Biobased Polyol with Self-crosslinking Functionality

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The need for green and environmentally safe coatings creates an opportunity for biobased raw materials. Vegetable oil polyols (VOPs) are the major source of biobased raw materials for making polyurethanes.[1]

Despite their wide commercial availability, they have not been utilized for making water-based polyurethane (PU) coatings, because, VOPs have no performance-enhancing functional group in the molecular architecture.[2] Therefore, they are unable to meet the stringent corrosion-, UV-, and solvent-resistance performance requirements.

In this short communication, we present a new class of biobased polyol with a crosslinking functional group that is free from toxic chemicals and has superior performance. This is achieved by reacting a keto acid with a glycidyl functional fluids derived from biobased sources. We also present the utilization of the polyol in making water-based polyurethane dispersion (PUD).

SYNTHESIS OF THE POLYOL

In a typical example as shown in *Scheme 1*, levulinic acid is reacted with glycidol to produce 2,3-dihydroxypropyl levulinate (Levupol-G).

Any epoxide functional fluid with two or more oxirane groups can be utilized and a myriad of polyol grades can be obtained. For example, the reaction of levulinic acid with epoxidized soybean oil would result in soy polyol with crosslinkable levulinic ester in the final product, as shown in *Scheme 2*.

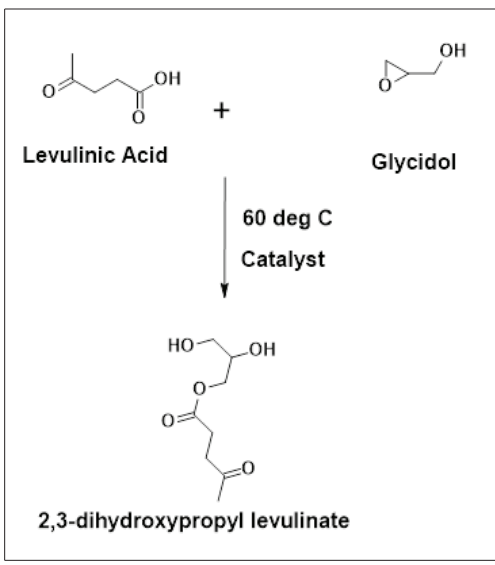
As shown in *Scheme 1* and *Scheme 2*, the polyol has hydroxyl groups that are necessary to react with polyisocyanates to form the polyurethane backbone. It also contains the performance-enhancing keto group that reacts with crosslinkers and provide the high-performance features.

We adopted Green Chemistry Principles[3] and the benefits of the polyol are: (a) 100% atom economical as there are no byproducts (b) it does not use any solvents, and (c) the product formed is highly pure, and no additional purification step is required.

The proprietary catalyst employed to make the polyol is highly effective for the epoxide ring opening with carboxylate nucleophiles. As a result, the ring opening reaction is fast, well-controlled, and produces the desirable product in quantitative yield.

There are no undesirable polyethers formed during the synthesis that would have otherwise adversely affected the product performance and cost. It was found the catalyst we used accelerated the product formation significantly compared to commercial control, as shown in *Figure 1*.

SCHEME 1—Synthesis of 2,3-dihydroxypropyl levulinate (Levupol-G)



SCHEME 2: Synthesis of Levupol-S from Levulinc acid and epoxidized soybean oil. (The structure of epoxidized soybean oil is for illustration only and does not represent the actual structure of the molecule; R^1 is triglyceride fraction.)

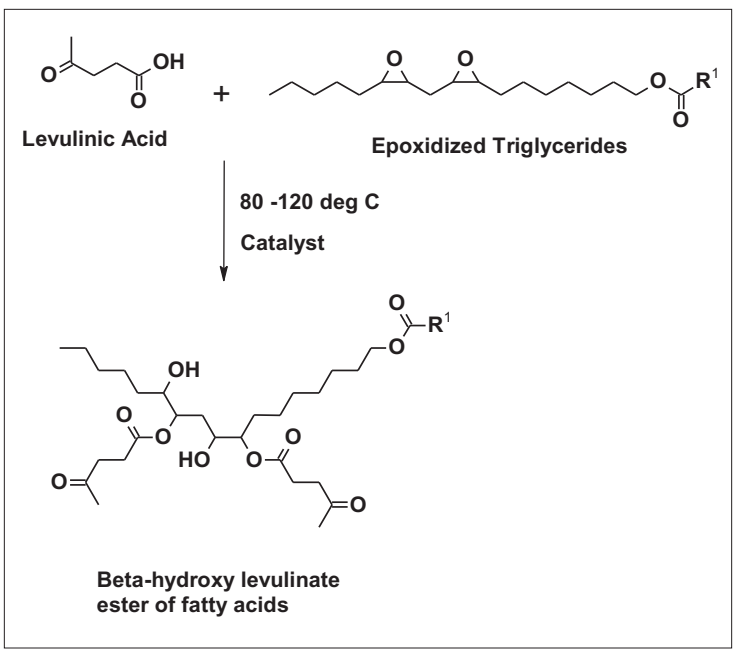


FIGURE 1—Effect of catalyst for the epoxide ring opening reaction with carboxylic acid nucleophiles

