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Functional soybean oil-based polyols as sustainable feedstocks for polyurethane coatings

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ABSTRACT

The development of renewable and viable alternatives to petroleum-based polymeric materials is a major challenge to the long-term environmental and waste management issues of the polymer industry. In this study, a technology platform composed of a series of efficient and quantitative thiol-ene reactions for preparing functional and sustainable polyols is proposed. First, a soybean oil (SO)-based polyol with two hydroxyl groups (MSO) was synthesized through a controlled thiol-ene click reaction between SO and 2-mercaptoethanol. Second, other functional groups, such as silane, fluorine or ethylene oxide units, were introduced to the MSO through another thiol-ene reaction between the MSO and thiol-terminated intermediates to afford SO-based functionalized polyols. The thiol-terminated intermediates were obtained using a Michael addition reaction between dithiol- and methacrylate-terminated compounds. Employing silane-modified MSO (SiMSO) as a representative functionalized polyol, preparation of polyurethane (PU) coatings was demonstrated. For comparison, PU coatings with commercially available poly(propylene glycol) (PPG) and MSO were also prepared. The thermal, physico-mechanical and anticorrosion properties of the PU coatings clearly demonstrated that coatings made with the silane groups had a better performance. PU coatings with SiMSO exhibited higher hardness, T_g, and adhesion strength than the PU coatings with MSO and PPG. Notably, incorporation of SiMSO improved the anticorrosion properties of the PU coating in a 3.5 wt% aqueous NaCl solution, probably due to the improved blocking and adhesion properties of the coating on mild steel panel. The present study demonstrates SO-based functional polyols as promising alternatives to conventional polyols to afford PU coatings with desirable properties.

1. Introduction

The replacement of petroleum-based raw materials with renewable resources is a major economic and environmental challenge (Gandini et al., 2016; Lligadas et al., 2010; Miao et al., 2014; Xia and Larock, 2010). Over the past decades, most of the starting materials for polymers have been derived from petroleum-based resources, which are widely regarded as unsustainable (Nohra et al., 2013). Environmental concerns, depleting world crude oil stocks, and increasing oil costs have triggered efforts to utilize bio-based resources for polymer production, since it is abundant and inexpensive (Pfister et al., 2011).

Several bio-renewable substances, such as vegetable oil (VO), cellulose, starch, sugar, and proteins have been considered as potential raw materials (Gandini, 2008; Tanaka et al., 2008; Zhang et al., 2014). Among them, VOs have gained considerable attention due to their unique chemical structure with unsaturation sites and ester groups. The unique structure of VO enables it to undergo various chemical transformations to produce materials with many applications (Wang et al., 2017). Taking advantage of this versatility, increasing efforts are being focused on the use of VOs as platform chemicals. VOs with hydroxyl, epoxy, amine, polyacid, isocyanate or silane groups have been prepared (Ionescu et al., 2015; Jaillet et al., 2013). Among them, the preparation of VO-based polyols has become attractive in terms of polymer synthesis (Alagi et al., 2016a; Alagi et al., 2016b; Alagi et al., 2017; Alagi and Hong, 2015). Polyols from VOs with hydroxyl functionalities were typically prepared by epoxidation, hydroformylation, ozonolysis, amidation, and transesterification reactions (Alagi and Hong, 2015; Desroches et al., 2012; Nohra et al., 2013; Pfister et al., 2011). However, the VO-based derivatives generally contained only one type of functionality on the molecule, which often limits the diversity of their potential applications.

Polyols are essential raw materials for polyurethanes (PUs), which

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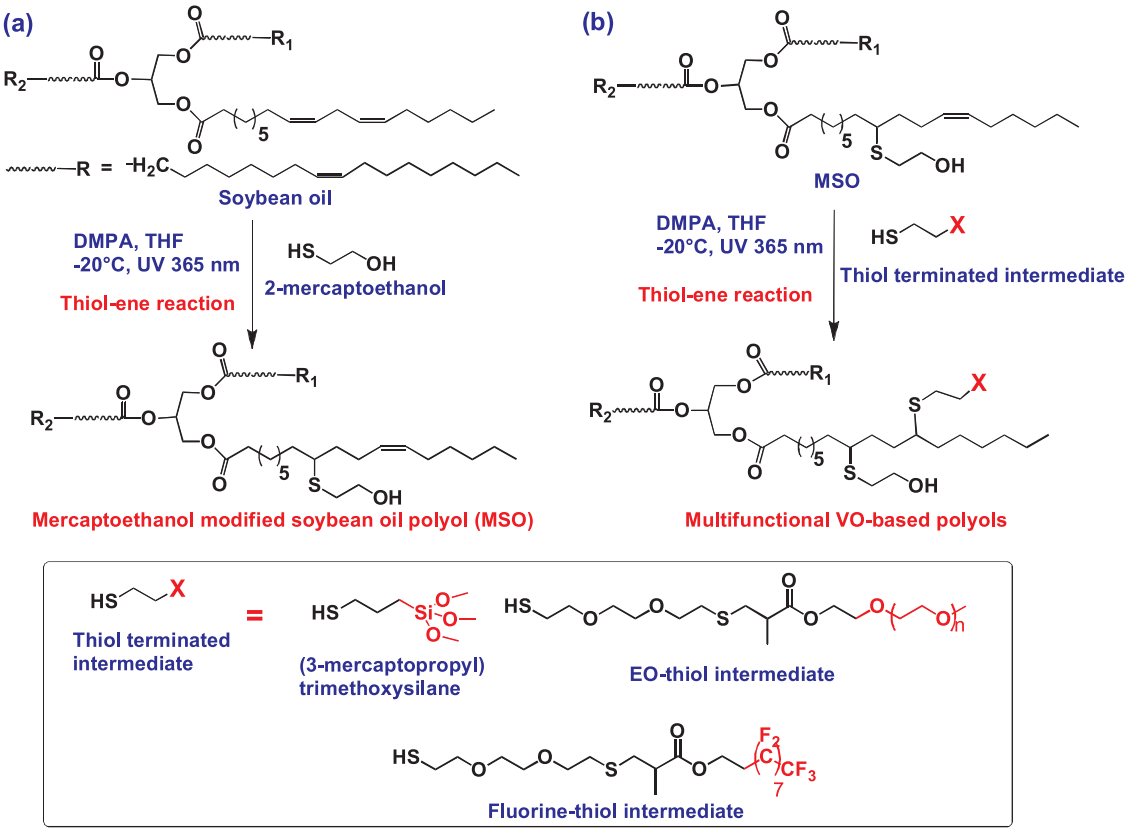

