UMassAmherst

Biomass-Derived Coatings Using Renewable, Low-Cost 1,5-Pentanediol

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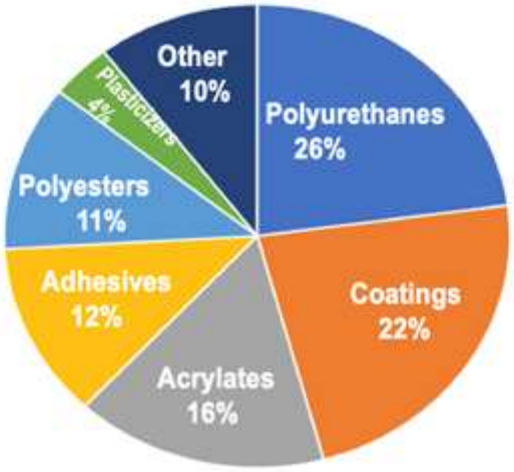
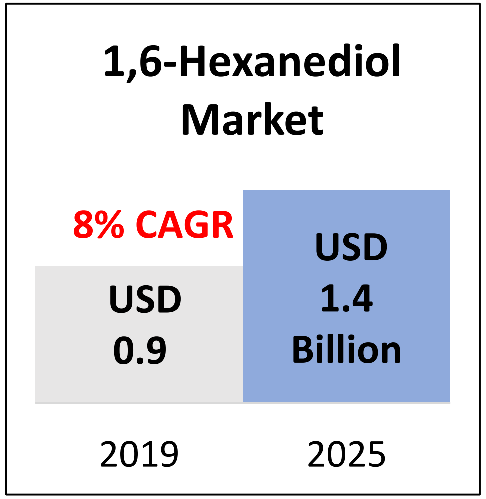
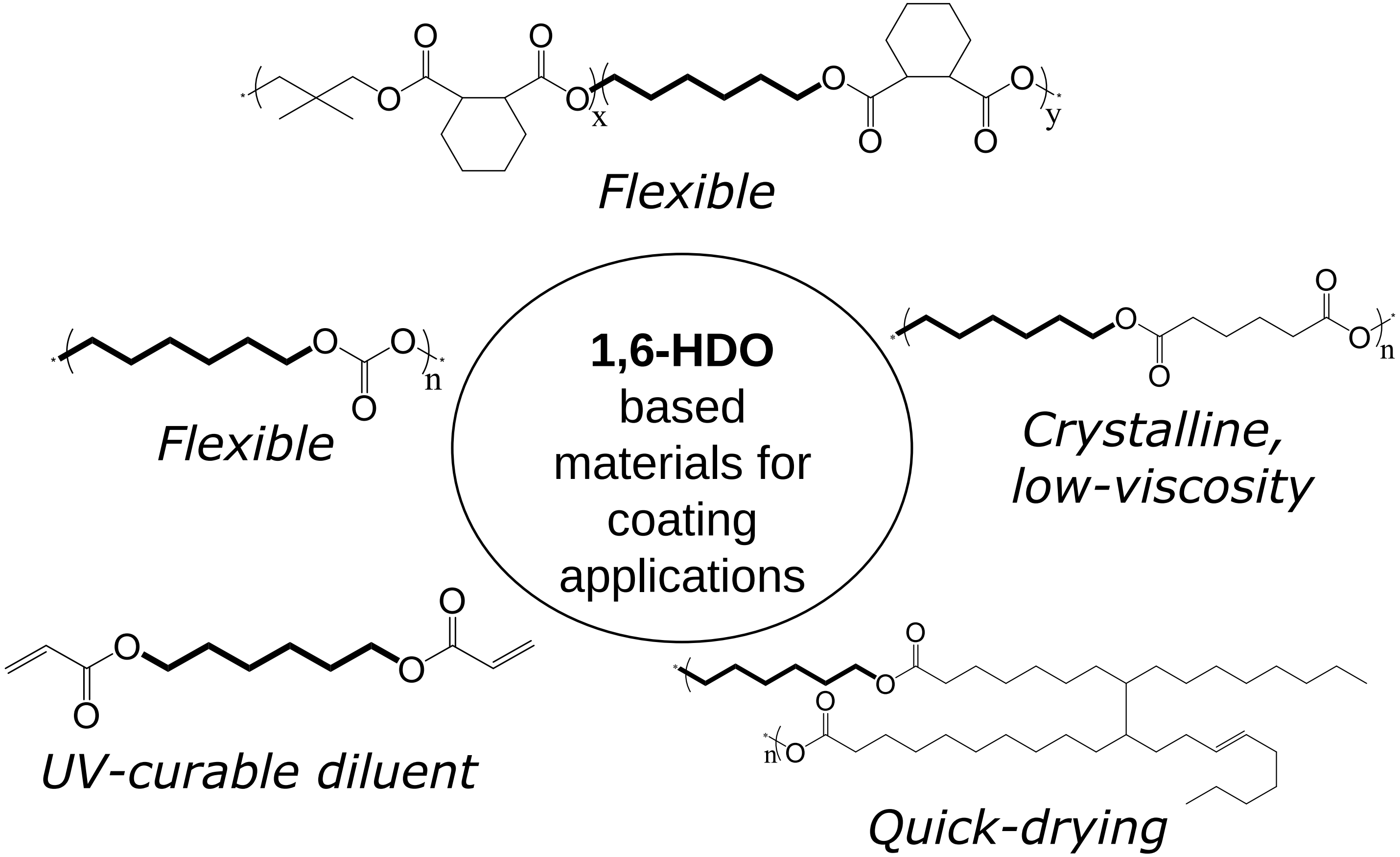
1,6-Hexanediol is a common monomer used in coating industry

