Emery Oleochemicals

Advantages of Azelate-Based Polyester Polyols and Their Performance Benefits in Model Polyurethane Coatings

Eric Geiger, Technical Director

Ep Eco-Friendly Polyols

Overview

- Background
  - Azelate (C_9 Diacid) and Dimerate (C_{36} Diacid) Polyols
  - Odd-Even Effect and Influence on Properties
  - Production Process and Performance Benefits

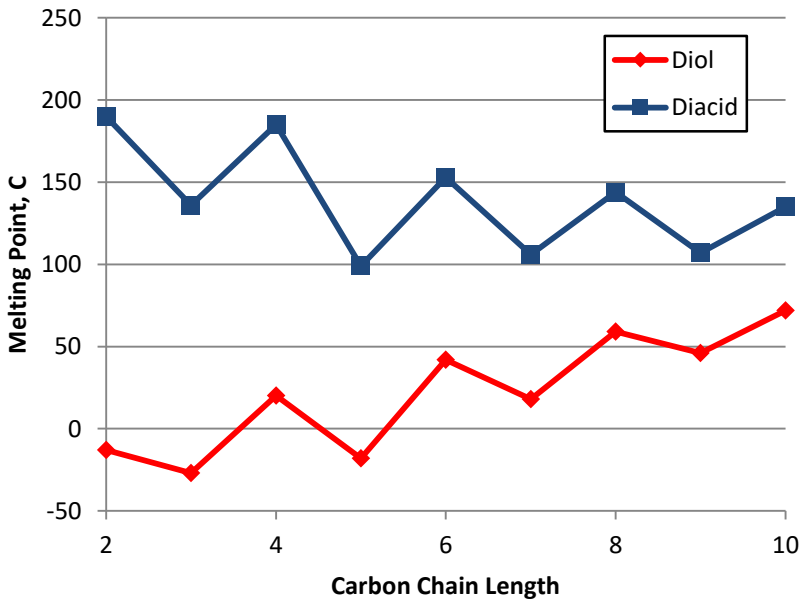
- Polyols for CASE Applications
  - Product Overview – Commercial and Experimental
  - Structure-Property Relationships
  - Model Formulation Comparisons
  - Performance Properties Achieved For Model Formulations

- Conclusions

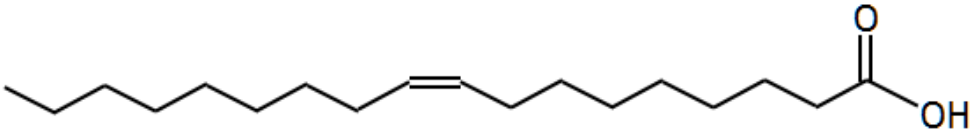
Background

- Aliphatic polyester polyol for PU most commonly based on adipic acid (C_6 diacid)
  - Petrochemical based, known to form lactone, high NOx emissions
  - No significant manufacturer using renewable feedstock
- Limited options for commercial aliphatic diacids
  - Succinic (C_4), Sebacic (C_{10})
  - Azelaic (C_9)
- Capitalizing on the "odd-even" effect in polyol structure-property

Odd-Even Effect: Melting Point of Linear Diols and Diacids vs. Carbon Chain Length



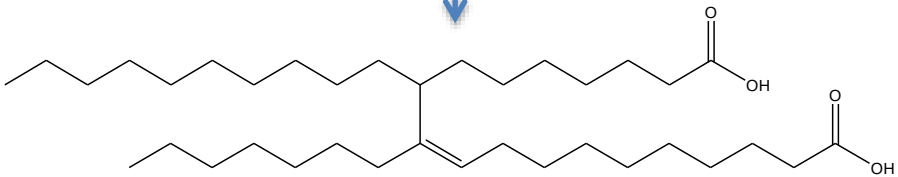
Azelaic Acid Production via Ozonolysis
Dimer Diacid Production via Addition

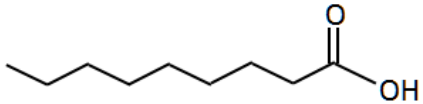


Oleic acid ($C_{18:1}$ monoacid from triglyceride)

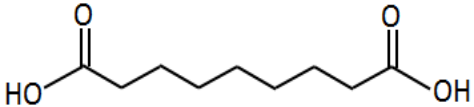
O_3, O_2

Cat, Δ





Pelargonic acid (nonanoic acid)

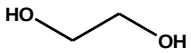


Azelaic acid (nonanedioic acid)

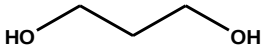
Representative structure:
Dimer diacid (C_{36} dibasic acid)

Esterification of Azelaic and Dimer Diacids

Glycols Used in Stepwise Polymerization

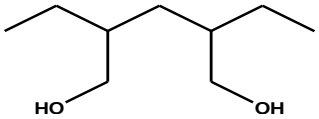


Ethylene Glycol
(EG)

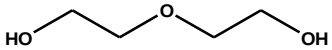


1,3-Propanediol
(PDO)

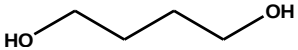
Neopentyl Glycol
(NPG)



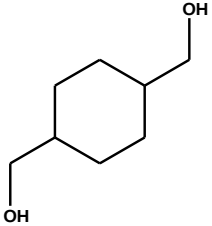
2,4-Diethyl
Pentanediol
(PD-9)



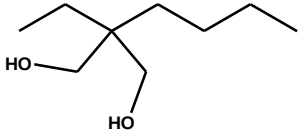
Diethylene Glycol
(DEG)



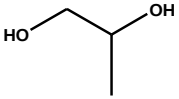
1,4-Butanediol
(BDO)



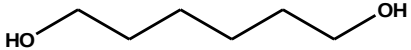
Cyclohexane
Dimethanol
(CHDM)



2-Butyl-2-Ethyl
Propanediol
(BEPD)



Propylene Glycol
(PG)



1,6-Hexanediol
(HDO)

