-1}is corresponds to -C=O of urethane groups with respect to biscarbamate connections.

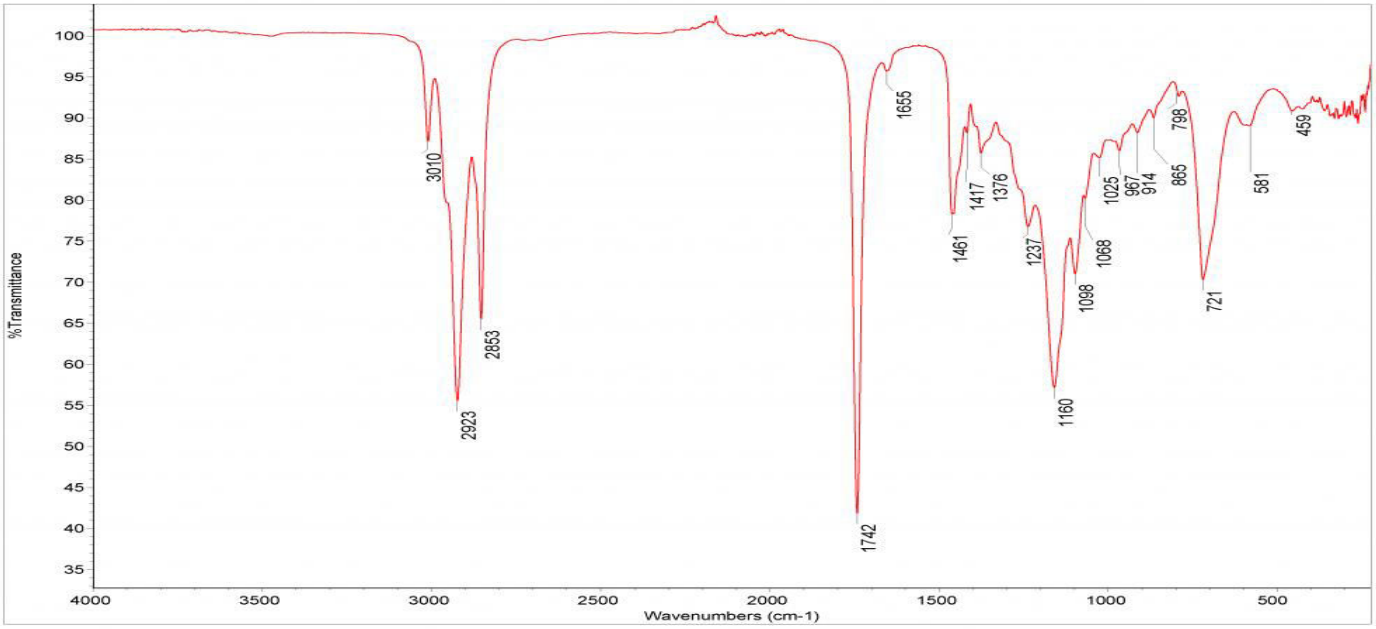


Fig. 3: FTIR spectrum of polyurethane synthesised from cottonseed oil

The top corresponding to the ester group of the triglyceride molecule observed at approximately 1742 cm^{-1} has transfered from 1718 cm^{-1} (observed in hydrolysed cotton seed oil); this is for the reason that of the consequence of H-bonding with the-NH group of the urethane moiety. These results authenticate the existence of H-bonding between-NH and -C=O groups. The peaks range from 2840-3020 cm^{-1}were corresponds to the –NH stretching vibration of imide group exist in the polyurethanes. These FTIR spectral data reveals the excellent formation of polyurethanes which was synthesised from cottonseed oil.

3.3. Characterization of ^{1}H NMR Spectra

The ^{1}HNMR spectra recorded for cottonseed oil, epoxidised cottonseed oil and cottonseed polyol. The ∂ region between 5 to 5.4 ppm indicate the existence of olephinic proton. This top 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 methylenic proton associated with -OH groups.

