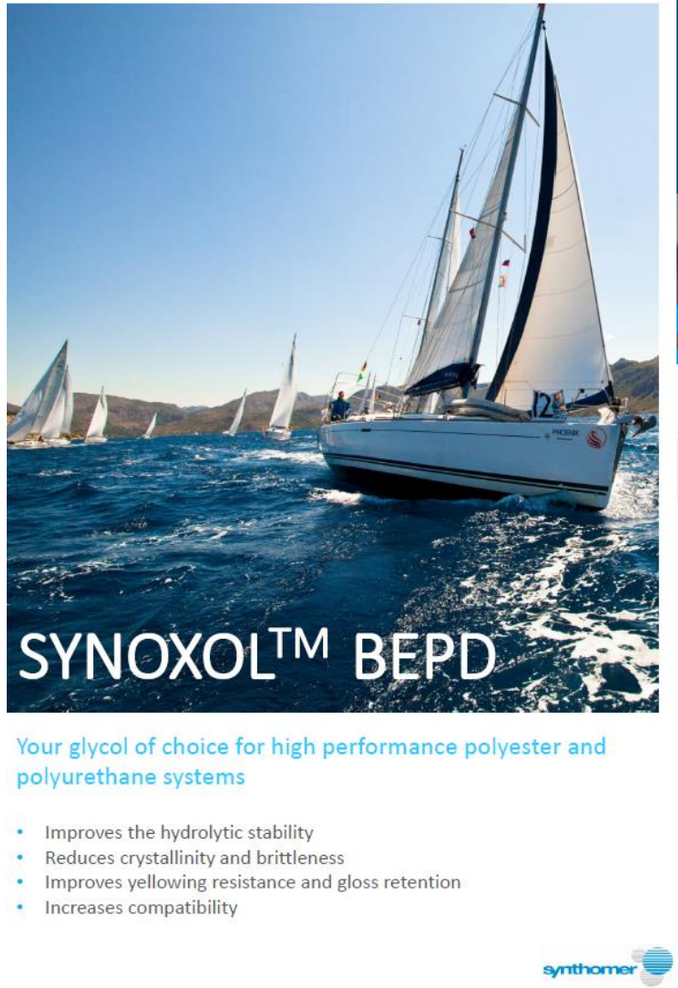
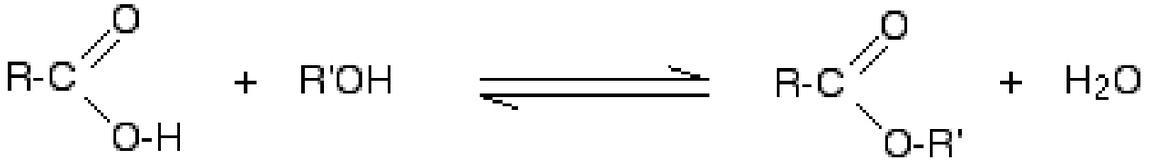
Synoxol™ BEPD in PIA based Gelcoats

Contents

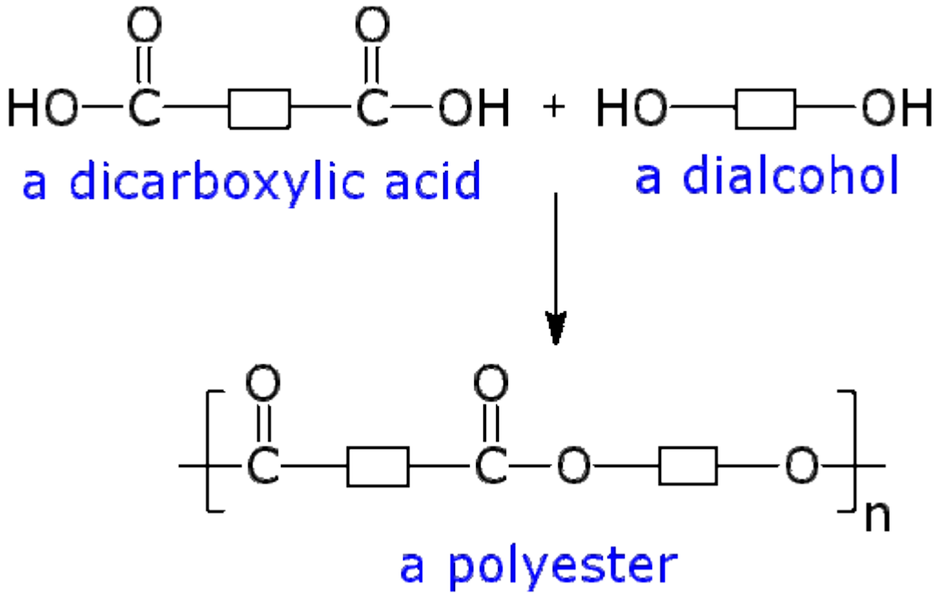


PES resin reaction

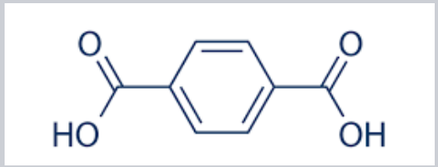
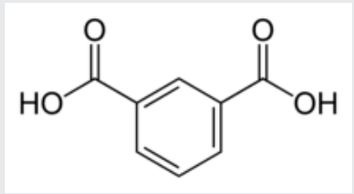
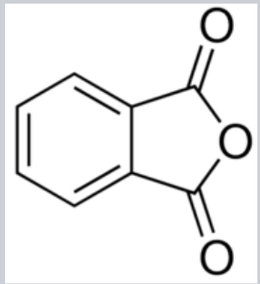
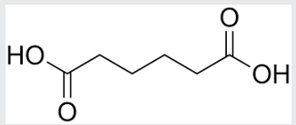
An ester is the reaction product of an acid reacted with an alcohol



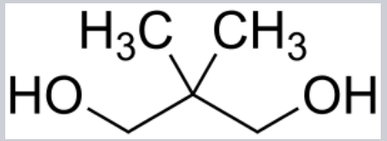
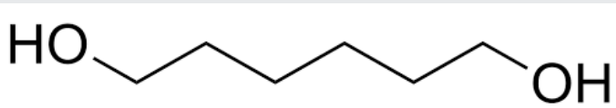
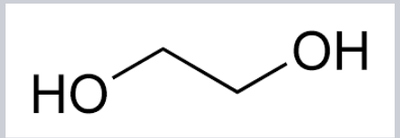
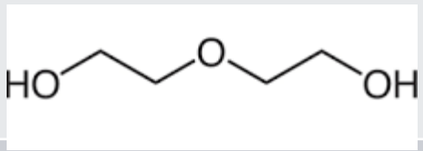
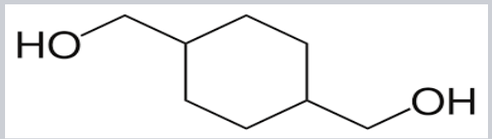
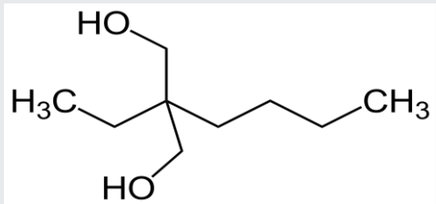
A polyester is therefore the reaction product of a diacid with a di-alcohol (otherwise known as a diol or glycol)