Polyols for CASE Applications

Typical Polyol Properties

	A	B	C	D	E	F
Molecular Weight (Daltons)	320	1000	2200	2200	410	1000
Diacid Used	Azelaic (C_9)	Azelaic (C_9)	Azelaic (C_9)	Azelaic (C_9)	Azelaic (C_9)	Dimer (C_{36})
Glycol Used	EG	EG	EG	EG	Glycerol	EG
Functionality	2.0	2.0	2.0	2.0	2.7	2.2
Hydroxyl Value (mg KOH/g)	350	105	50	50	370	105
Acid Value (mg KOH/g)	1.0	1.0	1.0	1.0	1.0	1.0
Brookfield Viscosity @ 25C (cP)	310	1320	5125	n/a*	1715	2600
Glass Transition Temperature (C)	-67	-58	-51	-54	-57	-59
Bio-content (wt%)	69	78	82	82	99	90

*Waxy solid at 25C, 500 cP @ 75C

Experimental Azelate Polyols

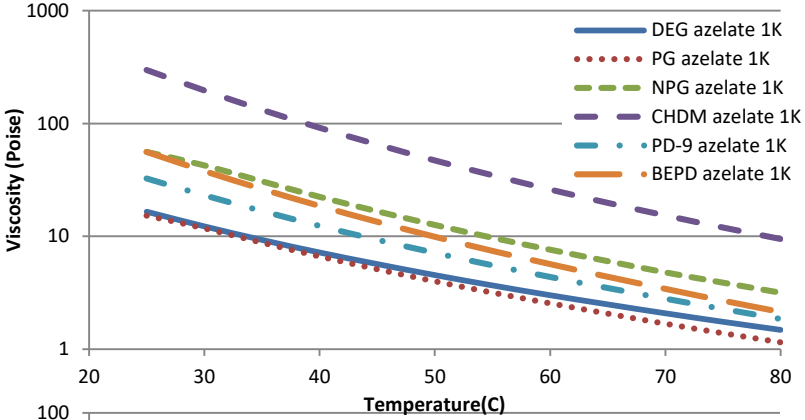
Typical Polyol Properties for 1000 MW diols

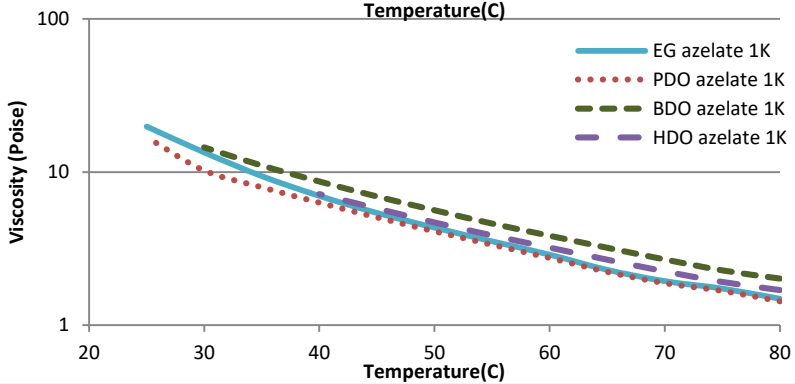
	Ethylene Glycol	Diethylene Glycol	Propylene Glycol	Propane Diol	Butane Diol	Hexane Diol	Neopentyl Glycol	Cyclo hexane Dimethanol	Diethyl Pentane Diol	Butyl Ethyl Propane Diol
Glycol Used	EG	DEG	PG	PDO	BDO	HDO	NPG	CHDM	PD-9	BEPD
Functionality	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
State @ 25C	Solid	Liquid	Liquid	Solid	Solid	Solid	Liquid	Liquid	Liquid	Liquid
Brookfield Viscosity @ 25C (cP)	n/a	1400	1500	n/a	n/a	n/a	4300	7100	2300	1900
Glass Transition Temperature (C)*	n/a	n/a	-55	-30	-45	-26	-61	n/a	n/a	n/a
Bio-content, calculated (wt%)	67	58	65	65	62	55	58	47	45	46

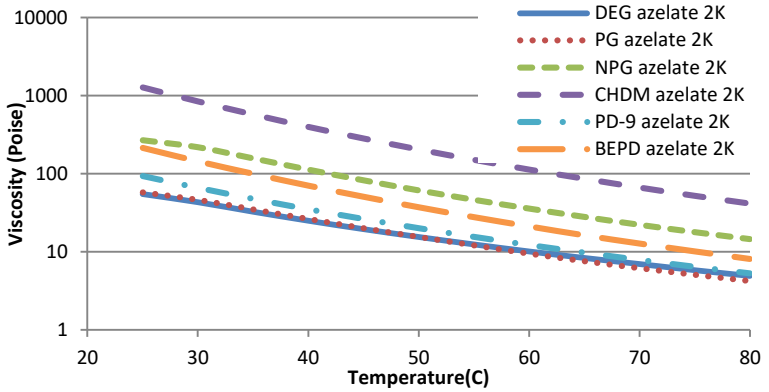
*Tg to be determined for some polyols, will be furnished upon request

