



# Metathesized palm oil: Fractionation strategies for improving functional properties of lipid-based polyols and derived polyurethane foams



Prasanth K.S. Pillai, Shaojun Li, Laziz Bouzidi, Suresh S. Narine\*

Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada

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## ABSTRACT

Palm oil metathesized triacylglycerol (PMTAG), the product of 1-butene cross-metathesis of palm oil stripped from it olefins, was fractionated using dry and solvent mediated crystallization. The fractionation yielded solid and liquid fractions (LF-PMTAG and SF-PMTAG, respectively) reminiscent of the stearin and olein portions of the natural palm oil. The polyol which was synthesized from LF-PMTAG (LF-Polyol) comprised ~30% more hydroxyl groups (diols, tetrols and hexols) and more short chain moieties than the polyol from SF-PMTAG (SF-Polyol). As a result, LF-Polyol presented a much higher OH value (184 mg KOH/g) than SF-Polyol (136 mg KOH/g) and more advantageous thermal and viscosity properties than SF-Polyol. The LF-Polyol was demonstrated to make improved rigid and flexible foams compared the polyol from PMTAG (PMTAG-Polyol) or from the natural palm oil. The rigid foam (RF) obtained with LF-Polyol presented compressive strength which was 1.5 times higher than the RF prepared with PMTAG-Polyol, indicating that the removal of stearin-like components can significantly increase the rigidity. The study demonstrate that controlled fractionation of PMTAG can produce customized functional feedstocks for enhanced polyurethane foams.

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## 1. Introduction

Concerns over sustainability, biodegradability, control of CO<sub>2</sub> emissions and the depletion of petroleum reserves are driving a strong demand for alternatives to petroleum as a feedstock for fuels and materials (Gandini and Lacerda, 2015; Hu and Li, 2014). Vegetable oils are a particularly promising alternative feedstock for the synthesis of polyols and polyurethanes because they are renewable, biodegradable, available in large quantities, and are relatively low-cost (Desroches et al., 2012; Zhang et al., 2015). A large body of literature investigating the utilization of vegetable oils for the synthesis of polyols and polyurethanes is currently available. Almost all natural triacylglycerol oils were tried for the synthesis of polyols and polyurethanes (Biermann et al., 2011; Desroches et al., 2012; Zhang et al., 2015). The polyols from vegetable oils are further used either neat such as in the case of soybean oil (Ji et al., 2015), canola oil (Narine et al., 2007) or palm oil (Zhou et al., 2015) or in blends with petroleum polyols to prepare polyurethanes. The latter

strategy has been used to produce rigid polyurethane foams such as from blends of rapeseed oil polyol and commercial petroleum polyol (Kurańska et al., 2015; Zieleniewska et al., 2015) as well flexible polyurethane foams such as with blends of castor oil polyols (Ugarte et al., 2014) or palm kernel oil polyols (Septevani et al., 2015). The goal of the current research approaches is to mitigate the inherent limitation of the natural vegetable oil feedstock due to the presence of saturated fatty acids and the internal nature of the double bonds of the unsaturated moieties which lead upon functionalization to dangling chains which after polymerization leads to incomplete crosslinking and imperfections in the polymer network (Narine et al., 2007; Zlatanić et al., 2002).

Palm oil is one of the most abundant and inexpensive renewable commodity oils in the world (Braipson-Danthine and Gibon, 2007; Septevani et al., 2015). A sustainable palm oil industry would make an economical alternative feedstock for many functional materials, particularly polyols and polymers. However, palm oil is a triacylglycerol (TAG) oil with a high saturation level (~50% saturated fatty acids) that limits greatly the hydroxyl value of the polyols derived from the native oil (Pawlik and Prociak, 2012). Several strategies have been employed to address these handicaps, including blending palm oil polyols with petroleum polyols (Pawlik and Prociak,

\* Corresponding author: Fax: +1 705 748 1652.  
E-mail address: [sureshnarine@trentu.ca](mailto:sureshnarine@trentu.ca) (S.S. Narine).

2012) and the recent utilization of cross metathesis of palm oil with 1-butene to produce terminal double bond feedstock (Pillai et al., 2016b).

Olefin cross metathesis enables the shortening of unsaturated fatty acids at the location of the double bonds, producing low molecular weight TAG products with terminal double bonds: structures that can yield polyols with primary hydroxyls on functionalization (Pillai et al., 2016b). Such terminal hydroxyls are free of pendant chains and therefore present reduced dangling chains and steric hindrances in subsequent polyurethane networks (Connon and Blechert, 2003; Mol, 2004). However, because the saturated fatty acid moieties of the palm oil (~50%) are not affected by the metathesis reaction, they remain as dangling chains after functionalization, limiting the hydroxyl number of its polyols and promoting steric hindrances in the resulting polyurethanes.