1,6-HDO market by applications at 2013







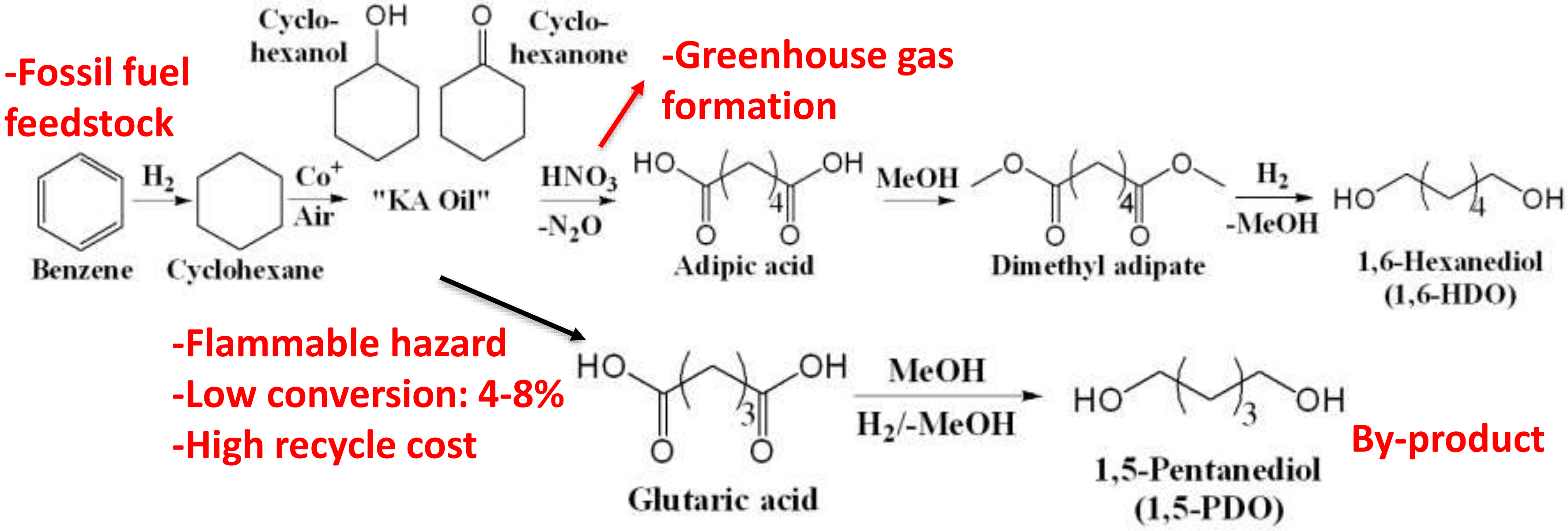
1,6-Hexanediol (1,6-HDO): a key monomer in coating building blocks

- Flexibility
- Crystallinity

1,6-HDO is from petroleum.

Pyran has developed a route to produce 1,5-Pentanediol (1,5-PDO) from biomass

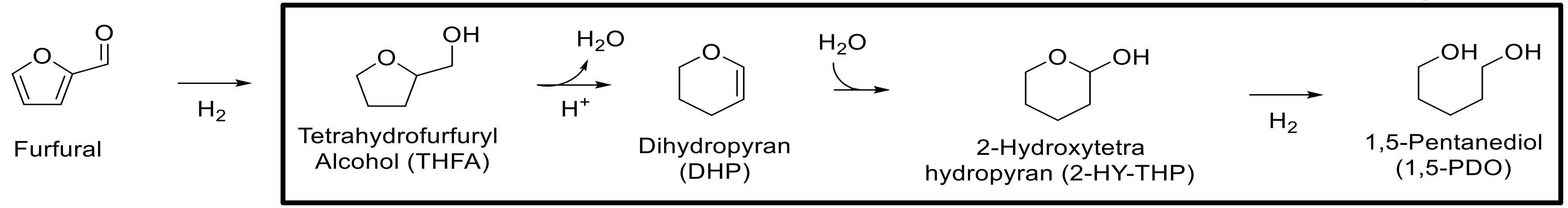
- 1,6-HDO and 1,5-PDO are currently produced from petrochemicals:



