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Bio-Based Polyurethane Containing Isosorbide for Use in Composites and Coatings

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14. ABSTRACT The purpose of this research is to formulate polyurethane 1) for use in composites or coatings that contain isosorbide as part or all of the polyol phase and 2) that can be easily molded or cast into a film at ambient conditions. Solubility studies were conducted to determine the maximum amount of isosorbide that could remain in solution with other diols. Formulation of polyurethanes using isosorbide as part or all of the polyol phase combined with monomers such as toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI) in the isocyanate phase. TDI reactivity at ambient conditions was too extreme, while IPDI was not reactive enough. Prepolymerized polyisocyanates were studied with isosorbide and compared with a commercial polyurethane coating. The dynamic mechanical analysis showed that isosorbide as a drop-in replacement for the commercial polyol increased the T _g 17 °C. However, ultraviolet exposure revealed that the polyurethane containing isosorbide does not perform as well as the commercial product with defects such as brittleness and delamination.					
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1. Introduction

Isosorbide is a renewable material derived from sorbitol, which is obtained from glucose. Isosorbide (Dianhydro-D-glucitol) is a nontoxic diol produced from bio-based feedstocks that is biodegradable and thermally stable. The purpose of this research is to formulate polyurethane for use in composites or coatings that contain isosorbide as part or all of the polyol phase and can be easily molded or cast into a film at ambient conditions. This research also explores the possibility of using isosorbide as a drop-in replacement for a commercial polyol in a polyurethane formulation. Research was iterative where results from the first phase lead to the material selection and experimental approach for the next phase.

2. Materials

The raw materials used in this study are detailed in Table 1.

Table 1 Summary of raw materials

Product Name	Chemical Type	Formula	Molecular or Equivalent Weight (g/mol)	CAS-No.
Dianhydro-D-glucitol (Isosorbide) (IS)	diol	C ₆ H ₁₀ O ₄	146.14	652-67-5
Dipropylene Glycol (DPG), mixture of 3 isomeric chemical compounds	diol	C ₆ H ₁₄ O ₃	134.2	2565-71-8
Ethylene Glycol (1,2-Ethanediol) (EG)	diol	C ₂ H ₆ O ₂	62.07	107-21-1
Glycerol Anhydrous	polyol	C ₃ H ₈ O ₃	92.09	56-81-5
Triethylamine (TEA)	catalyst	C ₆ H ₁₅ N	101.19	121-44-8
Dabco 33-LV (33% TEDA and 67% DPG)	catalyst	n/a	n/a	n/a
Surfynol DF-178 Defoamer (HAP-free and alkylphenol ethoxylated free)	defoamer	n/a	n/a	n/a
BYK-023 Silicone defoamer for aqueous systems	defoamer	n/a	n/a	n/a
Tolyene-2,4-diisocyanate (TDI) (Toluene-2,4-di-isocyanate)	Aromatic diisocyanate	C ₉ H ₈ N ₂ O ₂	174.16	584-84-9
Hexamethylene diisocyanate (HDI)	Aliphatic diisocyanate	C ₈ H ₁₂ N ₂ O ₂	168.19	822-06-0
Bayhydrol XP 7110E	Hydroxyl-functional polyurethane dispersion (PUD)	n/a	1100	n/a
Bayhydur 303, Water-dispersible	Aliphatic polyisocyanate based on HDI	n/a	equivalent wt. 218.0	n/a
Desmodur E 744	Aromatic polyisocyanate based on MDI	n/a	equivalent wt. 179	n/a
Desmodur L 67 BA	Aromatic polyisocyanate based on TDI	n/a	equivalent wt. 350	n/a
Desmodur L 75	Aromatic polyisocyanate based on TDI	n/a	equivalent wt. 315	n/a

3. Experimental Method and Discussion

3.1 Solubility Study

The materials discussed in this section are listed in Table 1. Isosorbide is a nontoxic diol and a white solid at room temperature.¹ Two diols were selected to use as a solvent with isosorbide. The first diol was dipropylene glycol (DPG), a mixture of 3 isomeric chemical compounds, and the second was ethylene glycol (EG), a liquid organic compound.² Glycerol, a polyol, was selected because it is polyfunctional, containing 3-hydroxyl groups, and is bio-based.³ Isosorbide was dissolved in the diols individually and in blends with glycerol at various levels. The Thinky ARE-250 conditioning mixer and Aquasonic sonicator 75D were used to create homogeneous blends of isosorbide at various percentages with the carrier diols/polyol.

