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Preparation of vegetable oil-based polyols with controlled hydroxyl functionalities for thermoplastic polyurethane

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ABSTRACT

Growing concerns over long-term environmental and waste management issues direct the use of renewable resources for sustainable polymers in the polymer industry. In this study, controlled preparations of vegetable oil-based polyols with predetermined primary hydroxyl functionalities ranging from 2 to 4 were attempted using a one-step thiol-ene click reaction between soybean oil (SO) and 2-mercaptoethanol (ME). The numbers of the primary hydroxyl functionalities in the SO-based polyols could be easily controlled by terminating the thiol-ene reaction at a particular reaction time and conversion of the carbon-carbon double bonds of SOs. The SO-based polyols were a mixture of SO molecules with different numbers of ME units, where the SO molecules with three and four ME units afforded thermoplastic polyurethanes (TPUs) with hyperbranched architectures. The TPUs exhibited increased glass transition temperature, moduli and tensile strength values, demonstrating that they were hard and tough elastomers. Relatively low tension set values, along with high elongation at break and low hysteresis values demonstrated the good elastomeric characteristics of the TPUs. The TPUs also exhibited excellent shape memory properties and film transparencies because of their hyperbranched architectures. This study demonstrates an efficient and controlled synthetic pathway for the preparation of unique polyols and polymers from renewable resources, enabling new applications of eco-friendly materials in high value-added technologies.

1. Introduction

The depletion of fossil fuel resources and environmental issues has triggered the search for renewable feedstocks and sustainable development [1]. Several bio-renewable materials, including cellulose, starch, proteins, natural oil, and sugar, have received much attention as potential raw materials [2–4]. Vegetable oil (VO) has been one of the most interesting renewable resources for both academic and industrial researchers because of its universal availability, inherent biodegradability and low price [5,6].

VO mainly comprises triglycerides and has three long chain fatty acids of different compositions depending on the oil sources. The physical and chemical properties of VO depend on the chain length and the number of double bonds of the fatty acids [7,8]. Carbon-carbon double bonds and ester linkages are two major functional moieties present in VO structures that are used for chemical transformations. VO is often chemically modified to introduce hydroxyl groups into the structures to generate polyols [9]. Polyols are essential raw materials for the synthesis of industrially important polymers such as

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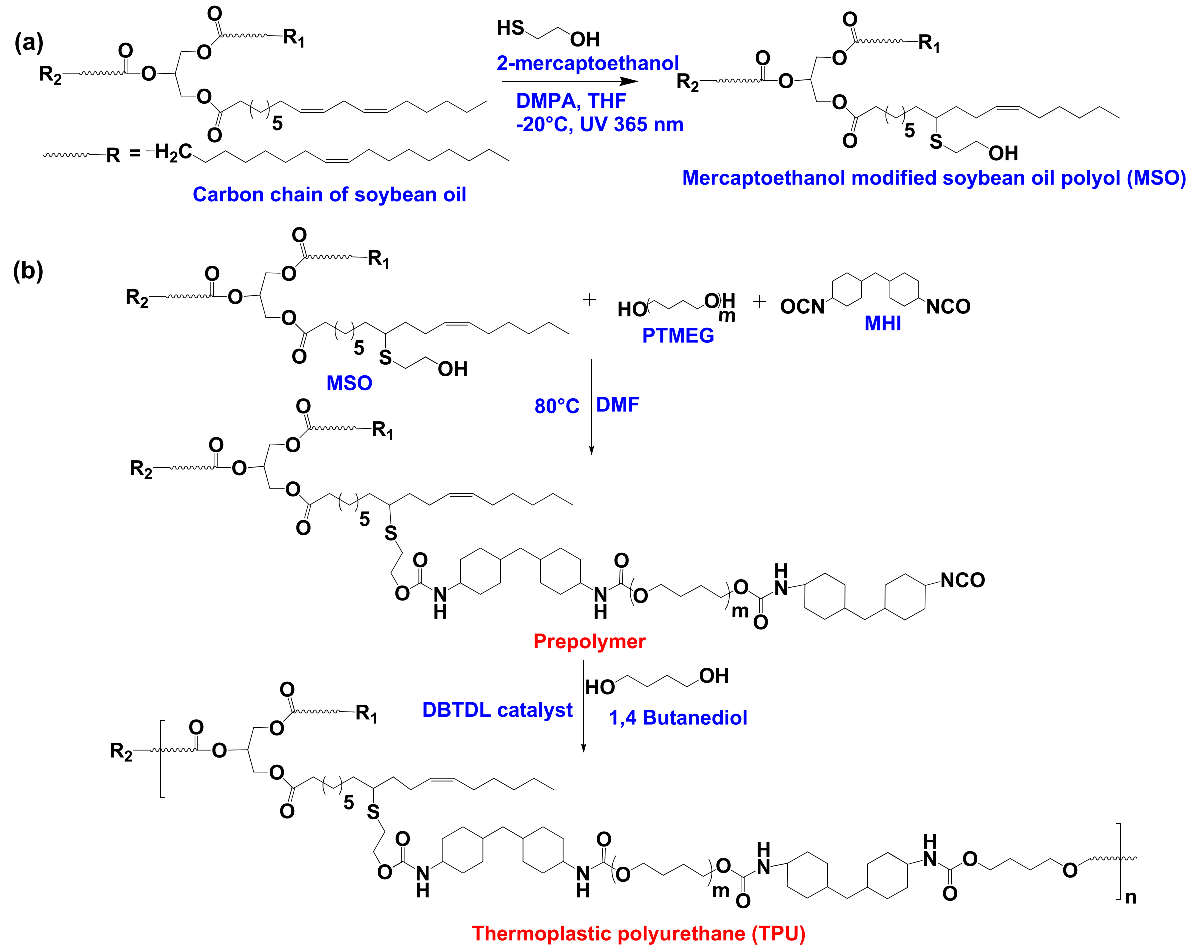

