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Metathesized palm oil polyol for the preparation of improved bio-based rigid and flexible polyurethane foams

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ABSTRACT

Polyols derived from 1-butene cross metathesized palm oil (PMTAG polyol) were used to prepare improved rigid and flexible foams. The chemical structure, thermal degradation, thermal transition behavior and compressive strength of the foams were determined using FTIR (Fourier Transform Infrared Spectroscopy), TGA (Thermogravimetric analysis), DSC (Differential Scanning Calorimetry) and texture analyzer, respectively. Their cellular structure was investigated by SEM (Scanning Electron Microscopy). Both the rigid and the flexible foams from the metathesized palm oil polyol displayed high thermal stability (T_{on} of degradation of ~253 °C) comparable to commercial and other vegetable oil polyol foams. The rigid foams from the polyol of PMTAG presented compressive strengths as high as 2.6 MPa, a value higher than similar foams prepared from palm oil polyol or highly unsaturated vegetable oils such soybean and canola oil based polyols. The flexible foams from the metathesized palm oil polyol displayed excellent flexibility with more than 90% recovery in thickness after compression.

1. Introduction

Palm oil is one of the cheapest and most produced oils in the world that is touted as a viable renewable feedstock for the economical industrial production of polyols and polyurethanes (Chuayjuljit et al., 2007; Ong and Goh, 2002; Pawlik and Prociak, 2012; Tanaka et al., 2008). The palm oil is composed of ~95% triacylglycerols (TAGs) and other minor components such as diacylglycerols (DAGs) (Lida et al., 2002; Ong and Goh, 2002; Santosa, 2008). The palm oil shows a balanced saturation (~50/50% of saturates/unsaturates) distributed in tri-unsaturated (4.8–9.8%), di-unsaturated (31.8–44.4%), mono unsaturated (38.5–50.3%) and saturated TAGs (Gunstone, 2011).

Because of its relatively high level of saturation, the palm oil does not lend itself easily to chemical modification, capping the degree at which it can be functionalized and hence the hydroxyl value of its polyols as compared to highly unsaturated TAG oils such as soybean oil (Lida et al., 2002). Furthermore, similar to most other natural oils, its double bonds are internal which result in polyols with secondary hydroxyl groups and dangling chains. Such polyols are less reactive toward polymerization, and known to lead to incomplete crosslinking and imperfections in the polymer network (Narine et al., 2007a; Zlatanic et al., 2002). The regions where dangling chains are present do not support stress when the sample is loaded, and act as plasticizers that reduce the rigidity of the polymer (Narine et al., 2007b; Zlatanic et al., 2002). In fact, the hydroxyl value and the position of the hydroxyl groups in the fatty chain, the molecular weight of the polyol and the presence of dangling chains, are the most important factors which affect the properties of polyurethanes (Guo et al., 2002; Narine et al., 2007b; Zlatanic et al., 2002).

Polyurethanes (PUs) are macromolecules containing urethane linkages (—NH—CO—O—) that are either formed based on the reaction of isocyanate groups and hydroxyl groups(Szycher, 1999), or via non-isocyanate pathways, such as the reaction of cyclic carbonates with amines (Guan et al., 2011), self-polycondensation of hydroxyl-acyl azides or melt transurethane methods (More et al., 2012). Judicious selection of reactants enables the production of a wide range of polyurethane products such as polyurethane elastomers (Kong and Narine, 2007), sheets (Kong and Narine, 2007), adhesives (Somani et al., 2003), coatings (Velayutham et al., 2009), and foams (Narine et al., 2007a) etc.

PU foams are light weight, have good insulation properties, excellent strength to weight ratio, and impressive sound absorbing properties (Szycher, 1999). Furthermore, their physical properties can be tailored to a large extent by varying the structure and com-

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position of the reacting monomers, amount of catalyst and other additives like glycerin, water etc., as well as the reaction conditions used in the foam formulation (John et al., 2002). In the case of water blown polyurethane foams, the reaction of water and isocyanate produces carbon dioxide gas which forms into small air bubbles. The diffusion of further carbon dioxide inflates the air bubbles leading to a well-defined cell structure (Doyle, 1971). PU foams are classified as rigid or flexible according to compressive strength value, and other parameters such cross link density and hydroxyl value (OH value) of the starting polyol (Szycher, 1999). The market for PU foams is very large and growing due to high demand across a wide range of industries such as automotive, building and construction, and packaging (Babb, 2012b; David et al., 2010). The worth of the global polymer foams market was \$82.6 billion in 2012 and is estimated to reach \$131.1 billion by 2018 (Firm, 2013). The specific polyurethane foam market which was valued at 46.8 billion in 2014 is expected to reach 72.2 billion by 2020 (Firm, 2015).

Traditionally, PU foams are prepared by the reaction of diisocyanates or polyisocyanates with petroleum-derived polyols (Szycher, 1999). The development of polyurethanes from renewable and environmentally friendly feedstock has become the subject of increasing research because of sustainability and other environmental concerns (Desroches et al., 2012). Vegetable oils are a particularly promising alternative feedstock for the synthesis of polyols and polyurethanes because they are biodegradable, available in large quantities, and are relatively low-cost (Petrović, 2008). A significant body of literature reporting on the synthesis of polyols and polyurethanes from natural oils is readily available (see for example PU foams from soybean oil (Tan et al., 2011; Zhang et al., 2007), safflower oil, corn oil, sunflower seed oil, linseed oil (Khoe et al., 1972), rapeseed oil (Hu et al., 2002), and cotton seed oil (Babb, 2012a)).