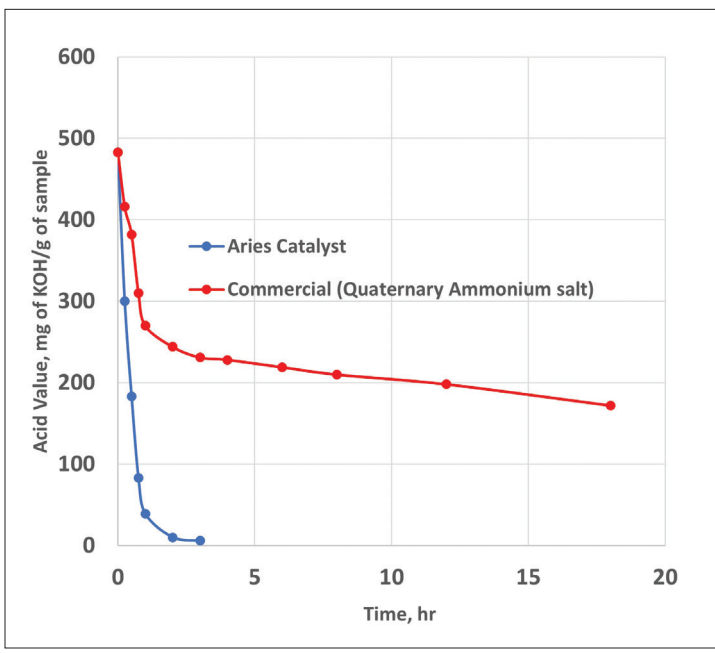


TABLE 1—Physical properties of Levupol-G and Levupol-S

PROPERTIES	LEVUPOL-G	LEVUPOL-S
Molecular Weight (Calculated)	190.19	1091
Number of hydroxyl functionality (Based on structure)	2	>3
Hydroxyl Value (mg KOH/g)	565± 15	138± 20
Acid Value (mg KOH/g)	0.3±1	6±2
Viscosity (cP) @25 °C Spindle# 4; 60rpm	200±10	980±40
Solubility in selected solvents (20% w/w solute concentration)		
Acetone	Soluble	Soluble
MEK	Soluble	Soluble
NMP	Soluble	Soluble
Cyrene	Soluble	Soluble

PROPERTIES OF THE POLYOL

The physical properties of different polyol grades are provided in *Table 1*.

REACTIVITY OF THE POLYOL TOWARD ISOCYANATES

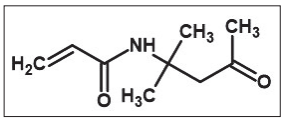
To determine their effectiveness towards reaction with isocyanates, we reacted specified polyol with toluene-2,-4 diisocyanate at NCO/OH ratio 1.05, dibutyl tin dilaurate (0.03 wt.%) catalyst in methyl ethyl ketone as solvent (monomer concentration is 30 w/w%).

Figure 2 compares the reactivity of isocyanates with different Levupol grades along with commercial polyol (Polyester polyol type with number average molecular weight 1100). It is observed that both the Levupol grades reacted with isocyanates efficiently, which is key for forming the polyurethane polymer. The percentage conversion was assessed by analyzing isocyanate content at specified time using the industry acceptable dibutyl amine back titration following the ASTM D 5155 – 01: Standard Test Methods for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates.

APPLICATION OF THE POLYOL IN MAKING SELF-CROSSLINKABLE WATER-BASED POLYURETHANE DISPERSION

Coating formulators are increasingly using PUD due to environmental and consumer awareness of the health risks associated with hazardous organic solvents. Coatings derived from PUD do not have adequate chemical and mechanical properties for some applications such as heavy-duty industrial applications. To overcome this challenge, water-based binders are often reacted with crosslinkers[4], and the resultant coatings exhibit similar or superior performance compared to their solvent-based counterpart. One of the best and widely studied crosslinkers for PUD is diacetone acrylamide, as shown in *Figure 3*.

FIGURE 3—Chemical structure of diacetone acrylamide



Generally, it is introduced into the polyurethane backbone via multiple steps and formulated with specified amount of adipic dihydrazide.[5,6] When the water evaporates from the coating, the ketone group of the diacetone acrylamide reacts with the hydrazide, resulting in the formation of a three-dimensional polymer network.[7] Concerns surrounding the toxicity of acrylamide and the technical challenges involved incorporating the acrylamide monomer to the PU backbone warrants a safer and process friendly biobased alternative.