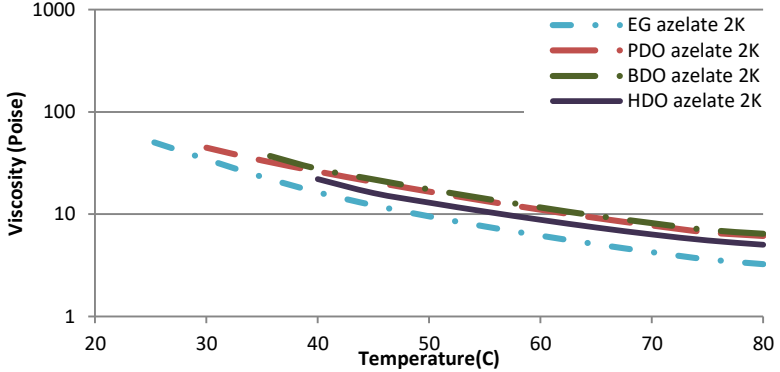
Rheology Studies Azelate Polyols

Temperature Ramp



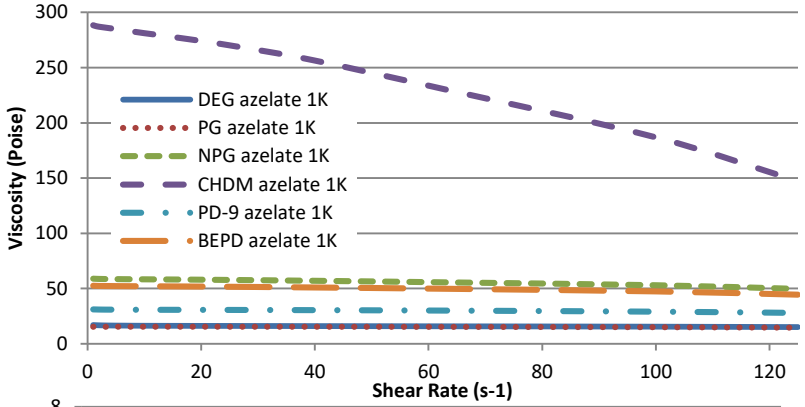


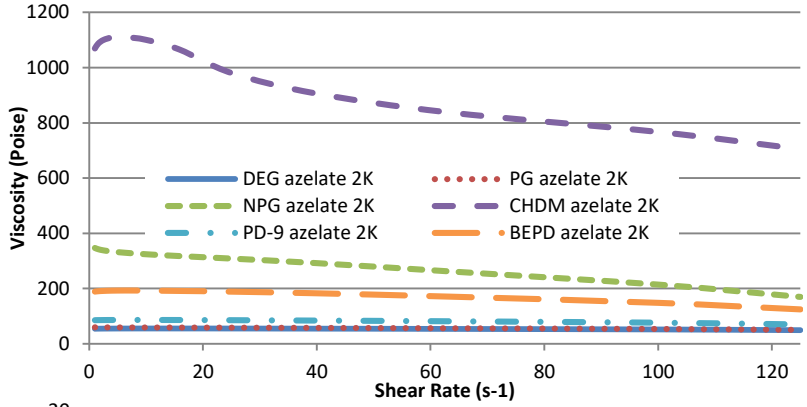


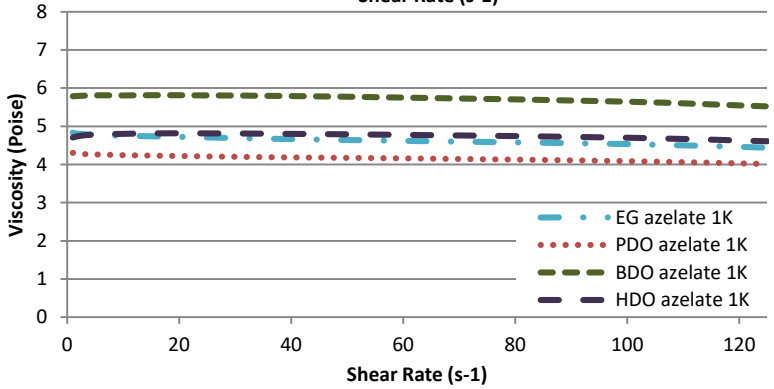


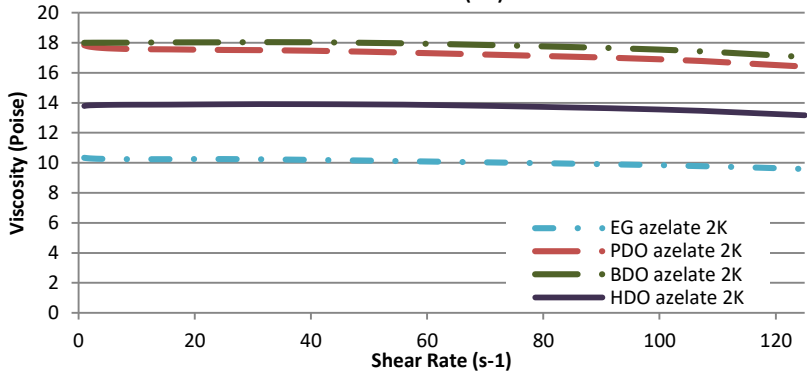
Rheology Studies Azelate Polyols

25C, 50C Shear Sweep





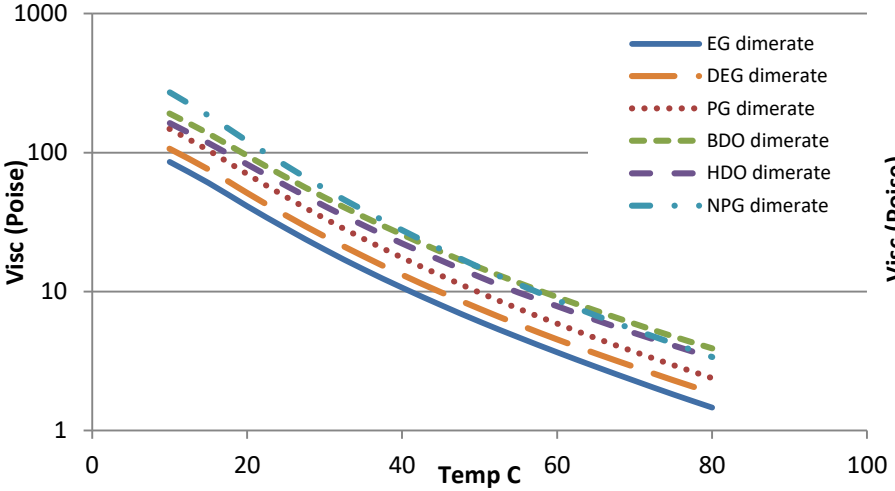


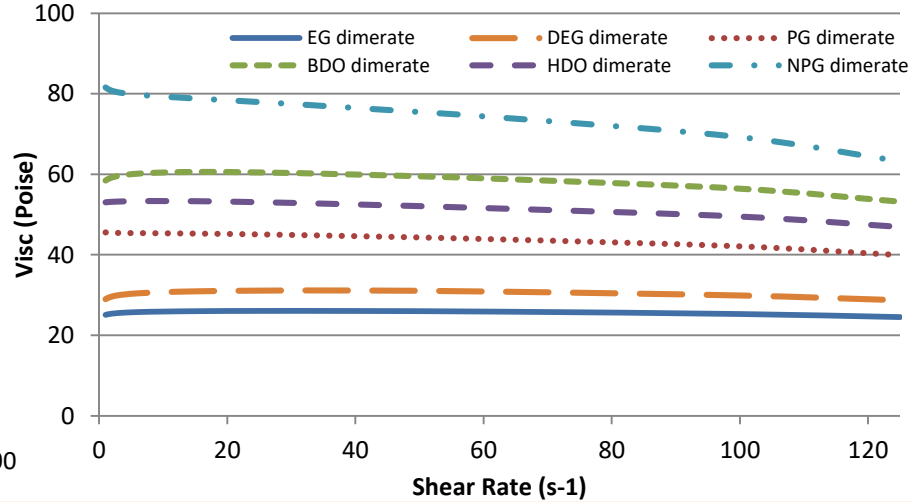


Rheology Studies Dimerate Polyols

Shear Sweep and Temperature Ramp 1000 MW Polyols

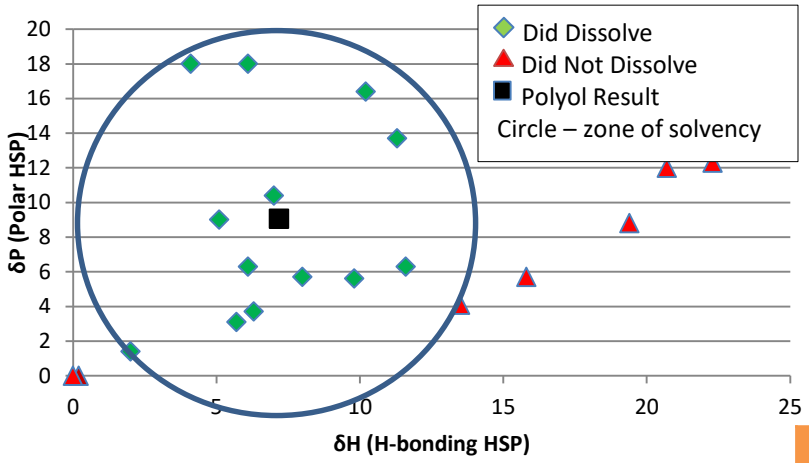
- Viscosity less dependent on glycol used than seen in azelates
- Viscosity trends up as glycol chain length increases
- NPG shows more shear thinning than others
- All dimerates are liquid at ambient





Hansen Solubility Parameters

Commercial Polyols



- B, C, and D Polyols
  - Common polar aprotic solvents were successful
  - Protic solvents and aliphatic hydrocarbons were unsuccessful
- F Polyol
  - Lower polarity due to dimer structure
  - Slightly higher H-bonding due to higher functionality
- A and E Polyols
  - Show more polar and hydrogen-bonding character
  - Only hydrocarbons failed to dissolve 14535 polyol
  - 14637 polyol showed more complex behavior, and even higher polar and H-bonding character

Chemistry	Polyol	MW (Dalton)	δ_D	δ_P	δ_H	R_0
EG Azelate	B	1000	17.0	9.0	7.2	8.0
EG Azelate	C	2200	17.0	9.0	7.2	8.0
EG Azelate	D	2200	17.0	9.0	7.2	8.0
EG Azelate	A	320	16.7	9.4	10.8	13.1
GLY Azelate	E	410	16.6	9.9	11.4	8.0
EG Dimerate	F	1000	16.7	5.8	7.9	8.9

Hansen Solubility Parameters

Experimental Azelate and Dimerate 1000 MW Polyols

