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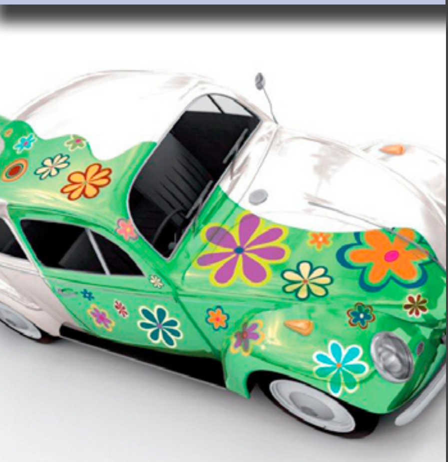

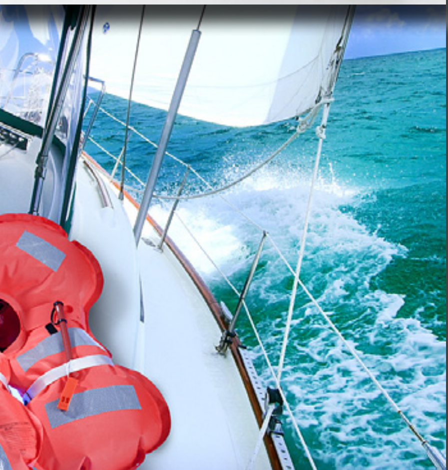

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KP VERLAG
ISSN 1867-3503

Technical Articles

Biosuccinium Sustainable Succinic Acid in TPU Applications Effect on Chemical Resistance

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Abstract

Biosuccinium (succinic acid, SA) is a unique 100% bio-based offering from Reverdia. The use of Biosuccinium increases the renewable content of polyurethane formulations and strongly reduces the carbon footprint, while maintaining the performance required in many applications.

Biosuccinium based polyester polyols can be formulated into polyurethane systems without extensive re-work. Several MDI-based TPUs were synthesized using a one shot method and evaluated at different hardness.

The mechanical properties and dynamic performance of these materials have already been discussed in detail before [1]. This article specifically focusses at the fact that TPUs based on Biosuccinium acid have been found to show excellent resistance to a set of chemicals that are commonly used in industry.

Introduction

Over the past decade the need for products made from "green materials" has intensified, driven by the need to respect generations to come and to be careful with the resources that are available. Also, the strong growth in demand for oil causes higher and more volatile oil prices, and has driven many purchasing organizations to search for alternatives. Both factors are forcing industry to more efficient ways to use, reduce, re-use and recycle materials, as well as to using renewable raw materials.

Non-governmental organizations push brand owners to source responsibly and corporations have made sustainability an integral part of their strategies. Renewable materials offer a potential way of improving the sustainable characteristics of the products that are made from them. All these megatrends have come together creating a unique situation propelling the growth of biobased chemicals.

Biosuccinium: Enabling Sustainable Polyurethanes

Biosuccinium sustainable succinic acid is produced by Reverdia, a joint venture between DSM and Roquette, using a proprietary low-pH yeast process. It is a 100 % biobased and renewable diacid.

Reverdia is the first and currently only company in the world operating a large scale facility for the commercial production of bio-based succinic acid. This new facility with a capacity of about 10kt is located on the Roquette site in Cassano Spinola, Italy and is operational since the end of 2012.

Typically, Biosuccinium can be used as an alternative to adipic acid and is regarded as a "near drop-in" as raw material for the production of polyester polyols and polyurethanes. Table 1 lists examples of polyurethane applications in which Biosuccinium can be applied, together with an indication of achievable biocontent and carbon footprint reduction.

Polyurethane application	Biocontent (typical)	CO_2 reduction / kg product	Applications
TPU	~25%	~20%	Running shoes, rollers, cable/wire
PU elastomer	~10%	~30%	Castor wheels, shoe soles
PU flexible foam	~30%	~45%	Flexible foam
PU adhesive	~5%	~20%	Construction
PU coatings	~5%	~15%	Wood and furniture coatings

Table 1. Indicative examples of Biosuccinium improving the environmental footprint of polyurethanes.

The carbon footprint reduction potential is based on the Biosuccinium LCA study [4] (cradle-to-gate, Copernicus Institute, Netherlands) which shows the carbon footprint of Biosuccinium (0.9 kg CO_2 equivalent/kg acid) to be much lower than fossil-based adipic acid (9.0 kg CO_2 equivalent/kg acid), which leads to potential carbon footprint reduction of about 8 kg CO_2-equivalent per kilogram of acid.

Performance characteristics of Biosuccinium based polyurethanes

In order to represent a feasible opportunity for improving the environmental footprint of polyesters and polyurethanes, of course also the performance characteristics should be suitable for the specific application.

