



# Metathesized palm oil & novel polyol derivatives: Structure, chemical composition and physical properties



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

## ARTICLE INFO

### Article history:

Received 3 October 2015  
Received in revised form 12 January 2016  
Accepted 5 February 2016  
Available online 13 February 2016

### Keywords:

Palm oil  
Metathesized palm oil  
Cross metathesis  
Metathesized triacylglycerol (MTAG)  
Polyol

## ABSTRACT

Metathesized palm oils are now a major source of fine chemicals; in particular due to the commercial production of 1-decene and 3,4-dodecene by cross metathesis of 1-butene and palm oil. This process results in the generation of a modified palm oil triacylglycerol (PMTAG) by-product, which has not been sufficiently studied. In this communication, the compositional analysis of PMTAG produced at a commercial scale is reported for the first time, and reveals that a percentage of the unsaturated fatty acids were shortened at the location of the double bond, producing a lower molecular mass TAG oil with terminal double bonds, and less steric hindrance compared to the natural oil. Furthermore, although PMTAG presented physical properties close to highly unsaturated vegetable oils, it retained a two-portion composition similar to palm oil, making its fractionation feasible with existing industrial methods. The epoxidation followed by hydroxylation of PMTAG resulted in a polyol comprising non-functional structures inherited from PMTAG and structures with diols, tetrols and hexols in which 50% of the hydroxyl groups were in terminal positions. The OH value (155 mg KOH/g), thermal stability (~370 °C), melting profile (offset temperature ~45 °C) and viscosity characteristics qualify the PMTAG polyol as a suitable substrate for the manufacture of a variety of materials including waxes, cosmetics and polyurethanes.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Growing concerns surrounding sustainability, biodegradability, control of CO<sub>2</sub> emission and other environmental problems are driving a strong demand for alternatives to petroleum as a feedstock for fuels and materials. Vegetable oils are advantageous in this regard because of their availability in large quantities, renewability and relative low cost (Lligadas et al., 2010). Furthermore, their triacylglycerol (TAG) structure is attractive for the chemical industry as it offers ready sites, such as the double bond and the ester, for chemical transformation (Biermann et al., 2000). There currently exists an important oleochemical industry that uses a large array of standard as well as novel chemical reactions on TAG oils to make a variety of fine chemicals and materials such as fuels, polymers, lubricants, waxes and cosmetics (Desroches et al., 2012; Gunstone, 2011; Petrović, 2008).

Palm oil is one of the cheapest commodity oils that that is abundantly available to be used as an alternative feedstock

to petroleum. It is primarily used in foods (Gunstone, 2011; Nagendran et al., 2000) and increasingly sought for the production of industrial materials. Palm oil is typically composed of 95% TAGs and 5% diacylglycerols (DAGs) and other minor components such as monoacylglycerols (MAGs) with a fatty acid profile ranging typically from C<sub>12</sub> to C<sub>20</sub> (Edem, 2002; Lida et al., 2002). It has a balanced saturation (~50/50% of saturates/unsaturates) (Ong and Goh, 2002; Santosa, 2008). Palmitic acid (P, C<sub>16</sub>:0) and oleic acid (O, C<sub>18</sub>:1) at ~43% and ~41%, respectively, are the main components of palm oil. Palm oil includes ~10% linoleic acid (L, C<sub>18</sub>:2), and trace amounts of linolenic acid (Ln, C<sub>18</sub>:3) and palmitoleic acid (C<sub>16</sub>:1). Other representative saturated fatty acids in palm oil are lauric acid (L, C<sub>12</sub>:0), myristic acid (M, C<sub>14</sub>:0), stearic acid (S, C<sub>18</sub>:0) and arachidic acid (A, C<sub>20</sub>:0). The TAG profile of palm oil shows a carbon distribution of C<sub>46</sub> to C<sub>52</sub> consisting of tri-unsaturated (4.8–9.8%), di-unsaturated (31.8–44.4%), mono unsaturated (38.5–50.3%) and saturated TAGs (Gunstone, 2011).