- Numerous reaction steps
- Greenhouse gas: N_2O
- Safety hazards
- 1,5-PDO cannot be produced on purpose (only as by-product)

- A novel route to synthesize 1,5-PDO from biomass:

Patented Reaction Steps



-Purity>98%

- Furfural produced from waste biomass
- Avoid toxic regents
- 90% lower GHG
- Only on purpose 1,5-PDO route

ZJ Brentzel, KJ Barnett, K Huang, CT Maravelias, JA Dumesic, GW Huber, Chemicals from Biomass: Combining Ring-opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural, ChemSusChem, (2017), 10, 1351-1355.

Low cost and renewable 1,5-PDO

Advantages of bio-based 1,5-PDO over 1,6-HDO:

- Sustainable
- Lower greenhouse gas emission
- Fewer reaction steps
- Low-cost, non-edible C5 platform chemicals (furfural)
- Lower cost

	Oil-based 1,5-PDO	Oil-based 1,6-HDO	Renewable 1,5-PDO
Monomers:			
Price:	**$5000/ton**	**$4000/ton**	**$3-4000/ton**

1,5-PDO based polyesters have opportunities for use in coatings

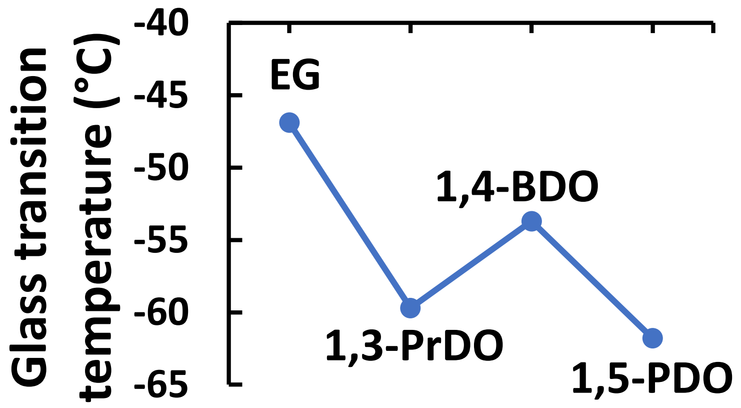
➢ **1,5-PDO based polyesters might be**

- **Flexible**
  - Long chain α,ω-diol, $-CH_2-CH_2-CH_2-CH_2-CH_2-$
  - Odd-even effect

  → 1,5-PDO + 1,6-HDO, or 1,5-PDO + adipic acid

  → lower glass transition temperature

Glass transition temperatures of adipate polyesters synthesized from various diols



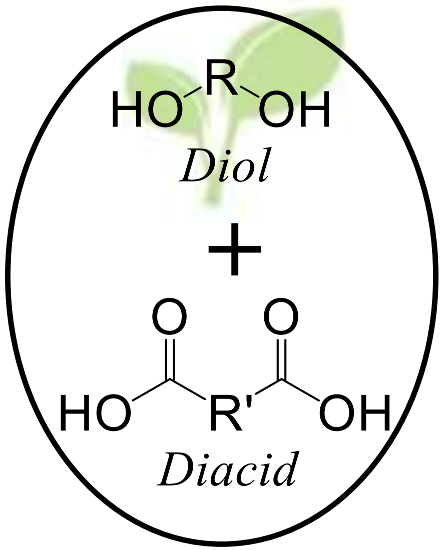
- **Crystalline**
  - Linear α,ω-diols with regular structure
  - Rapid drop in viscosity at melt transitions → high flow
  - Odd-even effect → lower melting temperature and crystallinity

➢ 1,5-PDO based polyesters impart cured coatings with:

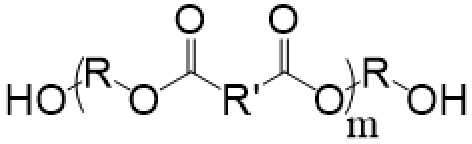
- Flexibility (e.g. solvent borne, powder, UV-cure, water borne coatings)
- Surface smoothness (e.g. powder coatings)

