FULL LENGTH ARTICLE

Preparation and characterization of polyurethane plasticizer for flexible packaging applications: Natural oils affirmed access

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Abstract Developing bio-renewable feedstock for polyurethane (PU) manufacturing and polymer industry as a whole has become highly desirable for both economic and environmental reasons. In this work castor oil (CO) and palm olein (PO) polyols were synthesized and partially used as renewable feedstock for the manufacturing of polyurethane plasticizing resin for printing ink applications. The chemical structure of the prepared polyols and polyurethanes were characterized using IR spectra and GPC and their solubility in common solvents was tested. As well, properties such as flexibility, mechanical properties, optical properties, heat seal and freeze resistance of these prepared printing inks were determined. The results indicated that the prepared printing inks from 50% synthesized polyurethane have high thermal stability, adhesion and excellent freeze resistance. The net technical properties of the new ink formulations are relatively comparable to the printing ink prepared from standard polyurethane plasticizer.

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1. Introduction

Polyurethane (PU) is a polymeric material that has versatile processing methods and mechanical properties. By proper selection of reactants, the resulting PU can range from flexible elastomers to high modulus plastics [1]. This wide range of properties makes PU an indispensable material in construction, coatings, consumer products, transportation, and medical devices [2]. Polyurethanes (PU) have numerous
applications in the coating industries because of their mechanical strength, excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance [3]. For printing inks, the primary binder is usually nitrocellulose. The stiffness of nitrocellulose requires the addition of plasticizers such as polyurethane in the ink formulation, polymeric plasticizers are incorporated into packaging inks to provide a non-migrating character, enhanced flexibility and mechanical properties, high temperature resistance, improved adhesion and resistance to water and deep freeze [4].

Similar to many polymeric materials, the production of PU relies mainly on the use of petroleum oil as the feedstock for its major components, hydroxyl-containing polyol and isocyanates. Over the last decade, as the price of petroleum oil increased, the costs of polymeric raw materials have risen steadily [5]. In contrast to the less predictable petroleum market, agriculture products, such as vegetable oils, have maintained relatively a stable price and supplies [6]. Thus, developing bio-renewable feedstock for PU manufacturing and polymer industry is highly desirable for both economic and environmental reasons [7,8].

In this respect, vegetable oils (VO) have important properties which make them valuable in the production of chemically polyols to replace petroleum-derived polyether and polyester polyols in PU production as well as in many other applications [9,10].

It is apparent that on a molecular level, these oils are composed of many different types of triglyceride, with numerous levels of unsaturation. In addition to their application in the food industry, triglyceride oils have been used for the production of coatings, inks, plasticizers, lubricants and agrochemicals [11–14].

Most of the previous works on bio-based polyurethanes using natural polyols were synthesized from modified soybean oil [1,3,15–17], castor oil [18,19], linseed oil, sunflower oil, palm oil [20–25] and rapeseed oil.

This work is concerned with the synthesis of PU plasticizers based on polyols originated from vegetable oil via epoxidation method followed by ring opening to be used in printing ink formulations. The investigation of physical properties of the obtained printing inks is shown and the obtained results were compared with the inks containing commercial PU plasticizers.

### 2. Materials and methods

#### 2.1. Chemicals

Poly tetramethylene glycol (PTMG) (MW = 2000 g/mol) as polyol was supplied by Investa-Spain, 1,4-butane diol (BDO) as chain extender, toluene diisocyanate (TDI) and dibutyltin dilaurate (DBTDL) as catalysts were purchased from Acros-Belgium, castor oil (CO) and palm olein (PO) were obtained from a local market. Ethyl Acetate, methanol and ethanol were obtained from (Petrochem-KSA), H_2O_2, formic acid and para toluene sulfonic acid were obtained from (Qualikem-India).

#### 2.2. Preparation of vegetable oil polyol

Figs. 1(a) and 1(b) represent the general structure of vegetable oils and the major triglyceride of castor oil, respectively and Fig. 1(c) represents the epoxidation method followed by ring opening route to synthesize vegetable-oil-based polyols.