Typical Acid Monomers used in PES Synthesis

Full Name	AKA	Structure	Benefits
Terephthalic Acid	TPA (or PTA)		Excellent Hardness, good weathering & flexibility
Isophthalic Acid	IPA (or PIA)		Excellent Weathering & Hardness
Phthalic Anhydride	PA		Good Flexibility & hardness
Adipic Acid	ADA (or AA)		Good Flexibility, reduces viscosity

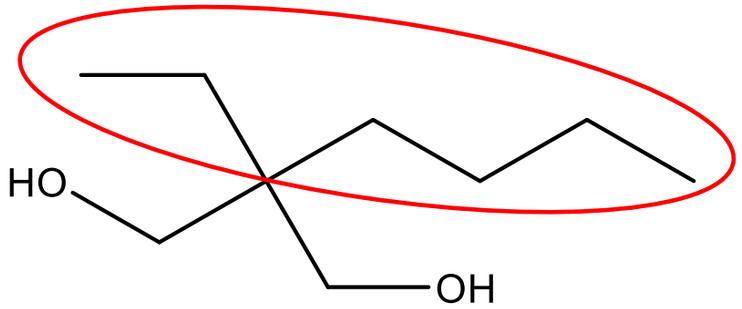
Typical Diol Monomers used in PES Synthesis

Full Name	AKA	Structure	Benefits
Neopentyl Glycol	NPG		Hardness, Weathering
1,6-hexanediol	HDO		Flexibility
Monoethylene glycol	MEG		Reduces viscosity & cost
Diethylene glycol	DEG		Reduces viscosity & cost
1,4-cyclohexane dimethanol	CHDM		Hardness
2-Butyl-2-ethyl-1,3 propanediol	Synoxol™ BEPD		Flexibility, Improved Hardness & Excellent Weathering

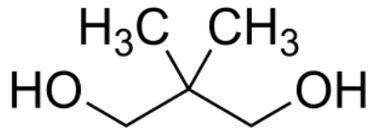
What is Synoxol™ BEPD

High performance glycol (diol) used in polyester, unsaturated polyester and polyester polyol synthesis

Structurally analogue to NPG



Synoxol™ BEPD



NPG

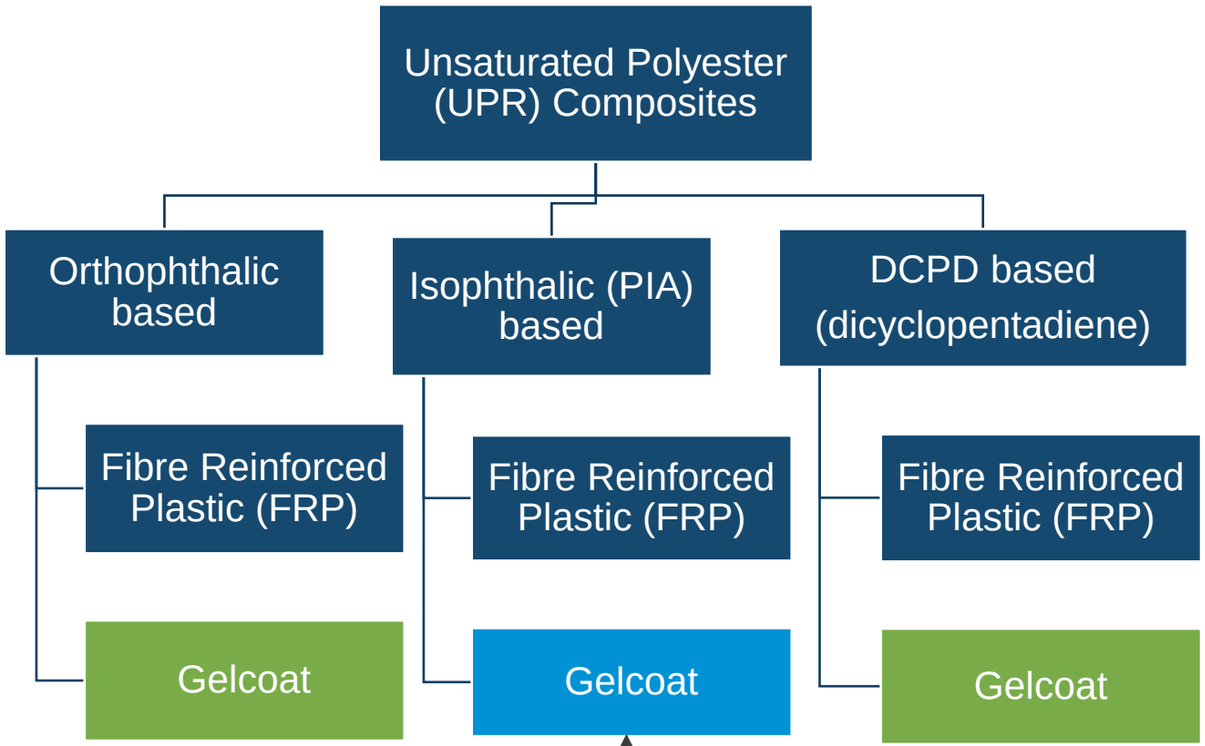
Most obvious difference between the two molecules is the increased chain length in the 2 position on the propanediol backbone

