Working towards high performance, sustainable polyurethanes

Clean up polyurethane production with renewable monomers that deliver an enhanced property profile.

Polyurethanes are a particularly versatile class of polymers, used to make products ranging from running shoes and wheels to car bumpers and carpet underlay. This versatility stems from complex but inherently flexible chemistry that offers enormous scope to tailor polymer properties. However, the feedstocks traditionally used are petrochemical based. Going forward polyurethane producers need a more sustainable range of options.

Roquette offers two plant-derived, renewable feedstocks that allow polymer chemists to develop polyurethanes that are not only more sustainable, but also better performing. Learn what you could do with bio-succinic acid and isosorbide.

Next generation feedstocks for polyurethane manufacture

Polyurethanes are synthesized by reacting a diisocyanate with a diol or polyol. With both monomers there is considerable scope to choose or synthesize molecules with an array of structures to enable the production of polyurethanes with closely tailored chemical, thermal and mechanical properties, for specific applications. As the industry rises to the challenges of a lower carbon economy, the goal is to refresh the palette of raw materials for polyurethane production with building blocks that deliver enhanced environmental credentials ***and*** higher performance.

Roquette, a global leader in plant-based chemistry, offers two products that meet this brief: BIOSUCCINIUM®, a 100% bio-based succinic acid, and POLYSORB®, a REACH-compliant, high purity isosorbide. Figure 1 illustrates the potential roles for these molecules in polyurethane chemistry.

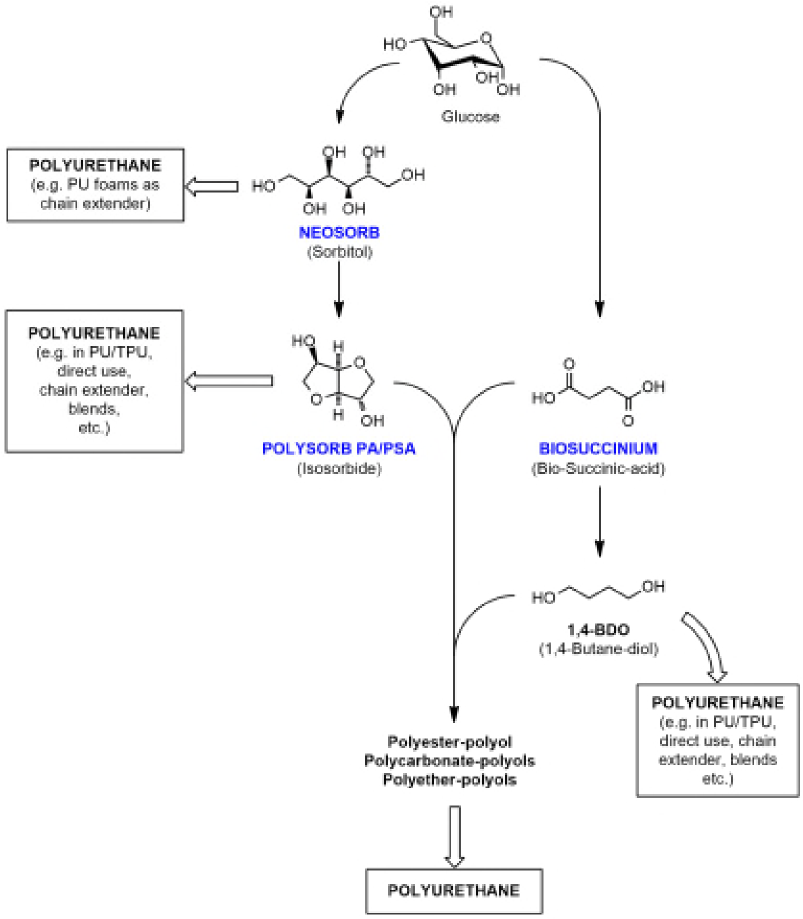

Figure 1: Renewable plant-based sources of succinic acid and isosorbide have an important role to play in the 'greening' of polyurethane chemistry.

