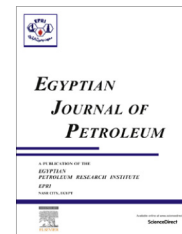


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FULL LENGTH ARTICLE

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

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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 $50\text{ }^\circ\text{C} \pm 2$. 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 $50\text{ }^\circ\text{C}$ 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

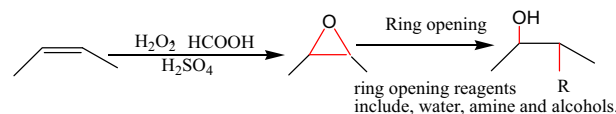


Figure 1c Epoxidation method followed by ring opening route to synthesize vegetable-oil-based polyols.

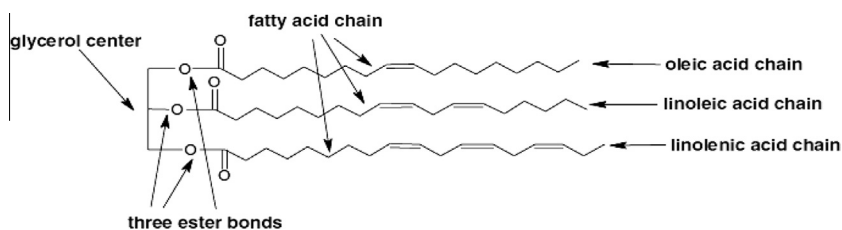


Figure 1a Triglyceride chain containing three fatty acids by a glycerol center.

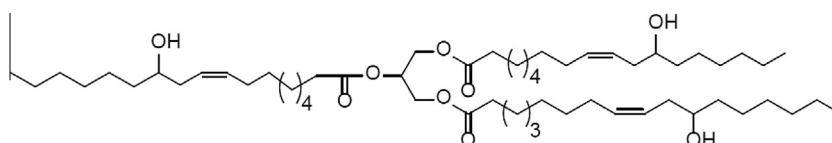


Figure 1b Major triglyceride of castor oil [12].

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