#### 2.2.1. Epoxidation of vegetable oils

Palm olein and formic acid were poured into a round bottom flask and mechanically stirred at a speed of 550 RPM and under controlled temperature through a water bath with a temperature of 50 °C ± 2. To start the epoxidation, hydrogen peroxide solution (30%) was gradually charged into the mixture during the first 5 h of reaction. The molar ratio of carbon double bonds to hydrogen peroxide (C=C : H_2O_2) was 1:1.7. After charging H_2O_2 was completed, the reaction continued by mixing and controlling the temperature at 50 °C for a further 5 h. Then, the mixture was cooled down and neutralized by adding the water. Ethyl acetate was used to enhance the separation of...

![Figure 1a](image_url) Triglyceride chain containing three fatty acids by a glycerol center.

![Figure 1b](image_url) Major triglyceride of castor oil [12].

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the oil product from water phase. The water and solvent were then distilled off under a rotary vacuum evaporator.

2.2.2. Preparation of vegetable oil polyol by ring opening with water

Epoxidized PO (50 g) was weighed into a round bottom flask. Deionized water (500 ml) and para-toluene sulfonic acid (21.5 g) were added then the mixture was stirred and heated to 100 °C for 7 h. The reaction mixture was poured into a separating funnel and was washed with NaCl solution (100 ml) and NaHCO₃ (100 ml). The aqueous layer was discarded and ethyl acetate (100 ml) was added to the organic layer. The organic layer was dried over anhydrous MgSO₄ and ethyl acetate (100 ml) was added to the organic layer. Deionized water (500 ml) and para-toluene sulfonic acid (21.5 g) were added then the mixture was stirred and heated to 100 °C for 7 h. The reaction mixture was poured into a separating funnel and was washed with NaCl solution (100 ml) and NaHCO₃ (100 ml). The aqueous layer was discarded and ethyl acetate (100 ml) was added to the organic layer. The organic layer was dried over anhydrous MgSO₄ and ethyl acetate (100 ml) was added to the organic layer. Deionized water (500 ml) and para-toluene sulfonic acid (21.5 g) were added then the mixture was stirred and heated to 100 °C for 7 h. The reaction mixture was poured into a separating funnel and was washed with NaCl solution (100 ml) and NaHCO₃ (100 ml). The aqueous layer was discarded and ethyl acetate (100 ml) was added to the organic layer. The organic layer was dried over anhydrous MgSO₄ and ethyl acetate (100 ml) was added to the organic layer. Deionized water (500 ml) and para-toluene sulfonic acid (21.5 g) were added then the mixture was stirred and heated to 100 °C for 7 h. The reaction mixture was poured into a separating funnel and was washed with NaCl solution (100 ml) and NaHCO₃ (100 ml). The aqueous layer was discarded and ethyl acetate (100 ml) was added to the organic layer. The organic layer was dried over anhydrous MgSO₄ and ethyl acetate (100 ml) was added to the organic layer.

2.3. Preparation of polyurethane resin

PUs were prepared via one shot method in which the blends of the PTMG 2000, vegetable oil polyol (50:50) and chain extended palm olein polyol (HPO).

2.4. Measurements

(1) Acid number and hydroxyl number were determined according to ASTM D1639-90 and ASTM D1957-90, respectively.

(2) The viscosity of the polyol and polyurethane were determined using the Brookfield digital viscometer model DV-E (ASTM D4878-88: Standard Test Methods for Polyurethane Raw Materials-determination of viscosity of polyols).

(3) Chemical structural studies were conducted using Bruker FTIR analyzer; ALPHA-Platinum FT-IR Spectrometer with ATR Platinum–Diamond sampling module.

(4) The molecular weights of the prepared polyols and polyurethanes were determined using GPC Agilent model 1515 pump system equipped with 1260 infinity refractive index detector and using THF as eluent operating with a flow rate of 1.00 mL/min at 35 °C. Column PL-gel 3 μm Mixed E 300 × 7.5 mm covering a molecular weight range of 600–30,000 mg/g was used and was calibrated using five polystyrene narrow standards.

(5) The water content of the polyol was determined using the Karl Fischer Titrator model Metrohm 870 Titrino plus according to (ASTM D4672-00(2006) el: Standard Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols).