Succinic acid: Polyester polyols, produced by reacting a diol with a dicarboxylic acid, are an important class of polyols for polyurethane synthesis. Using BIOSUCCINIUM® in place of adipic acid, the most commonly used dicarboxylic acid, reduces associated CO_2 by 8 kg/kg of acid. BIOSUCCINIUM® can be similarly used to make bio-based polyether polyols, polycarbonate polyols, and polycarbonate polyester polyols, either directly or via the synthesis of 1,4 butane diol.

Isosorbide: There are multiple roles for isosorbide in polyurethane production giving POLYSORB® broad and valuable potential. It can be used to make alternative diols or polyols, for example, a polyester polyol, polyether polyol, polycarbonate polyol or polycarbonate polyester polyol, or as the reactive diol, either alone or in a blend. Isosorbide is also an option for the specific task of chain extension, to increase molecular weight, or as an additive to otherwise modify polyurethane properties.

The following studies illustrate how these molecules have already been used to produce polyurethanes with advantageous properties.

Case study 1: Producing rigid bio-based polyurethane foams

A study, reported by researchers from Pittsburgh State University and Honeywell Federal Manufacturing and Technologies[1], demonstrates the value of isosorbide in the production of rigid polyurethane foams. In this work, isosorbide was dissolved in sucrose polyol, a polyether polyol routinely used to make rigid polyurethane foam, at concentrations of upto 40%. Images of the resulting foams are shown in figure 2 alongside data illustrating how properties change as a function of isosorbide concentration.

