Scaling the heights of sustainable PU
The rise of polyols from CO₂
Structure-property relationships of TPUs from bio-based C18 polyester polyols

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C18 polyols are a promising new class of bio-based high-performance building blocks for demanding PU applications where sustainability is important. They offer opportunities to produce easier-to-process polyurethanes for a wide range of CASE applications with good viscosity and performance characteristics.

Polyurethanes may display thermoplastic, elastomeric and thermoset behaviour, depending on their structures and morphology. As a result of the diversity of mechanical, physical, biological and chemical properties that are available, polyurethanes are widely used as rigid foams, flexible foams, coatings, adhesives, sealants and elastomers (CASE).

This work shows that Elevance Inherent C18 Diacid can be reacted with different diol co-monomers to produce polyols with a wide range of morphologies. These can be used to produce polyurethanes for many applications.

There is a growing demand from customers for materials with good properties that are made sustainably. Inherent C18 diacid is made from completely biorenewable carbon, and the corresponding C18 polyols range between 61–100%, depending on the source of the diol co-monomer(s).

Thermal properties of C18 polyols depend on constituent diol structures: linear aliphatic diols yield polyols with high melting temperatures, which may be useful in hot-melt adhesives and shape-memory polyurethanes. Branched aliphatic and ether-containing diols yield liquid/semi-solid polyols more suitable for PU coatings and elastomers.

This work shows that C18 TPUs with well-developed crystalline phases possess high ultimate tensile strength, tear strength, compression set, good resilience and good solvent resistance. In contrast to TPUs made from conventional polyester polyols, C18 TPUs displayed excellent hydrolytic stability at elevated temperature and humidity.

In terms of processability, the viscosity of conventional high-performance specialty poly-carbonate (PC) polyols is more than 30 times higher than comparable C18 polyols that yield TPUs with good properties. The lower viscosity of C18 polyols enables higher solids and low/zero VOC PU formulations to be produced.

Structure-property relationships of thermoplastic polyurethanes (TPUs) based on a series of different C18 polyols were benchmarked against a series of reference TPUs constructed from typical polyester, polyether, and PC polyol soft segments.

PUs are commercially valuable because of their outstanding mechanical properties, which stems from microphase separation between incompatible and immiscible hard and soft segments of the polymer. Hard segments serve as physical cross-linkers for soft segment domains, providing strength and stiffness. Soft segments confer elastomeric behaviour such as rebound and flexibility, ultimately leading to high tensile strength, tear

**Table 1: Characterisation data of C18 Polyols**

<table>
<thead>
<tr>
<th>Polyol code</th>
<th>n</th>
<th>AV (mg KOH/g)</th>
<th>OHV (mg KOH/g)</th>
<th>cP (°C)</th>
<th>Colour</th>
<th>Bio-based carbon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18-HD</td>
<td>2.0</td>
<td>&lt;1</td>
<td>59</td>
<td>850 (90°C)</td>
<td>82</td>
<td>&lt;200</td>
</tr>
<tr>
<td>C18-BD</td>
<td>2.0</td>
<td>&lt;1</td>
<td>56</td>
<td>976 (85°C)</td>
<td>85</td>
<td>&lt;200</td>
</tr>
<tr>
<td>C18-PDO</td>
<td>2.0</td>
<td>&lt;1</td>
<td>54</td>
<td>1182 (85°C)</td>
<td>80</td>
<td>&lt;200</td>
</tr>
<tr>
<td>C18-PG</td>
<td>2.0</td>
<td>&lt;1</td>
<td>54</td>
<td>760 (75°C)</td>
<td>62</td>
<td>&lt;200</td>
</tr>
<tr>
<td>C18-EPG</td>
<td>2.0</td>
<td>&lt;1</td>
<td>56</td>
<td>1230 (60°C)</td>
<td>38</td>
<td>&lt;200</td>
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<tr>
<td>C18-TPG</td>
<td>2.0</td>
<td>&lt;1</td>
<td>55</td>
<td>990 (60°C)</td>
<td>17</td>
<td>&lt;200</td>
</tr>
<tr>
<td>C18-BEPD</td>
<td>2.0</td>
<td>&lt;1</td>
<td>55</td>
<td>1447 (60°C)</td>
<td>18</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>

*average functionality

**Figure 1.** Polyol viscosity versus temperature curves at a constant 10 S⁻¹ shear rate (a) C18 polyols compared with PC polyols (b) viscosity reduction of PC-BEPD by blending in C18-BEPD.
resistance and good elongation properties. The abundance of raw materials available to produce PUs such as polyols, isocyanates and chain extenders allows processing behaviour and, more importantly, physicochemical properties of the polymers, to be tuned to meet the demands of various applications.