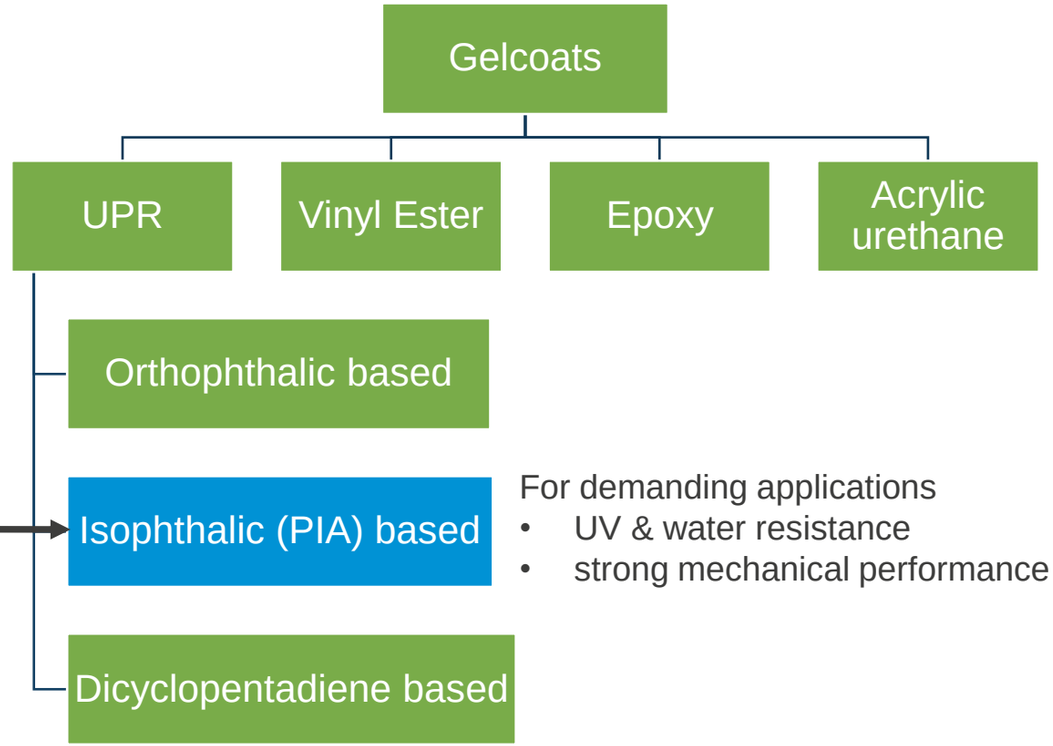
2-Butyl-2-Ethyl-1,3-Propanediol

CAS number: 25265-77-4
EC (EINECS) number: 204-1-117
HS number: 2905 39

SYNOXOL™ BEPD in PIA based Gelcoats

UPR Composites & Gelcoats by resin type





For demanding applications
- UV & water resistance
- strong mechanical performance

Synoxol™ BEPD positioned for PIA based UPR gelcoats

Target Applications



Transportation

Electrical enclosures

Engineered stone

Marble & solid surfaces

Swimming Pools

Windturbine Blades

Marine

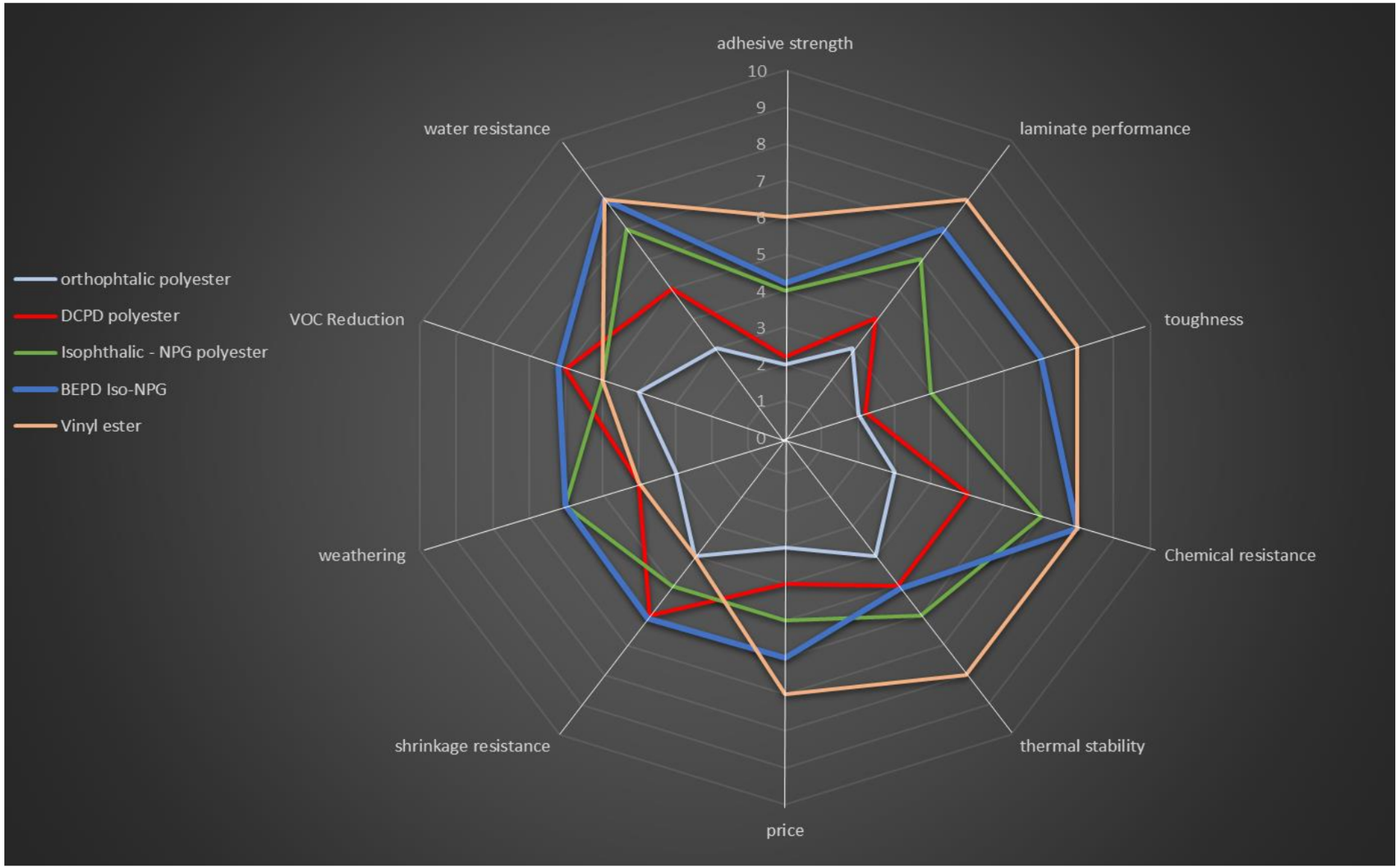

Construction

- Electrical enclosures
- Engineered stone
- Marble & solids surfaces
- Tub & Shower

Technology positioning

Synoxol™ BEPD provides:

- Excellent water resistance
- Routes to VOC reduction
- Good weathering performance
- Shrinkage reduction on par with DCPD resins



Value Propositions

Against other gelcoat technologies e.g. DCPD

- Enables formulation of **low VOC, low shrinkage gelcoats** similar to DCPD resins **without compromising** the benefits of Iso-NPG systems
- Delivers **excellent water resistance** approaching vinyl ester based gelcoats
- **Superior weatherability** compared to DCPD and Vinyl Ester systems

Against other PES gelcoats

- Up to **20% less water absorption** in comparison to isophthalic resin based benchmark consisting of NPG & other glycol blends
- Delivers **excellent aesthetics** - reduced shrinkage upon cure compared to traditional ortho & Iso-NPG gelcoats
- **15% increased weatherability** against the NPG analogue – over 1 year South Florida outdoor exposure - in isophthalic based UPRs
- **Flexural strength** improvement in isophthalic / styrene UPRs

- Presents an opportunity to formulate isophthalic based UPRs with similar aesthetics and styrene content to dicyclopentadiene (DCPD) based resins whilst preserving high durability & mechanical properties of the isophthalic resin.