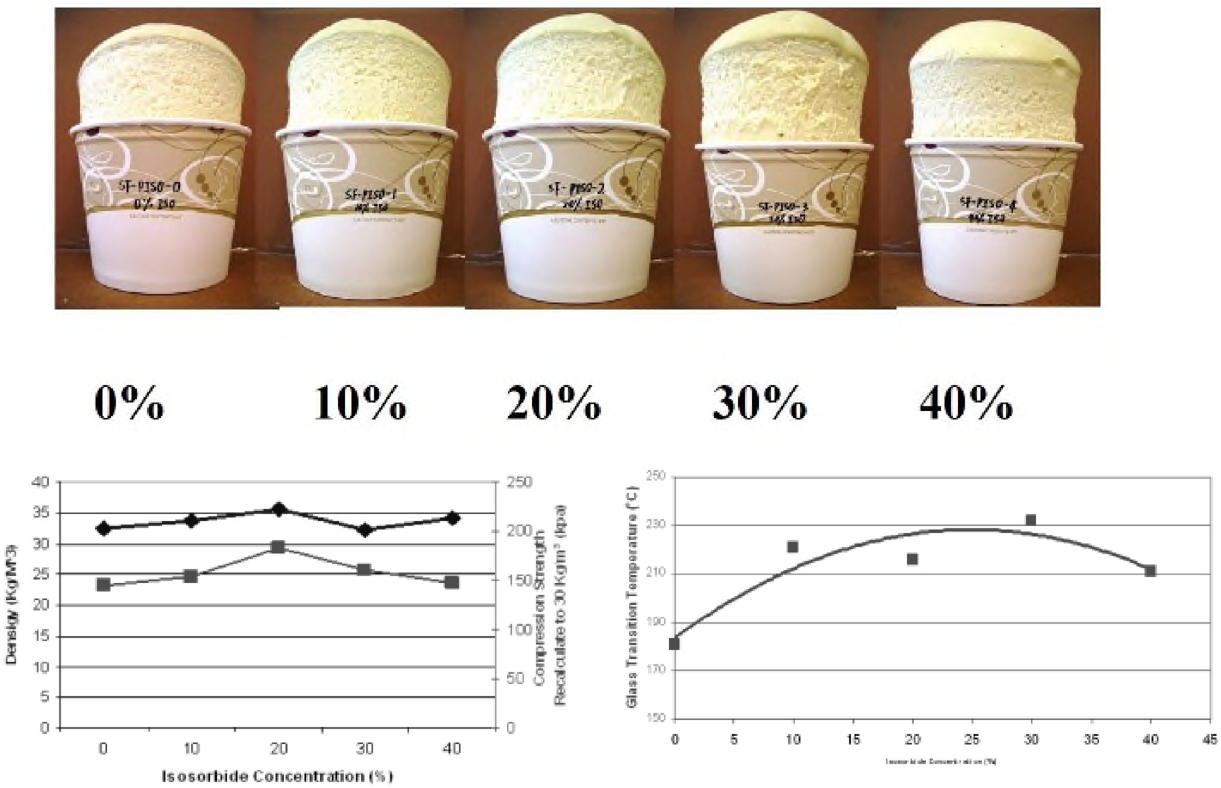

Figure 2: Isosorbide performs well in rigid polyurethane foams delivering an improvement in thermal properties with no impact on appearance and minimal effect on mechanical properties.

The inclusion of isosorbide has no impact on the appearance of the foam. Furthermore, both density and compression strength are minimally affected by isosorbide concentration; all the foams exhibited low friability and a closed cell content in the range 86 – 97%. Crucially though, isosorbide increases T_g, the glass transition temperature, an important metric indicative of potential in applications where thermal properties are relevant. The increase in T_g is therefore a valuable gain, one that isosorbide has successfully delivered for other polymers including PET[2] and that is unassociated with deterioriation in other vital characteristics.

The reserachers conclude in this work that isosorbide is 'a very valuable raw material for polyurethanes' both as described here and in the form of alkoxylated derivatives which were also investigated as part of the study[1].

Case study 2: Commercializing new polyols for polyurethane manufacture

Danimer Scientific, an innovative biotechnology company pioneering the development of sustainable biopolymers, has used isosorbide to develop and commercialize the Avio™ range of 100% bio-derived polyols. Two are already available, Avio™ 2426 and 2962 and two are awaiting TSCA (Toxic Substances Control Act) registration; all offer opportunities for enhancing polyurethane properties in a range of applications.

Data from an evaluation of the performance of Avio™ 2426 and 2962 in a 2K (two-component) solvent coating system is shown in table 1/figure 3. Coatings were formulated with an aliphatic polyisocyanate using ethyl acetate as the solvent, at a solids loading of 70%. The resulting systems were applied to panels at a thickness of 0.3 mm, catalyzed with 100 ppm dibutyltin dilaurate (DBTDL), and cured at room temperature for 24 hours and then at 70°C for 8 hours. Coatings were characterized via a range of tests and the results compared with data produced using a control system, a commercially available polyester diol (1,6 hexane diol (HDO)/neopentyl glycol (NPG) adipate) of comparable molecular weight.

Polyol	Taber abrasion	Crosshatch Adhesion	Shore A	Impact resistance	
				Intrusion	Extrusion
Avio™ 2426	2 mg/1000 cycles	5,5 (5.0)	96 , 99 (97.5)	>160, > 160 in/ibs	>160, > 160 in/ibs
Avio™ 2962	68 mg/ 1000 cycles	4,5 (4.5)	97, 97 (97.0)	80, 80 in/lbs	>160, >160 in/lbs
HDO/NPG	102 mg/1000 cycles	1,0 (0.5)	95, 89 (92)	140, 140 in lbs	140, >160 in lbs

- Test methods: ASTM D4060, 3359, 22402794

Control ester   Avio™ 2426

Table 1/Figure 3: 100% bio-derived polyols incorporating isosorbide show enhanced performance in a 2K coating system relative to a conventional polyurethane system.

All panels passed the Mandrel bend test indicating comparable flexibility. However, the bio-based coatings exhibit better abrasion resistance (Taber Abrasion), particularly in the case of the Avio™ 2426, and substantially better adhesion (Crosshatch Adhesion), relative to the control. Furthermore, both bio-based coatings have higher hardness (Shore A) with Avio™2426 additionally delivering better impact reistance; with Avio™2962 impact resistance is somewhat reduced. In solvent resistance tests the Avio™2426 coating also demonstrates superior performance to the control, especially with respect to Skydrol, a fire resistant aviation fluid.