The chemical nature of the polyol soft segment strongly influences PU properties. Polyols are predominantly grouped by functionality into polyether polyols or polyester polyols. Polycarbonate polyols represent a third group of materials used in the CASE sector. They provide excellent chemical, heat and weathering resistance, but present processibility challenges as a result of their high viscosities.

It is desirable to design polyols that provide an improved balance of resistance to hydrolysis and oxidation, while maintaining mechanical properties, ease of processing and improvements in sustainability. In this study, Elevance investigated a series of thermoplastic polyurethanes based on bio-based C18 polyols to benchmark against TPUs from traditional polyester, polyether and PC polyols. C18 polyols with diverse thermal properties can be produced by reacting C18 diacid with different diols. Low-melting C18 polyols are good candidates for applications in PU dispersion (PUD) coatings and thermoplastic elastomers, while crystalline C18 polyols with high, sharp melting points can serve as building blocks for shape-memory materials or be used as strengthening modifiers in polyether-based TPU elastomers. Importantly, biorenewable C18 polyols provide TPUs with excellent hydrolytic stability at low processing viscosities without compromising mechanical performance.

As shown in Table 1, the thermal properties of di-functional C18 polyols are mainly determined by the structure of the diol comonomers. Linear aliphatic diols, such as 1,6-hexanediol (HD), 1,4-butanediol (BD) and 1,5-pentanediol, give polyols with high melting temperatures (Tm) (≥80°C). This is probably a result of the high crystallinity, which arises from the compact packing of easily aligned polymer chains. When the methyl-branched aliphatic diol propane-1,2-diol (PG) or ether-containing dipropylene glycol (DPG) were used as comonomers, a significant drop of Tm was observed (62°C for PG and 38°C for DPG). This indicates there is some disruption of crystallinity by the methyl branches. Furthermore, diols with more methyl branches, or bulkier branches, lead to polyols with even lower Tm: tripropylene glycol (TPG) and highly branched butyl ethyl propane diol (BEPD) yield C18 polyols with melting points below ambient temperature, and those liquid/semi-solid polyols are well-suited for PU elastomer or coating applications.

No glass-transition temperatures were observed for C18 polyols down to -60°C. Polyols with low melt viscosities are preferred for most PU applications. Low viscosity eases processing and enables formulations at high solids and low-VOC without plasticisers, solvents or reactive diluents.

Polyl viscosity versus temperature plots inform the ideal processing window, which is critical for PU formulation. Such plots were generated for two low-melting C18 polyols, one produced with tripropylene glycol (C18-TPG), the other with butyl ethyl propane diol (C18-BEPD). These were compared with two PC polyols commonly used in high-performance coatings, PC-HD/1,5PD from a blend of hexane diol and 1,5-pentanediol, and PC-BEPD. The results are shown in Fig. 1 a. C18-TPG and C18-BEPD had much lower melt viscosities (2,600, and 5,700 cP, respectively) compared with PC-HD/1,5PD and PC-BEPD (32,900 and 185,800 cP) at 35°C. Comparing the two polyols designed with BEPD comonomers, PC-BEPD viscosity at this processing temperature is 30 times greater than C18-BEPD.

At 80°C, viscosities of C18 polyols were still only 10-20% of the values displayed for reference PC polyols. This is likely to be caused by the long chain architecture of C18 chains that have a reduced density of polar functional groups for the same average mass unit.