Objective is to evaluate 1,5-PDO in polyols and coatings

Monomers



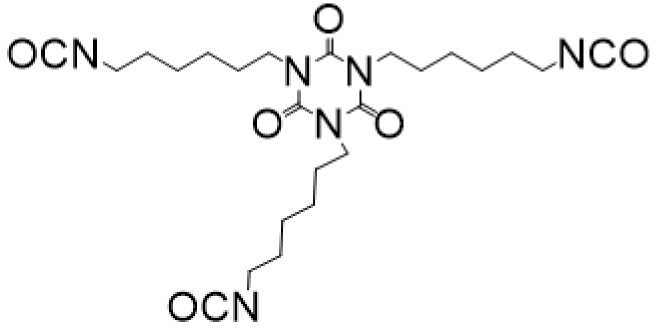
Polyols



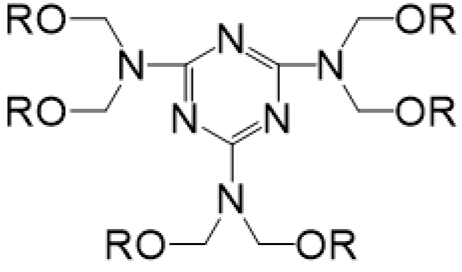
Polyester polyol

+

Curing agents

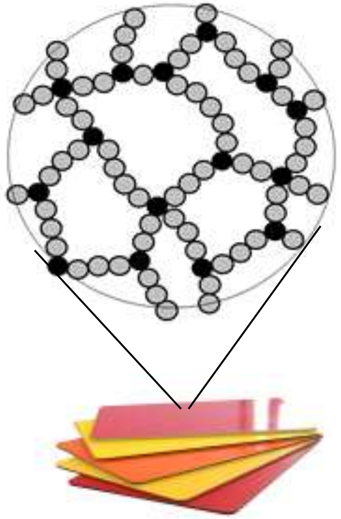


Isocyanate trimer



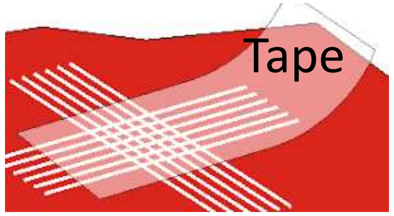
Melamine-formaldehyde

Crosslinked coatings

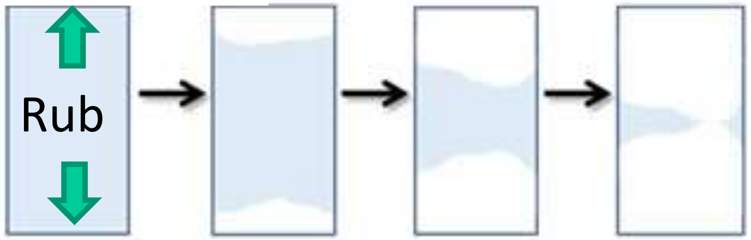


Flexibility

Pencil hardness



Adhesion strength



Solvent resistance

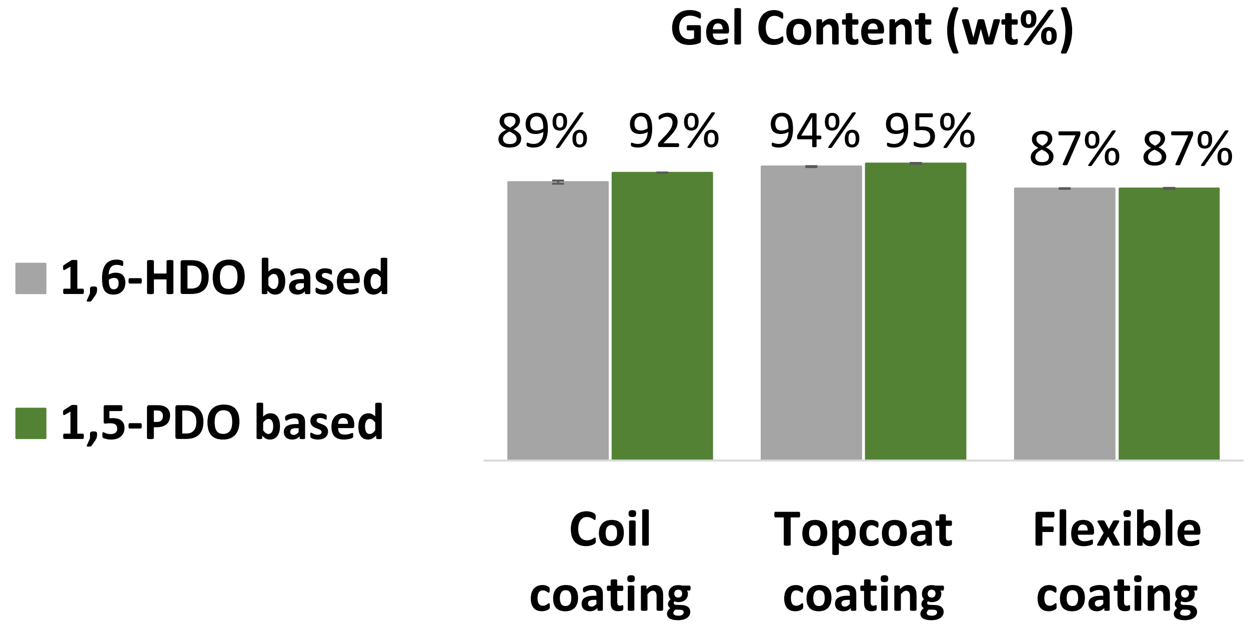
Lei Zheng, Daniel McClelland, Kevin Barnett, George W Huber, John Klier, 1,5-Pentanediol as a Biomass-based Monomer for Polyester Polyols, In preparation

