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Bio-based cationic waterborne polyurethanes dispersions prepared from different vegetable oils

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ABSTRACT

In this study, a series of bio-based polyols were prepared from olive, castor, corn, canola, rice bran, grape seed and linseed oil by thiol-ene photo-click reaction. The relationship between carbon-carbon double bonds in the backbone of vegetable oil fatty acid chains and the functionalities of the polyols was elucidated. The advantage and disadvantage between thiol-ene photo-click reaction and traditional methods for vegetable oil based polyols are summarized and compared. These bio-based polyols were used to prepare cationic waterborne polyurethane dispersions.

With the increase of the vegetable oil based polyols' hydroxyl values, the tensile strength, Young's modulus, T_g, water contact angle of the waterborne polyurethane films increase from 1 to 11 MPa, 10 to 395 MPa, 23 to 50 °C and 38° to 46°, respectively, but the elongation at break and thermal stability of them decrease. Thiol-ene photo-click reaction offers a bio-based platform to create a variety of waterborne polyurethanes that promises economic and environmental benefits.

1. Introduction

The replacement of traditional solvent-based polyurethanes (PU) from fossil feedstock with renewable waterborne polyurethane (WPU) has received much attention due to the growing concern toward the depletion of the world crude oil stock and health threat of the volatile organic compound (VOC) emission (Kim et al., 1994; Philipp and Eschig, 2012). Several renewable resources have been exploited for this purpose, including polysaccharides (starch and sugars), wood, protein and vegetable oils (Petersen and Gatenholm, 2011; Rabotyagova et al., 2011; Xie et al., 2013; Zhu et al., 2016).

Vegetable oils are among the most promising options because they are relative low price, low toxicity, and inherent biodegradability. Vegetable oils are tri-esters derived from glycerol and fatty acids containing 8～18 carbon atoms and 0～3 carbon-carbon double bonds depending on the plant kinds and growing conditions (Downing and Greene, 1968; Petrovic, 2008). Some oils inherently bear reactive functional groups, such as hydroxyl in castor oil and epoxy in vernonia oil. These vegetable oils are suitable to be used for producing polymers directly by free radical or cationic polymerization without the need of chemical modification (Barretta et al., 1993; Petrovic et al., 2005). However, most oils require chemical modification on the reactive sites (esters and carbon-carbon double bonds) in triglycerides prior to use as valuable monomers for polymer synthesis.

A variety of routes have been developed to introduce functionalities at reactive sites of fatty acid chains in the purpose of producing bio-based polyols for waterborne polyurethane dispersions (PUDs). For example, a series of vegetable oil based polyols have been successfully prepared with different functionalities and residual carbon-carbon double bonds via epoxidation/ring opening methods (Garrison et al., 2014). These polyols were used to prepare WPUs and it is found that the tensile strength, Young's modulus and toughness of the resulting PU films increase with the enhancement of the residual unsaturation. Hydroxylated tung oil has been synthesized using ester alcoholysis (Ren et al., 2015). The WPU films from the hydroxylated tung oil exhibit strong hydrophobic character. The synthesis of new diisocyanates and chain extenders from castor oil by thiol-ene reaction have been reported (Fu et al., 2014). And the resulting WPU films with high bio-based content (nearly 100%) demonstrate excellent thermal and hydrophobic properties.

The advantage and disadvantage between thiol-ene photo-click reaction and traditional method for vegetable oil based polyols are also summarized and compared in Table 1. The thiol-ene photo-click reaction is considered to be an efficient and green route to functionalize the

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Table 1
Comparison of different methods for vegetable oil based polyols.

	Epoxidation/ ring-opening	Ozonolysis /reduction	Hydroformylation / hydrogenation	Transesterification /amidation	Thiol-ene
Number of steps	2	2	2	1	1
Functionality	Secondary, tunable	Primary and terminal, 3	Primary, tunable	Primary and terminal, 2-3	Primary, tunable
OH number	70-340	200-260	140-210	150-400	190-330
MW	> 1000	400-700	900-1150	350-550	1000-1500
Viscosity	High	Low	Medium	Low	Medium
Reaction temperature	50-190 °C	RT	appro x .120 °C	120-220 °C	RT
Reaction time	Long	Medium	–	–	Medium
Organic solvent	Yes	Yes	No	Yes or No	No
Catalysis	Cheap	Cheap	Expensive	Cheap	Cheap
Reference	(Bakhshi et al., 2013; Dai et al., 2009; Xia and Larock, 2010; Zhang et al., 2013)	(Dumont et al., 2013; Omonov et al., 2011; Petrovic et al., 2005)	(Petrovic et al., 2010, 2008; Pfister et al., 2011)	(Chaudhari et al., 2013; Das et al., 2013; Kirpluks et al., 2013; Nohra et al., 2013)	(Caillol et al., 2013; Elbers et al., 2017; Feng et al., 2017)

RT-Room temperature, MW-Molecular weight.

vegetable oils for value-added polyols. First, only one step is needed to introduce the necessary functional groups into the vegetable oils. Second, mild and green conditions are conducted to initiate the reaction, that is, it could be performed at room temperature without any solvents or expensive catalysts. Finally, most of by-products or residual starting materials could be easily washed by water for high purity chemicals.