Table 2: Characterisation and mechanical properties of C18 TPUs and reference TPUs

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|---|---|---|---|---|---|---|---|---|---|
| | Tm | Tensile strength | Tear strength | Strain at break | Compression set | Resilience | Abrasion resistance | k | D |
| C6-BD | - | 30.9±1.6 | 800±20 | 660±10 | 13.8±3.9 | 74±1 | 55.1±0.5 | 0.11 | 5.94 | 0.070 |
| PCL | - | 20.9±2.4 | 610±30 | 630±20 | 14.6±1.6 | 67±2 | 64.2±0.8 | 0.02 | 6.13 | 0.084 |
| PC-HD/1,5PD | - | 28.0±1.6 | 670±50 | 630±20 | 26.3±2.5 | 72±1 | 18.4±1.3 | 0.15 | 3.37 | 0.056 |
| PMTG | - | 15.3±1.8 | 630±40 | 530±40 | 1.9±1.9 | 73±1 | 66.8±1.9 | 0.02 | 5.47 | 0.063 |
| C18-BD | 68 | 33.0±1.1 | 2180±120 | 660±30 | 28.8±0.8 | 88±1 | 35.0±3.0 | 0.04 | 3.28 | 0.089 |
| C18-PG | 55,57 | 29.8±1.8 | 1750±50 | 600±20 | 14.3±1.6 | 91±1 | 36.0±1.7 | 0.42 | 7.08 | 0.007 |
| C18-DPG | 33 | 21.1±1.9 | 1070±40 | 700±30 | 9.1±1.6 | 87±2 | 32.7±1.2 | 0.52 | 3.4 | 0.045 |
| C18-BEPD | 11 | 12.9±1.2 | 370±20 | 640±60 | 16.9±1.8 | 64±1 | 27.9±0.7 | 0.59 | 3.23 | 0.054 |

Note: a Measured using a Perkin Elmer DSC-7 under a purge of nitrogen gas with a heating rate of 5°C/min from -60°C to 200°C (second heating cycle). b Measured using Instron 5500R Model 1122 according to ASTM D-2240. c Measured using a Perkin Elmer DSC-7 under a purge of nitrogen gas with a heating rate of 5°C/min from -60°C to 200°C (second heating cycle). d Measured according to ASTM D-395. e Measured using a Perkin Elmer DSC-7 under a purge of nitrogen gas with a heating rate of 5°C/min from -60°C to 200°C (second heating cycle). f Measured using a Perkin Elmer DSC-7 under a purge of nitrogen gas with a heating rate of 5°C/min from -60°C to 200°C (second heating cycle). g Measured using a Perkin Elmer DSC-7 under a purge of nitrogen gas with a heating rate of 5°C/min from -60°C to 200°C (second heating cycle). h Dielectric constant (k) and dissipation factor (D) were measured using a Boonton Electronics 76A 1 MHz automatic parallel plate capacitor. The dielectric constant was calculated from the measured capacitance.
The low viscosity of miscible C18 polyols can lead to a significant viscosity reduction when used in blends with polycarbonate polyols, and may make solvents unnecessary. At low temperatures, the viscosity of PC-BEPD/C18-BEPD (6/4) blends was fairly close to that of PC-BEPD diluted by 10 wt % N-methyl-2-pyrrolidone, as shown in Figure 1b. This polyol mixture strategy could be useful for high solids and low-VOC PUD and solvent-borne PU coatings.

Testing TPU
We used these C18 polyols to produce a number of different TPUs. In all cases, we reacted the C18 polyols with 4,4'-methylene diphenyl disiocyanate (4,4’-MDI) and chain extender 1,4-butanediol (BD) at polyol/BD/4,4'-MDI equivalent weight ratio of 1/1/2.04.

We compared their properties to reference TPUs based on conventional polyols with similar Mn, including:

- a traditional polyester polyol poly(1,4-butylenediphenyl adipate) (C6-BD),
- specialty polyester polyol polycaprolactone (PCL),
- polyether polyol poly(tetramethylene oxide) (PTMG),
- and a PC polyol PC-HD/1,5PD.

The hard segment content of all TPUs was in the 28–36% range. TPU characterisation, including mechanical and electrical properties, are summarised in Table 2.

C18 TPUs generally exhibited good compression resistance and resilience.