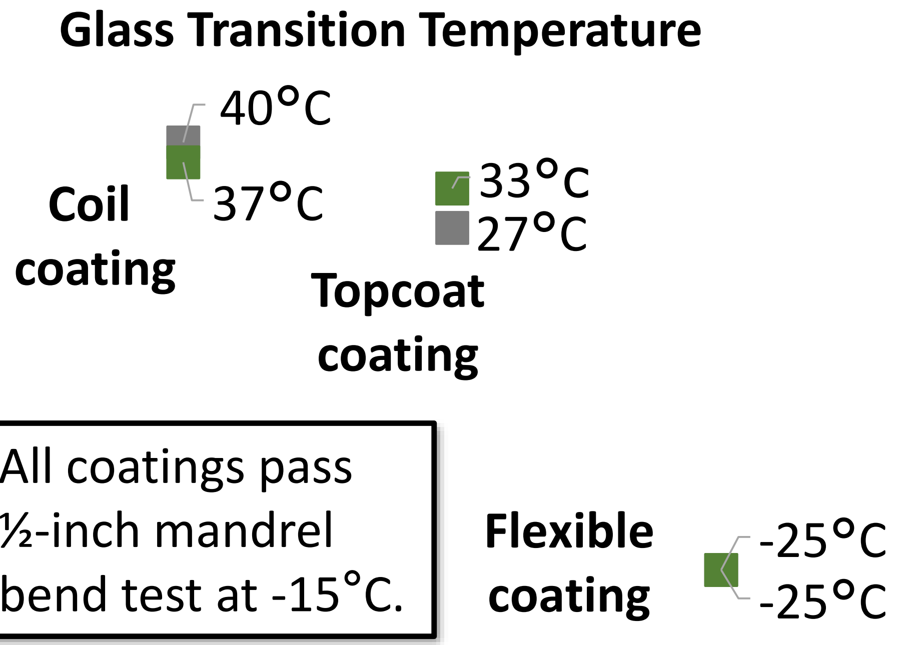
Compare biomass-derived polyols with 1,6-HDO based polyols

Sample	Polymer composition	$Ø_{bio}$ (%)	OH_v (mg KOH/g)	A_v (mg KOH/g)	M_n (Da)	Tm (°C)	Tg (°C)
BPDO1	**PDO**/NPG/HHPA/T-HDI	23.6	172	7	627	/	/
HDO1	**HDO**/NPG/HHPA/T-HDI	0	163	10	649	/	/
BPDO2	**PDO**/AA/HHPA	44.8	70	1.8	1498	/	/
HDO2	**HDO**/AA/HHPA	0	64	4	1604	/	/
BPDO3	**PDO**-Branched	21.1	45	6.2	8416	/	23±8
HDO3	**HDO**-Branched	0	41	8.2	8894	/	29±3
BPDO4	**PDO**/AA	46.8	31.7	1	3789	34/41 (64J/g)	/
HDO4	**HDO**/AA	0	34.3	0.8	3782	54 (87J/g)	/
BPDO5	**PDO**/AA/IPA	44.6	53.8	0.3	2028	/	-44±0.7
HDO5	**HDO**/AA/IPA	0	47.5	0.6	2300	/	-45±1.3