Chemistry	δ_D	δ_P	δ_H	R_0
EG Azelate	17.0	9.0	7.2	8.0
DEG Azelate	16.8	9.2	9.0	7.6
PG Azelate	16.7	8.7	9.7	11.5
PDO Azelate	16.6	7.7	6.7	7.7
BDO Azelate	16.9	8.5	8.2	11.2
HDO Azelate	16.6	6.9	6.6	9.4
NPG Azelate	16.7	8.7	9.7	11.5

Chemistry	δ_D	δ_P	δ_H	R_0
EG Dimerate	16.7	5.8	7.9	8.9
DEG Dimerate	n/a	n/a	n/a	n/a
PG Dimerate	16.6	5.1	7.6	9.0
BDO Dimerate	16.7	4.6	7.6	9.8
HDO Dimerate	n/a	n/a	n/a	n/a
NPG Dimerate	16.5	4.7	7.0	10.0

➢ Experimental Azelate Polyols

- EG azelate (experimental) results identical to commercial 1K, 2K polyols
- DEG azelate: alcohols successful
- PG and NPG azelate: alcohols successful, unsuccessful only in aliphatic hydrocarbon and DEG
- BDO azelate: larger HSP and R_0 values than expected, may be due to odd-even effect
- HDO azelate: cyclohexane successful

➢ Experimental Dimerate Polyols

- Dimerate results close to one another, less dependent on glycol used
- EG dimerate successful in DMF, other dimerates not
- BDO dimerate: unsuccessful in acetone
- NPG dimerate: hexane successful

Formulation of Azelate Polyols

Coatings Based on Model Formulations

- Simple model formulas to demonstrate polyol comparisons
  - 2K PU formulas, unpigmented/unfilled
  - Target similar formulations for each polyol chemistry for ease of comparison
  - Chain extend/crosslink with amine tetrol
  - Cure w/ HDI trimer, 1:1 vol
  - Apply via air spray from 50% MEK, DTM ground CRS, cure 1 d @ 70C

- Basic coating characteristics compared
  - Chemical resistance
  - Weathering resistance (QUV)
  - Hydrolysis resistance (solid elastomer)
  - Water Vapor Transmission (ASTM D1653)