The starting material of the present work derives from palm oil. It is the product of the cross-metathesis of palm oil with 1-butene in the presence of a 2nd generation Grubb catalyst. The palm oil metathesized triacylglycerol (PMTAG), stripped of short chain olefins, is a by-product of a large biorefinery process which makes 9-decenoic acid and 3,4-dodecenoic acid for the chemical industry. PMTAG and its polyols have been previously well characterized (Pillai et al., 2016b). PMTAG comprises approximately 25% terminal double bonds, 28% shortened unsaturated fatty acids, and ~47% of saturates inherited from the natural palm oil. PMTAG was easily converted into polyols by standard epoxidation and hydroxylation (Pillai et al., 2016b) which were then used to make improved rigid and flexible polyurethane foams (Pillai et al., 2016a,b). However, although the compressive strength of the foams was significantly enhanced due to the reduction of dangling chains associated with the terminal unsaturated fatty acids, undesirable long pendent chains were still present due to the relatively large number of saturates left from the natural oil. Opportunely, PMTAG is comprised of two relatively separate portions akin to the stearin and olein portions of the natural palm oil, indicating that it can be separated into high and low melting fractions. If a facile fractionation is possible, the low melting portion should contain less of the highly saturated components and therefore should make a feedstock which would help mitigate the problems associated with the plasticizing action of the dangling chains in rigid foams. The material should also be more easily processed because of a lower melting temperature and should present less steric hindrance during functionalization to produce polyol and also in crosslinking process to form polyurethanes.

Crystallization is one of the most effective and economical means for fractionating vegetable oils (Hamm, 1995). Crystallization fractionation consists of two steps, first the cooling of the liquid oil using specific processing conditions to a crystallization temperature and then removal of the solid fat from the liquid oil (Timms, 2005). During the cooling process, the high melting components of the oil crystallize first and these can be removed from the liquid oil via filtration or sedimentation. The parameters of an effective fractionation by crystallization are determined by the cooling rate, the crystallization temperature and the crystallization time (Dunn, 2011). Fractionation can be entirely from the melt (dry) or can be solvent mediated. Solvent aided crystallization, although more expensive, is more efficient and allows for facile filtration since the viscosity of the liquid oil is reduced when a solvent is present (Dunn, 2011). Furthermore, it can be advantageous if the solvent was a part of the further transformation of the material, such as in the synthesis of polyols. For this reason both solvent and dry crystallization methods were used to fractionate PMTAG in an attempt to optimize yield and composition of the fractions, particularly with respect to the synthesis of polyols and rigid polyurethane foams.

Several studies regarding the fractionation of palm oil by dry as well as solvent aided crystallization have been published (Hasmadi

et al., 2002; Kellens et al., 2007; Ramli et al., 2008). The present work reports on the fractionation of PMTAG and the synthesis of polyols from the fractions. The fractionation was performed by dry as well as solvent mediated crystallization for optimum yield and quality of the liquid fraction. Quality here refers to maximum unsaturation content. The polyols were synthesized by standard epoxidation and hydroxylation reactions, and characterized chemically and physically to determine their suitability as monomers for the preparation of polyurethane foams. The rigid and flexible foams were prepared with similar densities (~160 kg m<sup>-3</sup>) to allow for comparison. The urethane linkage of the foams was confirmed by FTIR. Their morphology, thermal decomposition and thermal transition behaviors were studied by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. The compressive strength of the foams were determined with a texture analyzer.

## 2. Materials and methods

### 2.1. Materials

PMTAG was provided by Elevance Renewable Sciences (ERS, Bolingbrook, IL). Dichloromethane (DCM), ethanol (anhydrous), toluene, potassium hydroxide, and sodium thiosulfate were purchased from ACP Chemical Int. (Montreal, Quebec, Canada) and used without further treatment. Formic acid (88 wt %) and hydrogen peroxide (30 wt% in H<sub>2</sub>O), iodine monochloride (95%), potassium iodide (99%), dibutyl dilaurate (DBTDL), glycerin (99.5%) and phenolphthalein were purchased from Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada). Perchloric acid (70%), *N,N*-dimethylethanolamine (DMEA) was purchased from Fisher Scientific, USA, diphenylmethane diisocyanate (MDI) from Bayer Materials Science (Pittsburgh, PA), and polyether-modified surfactant (TEGOSTAB B-8404) from Goldschmidt Chemical Canada. HPLC grade solvents were obtained from VWR International, Mississauga, ON.

### 2.2. Chemistry characterization techniques

#### 2.2.1. Titrimetric methods (OH value, acid value, iodine value)

Iodine and acid values of SF- and LF-PMTAG were determined according to ASTM D5554-95 and ASTM D4662-03, respectively. OH and acid values of the polyols were determined according to ASTM S957-86 and ASTM D4662-03, respectively.

#### 2.2.2. Proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR)

<sup>1</sup>H NMR spectra were recorded CDCl<sub>3</sub> on a Varian Unity-INOVA at 499.695 MHz using an 8.6 μs pulse with 4 transients collected in 16 202 points. Datasets were zero-filled to 64,000 points and a line broadening of 0.4 Hz was applied prior to Fourier transforming the sets. <sup>1</sup>H chemical shifts are internally referenced to CDCl<sub>3</sub> (7.26 ppm). The spectra were processed using spinwork NMR Processor, version 3.

#### 2.2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the foams were obtained using a Thermo Scientific Nicolet 380 FT-IR spectrometer (Thermo Electron Scientific Instruments, LLC, USA) equipped with a PIKE MIRacle™ attenuated total reflectance (ATR) system (PIKE Technologies, Madison, WI, USA.). Foam samples were loaded onto the ATR crystal area and held in place by a pressure arm. The spectra were acquired over a scanning range of 400–4000 cm<sup>-1</sup> for 32 repeated scans at a spectral resolution of 4 cm<sup>-1</sup>.

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