1,5-PDO and 1,6-HDO based polyols have similar coating properties

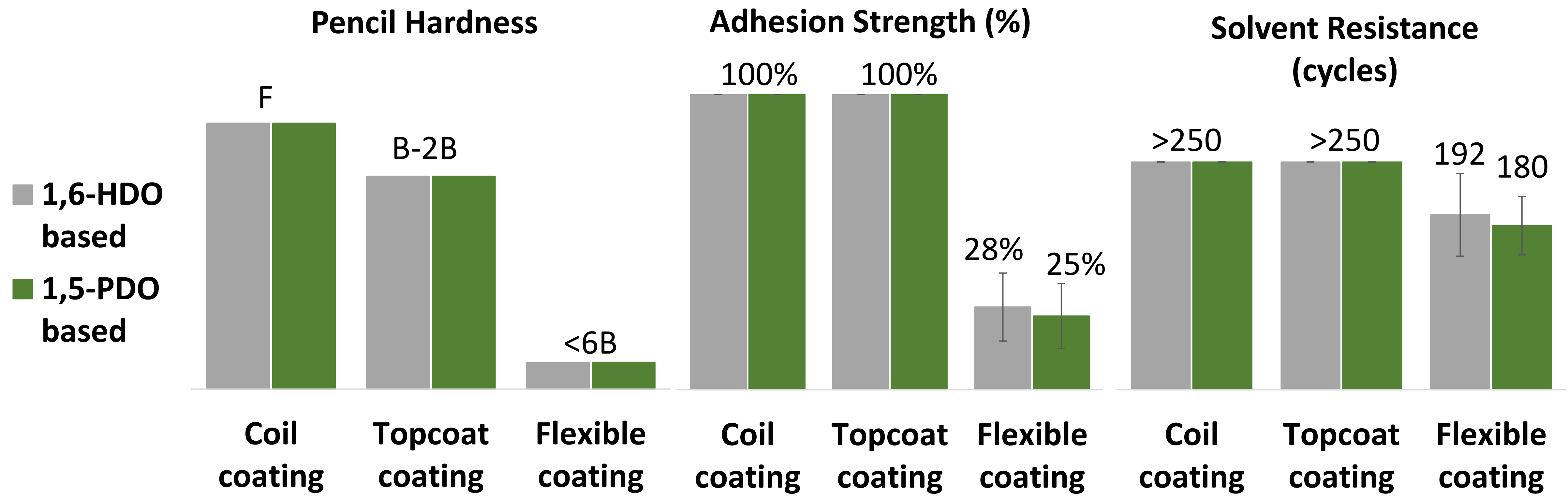
Formulation	Components
Coil Coating	**HDO- or PDO-branched polyols**/melamine resins/additives
Topcoat coating	**HDO- or PDO-based polyester-urethane polyols**/isocyanate crosslinker/additives
Flexible coating	**HDO- or PDO-based polyester polyols**/isocyanate crosslinker/additives





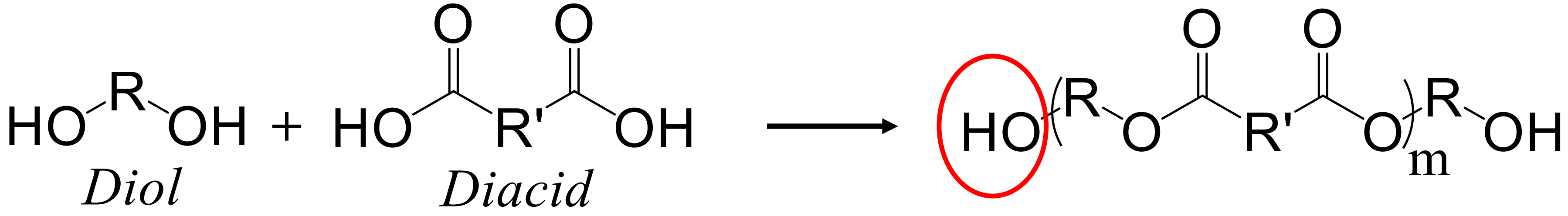
All coatings pass ½-inch mandrel bend test at -15°C.

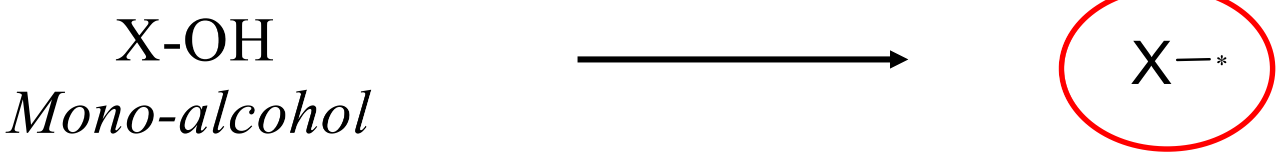
1,5-PDO and 1,6-HDO based polyols have similar coating properties