Scheme 1. Synthetic pathway for the preparation of MSO polyols (a) and TPUs (b).

polyurethanes (PUs) and polyesters [9]. Synthetic routes for the preparation of VO-based polyol includes epoxidation [10,11], hydroformylation [12,13], ozonolysis [14,15], transesterification [16,17], amidation [18,19], and thiol-ene coupling [20,21] reactions.

Indeed, most of the industries have developed their own brand of biobased polyols, VO-based polyols generated from thiol-ene reactions are interesting because of the simple single-step reaction that is utilized to introduce primary hydroxyl groups. Auvergne et al. prepared polyols with ~3.6 hydroxyl groups per triglyceride molecule from rapeseed oil using a thiol-ene reaction under ultraviolet (UV) light [21]. Caillol et al. also reported the application of a thiol-ene reaction to prepare soybean oil (SO)-based polyols [20]. Thiol-ene reactions are not limited to the hydroxyl functionalities of VO but are applicable for introducing a range of functionalizations, such as amine, epoxy, isocyanate, silane, and carboxylic acid groups [22].

PUs are one of the most important classes of polymer materials, which varies from thermoplastic to thermoset materials, and have a broad spectrum of applications [23,24]. Thermoplastic PU (TPU) is a class of PUs with several useful properties, including elasticity, transparency and recyclability. Most reported PUs with VO polyols are thermosets. Only a limited number of studies have demonstrated the synthesis of TPU from VO-based polyols [7,25].

The mechanical and thermal properties of PUs synthesized from VO-based polyols depend on the structure and crosslinking density of the polymer network [26,27]. Carme Coll Ferrer et al. compared the TPUs derived from VO-based polyols and petroleum-based diols and suggested that an increased crosslinking density resulted in increased glass transition temperature (T_g) values [26]. Furthermore, the incorporation of VO moieties in PUs enhanced their mechanical properties [28]. Therefore, control over the number and type of hydroxyl groups in VO-based polyols is important for the preparation of TPUs with target characteristics. In this study, the preparation of VO-based polyols with a predetermined number of primary hydroxyl functionalities was targeted via controlled thiol-ene reactions between SO and 2-mercaptoethanol (ME). The relationships between the hydroxyl functionalities of the VO-based polyols and the characteristics of the corresponding TPUs were also investigated.