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- European flexible foam industry
- Interview with L. Kjeldsen, Evonik
- Interview with T. Hankins, Huntsman
- Polyester polyols with recycled content
- Furniture fire solutions



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# Thermoplastic polyurethanes from renewable, long chain diacids

Driven by sustainability initiatives and increasing consumer demand for environmentally friendly products, thermoplastic polyurethane (TPU) manufacturers are actively searching for high-performance building blocks from bio-based resources. Herein, we report a novel class of renewable polyester diols designed to enable TPUs with exceptional solvent resistance and hydrolytic stability. These polyols were constructed from Elevance Inherent C18 Diacid, a linear long-chain aliphatic monomer based on renewable carbon. The hydrolytic stability, solvent resistance and mechanical properties are measured and compared to typical TPUs synthesized from shorter chain adipic acid. Remarkably, 90 % of the tensile strength was retained after hydrolysis in C<sub>18</sub>-based TPUs, suggesting polyether-like stability in a polyester-based TPU.

## 1 Introduction

Among specialty engineered thermoplastic elastomers, the unique chemistry of polyurethanes enables significant performance advantages in myriad applications, including construction materials, adhesives, coatings, durable consumer goods and medical devices. TPUs are segmented multiblock copolymers prepared by addition polymerization between soft segment diols (e. g., oligomeric  $\alpha,\omega$ -polyols) and hard segment diisocyanates with short-chain diol chain extenders. The resulting polymer morphology, hard segments chemically linked to soft segments and their corresponding thermodynamic phase separation, imparts

many of the outstanding mechanical properties seen in TPUs. Hard and soft segment designations stem from the fact that semi-crystalline hard segments have softening points well above room temperature while soft segments often have softening points below room temperature. The hard segments act as physical crosslinks, giving the material strength and stiffness, while the soft segments impart elastomer properties such as rebound and flexibility. For materials with relatively low hard segment content, the mechanical properties can be very soft and rubbery while increasing the hard segment gives harder, higher modulus polymers.

TPU properties depend significantly on the nature of the polyol soft segment (e. g., chemistry, molecular weight and mole per-

centage in the formulation). TPUs made from polyester polyols are known to display excellent mechanical properties, oxidative stability and chemical resistance. Susceptibility to hydrolysis, however, often represents a major durability concern for these materials, limiting their utility in applications exposed to humidity and aggressive weathering environments. For these reasons, TPU manufacturers often turn to polyether polyols for applications exposed to water, especially under acidic or alkaline conditions, often at the expense of decreased oxidative stability and solvent resistance. Consequently, the pursuit of novel strategies to enhance the hydrolytic stability of polyester-based urethanes is an active area of research. Increasing crystallinity (as with caprolactone polyols) or hydrophobicity (as with dimer acid polyols) has been explored with some success.

Caprolactone-based TPUs show better hydrolytic stability as the crystallinity provides resistance to acid and base solutions [1]. TPUs based on long chain dimer acid polyols (C<sub>26</sub>-C<sub>44</sub>) are known to be very hydrophobic compared to both polyethers and polyesters, and show good hydrolytic stability based on their very low water absorption [2]. These branched dimer acid polyols result in TPUs with rubbery, amorphous soft segments but with low Shore hardness. Ideally, polyols with a combination of both hydrophobicity and crystallinity would impart properties such as hydrolytic stability and higher Shore hardness values in TPUs.

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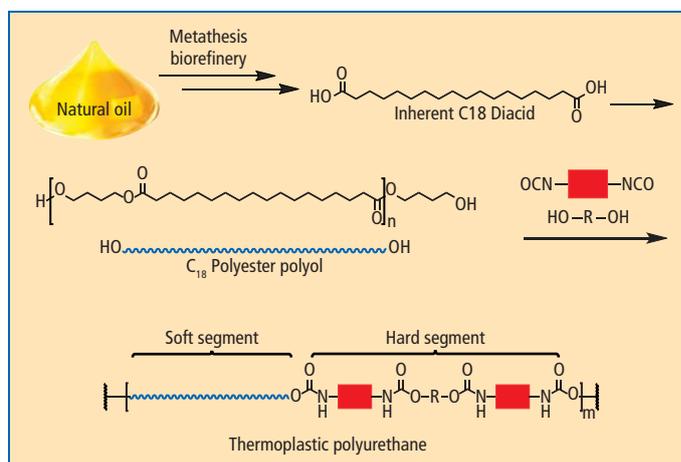
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**Fig. 1:** Renewable thermoplastic polyurethanes via the metathesis pathway