SYNOXOL™BEPD reduces VOC / Styrene emissions

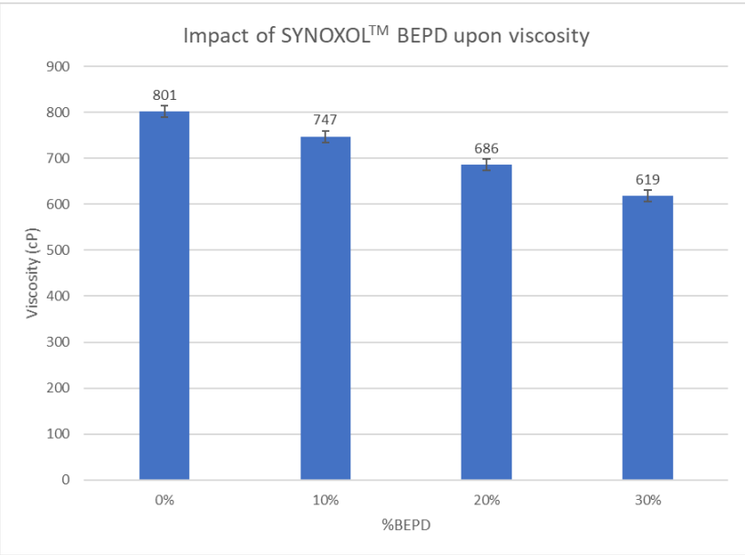
SYNOXOL™BEPD can reduce viscosity

Through replacement of NPG with SYNOXOL™ BEPD it is possible to reduce resin viscosity

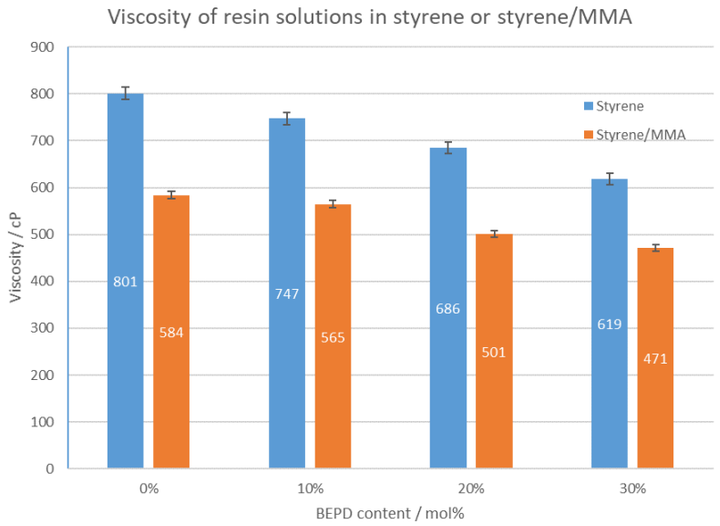
This reduction in viscosity is also observed in Styrene/ MMA blends

Additional replacement of 1,2-PG with MEG can further reduce viscosity

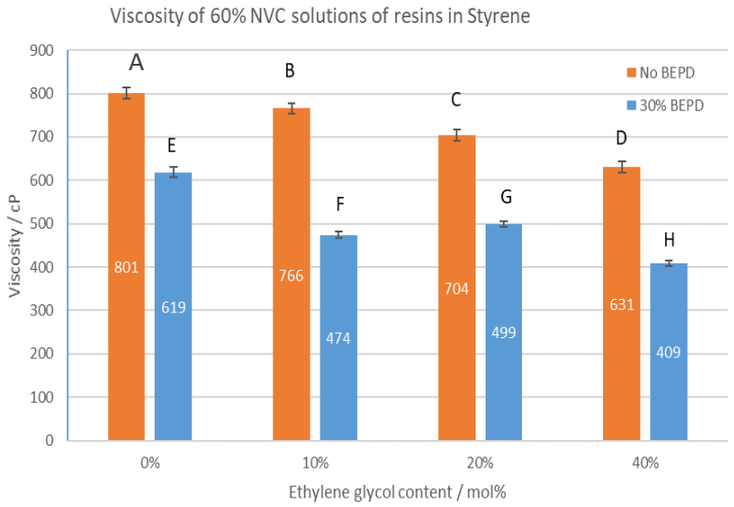
60% solids in Styrene



60% solids in Styrene and Styrene/MMA (25%/15%)