Scheme 1. Reaction scheme for the preparation of functionalized polyols through sequential thiol-ene reactions: First step, the preparation of MSO (a); second step, the preparation of functionalized polyols containing silane, fluorine or EO (b).

are one of the most important classes of polymer materials. With a global production of 18 Mt in 2016, PUs have ranked sixth in the annual worldwide production of polymers (Cornille et al., 2017). The applications of PUs vary from thermoplastic to thermoset materials, including coatings, adhesives, sealants, foams, insulation, and other automotive parts (Akindoyo et al., 2016; Chattopadhyay and Webster, 2009; Chung et al., 2016; Jin et al., 2016; Nohra et al., 2013). Among them, PU coatings have received considerable attention because of their excellent abrasion resistance, chemical resistance, toughness and low temperature flexibility (Alagi et al., 2017), which made PUs popular materials for automobile finishing and industrial maintenance (Chattopadhyay and Raju, 2007).

For coating application, silane is one of the most important and desirable functional groups. Moisture may hydrolyze the silane groups to afford silanols, which undergo condensation with other silanols or with functional groups on the substrate, resulting in efficient cross-linking and strong adhesion of the coating materials (Chaudhury et al., 1987; Dumée et al., 2014). Several studies have demonstrated the introduction of alkoxysilanes into VO-based polymers. 3-Aminopropyltrialkoxysilane was used as an end-capping reagent for VO-based PUs (Jena and Raju, 2007; Seeni Meera et al., 2013). Acrylated epoxidized soybean oil (SO) was shown to react with 3-aminopropyltriethoxysilane (Çolak and Küsefoğlu, 2007). Probably, castor oil with silane functionality can be a simple target due to its inherent secondary hydroxyl functionality (Allauddin et al., 2013; Fu et al., 2014). However, the type and number of hydroxyl functionality of castor oil are not so desirable for well-defined polymer synthesis.

Thiol-ene chemistry has been receiving increased attention because of its high efficiency and quantitative controllability (Alagi et al., 2016a; Alagi et al., 2016b; Hoyle and Bowman, 2010; Lowe, 2010). The addition of thiol groups to carbon-carbon double bonds (C=Cs) can be initiated thermally or photochemically by UV light (Caillol et al., 2013; Desroches et al., 2011; Ionescu et al., 2015). In our previous studies, we successfully demonstrated the preparation of well-defined SO-based polyols with a controlled number of primary hydroxyl groups by an efficient, quantitative and simple photo-initiated thiol-ene reaction (Alagi et al., 2016a; Alagi et al., 2016b; Alagi and Hong, 2015). The polyols were then successfully used for preparing thermoplastic PUs. In this study, we extend our strategy to demonstrate the preparation of the SO-based polyols with additional functional groups such as silane, fluorine and ethylene oxide (EO). In particular, the performance of alkoxysilane-modified SO-based polyol in PU coatings was evaluated. Through this study, an efficient and simple chemical toolbox is provided to allow an access to renewable and functional chemical building blocks for PUs with predetermined characteristics.

2. Experimental

2.1. Materials

SO (analytical standard), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), 2-mercaptoethanol (ME, > 99%), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (FMA, 97%), poly(ethylene glycol) methyl ether methacrylate (EOMA, number average molecular weight, Mn ~ 500 g/mol), (3-mercaptopropyl)trimethoxysilane (MTS, 95%), 2,2′-(ethylenedioxy) diethanethiol (DT, 95%), triethylamine (TEA, 99%), poly (propylene glycol) diol (PPG, Mn ~ 2000 g/mol), and dibutyltin dilaurate (DBTDL, 95%) were obtained from Aldrich (St. Louis, MO, USA) and used as received. Tetrahydrofuran (THF, > 99%, Daejung Chemicals, Seoul, Korea), dichloromethane (99.5%, Samchun Chemicals, Seoul, Korea), ethyl acetate (EA, 99%, Samchun Chemicals, Seoul, Korea), and *n*-hexane (95%, Samchun Chemicals, Seoul, Korea) were also used without purification.