Therefore, Biosuccinium has been evaluated as an alternative for adipic acid (AA) in polyester polyols and thermoplastic polyurethanes. Mechanical properties (tensile, abrasion, etc.) of Biosuccinium based polyurethanes have been reported before in detail [1] and were found to be very similar to adipate based thermoplastic polyurethanes. However, in that same evaluation it was also found that there are some properties of Biosuccinium based polyester polyols and polyurethanes that are significantly different than their adipate counterparts. Whether or not that is of practical value obviously depends on the actual application and its specific requirements, as is highlighted by the following two examples.

One example of such a differentiating performance characteristic is that succinic acid / 1,4-butanediol based polyols have been found to crystallize very easily, causing a high melting temperature and a relatively high viscosity of the polyol. While on one hand this may be require higher processing temperatures in TPU synthesis, at the same time this differentiating property may be of value in other applications, for example when the polyester is used in a (reactive) hot melt adhesive. Another example of differentiating performance characteristic, which will be highlighted in more detail in the following section, is the excellent chemical resistance of Biosuccinium based TPUs to many common chemicals.

Polyester polyols based on 1,4-butylene-adipate are commonly used for TPUs providing good overall properties including a good chemical resistance [3], but succinate TPUs were found to perform even better. In first instance the good chemical resistance manifested itself as an issue; it turned out that the 1,4-butylene-succinate polyester polyol cannot be dissolved in THF, a quite common solvent used for determination of acid and hydroxyl values by means of titration. Instead it was required to use less frequently used solvents such as chloroform or o-cresol.

In further investigations it was however found that not only the polyester polyol but also the final Biosuccinium based thermoplastic polyurethanes exhibits a high chemical resistance. This can for example be beneficial in such applications where the polyurethane gets in occasional contact with chemicals, such as safety boots and gloves, (automotive) hoses and tubing, but also in applications with intended contact with chemicals such as tubes and hoses for suction and delivery of chemicals, seals and gaskets, etc.

Also in some inks, where both the solvent and the polyester or polyurethane are an integral part of the final application the interaction between solid (polyester or polyurethane) and solvent (ie MEK) is highly relevant. Further details on the chemical resistance will be highlighted in more detail in the following section.

Experimental

The work presented here deals with straightforward standard formulations of polyester polyol and TPU (see table 1 and 2 for an overview). The formulations have not been optimized in order to allow for a direct comparison of succinic acid and adipic acid based TPUs.

Materials

The raw materials used in this study are Biosuccinium (Reverdia), adipic acid (Rhodia), 1,4-BDO (ISP/Ashland), 1,2-EG (Sabic) and MDI (standard grade). Polyols and diols were dried before use. MDI was used as received from the supplier.

Preparation and properties of Polyester Polyols

Succinic acid and adipic acid based polyester polyols were synthesized by polycondensation of the respective diacid with either 1,4-butanediol (B) or a combination of 1,4-butanediol with ethylene glycol (EB) and a metal catalyst.

Polyester polyols were prepared with Mn of approximately 2000 g/mol, and low terminal acid values. The compositions and properties of the polyols are described in Table 2.

Label	Diol	Di-acid	Renewable content (%)	OH Value [mg KOH/g]	Acid Value [mg KOH/g]	Melt Temp [°C]	Viscosity @ 75°C [cPoise]
B-AA	BDO	adipic acid	0	53.9	1.1	60	733
B-SA	BDO	Biosuccinium	~ 50	52.9	0.1	113	n.d.
EB-AA	EG + BDO(1)	adipic acid	0	56.0	1.3	17	579
EB-SA	EG + BDO(1)	Biosuccinium	~50	53.9	1.1	55	1284

Table 2. Overview of polyester polyol formulations and properties
(1): Mixture of ethylene-glycol and 1,4-butanediol in 50/50 molar ratio used in the polyol.

BDOSA polyol was not soluble in THF, which is commonly used as a diluent in GPC for determination of molecular weight distribution. This polyol was even found to be not soluble in most common solvents, including MEK, toluene, NMP, and DMF at very low concentrations. However, it was soluble in chloroform and o-cresol which are less frequently used as an diluent for GPC.
Melt temperature of the BDOSA polyol, as determined via DSC, were 113 °C, which are in line with values reported by Sonnenschein et. al. [2].

Preparation and properties of TPUs

TPUs were prepared using a one-shot process (see Table 3) by reacting the above mentioned polyester polyols with stoichiometric amounts of pure MDI and 1,4-butanediol as the chain extender, and an isocyanates index of 1.02. A typical 95 Shore A formulation was used (48% hard segment concentration).

Label	Polyol	Renewable content (%)	Process setup	Hardness(2) [Shore A]	Process completion
TPU1	B-AA	0 %	Standard	93	For all TPU's synthesis ran as expected
TPU2	B-SA	~20 %	Adapted(1)	93	
TPU3	EB-AA	0 %	Standard	90	
TPU4	EB-SA	~35 %	Standard	94	

Table 3. Overview of TPU formulations
(1): Required higher processing temperature due to the higher melting point of BDOSA-polyol.
(2): Standard formulations have been used targeting a hardness of 95 Shore A.

