European Polymer Journal 48 (2012) 2097–2106

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Novel polyurethane produced from canola oil based poly(ether ester) polyols: Synthesis, characterization and properties

Xiaohua Kong *, Guoguang Liu, Jonathan M. Curtis

Department of Agricultural, Food and Nutritional Science, 4-10 Agriculture/Forestry Centre, University of Alberta, Edmonton, Alberta, Canada T6G 2P5

ARTICLE INFO

Article history:
Received 2 May 2012
Received in revised form 16 July 2012
Accepted 23 August 2012
Available online 23 September 2012

Keywords:
Poly(ether ester) polyols
Canola oil
Polyurethane
Renewable resource

ABSTRACT

Two novel bio-based poly(ether ester) polyols (Liprol™ 270 and Liprol™ 320) with high functionality and low viscosity were synthesized from canola oil. A simple, two-step reaction sequence of epoxidation followed by hydroxylation and transesterification with 1,3-propanediol or 1,2-propanediol was used resulting in a versatile, low cost process. The chemical structures of the low molecular weight compounds in the polyols produced were identified by liquid chromatography–mass spectrometry (LC–MS) while the distribution of oligomers was elucidated by size exclusion chromatography (SEC). The feasibility of utilizing these polyols for the production of polyurethanes (PUs) was demonstrated by reacting them with commercial petrochemical derived diisocyanate. The physical properties of the PUs prepared were characterized by FTIR, dynamic mechanical analysis (DMA), modulated differential scanning calorimetry (MDSC), and thermo gravimetric analysis (TGA). It was found that Liprol derived PUs had high glass transition temperatures, good hydrolytic stability and alkali resistance, and formed highly cross-linked networks. This work is the first that establishes the production of polyols and their corresponding PUs from vegetable oil starting materials whose glycerol backbone was removed explicitly during the polyol synthesis reaction.

1. Introduction

Polyurethanes (PUs) are used by a wide range of industries including the construction, automotive and consumers goods industries, and in many diverse applications ranging from medical devices to coatings, etc. [1]. Conventionally, PUs are synthesized through the polyaddition reaction between compounds containing active hydroxyl groups, such as polyols, with organic isocyanates. The most common polyols in PU production are polyether polyols, and polyester polyols. Polyether polyols are generally formed by the addition of ethylene oxide and/or propylene oxide to polyfunctional starter molecules such as di-alcohols or di-amines. It is well-known that PUs obtained from polyether polyols have excellent physical properties such as their resilience to impact, low temperatures and hydrolysis, along with advantages due to their favorable cost of production. However, they are generally inferior in their strength, abrasion resistance, and heat resistance compared to PUs obtained from polyester polyols [2–4]. In order to overcome these drawbacks, there has been a considerable amount of research aimed at improving the strength and heat resistance of these PUs while maintaining the various physical properties imparted by the polyether polyols [5–9]. One method that is commonly used is to mix polyester polyols with polyether polyols. However, these two types of polyols are not always miscible and the physical properties of the PUs obtained from such polyols mixture may still be inadequate. Later, it was also proposed to modify polyether polyols by esterification of

* Corresponding author. Address: Lipid Chemistry Group (LCG), Department of Agricultural, Food and Nutritional Science (AFNS), University of Alberta, 4-10 Agriculture/Forestry Centre, Edmonton, Alberta, Canada T6G 2P5. Tel.: +1 780 492 3051.
E-mail address: xkong@ualberta.ca (X. Kong).

0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2012.08.012

the terminal groups of a polyether polyol using a strong basic catalyst [6,7]. However, the molecular weight distribution of the resultant polyols are wide and the tensile strength, impact resilience, and elongation at break of the PUs obtained from such a polyols is not satisfactory. Since the 1980s, several researchers have attempted to develop new synthetic procedures to produce poly(ether ester) polyols by developing more complex catalysts such as double metal cyanides [7–9]. The PUs prepared from such poly(ether ester) polyols have superior physical properties as compared with those PUs obtainable by using either polyester or polyether polyols alone [7].