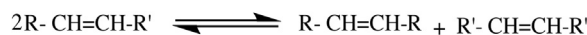
Despite high saturation, palm oil has been successfully transformed into a variety of industrial materials (Tanaka et al., 2008). It is increasingly used to make value added products such as soaps and detergents (Ogoshi and Miyawaki, 1985), lubricants (Chang et al., 2015; Shomchoam and Yoosuk, 2014), biodiesel (Abu-Hamdeh and

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

### Nomenclature

DDD	1,2,3-Triyl tris(dec-9-enoate)
DDdD	3-(Dec-9-enoxyloxy) propane-1,2-diyl dodec-9-enoate
DDL	3-(Dec-9-enoxyloxy) propane-1,2-diyl linoleate
DDO	3-(Dec-9-enoxyloxy) propane-1,2-diyl oleate
DDP	3-(Dec-9-enoxyloxy) propane-1,2-diyl palmitate
DDS	3-(Dec-9-enoxyloxy) propane-1,2-diyl distearate
DSS	3-(Stearoyloxy) propane-1,2-diyl bis(dec-9-enoate)
DDdDd	3-(Dodec-9-enoxyloxy) propane-1,2-diyl dec-9-enoate
DOO	3-(Oleoxyloxy) propane-1,2-diyl bis(dec-9-enoate)
DLO	1-Dec-9-oyl-2-linoleoyl-3-oleoyl- <i>sn</i> -glycerol
DOP	1-Decenoyl-2-oleoyl-3-palmitoyl- <i>sn</i> -glycerol
DdDdDd	1,2,3-Triyl tris(dodec-9-enoate)
DdDdS	3-(Dodec-9-enoxyloxy) propane-1,2-diyl distearate
DdDL	1-Dodecenoyl-2-decenoyl-3-linoleoyl- <i>sn</i> -glycerol
DdDdL	3-(Dodec-9-enoxyloxy) propane-1,2-diyl linoleate
DdDdO	3-(Dodec-9-enoxyloxy) propane-1,2-diyl oleate
DdDdP	3-(Dodec-9-enoxyloxy) propane-1,2-diyl palmitate
DdDP	1-Dodecenoyl-2-decenoyl-9-palmitoyl- <i>sn</i> -glycerol
DdLO	1-Dodecenoyl-2-linoleoyl-3-oleoyl- <i>sn</i> -glycerol
DdOP	1-Dodecenoyl-2-oleoyl-3-palmitoyl- <i>sn</i> -glycerol
MDP	1-Myristoyl-2-decenoyl-3-palmitoyl- <i>sn</i> -glycerol
MLP	1-Myristoyl-2-linoleoyl-3-palmitoyl- <i>sn</i> -glycerol
MMM	Trimyristoylglycerol
MMP	1,2-Dimyristoyl-3-palmitoyl- <i>sn</i> -glycerol
OOO	Triolein
OOL	1,2-Dioleoyl-3-linoleoyl- <i>sn</i> -glycerol
OOP	1,2-Dioleoyl-3-palmitoyl- <i>sn</i> -glycerol
OLO	1,3-Dioleoyl-2-linoleoyl- <i>sn</i> -glycerol
PLL	1,2-Dilinoleoyl-3-palmitoyl- <i>sn</i> -glycerol
PLP	1,3-Palmitoyl-2-linoleoyl- <i>sn</i> -glycerol
POL	1-Palmitoyl-2-oleoyl-3-linoleoyl- <i>sn</i> -glycerol
POO	1,2-Dioleoyl-3-palmitoyl- <i>sn</i> -glycerol
POP	1,3-Dipalmitoyl-2-oleoyl- <i>sn</i> -glycerol
POS	1-Palmitoyl-2-oleoyl-3-stearoyl- <i>sn</i> -glycerol
PPM	1,2-Dipalmitoyl-3-myristoyl- <i>sn</i> -glycerol
PPO	1,2-Dipalmitoyl-3-oleoyl- <i>sn</i> -glycerol
PPP	Tripalmitoylglycerol
PPS	1,2-Dipalmitoyl-3-steroyl- <i>sn</i> -glycerol
TAG	Triacylglycerol
SOO	1,2-Dioleoyl-3-stearoyl- <i>sn</i> -glycerol
SOS	1,3-Distearoyl-2-oleoyl- <i>sn</i> -glycerol