The first method included 1–3 mixing cycles at 2,000 rpm for 10 min each on the Thinky ARE-250 mixer, followed by a 2-min defoaming cycle. The second mixing method involved placing the sample vial in the Aquasonic sonicator 75D for 20–30 min. The temperature of the water was regulated between 25 and 50 °C. The parameters set for this solubility study were that the blends should remain in solution upon standing at room temperature for 24 h. The Thinky ARE-250 mixer proved ineffective for creating a homogeneous mixture. After 3 mixing cycles at 2,000 rpm for 10 min plus 2 min of defoaming, the blends were foamy, white, and contained noticeable amounts of undissolved isosorbide.

On the other hand, the Aquasonic sonicator mixing method resulted in clear, slightly yellow homogeneous blends. The temperature increase (25–50 °C) most likely helped the isosorbide dissolve into the carrier diols/polyol. After the mixing method was established, the maximum load of isosorbide in each individual carrier was determined. The maximum load of isosorbide was also determined in various combinations with the diol/polyol blends. Isosorbide at 50–70 wt% of the polyol blend was able to stay in solution upon standing for 24 h at room temperature. Mixtures containing isosorbide at 80–90 wt% did dissolve into solution but crystallized overnight.

3.2 Formulating with Monomers and Cure Study

The goal of this study was to formulate polyurethanes that would cure at ambient conditions. All of the raw materials discussed in this section are listed in Table 1. First, the polyol blends containing various amount of isosorbide (50–70 wt%) and

a single diol such as EG or DPG were mixed with the catalyst Dabco 33-LV, which is a mixture of 33% triethylene diamine (TEDA) and 67% DPG, and a monomeric diisocyanate.⁴ In addition to blending isosorbide with diols, glycerol was incorporated into some of the blends at various levels. The ratio of monomer to polyol blend was 1.1:1.0–1.5:1.0. Two of the monomers selected for this study were the aliphatic compound isophorone diisocyanate (IPDI) and the aromatic monomer toluene diisocyanate (TDI).^{5,6} The isosorbide/EG, isosorbide/DPG, and isosorbide/glycerol polyol blends formulated with IPDI did not cure after 24 h at room temperature. The ratio of IPDI to polyol blend was increased from 1.1:1.0 to 1.3:1.0 and 1.5:1.0. Only the mixture containing 1.5:1.0 partially gelled after 24 h at room temperature. This same cure behavior after 24 h was also observed in the isosorbide/EG/glycerol blends formulated with IPDI.

Polyol blends containing isosorbide and EG formulated with TDI reacted within a few minutes. The exothermic reaction caused foaming, and the resulting product was a rigid foam that cured in 1–4 min. Surfynol DF-178 (defoamer) was added to the formulation to help limit the foam in the reaction.⁷ Batches were placed in a silicone mold approximately 60 × 12 × 3 mm. In addition, a portion of the same batch was used to cast a 4-mil wet film onto a 3- × 6-inch glass plate. Samples were allowed to cure at 30 °C and 20% humidity for up to 7 days and post cured at 60 °C for 24 h. Formulations made with TDI showed slight gelling after 1–2 h at 30 °C, but after 7 days the samples were not completely cured. Placing the sample into 60 °C only caused foaming to the uncured portion (Fig. 1). While some of the films did cure without foaming, most of them were too brittle to be removed from the glass for further testing.

Samples were also made without isosorbide using just EG or DPG in the polyol phase, but the reactivity of TDI was the same. Glycerol at a level higher than 10 wt% of the polyol phase made the formulations too brittle. Because the TDI was so reactive, a suitable bar for dynamic mechanical analysis (DMA) testing could not be achieved with the established molding method in ambient conditions. However, differential scanning calorimetry testing indicated a range of T_g from 75 °C to 85 °C for samples containing isosorbide at various levels with no clear trend evident.