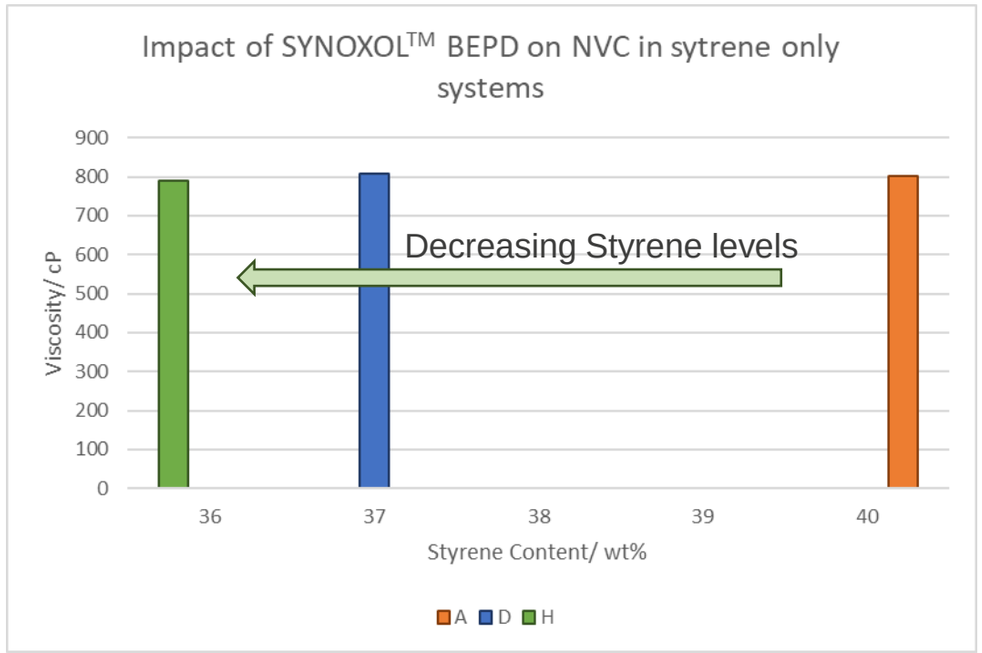


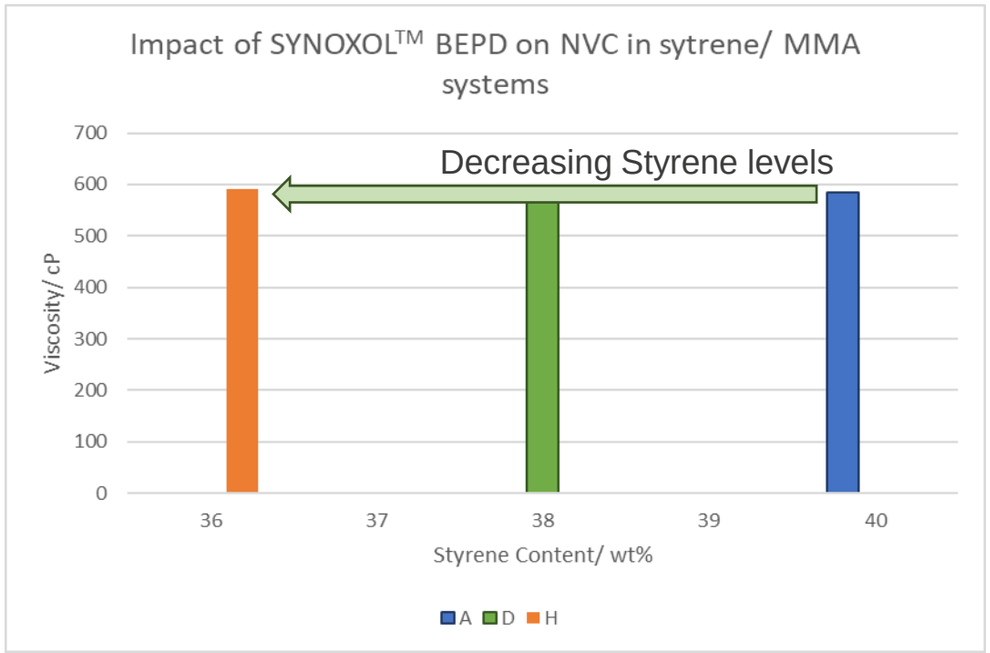
60% solids in Styrene



Lower viscosity leads to lower VOC emissions

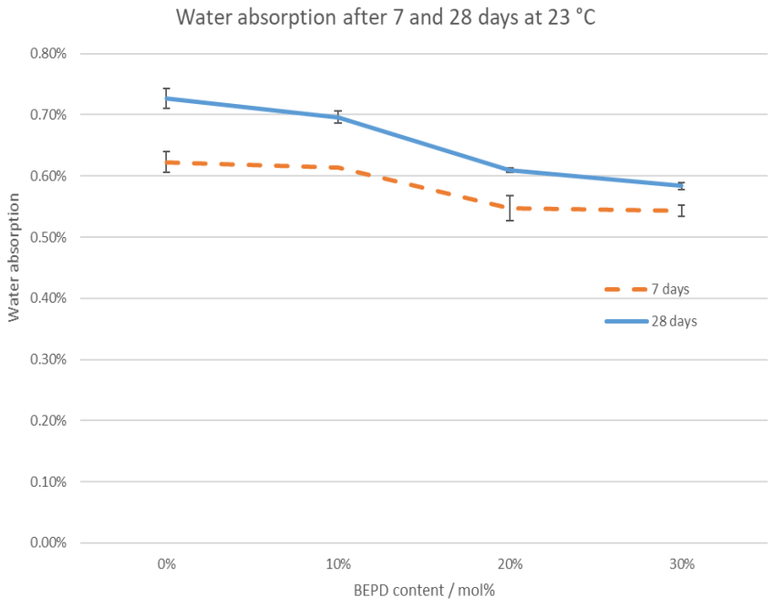
	monomers	resin/ wt %	styrene/ wt%	MMA/ wt%	Viscosity/ cP	% styrene reduction	% VOC reduction
A	0%BEPD, 0%MEG	60	40	0	801	0	0
D	30% BEPD, 0% MEG	63	37	0	809	7.5	7.5
H	30%BEPD, 40%MEG	64	36	0	790	10	10
A	0%BEPD, 0%MEG	60	25	15	584	37.5	0
D	30% BEPD, 0% MEG	62	24	14	595	40	5
H	30%BEPD, 40%MEG	64	23	13	590	42.5	10

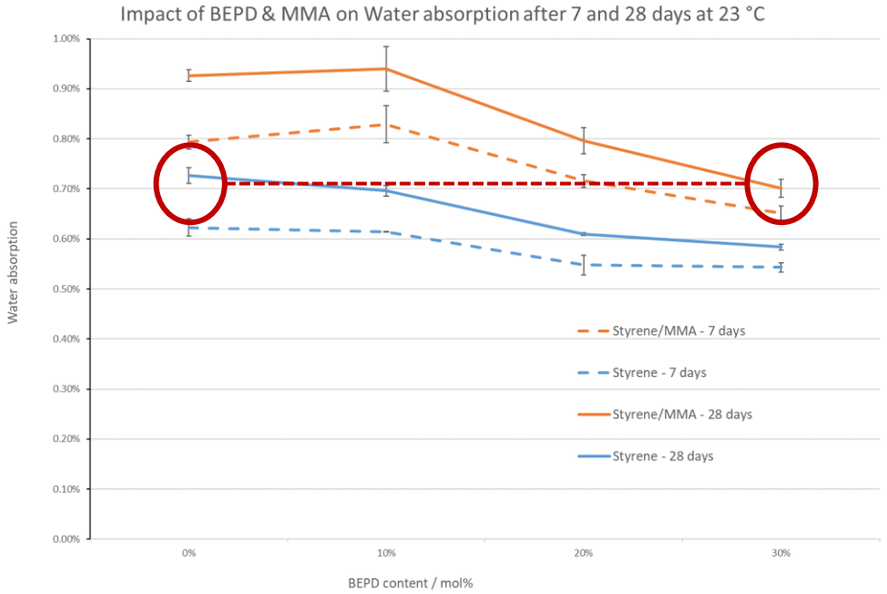


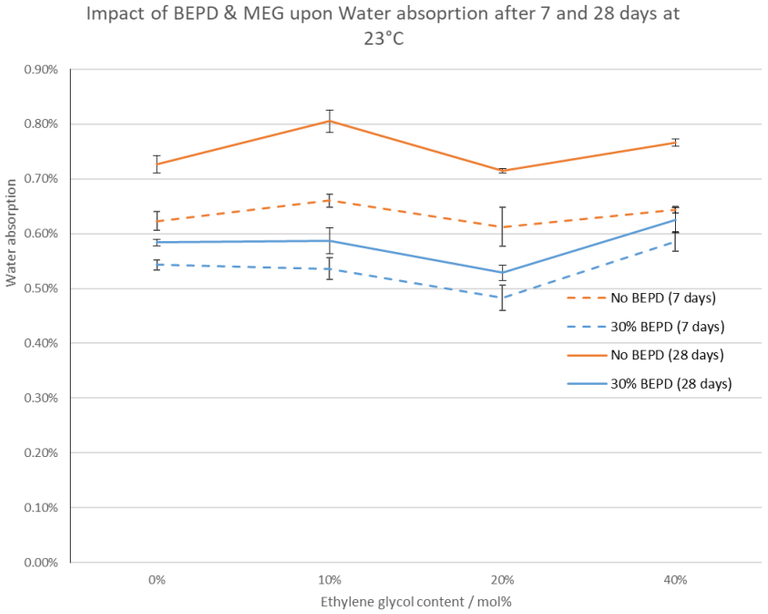


SYNOXOL™BEPD improves water resistance

SYNOXOL™ BEPD reduces water absorption







SYNOXOL™BEPD statistically proven to reduce water absorption above 20mol% addition levels