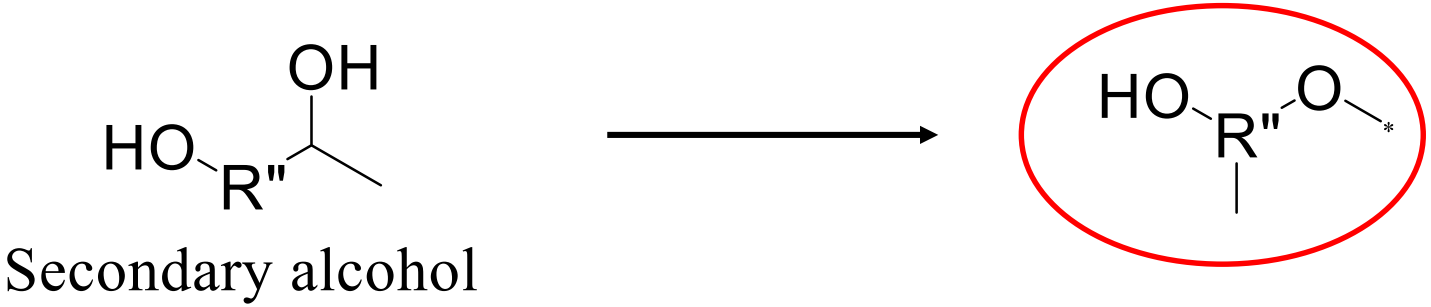
- Similar hardness, flexibility, adhesion strength and solvent resistance
- 1,5-PDO provides a lower cost, sustainable and non-petrochemical alternative to 1,6-HDO in coating applications.

Effects of possible impurities from biomass on polyols

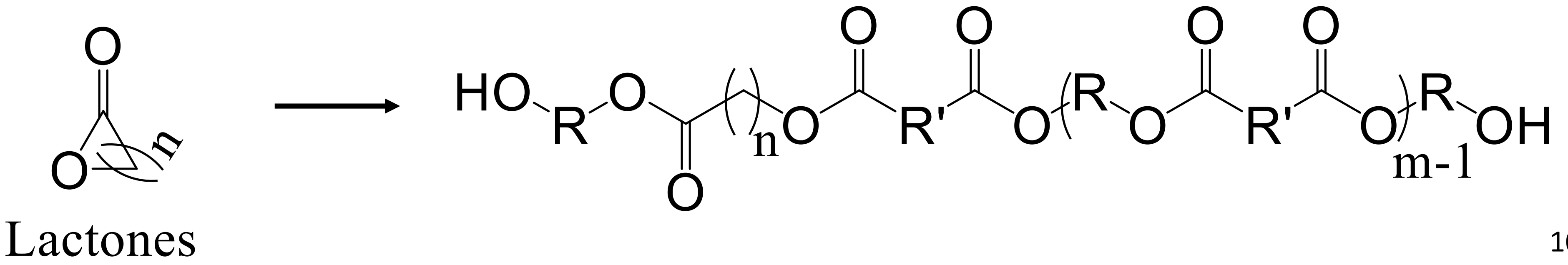




Dead ends



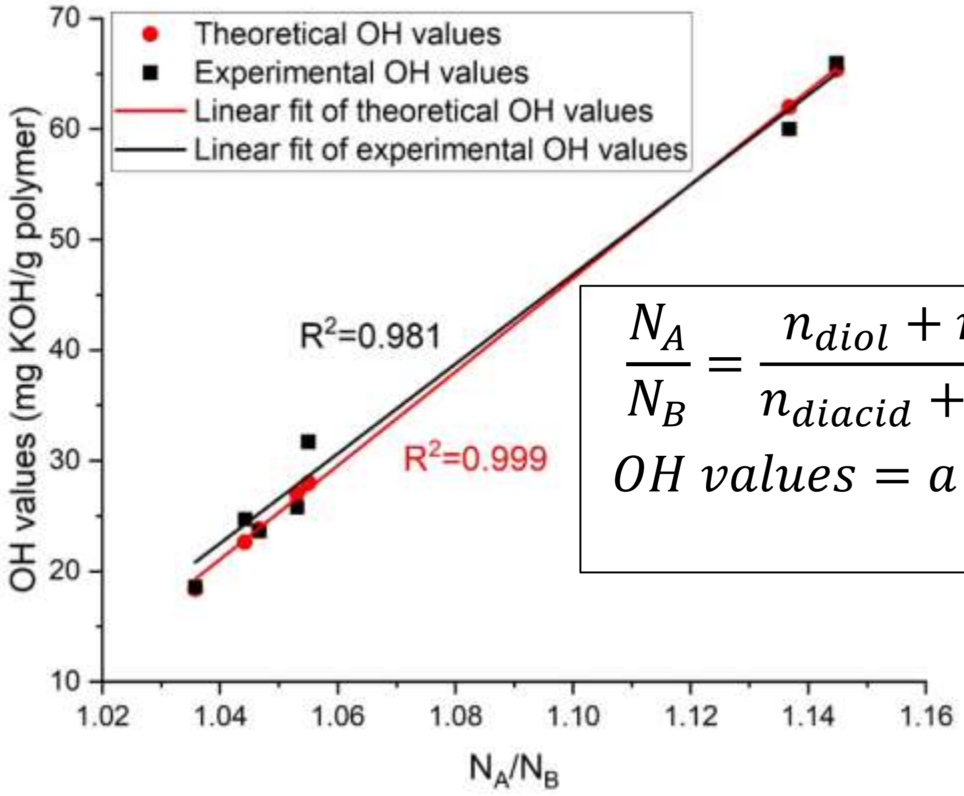
Less reactive



US 20140309461 A1
JP 2017014427A
N. Yoshinao, Catalysis Today, 2012

Lactones have no effect on polyol functionality

- Model polyesters: 1,5-PDO + adipic acid + 0%, 2%, 5%, 7%, 10% lactone
- Impurities were added "well above" any observed amount in order to observe outsized impact of impurities.