Alnefaie, 2015; Santosa, 2008) and surfactants (Tulathammakit and Kitiyanan, 2014), etc. Palm oil and its derivatives are also actively investigated as a feedstock for the synthesis of polyols to prepare polyurethanes (Chuayjuljit et al., 2007; Lee et al., 2007; Tanaka et al., 2008). However, its larger use for the production of polyurethanes is hindered because of its relatively higher saturation level (50% fatty acids) which cap the hydroxyl value of its polyols, adding to the structural limitations inherent to TAG oils (Lida et al., 2002). Typical palm oil-based polyols produced so far usually have hydroxyl values of less than 200 mg KOH g<sup>-1</sup> (Pawlik and Prociak, 2012), limiting their applicability in some polymer formulations, particularly in rigid polyurethane foams. Although some successful examples through chemical transformation of the natural oil are reported in the literature, such as for example, the transformation of the TAGs of the natural palm oil into monoacylglycerols (MAG) before functionalization and polymerization (Arniza et al., 2015; Tanaka et al., 2008), no significant breakthroughs have been made with palm oil in this area.



**Scheme 1.** Representation of olefin metathesis reaction.

The development of polyurethanes from renewable and environment-friendly feedstock is of particular importance as the market is large and growing due to high demand across industries such as automotive, building and construction, and packaging. The worth of the global polymer foams market was \$82.6 billion in 2012 and is estimated to reach \$131.1 billion by 2018 (General, 2013). A relatively large body of literature reporting on the synthesis of polyols and polyurethanes from natural oils is 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), palm oil (Chuayjuljit et al., 2007), cotton seed oil (Babb, 2012; Narine et al., 2007b)).

However, the development of polyol substrates and PU foams from natural oils is challenging. The introduction of hydroxyl groups at the positions of double bonds can be achieved by various methods (Desroches et al., 2012). Some of the methods are ozonolysis followed by hydrogenation (Narine et al., 2007a; Petrović et al., 2005), hydroformylation followed by hydrogenation (Guo et al., 2002; Petrović, 2008), epoxidation followed by ring opening (Dai et al., 2009; Pawlik et al., 2009) or bioconversion directly to polyols (Hou and Lin, 2013). These synthesis methods produce polyols of distinctive hydroxyl value, distribution and position of the hydroxyl groups which result in polyurethane networks with vastly different properties (Guo et al., 2002; Guo et al., 2006; Narine et al., 2007a). In many instances however, the functionalization of the double bonds leaves significant amounts of dangling chains because of their internal location on the fatty acids. The presence of relatively large amounts of non-reactive moieties further reduce the suitability of the polyols, especially to make rigid polyurethane foams because the regions where dangling chains are present do not support stress when the sample is loaded, and act as plasticizers that reduce polymer rigidity. These issues are generally mitigated through the chemical transformation of the natural oil and judicious choice of methods of synthesizing the polyols (Zlatanovic et al., 2002).

More research around the transformation of the natural oil such as targeted chemistry and processing techniques, is needed to increase the potential of palm oil as a viable source for polyols and polyurethane formulations. Olefin metathesis is an important organo-metallic modification technique that holds exceptional promise in oleochemistry for many industries. It is already used on TAG oils and fats to produce fine chemicals, substrates and materials, many of which serve as or are potential petrochemical replacements (Malacea and Dixneuf, 2010; Mol and Buffon, 1998; Rybak et al., 2008; Thomas et al., 2011). Olefin metathesis can increase the molecular diversify and reactivity of the natural oil, and therefore the potential for its transformation into functional materials.

Olefin metathesis (Scheme 1) is a reversible reaction involving the exchange of the alkylidene groups between the reactant alkene moieties in the presence of catalysts, typically transition metal complexes (Connon and Blechert, 2003; Malacea and Dixneuf, 2010).

Olefin metathesis is categorized further as self-metathesis and cross metathesis (Malacea and Dixneuf, 2010; Mol and Buffon, 1998). In the self-metathesis reaction (forward reaction in Scheme 1) the same olefin molecules react to produce two different olefin products. The self-metathesis of TAGs results in a complex mixture comprising linear oligomers (from dimer to pentamer), macrocyclic structures, cross-linked polymers, as well as trans-/cis isomers (Li et al., 2012a; Refvik and Larock, 1999). In a cross metathesis reaction (backward reaction in Scheme 1)

Download English Version:

<https://daneshyari.com/en/article/4512419>

Download Persian Version:

<https://daneshyari.com/article/4512419>

[Daneshyari.com](https://daneshyari.com)