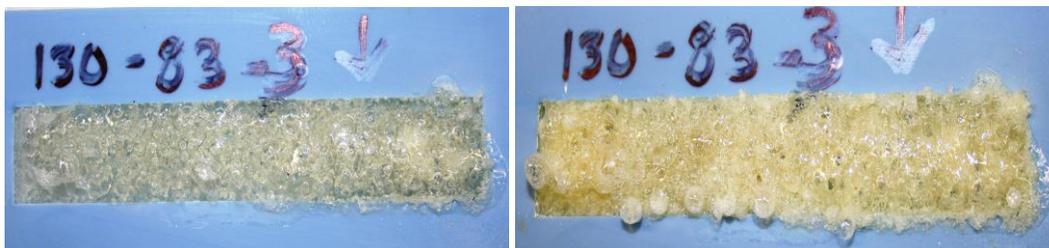


Fig. 1 Polyurethane with isosorbide and TDI room temperature cure (left) and after post cure (right)

3.3 Formulating with Polyisocyanates

To continue experimenting with films, some new materials were considered to replace the monomeric diisocyanate. These materials are prepolymerized to help facilitate a better end product. All of the raw materials discussed in this section are detailed in Table 1.

Bayhydur 303 is a solvent-free, water-dispersible aliphatic polyisocyanate resin based on hexamethylene diisocyanate (HDI).⁸ Desmodur E 744 is an aromatic polyisocyanate prepolymer based on diphenylmethane-diisocyanate.⁹ Desmodur L 67 BA is an aromatic polyisocyanate based on TDI and is 67% in butyl acetate.¹⁰ Desmodur L 75 is an aromatic polyisocyanate based on TDI and is 75% in ethyl acetate.¹¹ The ARE-250 Thinky mixer was used to create homogeneous blends of isosorbide, DPG, and TDI, which were then poured into silicone molds at room temperature. Again, efforts to make a bar for DMA testing at ambient conditions proved unsuccessful overall. Some samples were placed in a vacuum oven with 30 inches of Hg vacuum applied to help de-gas, which was ineffective. The bars contained significant voids and either did not cure thoroughly or expanded to twice the size of the mold. DMA was conducted on 2 different blends of Desmodur L 75, one with DPG as the only polyol component and one with a blend of isosorbide and DPG (Fig. 2). T_g of the DPG only sample was 52.79 °C, while the blended sample containing 12-wt% isosorbide had a T_g of 73.01 °C.