### 1.1 Inherent C18 Diacid

Based on the catalytic metathesis of natural oils such as palm oil and soy bean oil, we have developed “Inherent C18 Diacid”, a bio-based linear, long chain diacid (**fig. 1**) [3]. The metathesis pathway is expected to dramatically increase the availability of C18 Diacid and lower its cost. Natural oils, such as triglycerides, represent attractive feedstocks in terms of cost and abundance. While other bio-based building blocks for polymers are available [4], C<sub>18</sub> diacids offer unique properties due to the long aliphatic and oleophilic chain. Compared to the shorter chain alternatives, the products made from this diacid are hydrophobic. Furthermore, in contrast to dimer acid, polymers from linear C<sub>18</sub> diacid have high crystallinity and solvent resistance and are, in fact, insoluble in most common solvents.

In this study, we report on a new type of polyester urethane from Inherent C18 Diacid that exhibits a combination of good mechanical properties (due to the crystallinity of the polyol segment) and excellent resistance to hydrolysis (due to the hydrophobic long chain ester). A number of these TPUs based

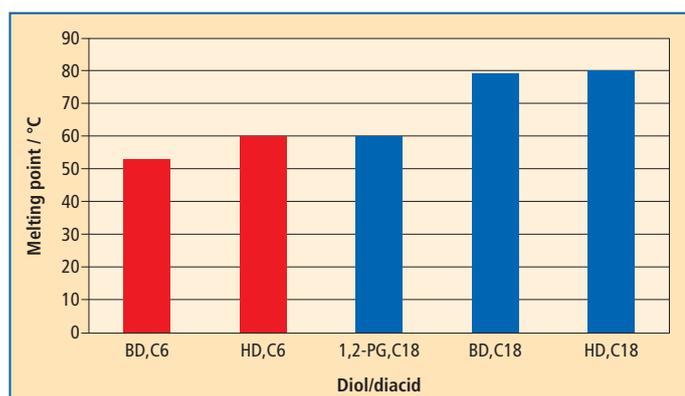
on common diols are synthesized and characterized. These C<sub>18</sub>-based TPUs have high crystallinity, tensile strength and solvent resistance compared to materials made from shorter chain diacids. The mechanical properties, solvent resistance, water absorption and hydrolytic stability of the TPUs from C<sub>18</sub> diacid are evaluated and compared to the properties of reference TPUs made from adipic acid.

## 2 Experimental

Polyester polyols were synthesized in the melt at 180 °C using a combination of diacid, diol and titanium isopropoxide as catalyst. Stoichiometry was adjusted according to the Flory equation to obtain a molecular weight of ~2,000 g/mol. The synthesis was carried out until the acid number was <1 mg KOH/g and the hydroxyl number reached a value close to 50 mg KOH/g. The reaction was monitored with collection of the water condensate and decrease in acid value. The resultant polyols were all hard, waxy, crystalline products at room temperature with sharp melting points. The melting points of the various compositions are shown in **figure 2**.

Various TPUs were synthesized via a one-step polymerization method according to the formulations shown in **table 1**. The polyols were conditioned to 75–100 °C, depending on the polyol melting point, and then placed into a Teflon speed mixer cup, also preheated to 100 °C and stirred with a FlackTek Speed Mixer. 1,4-butanediol (1,4-BD), which was conditioned at 75 °C, was added to the polyol as the chain extender. These two components were mixed for 20 s at 2,200 min<sup>-1</sup> and then placed in the oven at 100 °C. 4,4'-diphenylmethane diisocyanate (4,4'-MDI, Mondur M) was weighed and placed in the oven at 90 °C. When the components were conditioned at respective temperatures, 4,4'-MDI was added to the polyol chain extender mixture and immediately mixed for 20 s. At about 55 s from the time when isocyanate was added to the mixture of polyol and chain extender, the resin was poured into an aluminum mold lined with Teflon that was preheated to 120 °C and pressed immediately in a Carver Press, which was preheated to 120–140 °C.