- 30 mol% SYNOXOL™ BEPD reduces water absorption by 20%
- 30mol% SYNOXOL™BEPD sufficient to mitigate water absorption increase arising from use of MMA
- Replacing 1,2-PG with MEG has zero impact to water absorption providing SYNOXOL™BEPD is used

SYNOXOL™BEPD improves aesthetics

SYNOXOL™ BEPD improves aesthetics

Addition of SYNOXOL™ BEPD leads to a statistically significant reduction in shrinkage

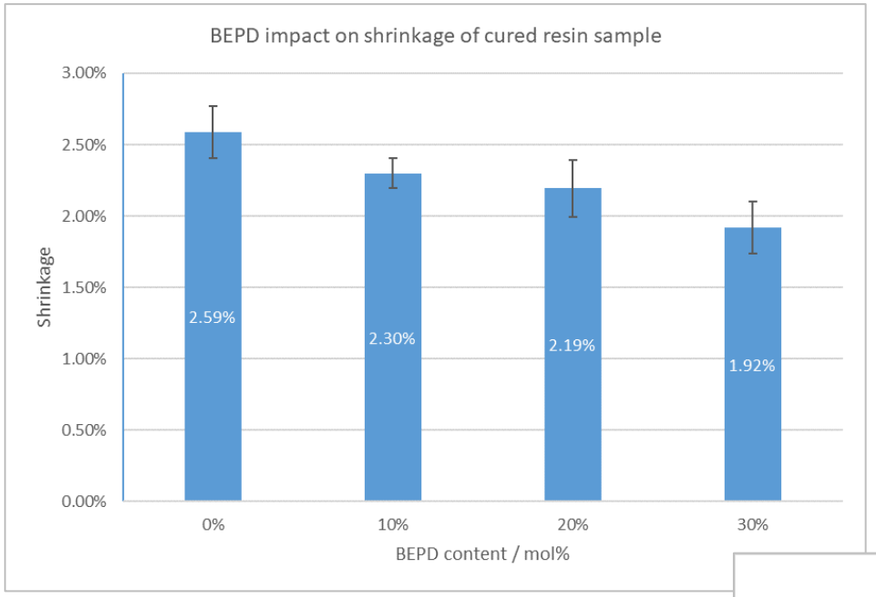
- 30mol% SYNOXOL™ BEPD results in a 25% reduction in the degree of shrinkage

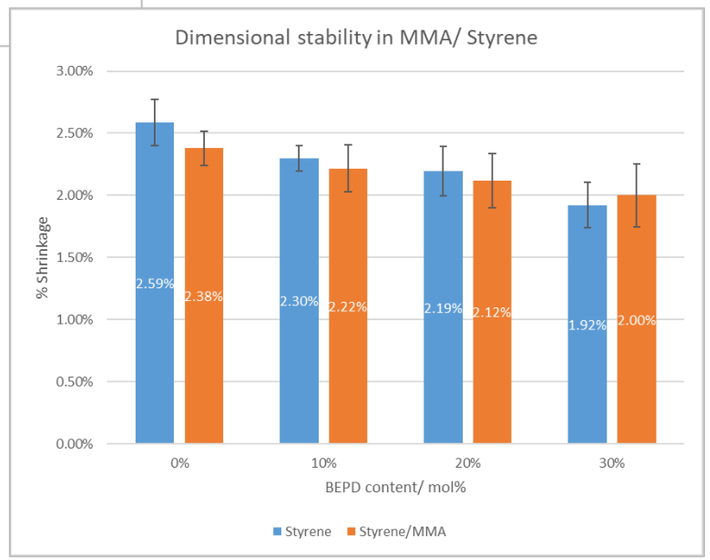
Degree of shrinkage is smaller in Styrene/MMA systems compared to Styrene only systems

- SYNOXOL™ BEPD still reduces shrinkage by 20%

Incorporation of MEG has zero impact upon SYNOXOL™ BEPD's impact on dimensional stability

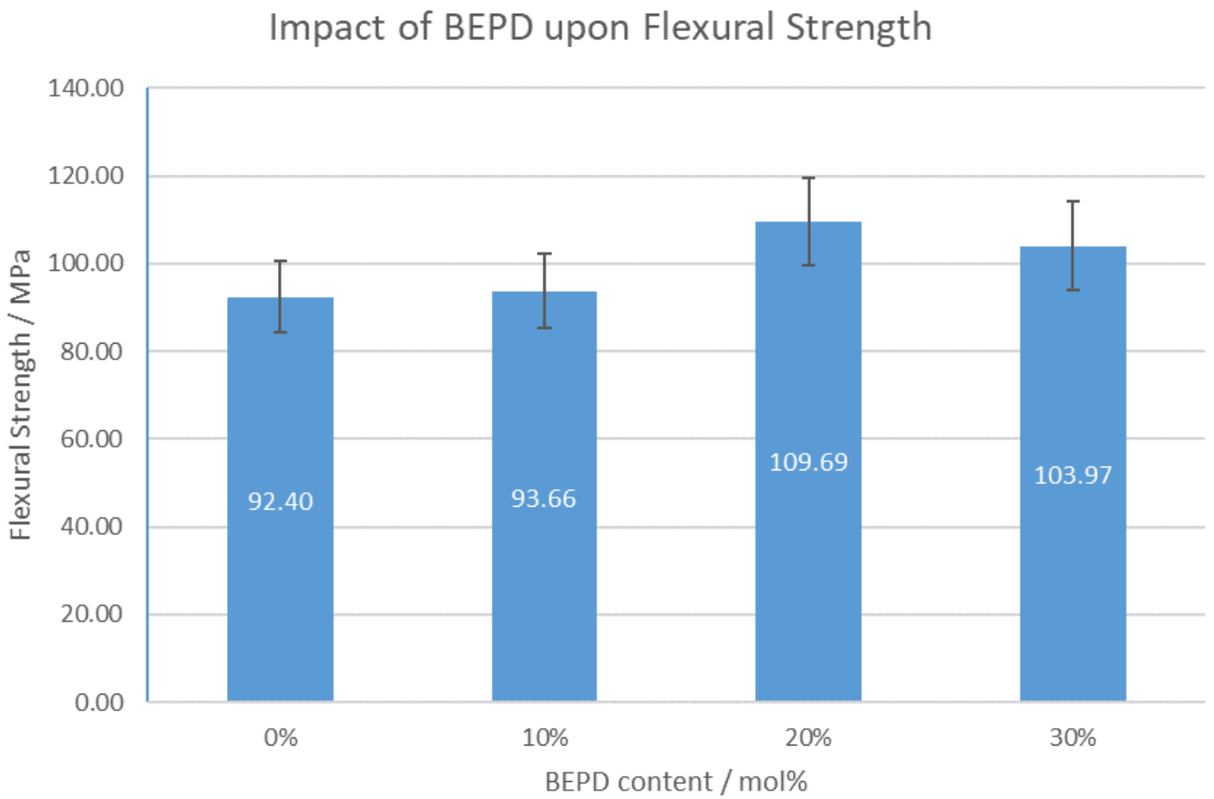
This leads to high gloss, low print-through solution even as styrene content diminishes