The adipic acid based polyols behaved as expected during the polymerisation. The succinic acid based polyols required some minor modifications in process setup due to the higher melting point of the butylene-succinate polyol, but nevertheless TPU's could be successfully produced at a hardness as expected.
From these TPUs plaques were produced by injection molding, from which test samples were punched for further characterization of TPU properties.
Tensile testing and abrasion resistance were characterized, as shown in Table 4.

Label	Polyol	Hardness [ShoreA]	Tensile stress [MPa@200,500,1000%, 200mm/min] MPa@200,500,1000%, 200mm/min] [MPa@200,500,1000%, 200mm/min]	Abrasion [mg mass loss, 500 cycles]	Exposure to Toluene Mass increase [%]	Exposure to 2-butanone (MEK) Mass increase [%]
TPU1	B-AA	93	10/15/30	0,034	16	54
TPU2	B-SA	93	12/20/38	0,061	5	23
TPU3	EB-AA	90	7/10/15	0,066	11	45
TPU4	EB-SA	94	15/20/35	0,070	3	29

Table 4: Mechanical properties and chemical resistance of the TPUs.

The resulting hardness and the tensile behavior of the TPUs are as expected, with the succinate TPUs being slightly higher in stiffness. More pronounced though is the difference in chemical resistance, represented by the mass increase of TPU samples after exposure to toluene and 2-butanone (MEK).

Solvent resistance was measured on specimens cut from a molded sheet, which were weighed (approx. 0,5 gram) and immersed in the solvents at room temperature. After 1 day and after 7 days, samples were taken out of the solvent and the mass increase determined (excess solvent was wiped of the sample with a tissue). In all occasions, equilibrium was reached after 1 day.

The mass increase for the succinate based TPUs is significantly less compared to the mass increase of the adipate based TPUs: ~70% reduction in toluene uptake and ~50% reduction in MEK uptake. Data from another study [1] confirms this excellent chemical resistance, for formulations for hardness of 67 Shore A (24% hard segment) and 87 Shore A (34% hard segment). Although the TPU with a 48% hard segment concentration the resulting hardness was as expected (see above), the TPUs with lower concentrations hard segment exhibited very high hardness: 55 Shore D at 24% hard segment concentration and 57 Shore D at 34% hard segment concentration (see Table 5).

This relatively high hardness for formulations based on 2000 g/mol BDOSA polyols, and hard segment concentration <40 %, has been reported before [1,2], and is believed to be caused by the higher degree of crystallinity of the BDOSA soft segments. In this case specimens (10 x 40 x 2mm) were again cut from a sheet, weighed and immersed in a range of different solvents, at room temperature. The samples were taken out after 1 day and 7 days of immersion. Their mass and dimension were measured.

Overall, the solvent resistance of TPUs based on BDOSA polyol is excellent, and although the high crystallinity may contribute to this, based on results of the 93 Shore A TPU it is expected that the high chemical resistance is retained even when soft segment crystallinity is decreased, for example by using polyols with lower molecular mass or by using copolyester polyols.

Label	Polyol	Hard Segment %	Hardness [Shore]	Toluene	Methyl ethyl ketone	Xylene	Ethyl acetate	Oil	Water
TPU5	B-AA*	23	67A	62	-	-	-	0	1
TPU6	B-SA	24	55D	3,04	13,7	1,1	11,7	0,6	1,0
TPU7	B-SA	34	57D	3.27	12,7	1,2	9,7	0,7	1,3
TPU8	B-SA	48	93A	5	23	-	-	-	-

Table 5: Solvent Resistance, mass gained, % (after 7 days)
*: Data taken from [5]

Conclusion

Biosuccinium is a potential alternative for (fossil-based) adipic acid as raw material for polyester polyols and polyurethanes. Biosuccinium is a 100% biobased and renewable raw material and has a much lower carbon footprint than fossil-based adipic acid – about 8 kg of CO_2 equivalents per kg of acid – which enables it to also substantially decrease the carbon footprint of polyurethanes and products made of it. Overall the properties of polyester polyols and performance characteristics of polyurethanes based on Biosuccinium are fairly similar to adipate based materials. Nevertheless there are some differences that either need to be improved, or differentiate in a positive way and can be turned into value in specific applications.

Examples of positively differentiating properties are fast and high degree of crystallization, which could be of value in adhesive applications, or improved chemical resistance which could be of value in applications where occasional or intended contact with chemicals occurs.

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Biography

Lawrence Theunissen

Lawrence Theunissen received a degree in Mechanical Engineering. He worked in the field of virtual product design and application engineering (CAD/CAE). He joined DSM in 2002, and since then managed application development activities for various business units in research and innovation environments. Since 2011 Lawrence works for Reverdia as Manager Application Development.

Richard Janssen

Richard Janssen is New Business Development Manager for Reverdia™ since 2010. He has a M.Sc. in Chemical Engineering and a Ph.D. in Particle Technology both from Delft University of Technology. He joined DSM Research in 2001 and since 2007 he has worked on innovation and new business development in the DSM Innovation Center.