Levupol can be partially or fully substituted in place of petroleum-based polyol for making PUD. In a typical experimental procedure, Levupol-G, dimethylol propionic acid-L (synthesized by neutralizing dimethylol propionic acid (DMPA) with triethylamine in equal molar ratio and the resultant liquid product DMPA-L[8] is used as made without any purification), were stirred at room temperature in a 500 ml reactor equipped with a dry argon spurge, a mechanical stirrer, a thermocouple, and a cold-water condenser.

The reactants were heated to 70 °C and charged with IPDI over a period of 1 hour. The ratio of NCO/OH was kept at 1.05 and the concentration of DMPA-L was 10% on total polymer solids. The reaction was held at 70 °C until the isocyanate content reached between 1% and 2%. The tertiary amine functional group in the DMPA-L acts as a catalyst and therefore there is no need for toxic tin catalyst for the polyurethane forming reaction. The pre-polymer was added to distilled water with stirring (600 rpm) to produce the water-based PUD. The property of the PUD is provided in *Table 2*.

The improved water and chemical resistance properties of the coating derived from the polyol and adipic dihydrazide suggest the keto group from the polyol reacted with the hydrazide functionality and formed a crosslinked polymer network. Structure-activity relationship studies are needed to fully optimize the coating performance.

SUMMARY

We utilized epoxide ring opening reaction with a carboxylic acid nucleophile and adopted Green Chemistry Principles to produce a novel biobased polyol with self-crosslinking functionality. To the best of our knowledge, this is the first report

FIGURE 2—Comparison of reactivity of Levupol grades with commercial polyols towards isocyanates

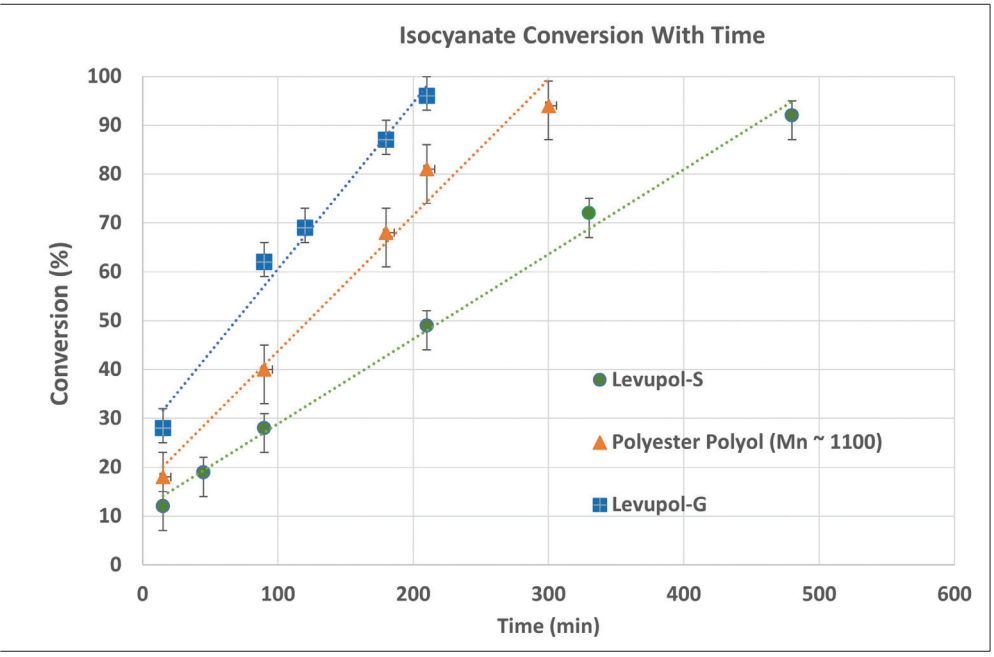


TABLE 2—Properties of PUD Derived from Levupol-G

PROPERTIES		LEVUPOL-G	LEVUPOL-G FORMULATED WITH 10 PHR ADIPIC ACID DIHYDRAZIDE (5% SOLUTION IN DI WATER)
Dispersion	Appearance	Transparent dispersion	Transparent dispersion
	pH	7.8	7.3
	Viscosity (cP) @25 °C Spindle# 2; 60rpm	230	202
	Solid content (%)	48	43
	T_g (°C)	43	Not determined
	Particle Size (nm)	80	96
Film	MEK DR	80	140
	Water resistance (immersion test)	Hazy in 24 hrs. Recovered in 2 hrs.	Translucent; Recovered in 2 hrs.

on making such unique biobased polyols and demonstrating their application potential to produce crosslink able polyurethane binder at ambient temperature.

Levupol-G and Levupol-S can be used to make water-based polyurethane; however, the right choice and concentration of the Levupol grade will be based on the final PUD product requirements namely solids, viscosity, particle size, thermal and mechanical properties. Levupol is a platform technology and based on the chemical structure of epoxide and carboxylic acid groups, a myriad of functional biobased polyols can be produced to meet the demanding requirements from the coating industry. ❊

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