$$\frac{N_A}{N_B} = \frac{n_{diol} + n_{lactone}}{n_{diacid} + n_{lactone}}$$

$$OH\ values = a - \frac{b}{k\frac{N_A}{N_B}+1}$$

Fraction of lactone	Tm(°C) ΔHm(J/g)	Tc(°C) ΔHc(J/g)
0%	33/40 62	11 62
2%	32/39 61	11 61
5%	32/38 58	6 56
7%	31/38 61	7 59
10%	31/38 60	7 58

➢ Lactones do not affect polyol functionality but lower crystallization temperature and crystallization enthalpy.

Mono-alcohols decrease the molecular weight of polyols

- Model polyesters: 1,5-PDO + adipic acid + 0%, 5%, 7% mono-alcohol
- Impurities were added "well above" any observed amount in order to observe outsized impact of impurities.

Fraction of mono-alcohol	Hydroxyl Value (mg KOH/g)	Acid Value (mg KOH/g)	Equivalent weight
0%	23.6	4	2033
5%	31.3	2.5	1660
7%	43.8	4	1174

$$DP = 1 + \frac{2N_B}{N_A - N_B + N_C}$$

When fraction of conversion=1

DP: degree of polymerization
N_A: moles of diols
N_B: moles of diacids
N_C: moles of mono-alcohols

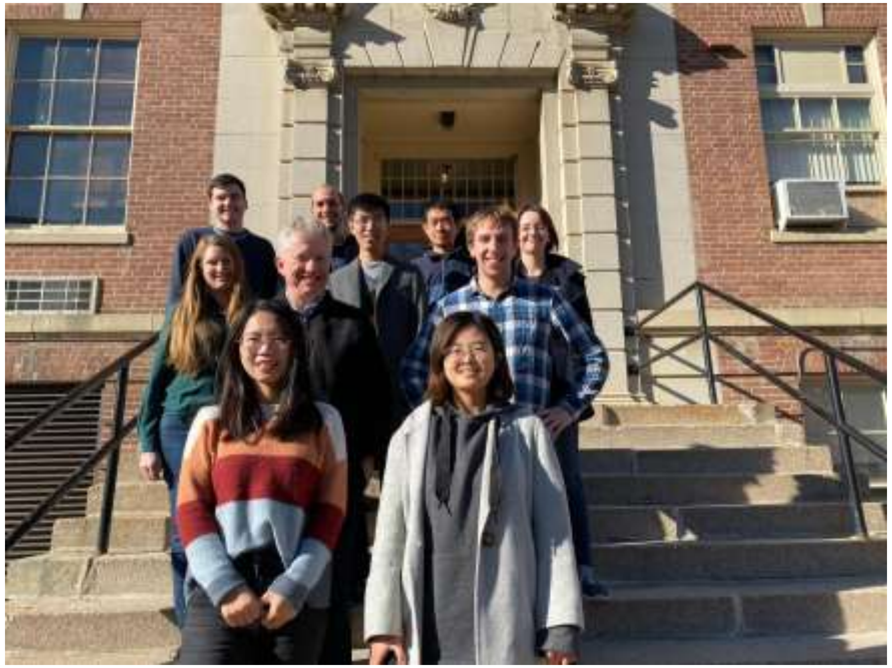
Pyran is scaling up biobased 1,5-PDO production

- Producing 10 tons of 1,5-PDO by quarter 1 of 2022
- This material will be available to potential partners
- Pyran looking for partners to continue to evaluate 1,5-PDO in polymer applications

Conclusions

- Renewable and highly pure (>98%) 1,5-PDO is successfully produced from biobased furfural.
- Biobased 1,5-PDO containing coatings have projected lower cost than incumbent 1,6-HDO or 1,5-PDO containing coatings.
- Renewable 1,5-PDO based coatings have similar properties to incumbent 1,6-HDO petroleum-based coatings.
- Impurities in biobased 1,5-PDO do not impact the polyol properties.
- 1,5-PDO can replace 1,6-HDO in coating applications.

Acknowledgments



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Thanks for listening!