For testing of mechanical properties (ASTM D412), TPU sheets were allowed to cure at ambient temperature for 2 h and were then transferred to a 100 °C oven. Sheets were cured at 100 °C for 20 h and then the molds removed from the oven. The sheets were allowed to cool to room temperature before removal from the mold. After removal, seven days were allowed to pass before any testing was conducted. The hydrolysis conditions were as follows: Dogbone samples were punched from the 2 mm thick plaque. Each dogbone was submerged in the hydrolysis medium (1 N NaOH), each in its own bottle. All the bottles were placed in a 70 °C oven and removed for testing after 7, 14 and 21 days. Hydrolyzed dogbones were equilibrated at ambient conditions for seven days before testing.



**Fig. 2:** Melting points of polyester polyols

**Tab. 1:** Formulation and processing of TPUs based on polyester polyols (2,000 g/mol), MDI and 1,4-BD chain extender

Formulation	BD-C6	HD-C6	BD-C18	HD-C18	1,2-PG-C18
Polyester polyol / g	77.0	77.0	78.3	76.3	79.3
4,4'-MDI / g	19.5	19.5	18.4	20.1	18.0
1,4-BD / g	3.5	3.5	3.3	3.6	2.7
Total / g	100	100	100	100	100
Hard segment concentration / %	23	23	22	24	21

For hardness testing, cylindrical “button samples” (6.5 cm x 2.0 cm x 1.3 cm) were prepared by casting of the degassed polyurethanes into a Teflon-coated mold with multiple cavities preheated at 120 °C. The mold was then covered with a Teflon-coated aluminum plate, transferred into an oven at 120 °C, cured for 2 h and then post-cured for 16 h at 100 °C.

### 3 Results and discussion

#### 3.1 Thermal characterization of polyester polyols and TPUs

DSC melting points of polyester polyols made from various diols and diacids are shown in **figure 2**. As expected, the polyols from  $C_{18}$  diacid have a higher melting point than those from adipic acid. All of the polyols are hard and waxy solids with sharp crystalline melting points.

TPUs were synthesized from both  $C_{18}$  polyols and  $C_6$  polyols in order to compare properties of the two. Hexane diol/ $C_{18}$  (HD-C18), butane diol/ $C_{18}$  (BD-C18), 1,2-propane diol/ $C_{18}$  (1,2-PG/C18), hexane diol/adipic (HD-C6), and butane diol/adipic (BD-C6) were all formulated at high weight percentage soft segment (78–80 %) in order to accentuate the contribution of a linear long chain  $C_{18}$  soft segment compared to the shorter  $C_6$ . The DSC results (**tab. 2**) show that the TPUs made from  $C_{18}$  diacid have semi crystalline soft segments compared to TPUs made from  $C_6$  diacid. The TPU made from BD-C6 is completely amorphous with lower, multiple glass transitions at  $-34\text{ }^\circ\text{C}$  and  $53\text{ }^\circ\text{C}$  and a higher glass transition of  $167\text{ }^\circ\text{C}$  (due to the isocyanate-based hard segment). The TPU made from HD-C6 is semi-crystalline with a glass transition of  $-37\text{ }^\circ\text{C}$  and a melting point of  $39\text{ }^\circ\text{C}$ . Of the  $C_{18}$  TPUs, only the polyurethane based on the branched diol, 1,2-PG, has a noticeable soft segment glass transition. The hard segment (isocyanate) properties appear to be relatively constant and independent of soft segment compositional changes indicating a high de-

gree of phase separation between hard and soft segments. Based on the separate and multiple transitions, neither the short chain ( $C_6$ ) nor long chain ( $C_{18}$ ) soft segments show appreciable miscibility with the hard segment.

#### 3.2 Mechanical property characterization of TPUs

Tensile mechanical properties of the TPUs were measured and shown to be strongly dependent on the chemical composition of the soft segment. A comparison of mechanical properties and Shore A hardness values of the TPUs from the two  $C_{18}$  polyols and HD-C6 polyol is shown in **table 3**. The results show that  $C_{18}$  retains hardness with significant improvement in tensile properties. Tensile strength at yield for the  $C_{18}$ -based TPUs is four times the tensile strength of the HD-C6 TPU. Moreover, the elongation at break of the materials is comparable, demonstrating that the  $C_{18}$ -based TPUs are elastomeric and yet also very strong and tough. This combination of properties may be attributed to the multi-phase structure observed in the DSC leading to both hard crystalline and softer elastomeric properties of the soft segment.