(6) Free NCO was followed qualitatively during the preparation of polyurethane by FTIR ANALYZER and was determined in the final product quantitatively by di-butyl amine titration method.

(7) Solubility in common solvents: The test was performed for the prepared polyurethane resin in which a 50:50 solution was prepared from the resin and common solvents such as ethyl acetate, ethanol, isopropanol and MEK.

(8) Solid Content: Determination of solid content was carried out according to ASTM D1644-06 using air drying oven DHG 9055 A model.

2.5. Coating characterization

The coatings were tested using the following techniques:

2.5.1. Printing ink formulation, application and film thickness

The printing ink was formulated according to the formulation given in Table 2 then it was applied on polypropylene, polyester and polyethylene milky films using hand coater 12. The film thickness was measured using KAFER micrometer and was found to be from 3 to 4 μm for all ink samples.

2.5.2. Flexibility and mechanical properties

2.5.2.1. Curling. The curling of the polypropylene printed ink film was carried out according to ASTM D4825-97.

2.5.2.2. Crinkle. The printed dry film was manually crinkled into a ball then unfolded to determine whether there are any cracks or discontinuities in the printed film or any flaking of the printed areas from the substrate. No cracks, discontinuities or flaking were visible.

2.5.2.3. Adhesion. Adhesion was measured according to ASTM D2252-03 and examined visually for the detached ink from the printed film.

2.5.3. Optical properties

2.5.3.1. X-rite measurements (color strength – ΔE – transparency). Printing ink strength, lightness and shade were measured using EXACT – PANTONE X-rite spectrophotometer, where; ΔE represents the differences between samples and standard in these three parameters.

2.5.3.2. Gloss. The gloss of the printed film was measured on the printed polypropylene film using BIUGED BGD 514 (60°) gloss meter.

2.5.4. Freeze resistance

Freeze resistance of the printed ink was carried out according to ASTM 2337-10 in which polyethylene milky printed film were immersed in water and placed in a chamber maintained at a temperature between −23 and −26 °C for 24 h. The printed films were examined with respect to visual appearance after aggressive abrasion test (10 times).

2.5.5. Heat sealing

Heat resistance of the printed ink during heat sealing was carried out according to ASTM F2029-00 using heat sealer HSBl – RDM EQUIPMENTS in which polyester printed film was sealed face to face at temperature range 160–200 °C, under 1 bar pressure for 2 s. The printed films were then examined with respect to the visual appearance (degree of distortion in the ink film) after cooling the sample to room temperature.
3. Results and discussion

3.1. Characteristics of palm and castor oils

The general structure of vegetable oils is shown in Fig. 1(a) which are triglycerides comprising three fatty acids joined by a glycerol center. Analysis of the unsaturated bond content in various oils indicated that palm oil is a convenient raw material for the synthesis of the polyols with its low and medium content of hydroxyl groups [20]. A low content of unsaturated bonds (LI = 50–55) in palm oils allowed the obtaining of products with hydroxyl numbers lower than 200 mg KOH/g and very low content of unreacted double bonds using the epoxidation method followed by ring opening [15,26]. Castor oil (CO) is primarily comprised of ricinoleic acid (>89%), which contains a hydroxyl group at the C-12 position and a carbon-carbon double bond between C-9 and C-10.21 The structure of ricinolein, the major triglyceride of castor oil, is shown in Fig. 1(b). The fatty acid distribution of palm olein and castor oil is shown in Table 1 [23].

Necessarily, polyols applied in flexible polyurethane resins should have a low functionality (2–3 OH groups/molecule) and/or medium molecular weights (Mn 1500–3000 g/mol) to decrease cross-linking density and to improve the elasticity of the final products [27].

3.2. Properties of VO polyols and polyurethanes

Epoxidation method followed by ring opening is the most widely studied reaction in which double bonds in the triglycerides were converted into oxirane ring, and then, they were further transformed into hydroxyl group via ring opening reaction using water or various mono-alcohols in the presence of an acid catalyst (Fig. 3(c)) [28,29]. The prepared polyols by epoxidation method are rich in hydroxyls, active methylenes and double bonds. These functional groups can undergo various chemical modifications; nonetheless, over the years, research has been focused mainly on the synthesis (involving – OH) and characterization of PU with applications as foams, lubricants, cosmetics, adhesives, plasticizers and coatings. These resins combine the advantages of flexibility conferred by long aliphatic triester chains of VO as well as polarity of hydroxyl moieties [10,30–34]. Moreover, the presence of hydroxyl groups is associated with extensive hydrogen bonding in VO polyols as evident by spectral studies as well as they impart good adhesion between the coating material and the substrate. [35].