Current research efforts revolve around finding the transformation routes that would increase the potential of the natural oils as viable sources for polyols and PU foam products. Such efforts include improving existing synthesis routes, developing new chemistries and optimizing processing conditions. Olefin metathesis is an example of such novel approaches that our research group is using as a platform for improved and more suitable feedstock for the formulation of bio-based materials, particularly polyols and PUs. The foams of the present work were formulated with a polyol obtained from a product of the cross-metathesis of 1-butene and palm oil (PMTAG) (so-called PMTAG polyol). The chemical and physical properties of the modified TAG material (PMTAG) and its polyol have already been reported (Prasanth et al., 2015).

PMTAG polyol is a relatively low molecular weight material comprising ~52% of functional hexols, tetrols and diols, with half of the hydroxyl groups in terminal positions (Pillai et al., 2015). The structures of the polyol with terminal hydroxyl groups were derived from 9-decenoic acid and those with internal hydroxyl groups (secondary hydroxyl groups) were formed from fatty acids like 9-dodecenioc acid and oleic acid (Pillai et al., 2015). The unique structure and composition of PMTAG polyol and related thermal and rheological properties indicated enhanced reactivity and kinetics that bode well for further transformation of the material at manageable reaction conditions into starters and materials for various polymer applications such as polyurethane foams. The polymerization of PMTAG polyol into PU foams as exemplified by a model hexol structure is shown in Scheme 1.

The present contribution reports on the preparation and characterization of rigid and flexible foams from PMTAG polyol. The effect of terminal hydroxyl PMTAG polyols on the physical properties of the polyurethane foams is particularly highlighted. Rigid foams with densities ranging from 93 $\mathrm{kg\,m^{-3}}$ to 250 $\mathrm{kg\,m^{-3}}$, and flexible foams with densities ranging from 106 $\mathrm{kg\,m^{-3}}$ to 193 $\mathrm{kg\,m^{-3}}$ were prepared and characterized by Fourier transform infrared spectroscopy (FTIR) to confirm the urethane linkage. The morphology of the foams was examined with scanning electron microscopy (SEM). Their thermal decomposition and thermal transition behaviors were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. The compressive strength of the rigid and the flexible foams were determined with a texture analyzer.

2. Materials and methods

2.1. Materials

PMTAG polyol (Pillai et al., 2015) was synthesized in our laboratory from PMTAG, a butene cross-metathesized palm oil product provided by Elevance Renewable Sciences (ERS, Bolingbrook, Il). Dibutin Dilaurate (DBTDL) and glycerin (99.5%) were purchased from Sigma–Aldrich, Canada, and perchloride acid (70%) from Fisher Scientific, Canada. *N*,*N*-Dimethylethanolamine (DMEA) from Fischer chemical (USA), diphenylmethane diisocynate (MDI) from Bayer Materials Science (Pittsburgh, PA), and polyether-modified surfactant (TEGOSTAB B-8404) from Goldschmidt Chemical Canada.

2.2. Polymerization method

The amount of each component of the polymerization mixture was based on 100 parts by weight of total polyol. All the ingredients, except MDI, were weighed into a beaker and then MDI was added to the beaker using a syringe. The ingredients were then mechanically mixed vigorously for 8 to 20 s and then poured into a cylindrical Teflon mold (60 mm diameter and 35 mm long), which was previously greased with silicone release agent. The mold was sealed with a hand tightened clamp. The sample was cured for four (4) days at 45 °C and post cured for one (1) day at room temperature. Rigid and flexible foams of different densities were prepared using the same polymerization protocol and formulation recipe. During the polymerization step, the amounts of mixture was controlled to achieve the desired densities. The polymerization protocol such as formulation recipe and the curing conditions were chosen based on our previous work (Narine et al., 2007a), so as to compare the foams that were produced by similar polymerization method. But the same polyol can be used for the preparation of foams industrially by suitable alterations in the polymerization protocol (Narine et al., 2015).

2.3. Chemistry and physical characterization techniques

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were obtained with a Thermo Scientific Nicolet 380 FTIR spectrometer (Thermo Electron Scientific Instruments, LLC, USA) equipped with a PIKE MIRacle$^{\mathrm{TM}}$ attenuated total reflectance (ATR) system (PIKE Technologies, Madison, WI, USA.). Solid samples were loaded onto the ATR crystal area, and sample spectra were acquired over a scanning range of 400–4000 $\mathrm{cm^{-1}}$ for 32 repeated scans at a spectral resolution of 4 $\mathrm{cm^{-1}}$.

2.3.2. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was carried out on a TGA Q500 (TA Instruments, DE, USA) equipped with a TGA heat exchanger (P/N 953160.901). Approximately 8.0–15.0 mg of sample was loaded onto the open TGA platinum pan. The sample was heated from 25 to 600 °C under dry nitrogen at a constant rate of 10 °C/min.