SYNOXOL™BEPD improves flexural strength

Synoxol™ BEPD improves Flexural strength



Replacing NPG with Synoxol™ BEPD at a level
≥ 20 mol% gives a statistically significant increase in flexural strength of 14%

No additional changes observed when tested in MMA or MEG systems

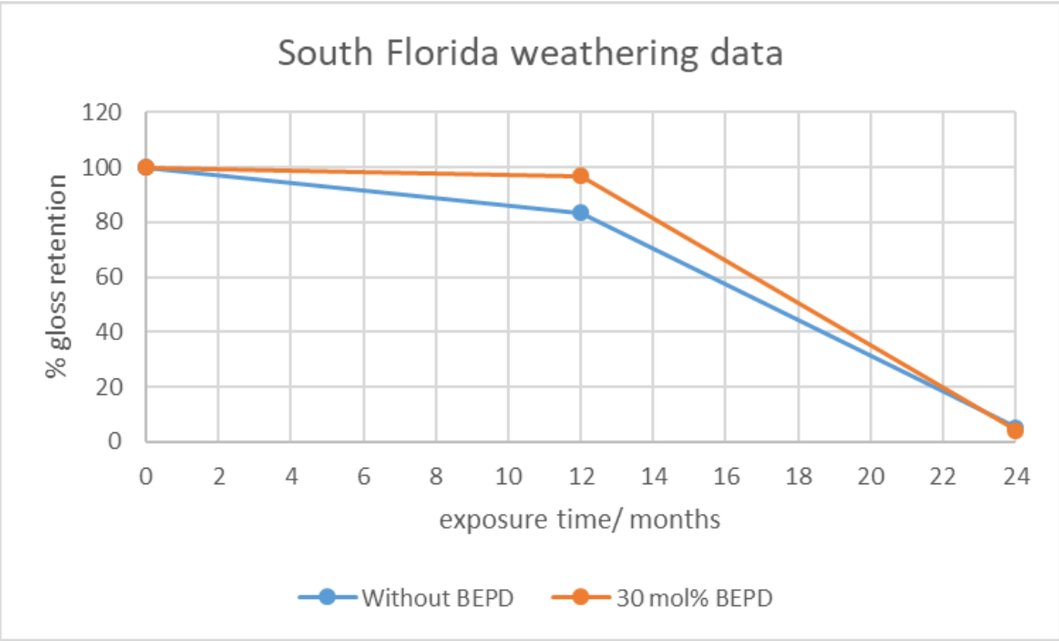
SYNOXOL™BEPD improves weatherability

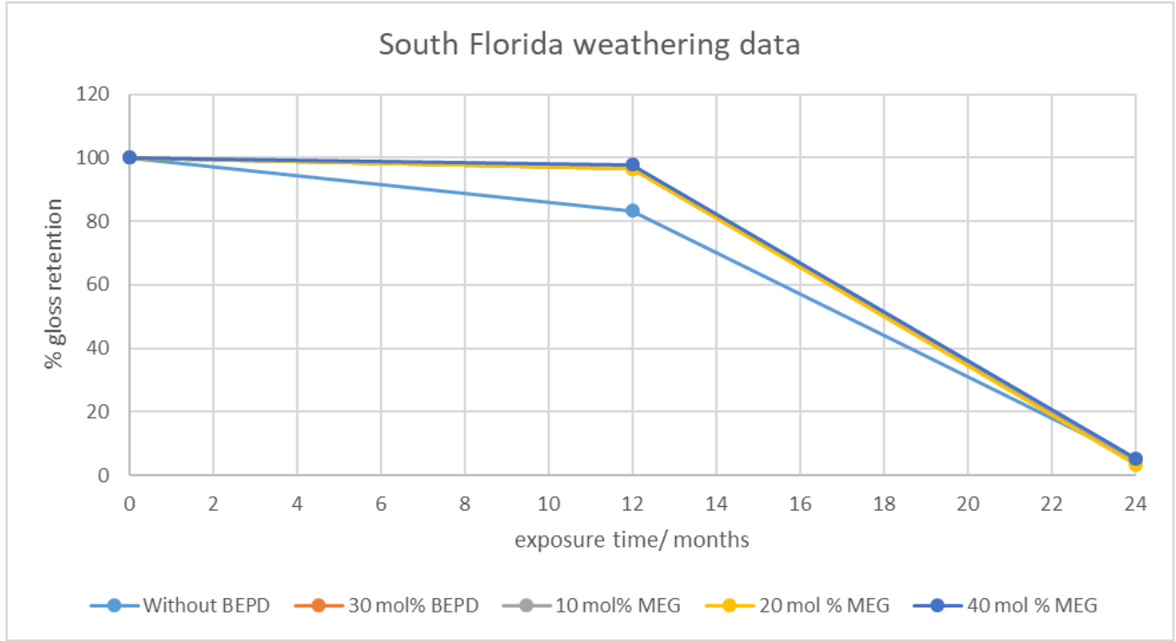
Synoxol™BEPD improves weatherability

Selected resins used to prepare gelcoats for exposure at South Florida for 24 months:

Inclusion of 30mol% BEPD lead to a 15% increase in gloss retention after 12 months of Florida exposure

Incorporation of MEG up to 40mol% leads to no negative impact in gloss retention





Summary

Replacing NPG with SYNOXOL™ BEPD allows the formulation of higher molecular weight, lower viscosity and high solubility gelcoats without any negative impact upon performance or mechanical properties.

These properties can be used to reduce Styrene emissions & overall VOC content; whilst maintaining high performance for demanding applications

Incorporating MEG can also lower the viscosity of the resin; resulting further reduction of Styrene