Model Coating Properties

Azelate vs. Alternative

- Azelate-based systems give soft, glossy coatings, transparent films, acceptable adhesion DTM, good compatibility with amine tetrol chain extender
- Azelate-based systems show large variation in gel time depending on glycol used to form azelate, improved compatibility with chain extender compared to adipate
- Finished products using azelate polyols may require less solvent for reactivity moderation (potential benefits include lower VOC or longer pot life)

	B	DEG adipate	DEG azelate	PG azelate	NPG azelate	CHDM azelate	PD-9 azelate	BEPD azelate
Gel time (hr)	0.75	0.25	4	0.75	5	0.75	2.5	1
Film quality	clear, good quality film	clear, surface drag, some phase sep	clear, good quality film	clear, good quality film	clear, good quality film	clear, good quality film	clear, good quality film	clear, good quality film
Pencil hardness	3B	2B	3B	3B	2B	F	B	B
Gloss 60°	105	99	102	101	100	105	104	104

Azelate Polyol Coating Chemical Resistance

24 Hour Spot Test

	B	DEG adipate	DEG azelate	PG azelate	NPG azelate	CHDM azelate	PD-9 azelate	BEPD azelate
Acetic acid, glacial	G	NR	NR	NR	NR	NR	NR	NR
Chloroform	E	E	NR	NR	NR	E	NR	NR
DEET (Insect repellent)	G	G	G	G	G	E	G	E
Dimethylformamide	E	NR	NR	NR	NR	E	E	G
Disinfectant	E	G	G	E	E	E	E	E
Hydrochloric acid 37%	G	E	NR	G	G	NR	NR	NR
Ketchup	E	G	G	E	E	E	G	E
Methanol	E	E	E	E	E	E	E	E
Methylene chloride	G	E	NR	NR	NR	NR	NR	NR
Skydrol LD-4	G	G	G	G	G	E	G	G
Sodium hypochlorite 8% (bleach)	E	G	E	E	G	E	E	E
Sulfuric acid 30%	G	NR	NR	E	E	E	E	E
Sunscreen lotion	G	G	G	G	G	E	G	E
Vinegar	G	G	G	G	G	E	G	E

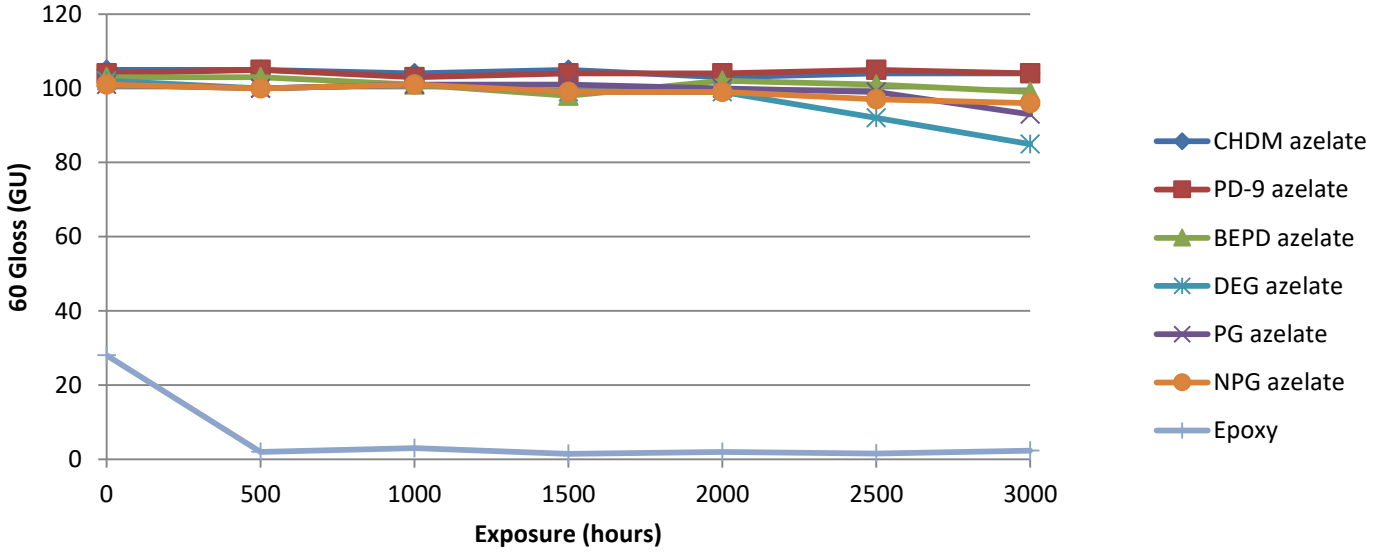
E = Excellent
G = Good
NR = Not recommended

- 32 different individual chemicals or substances used for this testing included
  - Acids & Bases
  - Polar aprotic solvents
  - Hydrocarbons
  - Polar and non-polar organics
  - Aqueous mixtures
  - Commonly encountered substances
- PU based on azelate polyols showed
  - Excellent resistance to aliphatic and aromatic hydrocarbons, glycols, water, polar aprotic solvents, bleach
  - Least differentiation against acids and chlorinated solvents
  - Strongest performance against bases
  - CHDM azelate PU notable for Skydrol

Accelerated Weathering (QUV)