The compression set of C18 TPUs was lower than that of other reference TPUs (55–67%). Of C18 TPUs (28–36%) were higher than that of PTMG TPU. Resilience values of C18 polyols, all of which were much higher, at 86-91 Shore A. However, this could change because, Traditionally, many polyester-based polyurethanes are produced using adipic acid and they suffer from poor hydrolytic stability at elevated temperatures and high humidity. This ultimately results in loss of mechanical properties over time.

Elastomeric C18-BEPD TPU with a low Tm (8°C) and reference TPUs exhibited moderate hardness, 64–74 Shore A, while the hardness of crystalline TPUs based on other C18 polyols was higher, at 86–91 Shore A.

In terms of abrasion resistance, C18-BD TPU showed comparable performance to the reference TPUs.

Electrical insulation properties are important in various electrical encapsulation applications. The dielectric constant (κ) and dissipation factor (D) values for most C18 TPUs were lower than the PC-HD/1,5PD TPU, all of which were lower than the polyester- and polycarbonate-based reference TPUs, indicating that hydrophobic C18 TPUs have better electrical insulation properties.

Representative stress–strain curves of C18 TPUs and reference TPUs are shown in Figure 2. All reference TPUs were elastomeric materials at room temperature; there was no yield point observed in the stress–strain measurements.

Crystalline C18 TPUs exhibited yield at low strain, which could be expected as a result of the use of solid C18 polyols as the soft segment (Table 1). The tensile strength of these TPUs was, therefore, high. However, C18-BEPD TPU was elastomeric and did not yield. This is because of the low Tm of the polyol.

All the TPUs showed strain at break values between 530% and 710%. It was notable that yield points observed for crystalline C18 TPUs at ambient temperature were absent when tested at 70°C (as shown in Figure 2b). This indicates that they could be used as shape-memory materials. Moreover, the crystalline nature of those C18 TPUs leads to significantly higher tear strength than reference TPUs, and also suggests that those solid C18 polyols at room temperature could, potentially, be used in hot-melt adhesives.

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However, this could change because, although polyurethanes produced with C18 polyols are polyester-based, C18 acid is more than six orders of magnitude less soluble in water than adipic acid, a C6 diacid.

We subjected TPUs in our test to high temperature stress tests. In this study, the difunctional C18 polyols were synthesised targeting a hydroxyl value (OHV) = 56 mg KOH/g or number average molar mass (Mn) ~ 2000 g/mol.

Viscosities of polyols were measured using a 50 mm parallel plate viscometer with a 1000 µm geometry gap. All samples were equilibrated at the starting temperature for 30 seconds before data collection. The temperature ramped up from 25 or 35°C depending on the polyols to 100 °C at a rate of 5 °C/min, and the shear rate was constant at 10 s⁻¹.

After the polyols were produced, we reacted them with diisocyanate to produce TPU sheets and round-bottom samples for physical testing. These were compared with test samples made from reference TPUs.

Sheets were prepared using a laboratory compression moulding method. Degased preheated polyol and a chain extender were weighed into Speed Mixer cup and mixed for 30 seconds and subsequently heated for 15 minutes in an air-circulating oven at 100°C. Liquid isocyanate conditioned at 70°C was added via syringe to the mixture of polyol and the chain extender. Small amounts of tin catalyst Dabco T-12 were added to some polyurethane systems to speed up polymerisation and adjust gel time. Gel time, in most cases, was about 12 minutes. All components were mixed and transferred into an aluminium mould covered with a Teflon sheet that was preheated at 120°C. At gel time, the mould was closed and the TPU cured for 2 hours at 120°C. Afterwards, the samples were post-cured for 16 hours at 100°C in an air-circulation oven. After post-curing, the samples were aged for seven days at ambient atmosphere prior to testing.

Experimental

We produced a range of difunctional C18 polyols [4] through polycondensation of Inherent C18 Diacid with various diols. This generated a number of C18 polyester polyols with diverse structures and physical properties which could be used in real applications.

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temperature and humidity. All the TPUs were tested for tensile properties before and after exposure to a 70°C and 95% relative humidity (RH) atmosphere for 7 days. The results are shown in Figure 3.