In summary, the new bio-based polyols deliver polyurethane coatings with substantially enhanced properties, with excellent adhesion, solvent resistance, toughness and impact resistance, with no loss of flexibility.

Testing with other polyurethane systems, with polyurethane dispersions, thermoplastic urethanes (TPUs) and UV cure urethane acrylate oligomers has also shown promise demonstrating the broader application and value of the new polyols.

Case study 3: Evaluating bio-based succinic acid in thermoplastic polyurethane (TPU) formulations.

Formulations containing varying amounts of bio-based succinic acid were assessed as TPUs for the production of acoustic foams in a project initiated by Adler Plastics (Naples, Italy), a premier Italian company producing acoustic and thermal comfort for vehicles, and the Institute of Polymers, Composites and Biomaterials (IPCB, Potici, Italy), part of the Italy National Research Council. A range of polyester polyols were produced by reacting various diols (1,4 butanediol (BDO), HDO, and 1,3 propanediol (PDO)) with bio-based succinic acid (Su) alone and in combination with adipic acid (Ad) and sebacic acid (Se). All systems readily produced polyester polyols with predictable, tunable properties.

		BDO-Ad	BDO-Se	BDO-SeSu(50)	BDO-SeSu(33)	PDO-Su	HDO-Su
Hardness	Shore A	87	96	90	95	93	90
Tensile Strength	MPa	39	33	39	37	40	22
Elongation at break	%	685	564	781	743	934	692
Tear Strength	N/cm	1344	1328	1330	1491	1342	1212
Resilience	%	44	46	48	41	25	36
Compression Set	Cb%	16	12	16	18	22	31
Abrasion Loss	mg	3.9	4.3	2.7	2.1	3.8	2.7

Table 2: Incorporating bio-based succinic acid improves the mechanical properties of TPU acoustic foams while simultaneously maintaining hydrolysis resistance and enhancing sustainability.

Table 2 shows the mechanical properties of the foams made using the various formulations. All exhibit acceptable mechanical properties but the BDO-SeSu(50) offers the best overall performance; hydrolysis resistance was also maintained (data not shown). These results illustrate the ability of the bio-based succinic acid to deliver greater sustainability along with improved polyurethane characteristics.

Looking ahead

The ongoing use of polyurethanes in a low carbon economy depends on the introduction of sustainable chemical building blocks that enable full access to the diverse range of materials that this inherently flexible chemistry can deliver. Roquette offers two biobased feedstocks that meet the need for feedstocks that combine sustainability with better polyurethane performance. BIOSUCCINIUM® and POLYSORB® are already delivering benefit for those leading the way in polymer innovation and present multiple opportunities for those shaping polyurethane production for the future.

For more information on bio-succinic acid or isosorbide from Roquette: click here.

References:

[1]M. Ionescu et al. ‘New Isosorbide Derivatives for Biobased Polyurethanes’ *Polyurethanes 2011 Technical Conference,* September 26-28, 2011, Nashville, Tennessee.
[2] ‘Improving the performance and sustainability of PET with POLYSORB® Isosorbide’ Available for download at: https://www.roquette.com/media-center/resources/article-isosobide-improve-performance-and-sustainability-of-pet

About Roquette: "Offering the best of nature"

Roquette is a global leader in plant-based ingredients, a pioneer of plant proteins and a leading provider of pharmaceutical excipients. The group addresses current and future societal challenges by unlocking the potential of nature to offer the best ingredients for food, nutrition and health markets.

In collaboration with customers who are also passionate about the ongoing food revolution, Roquette contributes to developing a whole new gastronomy that meets consumers' demands. In the pharma sector, Roquette offers solutions that play a critical role in medical treatments that cure and save lives.

Thanks to a constant drive for innovation and a long-term vision, the group is committed to improving the well-being of millions of people all over the world while taking care of resources and territories.

Founded in 1933, Roquette is a family-owned company which operates in more than 100 countries, has a turnover of around 3.5 billion euros, and employs 8,360 people worldwide. For more information, visit www.roquette.com.