The tensile strength of TPUs based on the BD-C18 polyol and HD-C6 was measured at elevated temperatures. At  $50\text{ }^\circ\text{C}$ , the BD-

C18 TPU retains 60 % of its initial strength and at  $70\text{ }^\circ\text{C}$  30 % of its initial strength compared to only 30 % retention for HD-C6 TPU. The improved high-temperature performance is likely attributed to the higher melting point of the soft segment.

#### 3.3 Chemical and water resistance

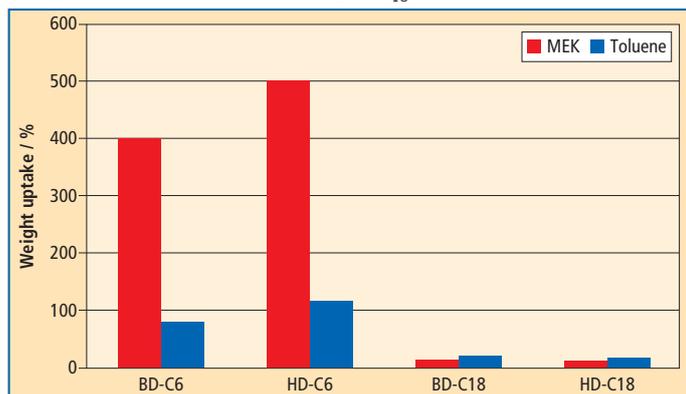
Chemical resistance of the TPUs was tested in polar organic solvents (e. g., MEK, toluene) (**fig. 3**). The resistance in water, acid and base, is shown in **table 4** and **figure 4**. The TPUs based on  $C_{18}$  polyols are much more solvent resistant in both polar solvents such as MEK and less polar solvents such as toluene while TPUs based on adipic acid completely disintegrated in MEK.  $C_{18}$ -based TPUs pick up only 13 % by weight after toluene exposure for seven days, making them four to five times more resistant to toluene than TPUs from adipic acid. The  $C_{18}$  TPUs were also more resistant to water, acid and base than  $C_6$  TPUs. This is most likely due to the high crystallinity and hydrophobicity of the soft segment in  $C_{18}$  diacid-based TPUs.

Tensile samples of TPUs based on 1,2-PG/C18 and BD/C6 were subjected to rigorous alkaline conditions (1 N NaOH at  $70\text{ }^\circ\text{C}$  at various durations) to accelerate hydrolysis. These conditions are known to result in a reduction of ten-

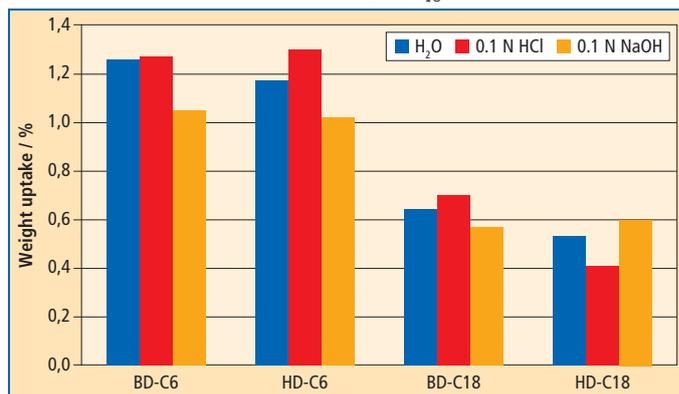
▼ **Tab. 2:** DSC results for TPUs based on polyester polyols (2,000 g/mol), MDI and 1,4-BD chain extender

TPU Sample	BD-C6	HD-C6	BD-C18	HD-C18	1,2-PG-C18
$T_g$ (soft segment) / $^\circ\text{C}$	-34.53	-37	Not observed	Not observed	18
$T_m$ (soft segment) / $^\circ\text{C}$	Not observed	39	67	67.79	52
$T_m$ (hard segment) / $^\circ\text{C}$	167	160	157	154	165

▼ **Fig. 3:** MEK and toluene uptake of  $C_6$  and  $C_{18}$  TPUs after seven days



▼ **Fig. 4:** Water, acid and base uptake of  $C_6$  and  $C_{18}$  TPUs after seven days



sile strength in polyester-based TPUs. The tensile properties of 1,2-PG/C18 TPU and BD/C6 TPU after 0, 7, 14 and 21 days are shown in **figure 5**. The BD/C6-based TPUs show a 57 % drop in tensile strength and 50 % drop in elongation after 21 days indicating degradation by hydrolysis. This degradation is typical for polyester-based TPUs and limits their use in aggressive, high humidity environments. The 1,2-PG/C18-based TPU shows very little degradation even after 21 days. This excellent resistance to hydrolysis is most likely a result of the increased hydrophobicity (leading to lower alkaline uptake) and the decreased number of ester groups in the long C<sub>18</sub> methylene chain

and is more typical of a polyether or polycarbonate-based TPU [5].