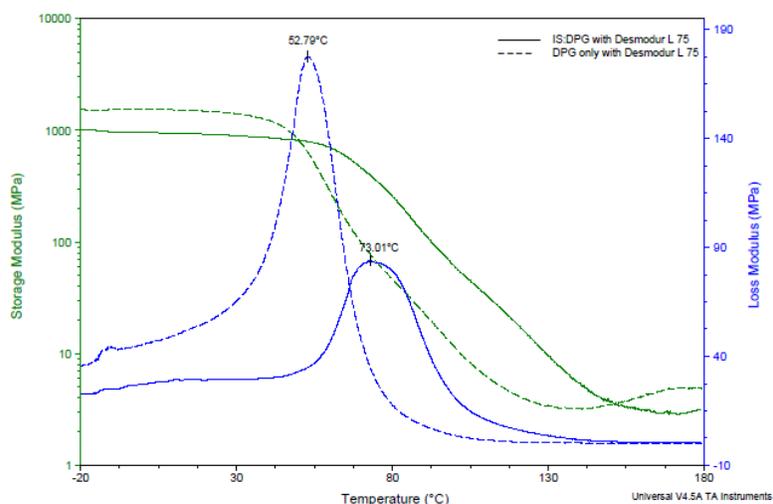


Fig. 2 DMA comparison of Desmodur L 75 blends with isosorbide and DPG

Bayhydur 303 (aliphatic polyisocyanate) was used to make a polyurethane coating containing isosorbide blended with Bayhydrol XP-7110E at various percentages (25%, 50%, 75%, and 100%) of the polyol phase. Bayhydrol XP-7110E is an OH-functional polyurethane dispersion dissolved in water/n-methyl-2-pyrrolidone.¹² The application is commonly used as the reaction partner for Bayhydur polyisocyanates in 2-component waterborne polyurethane low-VOC (volatile organic compound) coatings. Since the polyol is an aqueous dispersion, glycol was not needed to dissolve the isosorbide. Approximately 1 g of water (already present in the final polyurethane formulation) was used to pre-dissolve the 100% isosorbide formulation. The water-dispersible blend was mixed on a high-speed disperser until homogeneous. A wet film was cast on a glass plate with a 4-mil Bird applicator. The films were cured at room temperature for a minimum of 7 days and delaminated from the glass plate with a razor blade. The free film was post cured for 24 h at 60 °C prior to testing. Isosorbide content did not seem to affect the ability to apply the coating evenly to the glass plate. The baseline and the film containing isosorbide at 25 wt% in the polyol phase dried clear while the films containing isosorbide at 50–100 wt% in the polyol phase dried with a white haze.

DMA was conducted on cured free films using a tension film clamp on a TA 2980 (Fig. 3). A piece of cured free film was cut to the rectangular dimensions of 7 × 20 mm and a thickness of 0.065–0.075 mm. Test parameters were from –20 to 180 °C with a temperature ramp of 2 °C/min and oscillation frequency of 1 Hz.

The amplitude was 1/500 of the sample length. For a 5.0:1.0 (Bayhydur 303/isosorbide) index, the calculated maximum isosorbide content was 6.28 wt% of the dry film, which was 100% of the polyol phase (Fig. 4). Index is the ratio of isocyanate to hydroxyl functionality. A ratio of 1.0:1.0 is appropriate for solvent-based polyurethane, whereas a ratio of 1.1:1.0 is the starting point for aqueous-based polyurethane due to the competing side reaction of isocyanate with water. The US Army Research Laboratory found that an index ratio of 5.0:1.0 provided better properties and performances for some military requirements.

The DMA analysis showed that isosorbide as a drop-in replacement for the commercial polyol increased the T_g (E'') by 17 °C, increased the $\tan \delta$ by 7 °C, and increased the storage modulus in the rubbery region (E') by 13 MPa (Fig. 4 and Table 2).