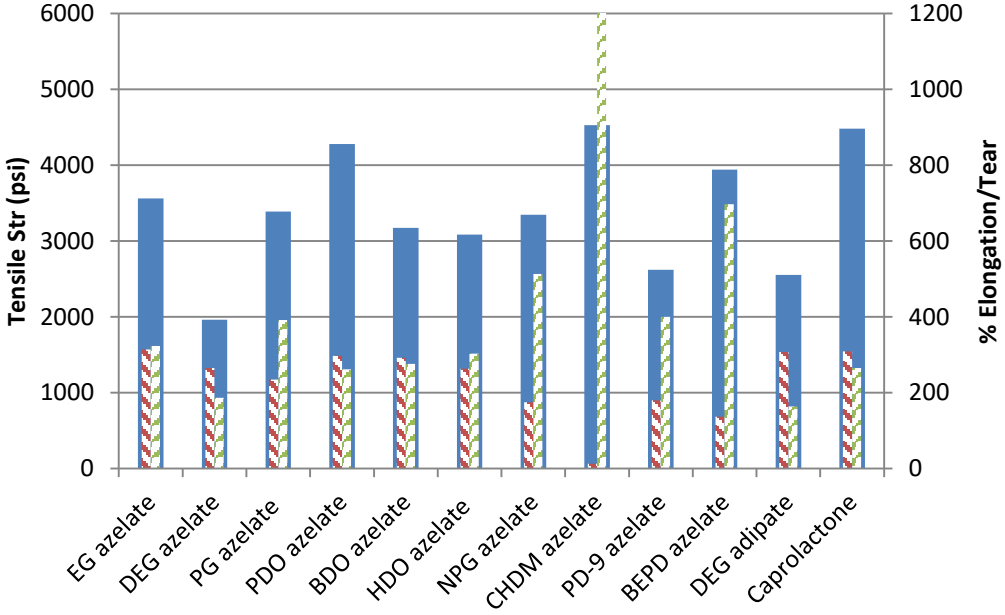
DTM Panels, evaluated at 3000 hr exposure, 500 hr intervals

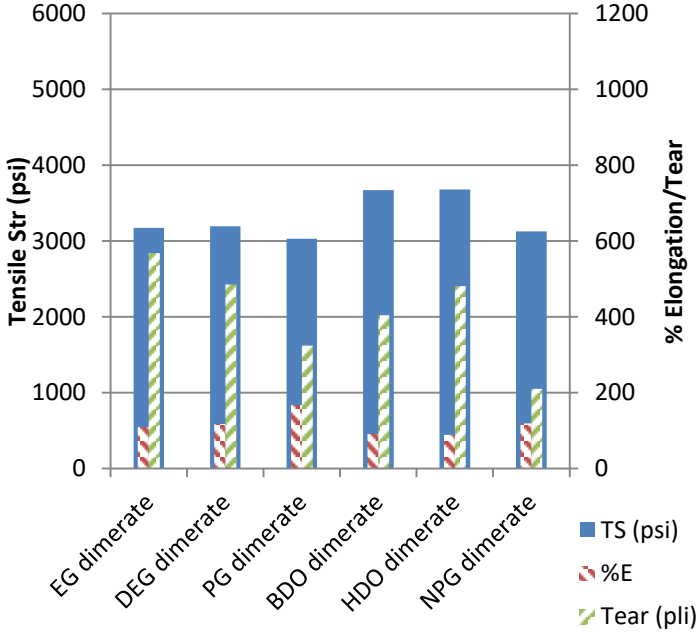
- Azelate polyol samples' gloss retention was excellent after 3000 hours. No chalking or discoloration were noted for any of the azelate polyol systems.
- Epoxy control discolored, chalked



Solid Elastomer Tensile Properties

Initial Tensile Strength, Elongation, C-Tear

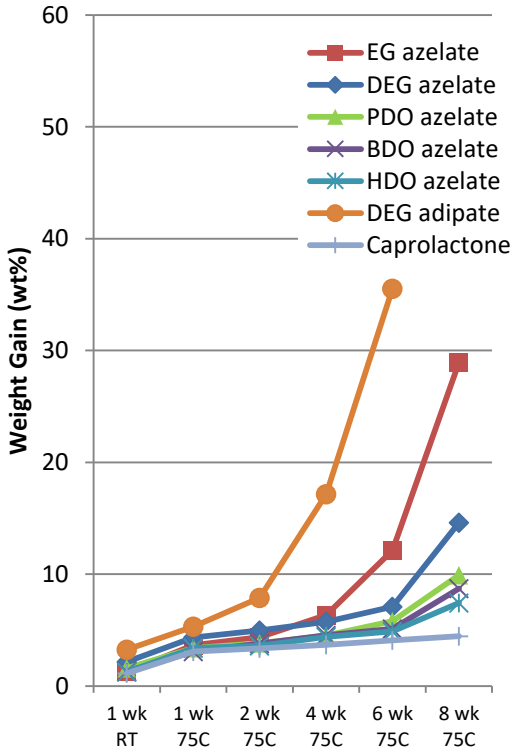


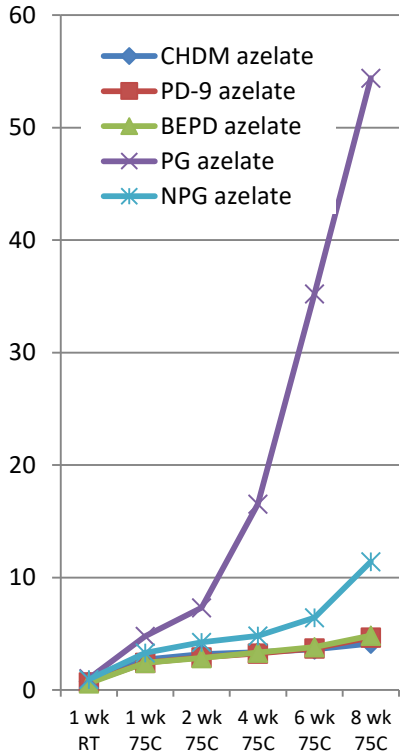


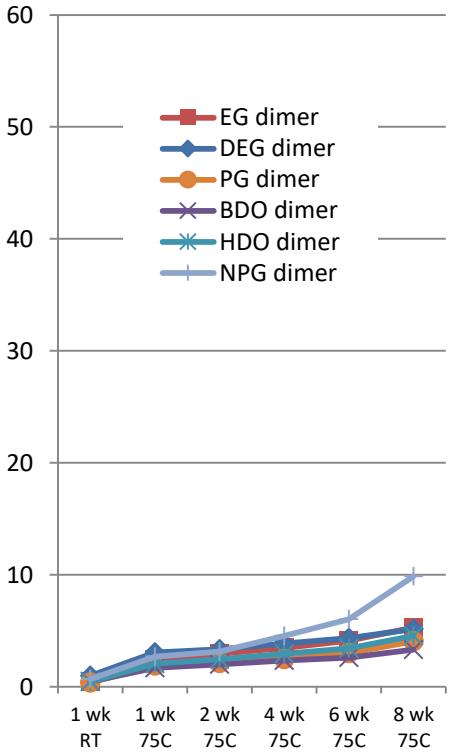
*CHDM Azelate sample tested at 2”/min, all others @ 20”/min