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Fatty acid distribution of several common oils [15].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Myristic</td>
</tr>
<tr>
<td>Palm olein</td>
<td>12</td>
</tr>
<tr>
<td>Castor</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Formulation of printing ink.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Components</td>
<td>Weight% (gm)</td>
</tr>
<tr>
<td>Cyan RMF2-cyan ink paste</td>
<td>60</td>
</tr>
<tr>
<td>Varnish FLV-nitrocellulose varnish</td>
<td>8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>8</td>
</tr>
<tr>
<td>Methoxy propanol</td>
<td>10</td>
</tr>
<tr>
<td>Polyurethane plasticizer</td>
<td>14</td>
</tr>
<tr>
<td>Total weight</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Properties of the prepared polyols and polyurethanes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyols</td>
<td>C–C</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>PTMG2000</td>
<td>–</td>
</tr>
<tr>
<td>Castor oil</td>
<td>3.1</td>
</tr>
<tr>
<td>HPO polyol</td>
<td>0.9</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td></td>
</tr>
<tr>
<td>PU STD</td>
<td>–</td>
</tr>
<tr>
<td>PU PTMG</td>
<td>–</td>
</tr>
<tr>
<td>PUHPO100%</td>
<td>–</td>
</tr>
<tr>
<td>PUHPO50%</td>
<td>–</td>
</tr>
<tr>
<td>PUHPO100%</td>
<td>–</td>
</tr>
<tr>
<td>PUHPO50%</td>
<td>–</td>
</tr>
</tbody>
</table>

* Fn – Functionality.
The acid number, OH numbers, functionality, viscosities and water contents of the polyols are presented in Table 3. Acid number is a sensitive value to correct the value of hydroxyl number in order to obtain the real value for OH. A special characteristic of all polyols is the fact that practically all of them are liquid at room temperature or at low temperatures (40–60°C). This fact is an important technological advantage, because high molecular weight polyurethane polymer is obtained using only low viscosity liquid intermediates, which are easy to process. Moreover, the viscosity gives an indication of the processability of a polyl.

Hydroxyl value of polyl is an indication for quality control during the production of polyurethane. In this study, the obtained polyols showed moderate OH numbers. Accordingly,
the results showed the presence of double bonds in the polyol molecules, which might result in the rubbery properties of PU. Table 4 depicts the technical requirements for polyols used in polyurethane flexible and elastomer industry. The prepared polyols have a higher hydroxyl number than the petroleum-based polyol, but according to the study of Petrovic et al. most polyols with OH numbers of about 200 and less give semi-rigid polyurethanes of a moderate or low crosslinking density when crosslinked with a diisocyanate [10]. Consequently, as crosslinking density decreases the polyurethane flexibility increases [16].

3.3. Chemical structure formulations

Fig. 2(a) shows the FTIR spectra obtained for the prepared polyols, which exhibited an increase in OH peak at 3450 cm⁻¹ with a disappearing of epoxy peak at 844 cm⁻¹ as the reaction time increased. The spectra showed that double bonds still present in the polyol molecules, which may give the reaction time increased. The spectra showed that double bonds still present in the polyol molecules, which might result in the rubbery properties of polyurethanes to the PUs [37].

The FTIR spectra of all the polyurethane polymers with various soft segments are presented in Fig. 2(b). The figure reveals that the distinguished absorption band due to NCO bonds still present in the polyol molecules, which may give the reaction time increased. The spectra showed that double bonds still present in the polyol molecules, which might result in the rubbery properties of polyurethanes to the PUs [37]. Consequently, as crosslinking density decreases the polyurethane flexibility increases [16].