3.4. Mechanical Properties

The static mechanical properties of synthesised polyurethane at optimum NCO-to-OH ratio obtained as: 15.29 MPa of tensile strength (σ), 4.49 MPa of modulus (*E*) and %elongation as 93.47 (*%E*). The mechanical performance were due to the number of urethane and/or urea groups, virtual or physical crosslinking, intra and intermolecular interactions, and phase mixing or separation. Issac et al observed that tensile strength (r) and modulus (E) improved whereas % elongation (%El) at break diminished as the NCO-to-OH ratio increased [9]. This is because of increasing H bonding, dipolar interaction, crosslinking density, and urea groups with growing NCO-to-OH ratio; these strengthen the PU matrix and make it more dense and rigid.

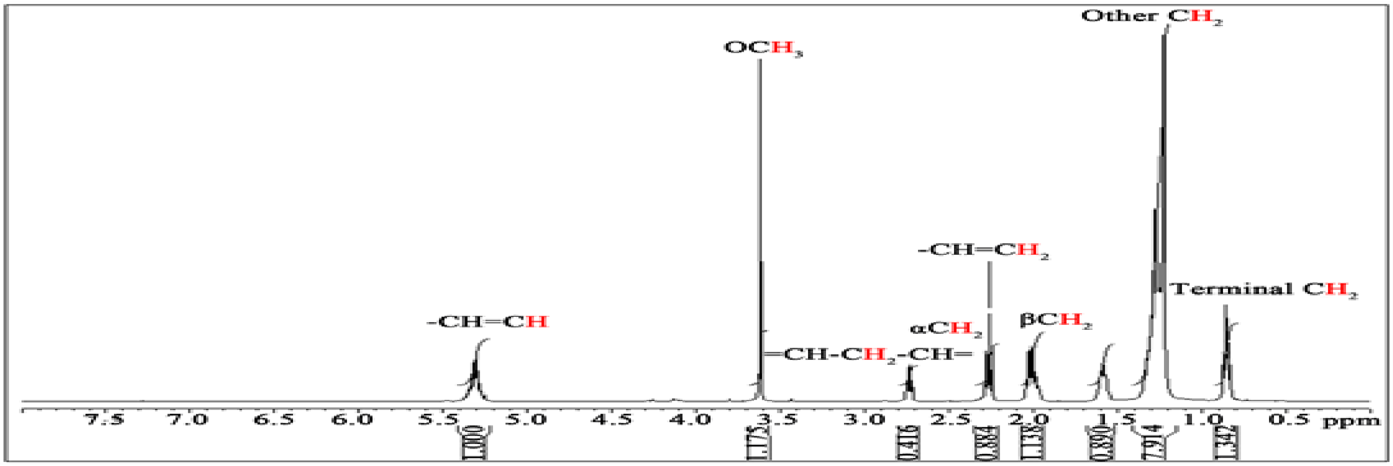


Fig. 4: ^{1}H NMRspectrum of cottonseed oil

4. CONCLUSION

An economic synthetic routes were proposed and executed for the synthesis of polyurethanes from bio-resource namely *Gossypiumhirsutum L.* (cotton) seed oil. FTIR and 1H NMR spectral reports were strongly supports the efficient formation of respective epoxides and polyols, i.e., hydroxylated cottonseed oil. Also the FTIR spectrum of final product found to be more pure formation of polyurethanes and hence favoured the present synthetic pattern. In addition to that well aggregated polymeric properties of tensile strength (15.29 MPa), modulus (4.49 MPa) and %elongation (93.47) were obtained. These findings concludes that synthesised polyurethane based from *Gossypiumhirsutum L.* (cotton) seed oil demonstrates flexible and excellent physical, chemical and mechanical properties, which may increase their requirement in coatings applications and other areas such as foam, elastomers, adhesive, ink, paints, etc.

5. ACKNOWLEDGMENT

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