The properties of WPUs are strongly determined by the types of chain extenders, isocyanates and polyol as well as their content. The PUDs containing ionic groups at the polymer chain termini exhibit the smallest dispersion size, the highest dispersion stability and viscosity. But the positions and concentration of the ionic groups do not influence the thermal and mechanical properties of the PU films (Lee and Kim, 2009). Jatropha oil based polyols with OH number ranging from 138 ~ 217 mg KOH/g and a series of WPUs therefrom have been synthesized (Saalah et al., 2015). The resulting WPU films behave from elastomers to rigid plastics with the increase of OH numbers. Soybean oil based WPUs with different chain extender content from 5.4 to 6.9% have been prepared (Lu and Larock, 2008). Increasing chain extender content enhances the glass transition temperatures and tensile strength of the resulting PU films due to the enhancement of the hard segment content, but decreases the thermal stability of the films as a result of the increase of labile urethane groups.

The vegetable oil based polyols have been common used for the preparation of WPU, but the OH numbers of all the polyols that have been reported are relatively low (Garrison et al., 2014; Saalah et al., 2015). This arises from that high OH numbers of the polyols may result in gelation and high cross-linking, which is relatively difficult to disperse the high cross-linking PU into the water.

To develop WPU with high performance as well as enlarge the applications of the vegetable oils, a series of polyols with OH number ranging from 190 to 305 mg KOH/g have been synthesis via thiol-ene reaction and a series of cationic PUDs were prepared therefrom. The polyols were prepared from different vegetable oils, including olive, castor, corn, canola, rice bran, grape seed and linseed oil, because of the different content of C=C bonds, abundant availability and relatively low cost of these oils. The chemical structure and properties of the polyols were characterized by proton nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR). N-methyl diethanolamine (MDEA) was used as chain extender in the preparation of the cationic PUDs. The particle size and zeta potential of the PUDs are characterized by zetasizer and the properties of the resulting films were characterized by dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and tensile testing. The effect of hydroxyl numbers and chemical structure of polyols from different vegetable oils on the particle size of the PUDs and thermo-physical, thermal stability, and mechanical properties of the corresponding PU films was investigated.

2. Materials and methods

2.1. Materials

Canola, rice bran and grape seed oil were purchased from Jinan Quanrun Rose Product Co., Ltd. Olive oil was purchased from Chengdu Kelong Chemical Reagents Factory. Castor oil, sodium chloride (NaCl) and dibutyltindilaurate (DBTDL) were supplied by Tianjin Fuyu Fine Chemical Co., Ltd. Corn oil was obtained from Jiangxi Yipusheng Pharmaceutical Co., Ltd. Linseed oil was purchased from Tianjin Guangfu Fine Chemical Research Institute. The basic chemical characteristics of the vegetable oils are summarized in Table 2. 2-Mercaptoethanol (ME) (> 98%) was obtained from Alfa Aesar (China) Chemicals Co., Ltd. 2-Hydroxy-2,2-dimethylacetophenone (1173) was supplied by Ryoji Organic Chemical Co., Ltd. Ethyl acetate was purchased from Shanghai Titan Scientific Co., Ltd. Magnesium sulfate ($MgSO_4$) was supplied by Tianjing Damao Chemical Reagents Factory. Isophorone diisocyanate (IPDI) and N-methyl diethanolamine (MDEA) were obtained from Guangdong Wengjiang Chemical Reagents Co., Ltd. Acetic acid (HAc) and methyl ethyl ketone (MEK) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd and Tianjin Hongda Chemical Reagents Factory, respectively. All materials were used as received without further purification.

2.2. Synthesis of vegetable oil based polyols

As showed in Scheme 1, Vegetable oil based polyols were prepared via thiol-ene photo-click reaction in a home-made reactor under the optimized conditions previously reported (Feng et al., 2017b). Different vegetable oils (5 g) were respectively mixed with ME in the 30 ml

Table 2
Basic chemical characteristics of the vegetable oils.

Materials	Grade/ purity	Density (g/ ml)	Saponification value (mg KOH/g)	CAS number
Grape seed oil	First grade	0.92-0.93	126	85594-37-2
Canola oil	First grade	0.91-0.92	132	8002-13-9
rice bran oil	First grade	0.91-0.93	128	68553-81-1
Olive oil	AR	0.91-0.92	190-195	8001-25-0
Castor oil	AR	0.96-0.97	176-186	8001-79-4
Corn oil	First grade	0.92-0.93	/	8001-30-7
Linseed oil	AR	0.93-0.94	/	8001-26-1