Polyols normally used in PU synthesis are made from chemical intermediates derived from petroleum or natural gas. Recently, with the increasing emphasis on issues concerning waste disposal and depletion of non-renewable resources, the importance of using renewable resources in industrial processes has become very clear from a standpoint of sustainability. In the quest for sustainable chemistry, there are in particular, increasing demands for replacing or complementing the traditional petrochemical raw materials with renewable raw materials in the production of polymers [10–17]. Utilization of bio-based polyols, especially natural oil polyols, in the manufacture of PU products has increased significantly [18–20]. However, the preparation of polyols from fatty acids and natural oils for general PU use has been centered on polyester [21–28] or polyether polyols [29,30], while limited attention has been paid to the preparation of poly(ether ester) polyols from these kinds of feedstocks. To the best of our knowledge, the one instance of branched poly(ether ester) polyols (Sovermol 1092) from renewable feedstocks was launched by Cognis in 2008, with no clear molecular structure reported [31]. In addition, most of the current commercially available bio-based polyols, for example castor oil, Agrol® series from BioBased Technologies and Soyol® ''Bio-Renewable'' polyols from Urethane Soy Systems Company, have hydroxyl numbers lower than 250 mg KOH/g and a few have hydroxyl numbers higher than 200 mg KOH/g. The hydroxyl number is one of the key parameters that impacts the property of polyurethane materials made with such polyols. Viscosity is another parameter that can also have greater impact on the processing and production effectiveness and the mixing quality in the preparation of polyurethane materials. For example, it would be favorable to use low viscosity polyols in a spray process or a reaction injection molding process or high pressure molded foam process. Therefore, there is a need to synthesize polyols having a high hydroxyl number and at the same time offering relatively low viscosity, in the range of 0.1–10 Pa s at 25 °C. In the traditional preparation of vegetable oil-derived polyols *via* the epoxidation of double bonds, the hydroxyl number relates to the consumption of double bonds in the unsaturated fatty acid chains and it is normally difficult to obtain a vegetable-oil-derived polyol with a hydroxyl number higher than 250 mg KOH/g. On the other hand, one generally finds that higher hydroxyl containing polyols also give a higher viscosity. It is thus a challenge to synthesize vegetable oil-derived polyols having at the same time both high hydroxyl number and low viscosity.

In this work, bio-based poly(ether ester) polyols were synthesized through epoxidation followed by hydroxylation (esterification) reactions, starting from canola oil and other renewable content (i.e. 1,3-propanediol and 1,2-propanediol) and using a cheap and efficient procedure, and a strong acid catalyst. An important consideration in selecting 1,3-propanediol and 1,2-propanediol is that both of these diols derived from renewable resources are currently commercially available [32,33]. Hence, polyols produced primarily from vegetable oil and bio-based diols could have a biomass-derived content approaching 100%. In addition, the process used here differs from conventional hydroxylation routes in which only the double bond sites were used for introducing hydroxyl groups. Instead, the presence of strong acid as well as the excess amount of diol also promotes transesterification reactions with the epoxidized triacylglycerol (TAG) structures in addition to the ring opening process. This results in many extra sites for hydroxyl groups to be introduced onto the fatty acids chains, as explained further below. Therefore, polyols synthesized using these routes possess low molecular weight, high hydroxyl number and low viscosity. By selecting different types of diols, a variety of polyol structures could be obtained which impart different properties when converted into the ultimate PU products.

2. Experimental section

2.1. Materials

The canola oil (Safeway® or Canola Harvest® brand or equivalent) used in this study was purchased from a local grocery store. Unrefined crude castor oil was obtained from CasChem Company, USA. Hydrogen peroxide (35%), formic acid (85%), sodium sulfate anhydrous, sodium bicarbonate and 1,2-propanediol (propylene glycol, technical grade) 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. Tritricosanoin (Mw = 1,101.88 g/mol), distearin (Mw = 625.00 g/mol) and monostearin (Mw = 358.56 g/mol) with purity $\geqslant$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

Canola oil was epoxidized by performic acid generated *in situ* by reaction of hydrogen peroxide with formic acid, as described elsewhere [34]. The time (around 19 h) for complete epoxidation of the canola oil was verified by LC–MS. The dried epoxidized canola oil (ECO) were added to a stirred solution of 1,3-propanediol in a 1:10 M ratio with concentrated sulfuric acid present at a final concen-