Solid Elastomer Hydrolysis Resistance

Water Soak 75C - Water Uptake

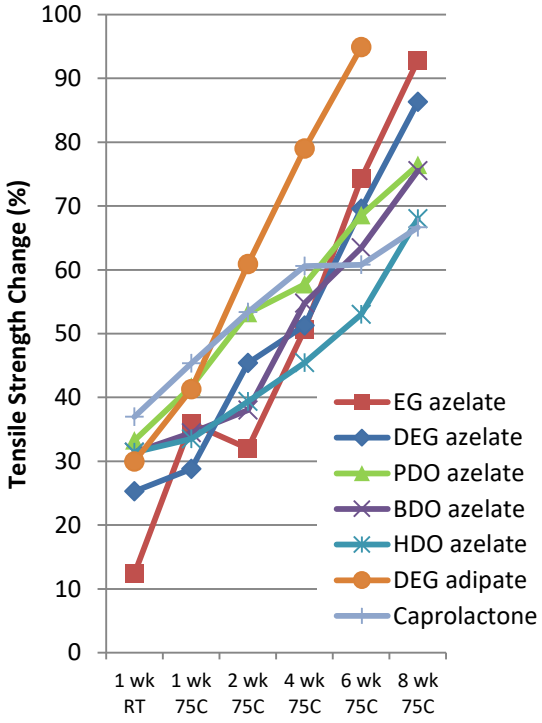


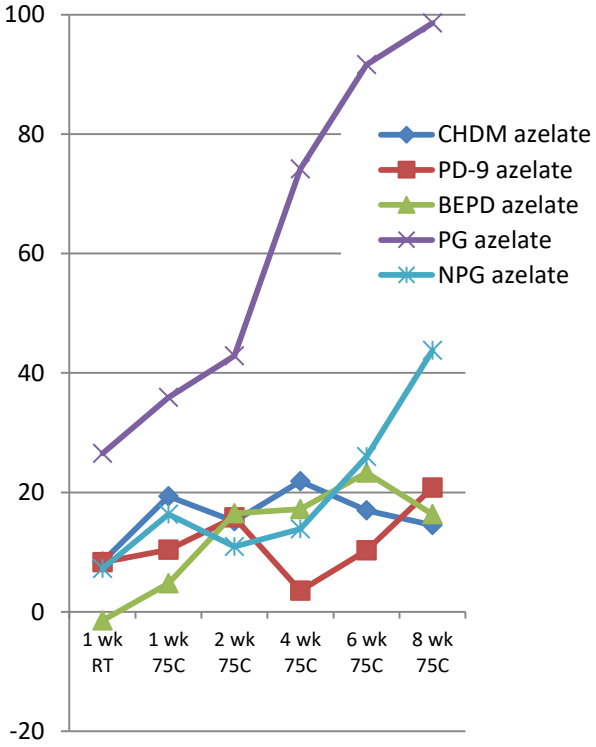


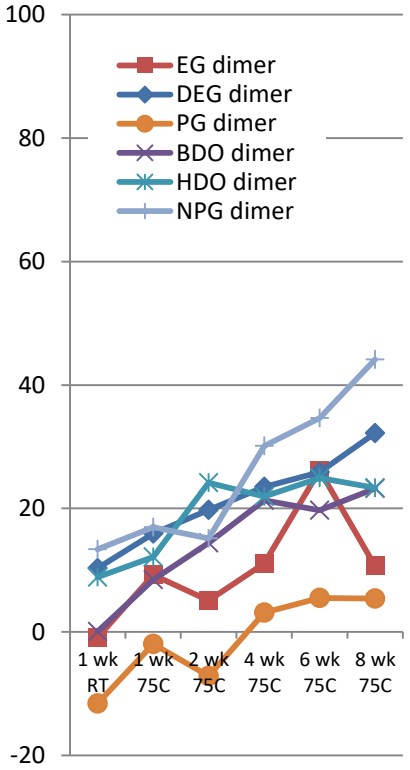


Solid Elastomer Hydrolysis Resistance

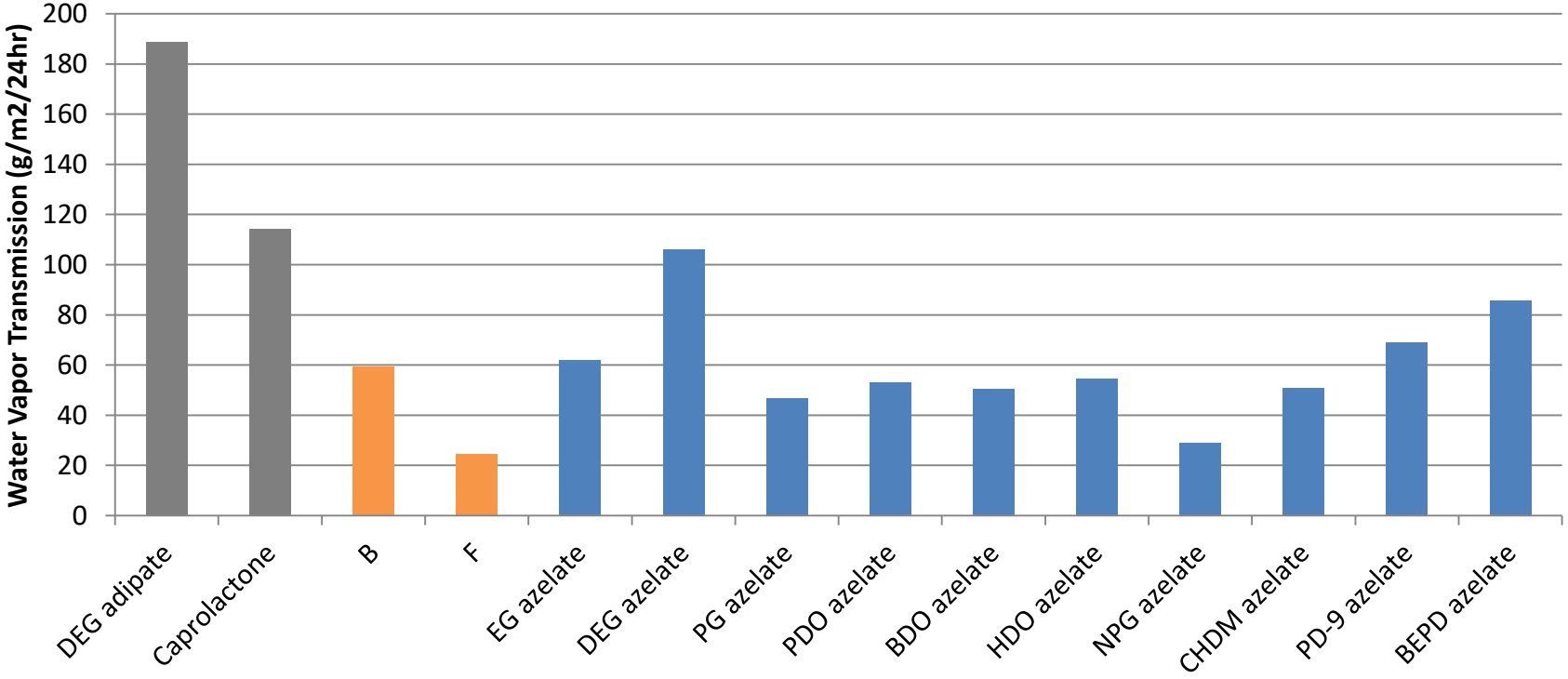
Water Soak 75C - Tensile Strength Loss







Water Vapor Transmission
ASTM D1653 Procedure B



Conclusions

- Azelate and dimerate polyol structure-property relationships
  - Choice of glycol used and how this affects polyol properties and performance
  - Compare to alternative commercial chemistry where possible

- Azelate and dimerate polyols offer application and performance benefits over alternative commercial chemistry
  - More hydrophobic and hydrolytically stable than alternative polyol
  - Versions with branched diol offer potential for high performance with improved formulation, ease of handling and use
  - Flexibility in the backbone, with very low Tg
  - Unique chemistry available in polyesters with alternative glycols
  - High renewable carbon content

