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Preparation and characterization of high-solid polyurethane coating systems based on vegetable oil derived polyols

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ABSTRACT

A series of bio-based polyols with high functionality and low viscosity were synthesized from 5 different vegetable oils (refined or crude). Their chemical structures and the distribution of oligomers in these polyols (known as Liprol™) were characterized. Liprol structures varied due to the fatty acid profile of the starting oils and their overall degree of unsaturation, along with the extent of oligomerization during their formation. These polyols were then used as starting materials for the production of high-solid content polyurethane (PU) coatings, by reacting them with commercial petrochemical derived diisocyanate and other additives. All of the PU coatings obtained had a bio-based content of around 60% and showed good thermo-mechanical and mechanical properties. NuLin® flax PU, made from oil with the highest linolenic acid content, had the highest glass transition temperature, high contact angle with water, good abrasion resistance and Shore hardness, low degree of solvent swelling and formed highly cross-linked networks.

1. Introduction

Polyurethanes (PUs) have found ubiquitous applications in many diverse areas such as elastomers, foams (flexible, semirigid, and rigid), coatings, adhesives, and fibers [1,2]. In the coatings industry, PUs exhibit excellent abrasion resistance, low temperature flexibility, toughness, chemical and corrosion resistance, and a wide range of mechanical strength. Because of these characteristics, PU coatings have extensive applications from automobile finishing to industrial maintenance to chemical resistant coatings [3]. It is commonplace to synthesize PUs through the mixing of a hydroxyl-functionalized monomer with a second monomer containing an isocyanate group, which will react to form a urethane linkage. The key to polyurethane versatility lies in the nature and the molecular characteristics of the reactants, i.e., polyol and isocyanate. Petrochemical-based polyester, polyether, and acrylic polyols are the main types of polyols used in PU coatings production. In general, polyesters and acrylics polyol produce very tough polyurethane films under proper curing conditions and are among the most widely used polyols for high performance coatings [1]. Polyether polyols are used in highly flexible systems such as sealants and other interior applications or to the formulation of primers [1].

To date, polyols used in polyurethane industry are typically of petrochemical origin. However, there is now an increasing worldwide demand for the finite resources of crude oil, which commands high but unstable prices. The resulting trend toward the use of more sustainable and environmentally friendly raw materials means that there is an excellent opportunity for polyols derived from renewable feedstock like vegetable oils to enter into the PU market [4–13]. Traditional vegetable oil-based PUs have been prepared by treating diisocyanates with castor oil, which naturally possesses hydroxyl groups [2]. Castor oil-based PUs have broad applications in PU foams, interpenetrating polymer networks, and PU coatings [14–17]. In addition, vegetable oil-based urethane varnishes, urethane alkyds which are typically prepared by using diisocyanate, monoglyceride, and phthalic anhydride, have been used for decades [18]. During the past few years, a variety of chemical modifications to the double bond sites of vegetable oils have been studied to derive multiple hydroxyl functional derivatives, which are used as polyols in PU preparation [19–25]. Of all the reported reaction pathways, epoxidation is one of the most important reactions to functionalize double bonds and epoxide ring-opening reactions can lead to numerous products [26]. For example, secondary hydroxyl groups can be created on fatty acids from the reactions between epoxides and compounds containing active hydrogen atoms, such as monoalcohols, amines, and carboxylic acids [27]. If diol or triol was used as nucleophile for epoxide ring opening, then both primary and secondary hydroxyl functions could be inserted on each epoxide group of triglyceride [21,28]. However, several issues are raised when using polyfunctional molecules, for

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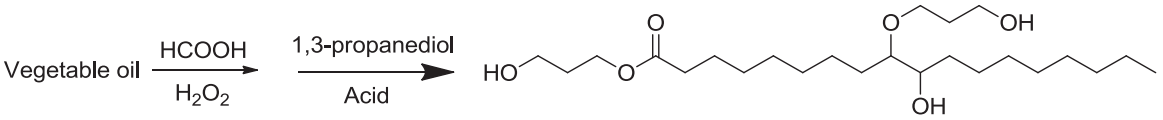

Scheme 1. Representative chemical structure of polyols synthesized from vegetable oil.

