



TECHNICAL BULLETIN

Susterra® Propanediol: A Renewable Resource for Unsaturated Polyester Resins

Opportunities for Susterra® propanediol (1,3-propanediol) in unsaturated polyester resins (UPR's) can be derived from a technical value proposition and physical / mechanical tests as presented in this study. Susterra® propanediol renewably-sourced propanediol from DuPont Tate & Lyle Bio Products is a 100-percent renewably sourced ingredient made from corn sugar. Formulation experiments led to a general recommended formulation window for Susterra® propanediol in UPR's. Less reactive resins (PA/MA = 1.5/1.0) may be based on Susterra® propanediol alone. In resins of intermediate or high reactivity (PA/MA = 1.0/1.0 to 1.0/1.5), about 20-40 wt% 1,2-propanediol (1,2-PG) on total diol is necessary to keep the UPR/styrene products non-crystalline and shelf stable. This corresponds to a level of 10-25 wt% Susterra® propanediol in the final thermoset product. The exact level depends on the specific recipe, including types and levels of glycols and phthalic fragments. Three recipes were selected for reactivity studies (60 wt% in styrene), and physical and mechanical property testing. Two recipes have a PA/MA ratio of 1.5 (Table 1). In these two recipes, Susterra® propanediol and 1,2-PG are compared directly (UPR-Susterra® propanediol) and (UPR-1,2-PG). A third recipe (UPR-80/20 mix) is more reactive (PA/MA = 1) and contains a mixture of diols (Susterra® propanediol/1,2-PG = 8/2). Complimentary properties of these three recipes point towards unique opportunities and applications of Susterra® propanediol, and are summarized as follows:

Processing of UPR's: Susterra® Propanediol vs. 1,2-PG

- The higher boiling point of Susterra® propanediol gives production benefits such as shorter batch times or less loss of glycol.
- Susterra® propanediol slows down the viscosity build of the UPR polymer during synthesis.
- Susterra® propanediol decreases the isomerization rate of maleic units in the UPR. This effect is amended by additives or procedural optimizations. Thus, negative impact on end-use properties (e.g.; hydrolytic stability) is prevented.
- Susterra® propanediol lowers the glass transition T_g of the non-cross linked UPR to a value well below room temperature, rendering the Susterra® propanediol based UPR sticky, rather than glassy.
- No differences in viscosity have been observed between UPR's based on Susterra® propanediol or 1,2-PG at 60 wt% in methylcellosolve or styrene.
- Susterra® propanediol slightly reduces the SPI gel and cure times and increases the peak exotherm. End-use properties of UPR's: Susterra® propanediol and 1,2-PG
- Susterra® propanediol gives cross linked UPR casts that are colorless (no yellowing observed) and clear.

- The glass transitions (T_g's) of Susterra® propanediol and 1,2-PG based UPR's are similar. However, 1,2-PG containing UPR's show a small melt transition, absent in UPR Susterra® propanediol.
- No differences in the Barcol hardness of UPR-1,2-PG, Susterra® propanediol, and -80/20 mix were observed
- Susterra® propanediol lowers the heat deflection temperature of a UPR/styrene thermoset.
- Susterra® propanediol lowers the tensile modulus, while corresponding thermosets show higher values for tensile strength and elongation.
- Similarly, Susterra® propanediol lowers the flexural modulus, while a higher value for flexural strength is obtained.
- Susterra® propanediol lowers the compressive strength of a UPR/styrene material.
- Susterra® propanediol slightly decreases the stiffness and increases the flexibility of a cross linked UPR without being detrimental to other mechanical properties.

Property	Unit	UPR Description		
		UPR-1,2-PG	UPR-Susterra® Propanediol	UPR-80/20 Mix
Recipe				
PA	mole %	1.2	1.2	1
MA	mole %	0.8	0.8	1
Susterra® Propanediol	mole %	0	2.2	1.76
PG	mole %	2.2	0	0.44
Analysis				
Acid number	mg _{koh} /g	12	10	11
Molecular weight M _n	g/ mol	2,285	2,554	4,572
Molecular weight M _w	g/ mol	8,094	9,454	15,088
Polydispersity DP		3.5	3.7	3.3
Isomerization	%	96	91	90
Glass transition T _g of UPR	°C	33	0.25	6.9
Viscosity, 60 wt% in methylcellosolve	cP	366 ± 2.7	375 ± 2.2	774 ± 5.4
Reactivity at 60 wt% in styrene				
Solid level	wt%	61	59.9	59.7
Garner Hold viscosity	-	P	P ² -Q	P-Q
Viscosity, 60 wt% in methylcellosolve	cP	316 ± 2.6	358 ± 2.5	660 ± 4.9
SPI gel time	min:sec	3:47 ± 0:08	3:39 ± 0:03	3:08 ± 0:06
SPI cure time	min:sec	3:19 ± 0:02	2:24 ± 0:04	1:45 ± 0:03
SPI total time	min:sec	7:06 ± 0:08	6:03 ± 0:01	4:53 ± 0:03
SPI exotherm	°C	195.1 ± 2.1	215.2 ± 0.2	230.6 ± 0.6

Table 1 Overview of UPR Processing Properties

Property	Unit	UPR Description		
		UPR-1,2-PG	UPR-Susterra® Propanediol	UPR-80/20 Mix
Recipe				
PA	mole eq.	1.2	1.2	1
MA	mole eq.	0.8	0.8	1
Susterra® Propanediol	mole eq.	0	2.2	1.76
PG	mole eq.	2.2	0	0.44
Physical Properties (cross linked at 60 wt% with styrene using 1 wt% BPO crystals)				
Yellowness index YI	-	5.97 ± 0.10	1.61 ± 0.10	2.10 ± 0.16
mp and ΔH	°C, J/g	-44.1, 0.090	none observed	-45.0, 0.087
Glass transition T _g	°C	-19.7, 86.3	-19.3, 85.1	-19.4, 110.8
Mechanical Properties (cross linked at 60 wt% with styrene using 1 wt% BPO crystals)				
Bar col hardness	-	64.9 ± 1.5	63.8 ± 1.8	65.0 ± 1.4
Heat deflection temperature	°C	75.2 ± 0.42	67.2 ± 0.90	91.4 ± 0.71
Tensile strength	MPa*	44.4 ± 2.8	70.0 ± 2.2	50.7 ± 5.9
Tensile modulus	MPa*	3,866 ± 341	3,223 ± 282	3,810 ± 200
Elongation	%	1.21 ± 0.16	2.88 ± 0.20	1.57 ± 0.26
Flexural strength	MPa	67.1 ± 5.6	112.7 ± 6.5	95.9 ± 7.4
Flexural modulus	MPa	4,161 ± 164	3,548 ± 177	3,638 ± 187
Compressive strength	MPa	131.3 ± 4.2	103.7 ± 3.3	112.7 ± 1.5
Hydrolytic stability	Only preliminary experiment performed			

* Mpa = 1.45 kpsi

Table 2 Overview of UPR End-Use Properties

DuPont Tate & Lyle Bio Products is a joint venture between DuPont, a global science company, and Tate & Lyle, a world leader in corn, wheat and sugar derived ingredients. By bringing together the unrivaled track record of DuPont in the integration of biology, engineering and materials science, and the technical excellence of Tate & Lyle in fermentation of natural products, scientists and engineers from the joint venture have developed a process that uses corn instead of petroleum-based feedstocks to produce 1,3 propanediol, or Bio-PDO. DuPont Tate & Lyle Bio Products provides renewably sourced ingredients that do not compromise product performance.

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