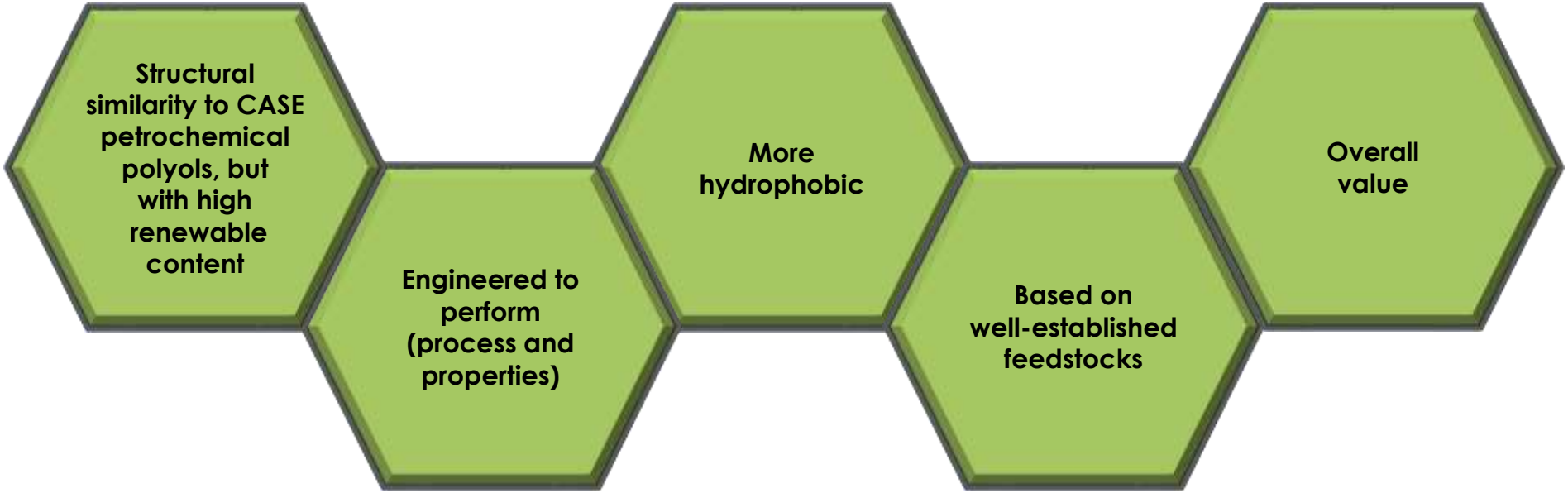
- Model formulations based on azelate and dimerate polyols offer:
  - Excellent combination of moisture, chemical and UV resistance
  - Good to excellent elastomeric properties, depending on the diol
  - Low water pick up, good retention of properties
  - Low water vapor transmission
  - High gloss

Emery Oleochemicals has commercialized azelate and dimerate polyols to meet the market demand for performance-oriented polyols that also offer the benefit of sustainability due to high renewable carbon content. Ongoing development is revealing new approaches for high-performance renewable content polyol products to meet the evolving needs of the polyurethane industry.

Renewable CASE Polyols

Performance Benefits

Unique polyol technology platform based on naturally-derived azelaic acid or dimer diacid. Produced with similar structure/method to petrochemical polyester polyols, providing a high degree of design freedom and ease of use.



THANK YOU

For more information, contact:
efp.americas@emeryoleo.com