## 4 Conclusion

TPUs based on Elevance C<sub>18</sub> polyester polyols represent a new class of polyester-based urethanes that show both good mechanical properties combined with superior hydrolytic stability. The C<sub>18</sub> polyester polyols produced TPUs that are semi-crystalline and tough with good solvent resistance and hydrolytic stability. We believe this improved hydrolytic stability and resistance to polar solvents is

due to a combination of hydrophobicity and reduced number of ester linkages, intrinsic to polyols with long linear aliphatic chains. Other physical properties such as thermal properties, Shore hardness and elongation are similar or improved compared to typical polyester TPUs. Due to crystallinity in the soft segment, the C<sub>18</sub>-based polyols have high tensile strength and strength retention at elevated temperature.

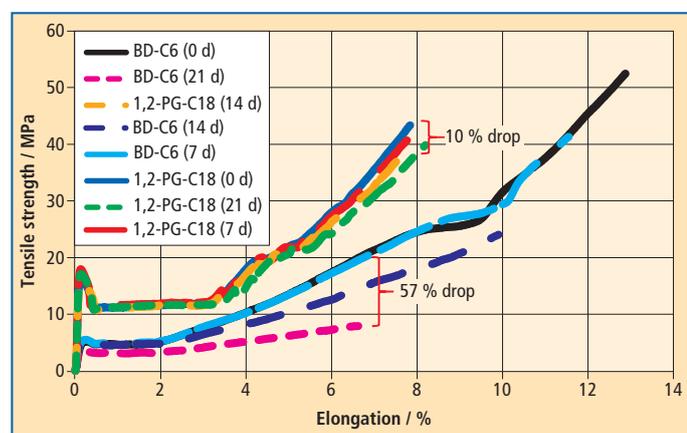
The ability to withstand high temperatures and high humidity environments without degradation is needed in the majority of urethane applications, including automotive adhesives, athletic equipment, footwear, oil field pipelines, flexible tubing and high-performance coatings. C<sub>18</sub>-based TPUs will allow the polyurethane market to expand product offerings in these demanding applications with renewable materials.

## 5 Acknowledgment

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**Fig. 5:** Tensile properties of TPUs from BD-C6 and 1,2-PG-C18 after 0, 7, 14, and 21 days in 1 N NaOH (70 °C)

**Tab. 3:** Comparison of semi-crystalline TPUs made from Inherent C18 Diacid and C<sub>6</sub> diacid

TPU properties	TPU based on HD-C6	TPU based on 1,2-PG/C18	TPU based on BD-C18
Hard segment concentration / %	22	20	22
Soft segment concentration / %	78	80	78
Shore A hardness	89	94	92
Shore D hardness	43	55	54
Ultimate tensile strength / MPa	16	43	32
Tensile strength at yield / MPa	4	17	14
Elongation at break / %	819	780	724
Toughness / MJ/m <sup>3</sup>	66	160	151
Tensile strength at yield / MPa (25 °C)	4	17	14
Tensile strength at yield / MPa (50 °C)	1.1	NA	8
Tensile strength at yield / MPa (70 °C)	0.9	NA	5

**Tab. 4:** Solvent resistance of TPUs made from Inherent C18 Diacid vs. TPUs from adipic acid (weight gain in % after seven days)

Solvent	TPU based on BD-C6	TPU based on HD-C6	TPU based on BD-C18	TPU based on HD-C18	TPU based on 1,2-PG-C18
H <sub>2</sub> O	1.26	1.17	0.64	0.53	0.35
MEK	399.57	Disintegrated	13	11.43	19
Toluene	79.18	116	20	17.07	40
0.1 N HCl	1.27	1.30	0.70	0.41	NA
0.1 N NaOH	1.05	1.02	0.57	0.60	0.30

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