instance, oligomerization occurs between triglycerides bearing primary hydroxyl functions and epoxided triglycerides. In another approach, primary hydroxyl groups on fatty acids may be created from the hydrogenation of aldehydes, which are made from the hydroformylation of double bonds [25]. Also, vegetable oil-based polyols for PU preparations, oligomeric polyether polyols are produced by polymerization of epoxidized methyl esters of fatty acids [23,29]. Ozonolysis is another method that has been reported to obtain terminal primary hydroxyl groups [22,24,30]. Petrovic and Javni [31] reported the use of soybean oil based polyols synthesized from epoxidized soybean oil and polymeric 4,4′-diphenylmethane diisocyanate (pMDI) to make coatings with good adhesion and hardness. However, of these vegetable oil derived polyols, the functional hydroxyl groups have been only introduced to the double bond sites of the unsaturated fatty acid chains and it is normally difficult to obtain a natural oil derived polyol with a hydroxyl number higher than 250 mg KOH/g. In addition, a primary drawback associated with the use of these vegetable oil-based polyols for many coating applications is their relatively high molecular mobility, as well as the presence of pendent dangling chains, which lead to relatively low glass transition temperatures (T_g) and a low modulus [27]. As a means to increase the thermo-mechanical properties of vegetable oil-based coatings it was of interest to produce novel PU materials which contain less fatty acids derived pendent chains. Recently, novel bio-based poly(ether ester) polyols known as Liprol™ (Scheme 1) [20,32] have been synthesized by our research group and are being commercialized[1]. These are made by epoxidation followed by hydroxylation (esterification) reactions, starting from canola oil and 1,3-propanediol/1,2-propanediol, both of which are commercially produced from renewable resources. In this way, polyols have been synthesized that have low molecular weights, high hydroxyl numbers and low viscosities. These characteristics are mainly attributed to the following reactions: (1) acid catalyzed ring-opening/hydroxylation of the epoxide groups; (2) transesterification reactions of the glycerides with diols resulting in addition of extra hydroxyl groups into the resultant polyols. As a result of these features, the polyurethanes made from these polyols contain few pendent chains and form highly cross-linked networks with a high T_g and modulus.

Vegetable oils are mainly composed of triacylglycerides, i.e. a glyceride in which the glycerol is esterified by three fatty acids, usually with chain lengths of 16, 18 or 20 carbon atoms and 0–3 C=C double bonds. Plant oils contain different fatty acid compositions depending on the variety and to some extent the growing conditions [33]. The location and abundance of unsaturation within the oil is of paramount importance for polyol formation since the double bonds are the precursors to the formation of hydroxyl groups. The degree of unsaturation is typically expressed by the iodine value (i.e., the amount of iodine in grams, which can react with double bonds present in 100 g of sample). In general it is to be expected that the higher the iodine value of the starting oil, the higher the hydroxyl value of the polyols that are derived from it will be. However, both the location of the double bonds and the degree of oligomerization during polyol formation will also affect the final hydroxyl value.

In the present study, we derived a series of vegetable oil-based polyols from refined canola and sunflower oils, and camelina, Linola® 2090 flax and NuLin® 50 flax crude oils using the established Liprol™ synthetic routes. Canola and sunflower oils have similar fatty acids composition, i.e. oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3), but in different proportions. Camelina oil has not only 18 carbon fatty acid chains, but also chain lengths of 20 carbons, i.e. eicosenoic acid (C20:1). Linola is an engineered flax with a low linolenic acid (approximately 2%) [34], whereas NuLin is a new flax with enhanced linolenic acid levels [35]. Therefore, Linola 2090 flax has the lowest iodine value in flax oil family, whereas NuLin 50 flax has the highest iodine value of all oils used in this work. All of these polyols were used to prepare PU coatings by reacting with pMDI and other additives needed to produce a coating with desirable properties. The properties of these PU materials were evaluated by testing their thermo-mechanical behavior, tensile strength, hardness, adhesion and abrasion resistance. A key objective of the work presented here is to evaluate the effect of changing the plant oil feedstock used in making Liprol polyol on the properties of PU coatings.

2. Experimental

2.1. Materials

The canola oil (Safeway® or Canola Harvest® brand or equivalent) used in this study was purchased from a local grocery store. Sunflower oil was obtained from Bunge Oil, Canada, flax oil (Linola 2090 and NuLin 50) were supplied by Viterra Inc. Canada, and Camelina oil was sourced from Linnaeus Plant Sciences Inc. Canada. Of all these vegetable oils, only canola and sunflower oil are refined for human consumption. Hydrogen peroxide (35%), formic acid (85%), sodium sulfate anhydrous, and sodium bicarbonate were obtained from Univar, Canada. Ethyl acetate (ACS grade), sodium hydroxide (ACS grade), sodium chloride (ACS grade) and sulfuric acid (ACS grade) were obtained from Fisher Scientific, USA. 1,3-propanediol was obtained from DuPont Tate and Lyle, USA. BYK A530 was generously supplied by Air Product, Canada, Abolith MS C-350 was provided by Alberdingk Boley Inc., USA and Imsil 1240 was supplied by Unimin Corporation, USA. Tritricosanoin (Mw = 1101.88 g/mol), distearin (Mw = 625.00 g/mol) and monostearin (Mw = 358.56 g/mol) with purity ≥99% were obtained from Nu-Chek Prep. Inc. (USA) and used as calibration standards for size-exclusion chromatography (SEC). The polymeric aromatic diphenylmethylene diisocyanate (pMDI, Mondur MRS) was sourced from Bayer Corporation, Pittsburgh, PA, USA. The NCO content of pMDI was 31.5 wt% and its functionality was 2.6 as provided by the supplier.

2.2. Synthesis of polyols

The vegetable oils selected were first epoxidized by performic acid generated in situ by reaction of hydrogen peroxide with formic acid, as described elsewhere [32]. The time for complete epoxidation of the vegetable oil (in the range of 19–48 h depending on the unsaturated degree of the starting oils) was verified by LC/MS. The dried epoxidized vegetable oil was then added to a stirred solution of 1,3-propanediol in a 1:10 M ratio with concentrated sulfuric

[1] Consolidated Coatings Corp., Vancouver, BC, Canada.