3.4. Molecular weight determinations by gel permeation chromatography (GPC)

The molecular weight of palm olien polyol prepared in this study was determined by gel permeation chromatography at room temperature using PS standards (Agilent). Number average molecular weight (Mn) and molecular weight polydispersity index (PDI) were affected by the conversion of oxirane groups into hydroxyl groups and oligomerization degree. There are two major fractions in the GPC chromatogram of the palm olien polyol (Fig. 3). The dominant peak corresponds to the hydroxyl derivative of triglyceride with average functionality of ca. 2.5. The second broad peak in GPC (minor peak) corresponded to dimers and trimers and maybe related to both the variations in fatty acid substituent and the completion of the reaction. That was further confirmed through the determination of the isocyanate value through the butyl amine titration method.

Polyurethanes are capable of forming several kinds of hydrogen bond, either hard segment-hard segment or as hard segment-soft segment bonds as the NH groups may form hydrogen bonding with the urethane carbonyl group C=O, ester carbonyl C=O (oil), or ether oxygen C–O–C (PTMG). From FTIR spectra studies of the polymers (Fig. 2(b)), the C=O absorption band appears at 1733–1719 cm⁻¹ and splits into two in each case, the NH broad absorption bands appear at 3330–3410 cm⁻¹ for polyurethane polymers with the chain extender BD. This broadening of the band may be due to the overlap of NH and OH frequencies and also due to the presence of hydrogen bonding. The bands at 870 cm⁻¹ and 730 cm⁻¹ may be due to the disubstituted aromatic ring of TDI [18,38].

The phase separation in polyurethanes can be characterized by the measurement of the intensity and position of the hydrogen-bonded NH stretching vibrations. Usually, a significant amount of N–H…O–C (urethane) hydrogen bonding indicates an extensive phase separation. Thus, the tendency of phase separation increases with the increase in the hard-segment content. The C=O stretching frequencies are very complex for such polyurethanes as they are influenced by C=O stretching and C–C–N deformation as well as N–H bending [19].

Table 5 Properties of printing inks with standard and prepared polyurethane plasticizer.

<table>
<thead>
<tr>
<th>Properties of printing inks with standard and prepared polyurethane plasticizer.</th>
<th>Flexibility and mechanical properties</th>
<th>Optical properties</th>
<th>Thermal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curling</td>
<td>Crinkle</td>
<td>Adhesion</td>
<td>ΔC:ΔS%</td>
</tr>
<tr>
<td>Ink with PU STD</td>
<td>No Curling</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Ink with PU PTMG</td>
<td>No Curling</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Ink with PU CO 100%</td>
<td>No Curling</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Ink with PU CO 50%</td>
<td>No Curling</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Ink with PU HPO 100%</td>
<td>No Curling</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>Ink with PU HPO 50%</td>
<td>No Curling</td>
<td>C</td>
<td>D</td>
</tr>
</tbody>
</table>

A: no ink removal; B: less than 5% ink removal; C: more than 5% ink removal; D: failed.
oligomerization of a small fraction of palm oil polyol during the modification [21].

The shoulder on the left side of main peak indicates oligomerization has taken place during the ring-opening reaction between unreacted epoxies in PO and newly formed hydroxyl groups in PO polyol, resulting in a higher molecular weight. As the reaction proceeded, the molecular weight was expected to slightly increase so that the left shoulder became more significant to contribute to the further ring-opening of the remaining epoxy groups by the resulting secondary hydroxyl group in PO polyol, resulting in a higher cross-linking [39].

3.5. Coating properties

The properties of printing inks with standard and prepared polyurethane plasticizer are summarized in Table 5. The results indicated that polyurethane plasticizer were prepared successfully by the partial substitution of petroleum polyols with vegetable oil polyols, castor oil and palm oline, given a very comparable mechanical, optical, thermal and freeze properties.

4. Conclusion

A serious attempt of inducing some vegetable oils (castor and palm oil) as a safe and environment friendly polyol to partially replace the petrochemical polyol aimed to prepare polyurethane resins as utilized as specific inks for the printing industry of synthetic films. All prepared ink samples showed high thermal resistance up to 120 °C. Moreover, the results revealed that ink samples with 50% PU CO are better than those with the same ratio of PU HPO, which confirm the possibility of the utilization of vegetable oil-based PU in the printing ink formulations.

References