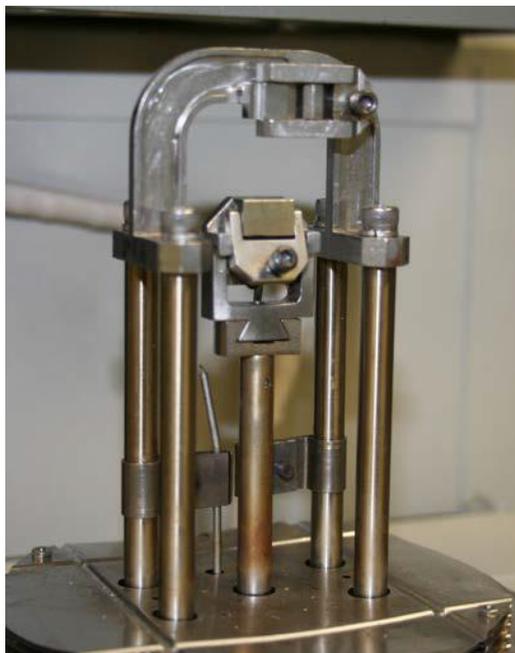


Fig. 3 Tension film clamp for DMA testing

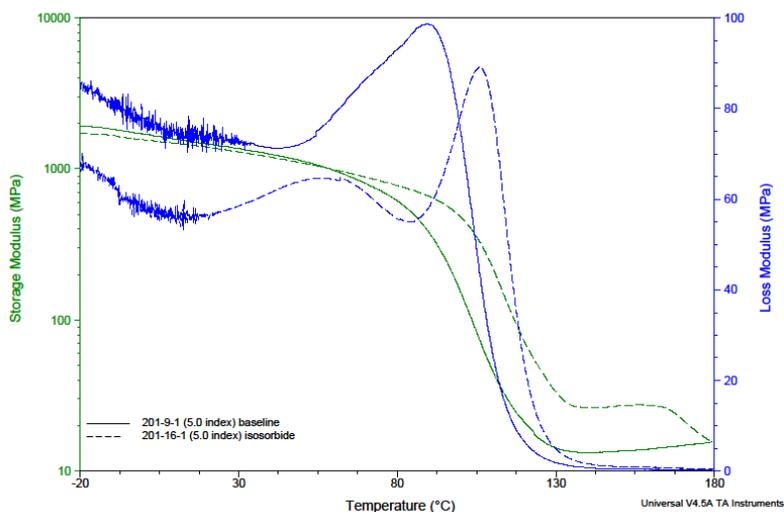


Fig. 4 DMA of film containing isosorbide compared with commercial baseline

Table 2 DMA summary of results for coatings in Fig. 4

Description	Index	E' @ 25°C (MPa)	Peak of E'' (°C)	Peak of Tan Delta (°C)	Rubbery T (°C)	Rubbery E' (MPa)	M _c (g/mol)
baseline	5.0	1436 ± 32	89 ± 1	107 ± 1	136 ± 3	13 ± 2	764 ± 75
isosorbide	5.0	1324 ± 15	106 ± 1	114 ± 1	153 ± 9	26 ± 0.07	405 ± 10

The ultraviolet (UV) exposure testing is done using Q-Lab's QUV/spray instruments in accordance with ASTM G154.¹³ This instrument is used to determine how a coating will fare when exposed to UV light. The test apparatus uses florescent bulbs that emit radiation concentrated at 340 nm. The test parameters were set for 0.77 W/m² with an 8-h light phase at 60 °C and a 4-h 100% relative humidity condensation phase in darkness at 50 °C. After 500 h of the continuous test cycles, the coating containing isosorbide had noticeable yellowing, brittleness, blushing, and some delamination from the glass plate substrate (Fig. 5), while the baseline coating sample had no negative results after the QUV test was completed. Commercial polyol systems such as Bayhydrol XP 7110E have numerous additives to assist with rheology, defoaming, substrate wetting, adhesion, flexibility, hardness, strength, and light stability. Specific formulaic content of these commercial products are proprietary.



Fig. 5 Commercial coating (left) and isosorbide coating (right) after QUV exposure

4. Conclusions

Isosorbide dissolved in other diols such as DPG and EG can be achieved at levels up to 70 wt%. Blending these isosorbide/diol mixtures with monomers such as IPDI or TDI under ambient conditions resulted in 1 of 2 outcomes: either the resin does not cure or the exothermic reaction is so intense that the mixture cured into a rigid foam in a matter of minutes. The coating made with isosorbide and Bayhydur 303 produced the only viable film for testing. This may be due to the water-dispersible characteristic of the commercial polyisocyanate. The coating that contained 100% isosorbide in the polyol phase had increased T_g (106–114 °C) and increased E' in the rubbery region compared with the baseline (Table 2). Dirlikov and Schneider¹⁴ reported T_g of 110 °C and T_m of 190 °C when reacting isosorbide with HDI in dimethyl sulfoxide solvent in the presence of tri-*n*-butylamine. However, the coating did not perform as well after exposure to QUV testing. The film containing isosorbide had signs of yellowing, brittleness, blushing, and some delamination from the glass plate substrate. The baseline film remained unchanged after 500 h of QUV exposure. Isosorbide as a drop-in replacement for the commercial polyol can increase modulus and T_g but decreases UV and moisture resistance.

Based on the findings in this study, further investigation into use of isosorbide in polyurethane synthesis will focus on preparation of prepolymers based on isosorbide. Meyborg et al.¹⁵ studied the use of isosorbide alone and blended with other low-molecular-weight diols as chain extenders. Given that most military applications of polyurethane use a high isocyanate-to-hydroxyl functionality to maximize cross-linking and other performance parameters, the work done by Bachmann et al.¹⁶ to prepare diisocyanates based on isosorbide is of particular interest.

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List of Symbols, Abbreviations, and Acronyms

DMA	dynamic mechanical analysis
DPG	dipropylene glycol
E	modulus of material
E'	storage modulus
E''	loss modulus
EG	ethylene glycol
HDI	hexamethylene diisocyanate
IPDI	isosporone diisocyanate
M _c	density between cross-links
MPa	Mega Pascal
Tan (δ)	ratio of loss modulus to storage modulus
TDI	toluene diisocyanate
T _g	glass transition temperature
T _m	melting temperature
UV	ultraviolet

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