We evaluated the hydrolytic stability of each material by measuring tensile strength coupled with weight change caused by water uptake after exposure.

All C18 TPUs exhibited minimum weight gain after the test. This was a result of the high hydrophobicity of the long aliphatic C18 chains which contain fewer functional groups for each of the hydrophobic backbone repeat units. Tensile test results showed that C18 TPUs based on C18-BD, C18-PG and C18-BEPD retained between 41% and 47% of the original strength after the exposure. This compares with the PC-HD/1,5PD reference TPU, which retained 53%.

In contrast, C18-DPG TPU retained only 22% of its original tensile strength after the exposure. This is possibly caused by greater water uptake resulting from hydrogen-bonding of ether functional groups in the polymer backbone, which increases the propensity for hydrolysis.

In sharp contrast, reference TPUs based on less hydrophobic polyester polyols, C6-BD and PCL, failed after 7 days of exposure: the tensile bars were too soft to test. Well known for its high hydrolytic stability, reference PTMG TPU showed the highest retention of tensile strength (96%) despite the high weight change resulting from water uptake.

We tested the solvent resistance of C18 TPUs by immersing (10 x 40 x 2mm) specimens in non-polar oil and the relatively polar solvent methyl ethyl ketone (MEK) at room temperature for 3 days. The samples were then removed, dried, and weighed.

As shown in fig. 4b, in oil, semi-crystalline C18 TPUs gained little weight, as did reference TPUs based on polyester and PC polyols, while the long alkyl branches in the non-crystalline C18-BEPD TPU lead to more oil pick-up.

The PTMG-based TPU absorbed an even greater amount of oil, despite its greater hydrophilicity than C18 TPUs. Linear C18-BD TPU exhibited the smallest weight increase in MEK. This could be a result of high soft segment crystallinity, which leads to excellent barrier properties. Branched C18-PG TPU absorbed much more MEK than C18-BD TPU, but still much less than all the reference TPUs. For C18 TPUs that have more or longer alkyl branches, lower solvent resistance is expected.

REFERENCES

This is an edited version of the paper presented by Elevation at the CPI Meeting in New Orleans in October.

Correction:
Kangnam Chemical has asked Urethanes Technology to correct its location and the name of one of its employees featured in the article Kangam Chemical Running the race, which appeared on page 27 of the last issue.

We are happy to confirm that the company is called Kangnam Chemical, that it is located South of Seoul and the family name of Mr Kwang-Soon Hwang is Kwang and not Hwang.

Biographies
Yanzhao Wang is a scientist at Elevation Renewable Sciences and received his Ph.D. in organic chemistry from the University of California, Santa Barbara for new methodology development based on transition metal catalysis. He then transitioned to the design and development of polyurethane and polyolefin elastomers for long-term biomedical applications as a postdoctoral fellow at the University of Minnesota Twin Cities. He has more than 20 peer-reviewed publications and patents. His work at Elevation includes studying structure–property relationships between novel natural oil metathesis-based monomers and prepolymers, and developing biorenewable high-performance polymers.

Dr. Aisa Sendjarevic is a Research Director at Troy Polymers, Inc., a consulting and contract R&D laboratory specializing in polyurethanes. She has authored more than 80 technical articles (papers, book chapters and conference proceedings) and 14 US patents. She has more than 30 years of research experience in isocyanate-based polymers and polyurethanes. Her research experience includes development of novel materials for medical, space, automotive, transportation and other industries. Specific interests include syntheses of isocyanate-based polymers and co-polymers of defined chemical structure and properties; morphology and structure property relationships in polyurethane elastomers, coatings and adhesives; polyurethanes based on renewable components.

Paul A. Bertin holds the title of R&D Group Leader, Innovation at Elevation Renewable Sciences. He received his Ph.D. in organic chemistry from Northwestern University for the development of polymer-based nanostructures from ring-opening metathesis polymerisation. He is the author or co-author of more than 40 research publications, patents and patent applications. His research interests are diverse and, broadly, include sustainable chemistry, hybrid organic-inorganic materials, and advanced functional macromolecules.