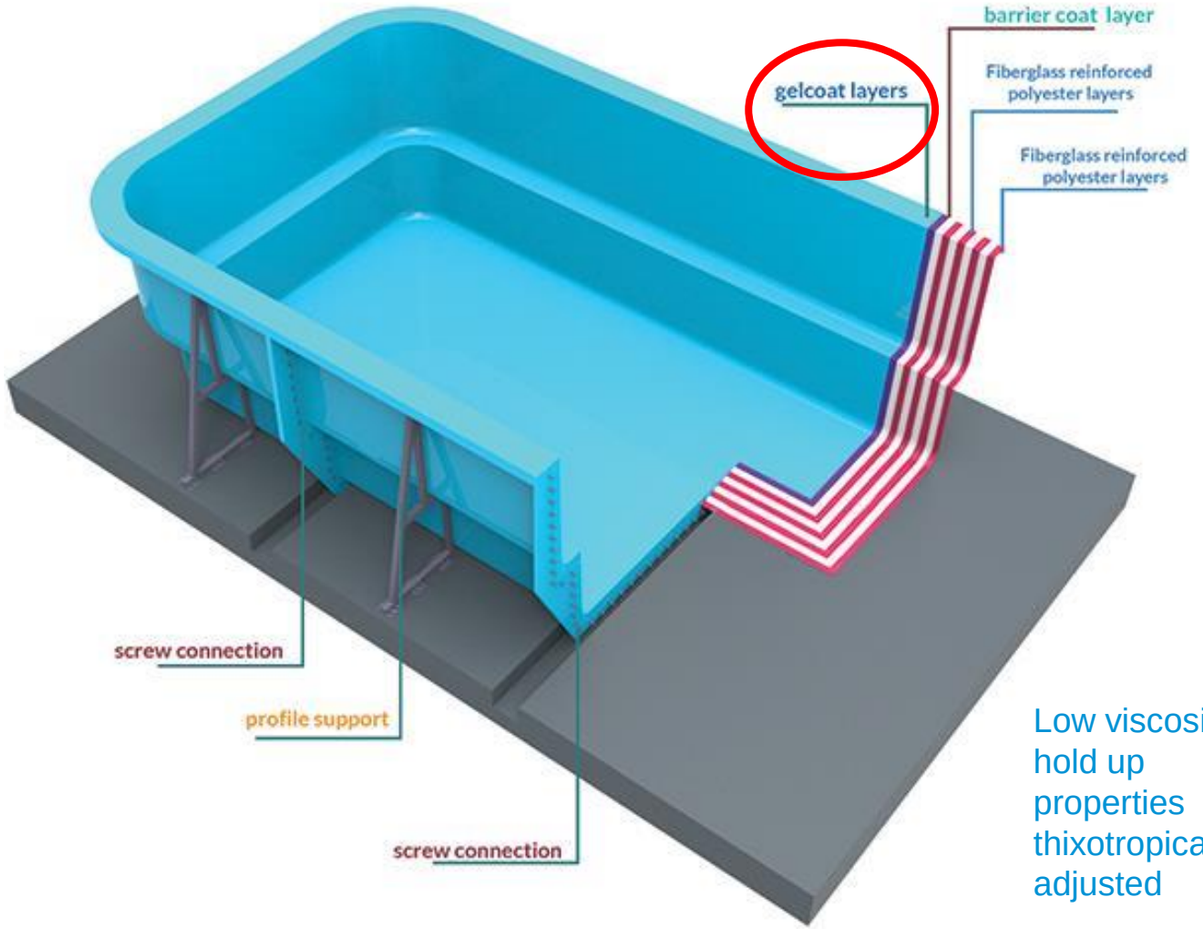
Adding MEG also offsets some of the price increase incurred by the introduction of Synoxol™ BEPD

We have the majority of the in-house supporting data for this, along with the details discussed as part of the lapsed INEOS patent (EP1131372)

Commercial applications of BEPD in Gel coats

Synoxol™ BEPD

Swimming pools (and sanitaryware)



FEATURES

Low viscosity resin,
negates to use of excessive solvent
Instead, sag / hold-up with a thixotrope

- Good flow/levelling properties
- Excellent atomization and general spraying characteristics
- Rapid air release
- Highly resistant to pre-release
- Good sag resistance
- Highly resistant to triping/wrinkling
- Excellent interlaminar adhesion
- Excellent UV resistance
- Good gloss retention

BENEFITS

Low viscosity, hold up properties thixotropically adjusted

- Easy control of film thickness
- East to apply with industry standard spray equipment
- Minimal air entrapment
- Increased tolerance to application variability
- More consistent film thickness
- Improved part quality. Increased tolerance to application variability
- More tolerant to application variability

Resistance to shrinkage upon cure ←
UV durability ←
Water resistance ←

- Reduces the incidences of delamination
- Articles retain their original colour for longer
- Superior appearance during service life

Synoxol™ BEPD

Marine (Yachts and boats)

Production & Application Benefits

Low VOC – Low Styrene Content

Defect free moulding
Flexural strength
Lower shrinkage upon cure

Lower viscosity
Ease of infusion
Ease of Application (Repair & New-Build)

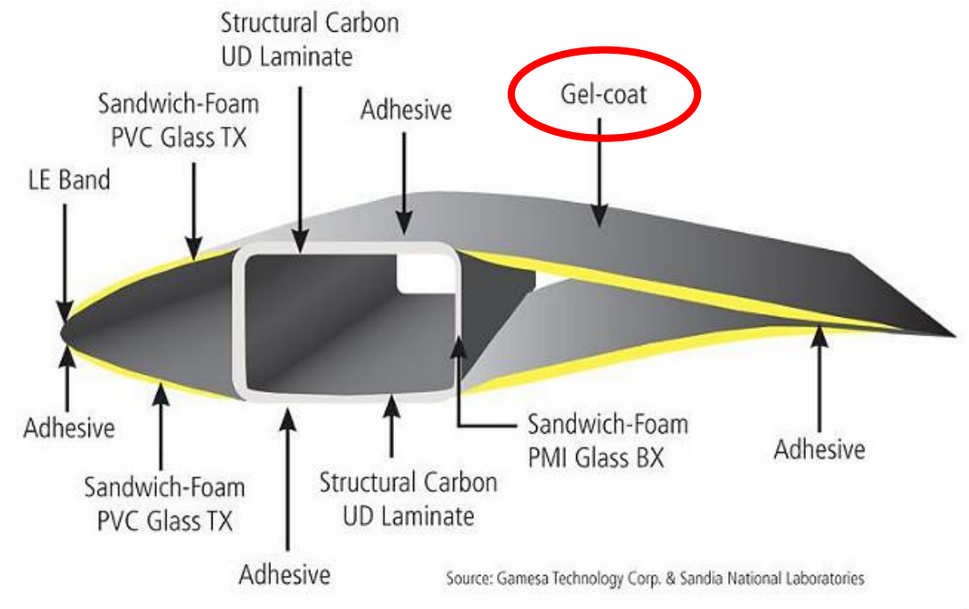
Performance Benefits

Water resistance

UV Resistance Weatherability

Synoxol™ BEPD

Windturbine Blades



Rain erosion performance
Flexibility + Hardness → Impact resistance

Defect free moulding
Flexural strength
Lower shrinkage upon cure

Lower viscosity
Ease of infusion – High processing speeds

Water resistance & Weatherability

Materials for Wind Turbine Blades: An Overview

Leon Mishnaevsky Jr. *, Kim Branner, Helga Nørgaard Petersen, Justine Beauson, Malcolm McGugan and Bent F. Sørensen

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Thermoset based composites represent around 80% of the market of reinforced polymers. The advantages of thermosets are the possibility of low temperature cure and lower viscosity (which eases infusion and thus, allowing high processing speed).

Initially, polyester resins were used for composite blades. With the development of large and extra-large wind turbines, epoxy resins replaced by polyester and are now used most often matrices of wind blade composites.

Still, recent studies (e.g by DSM Composite Resins) support arguments for the return to unsaturated polyester resins, among them, faster cycle time and improved energy efficiency in the production, stating that the newly developed polyesters meet all the strength and durability requirements for large wind blades

Appendix

UPR formulations

Unsaturated Polyester Resin	A	B	C	D	E	F	G	H	I	J
Neopentyl glycol (NPG) / g	332.6	335.1	337.6	342.8	152.6	153.7	154.7	156.9	269.1	209.2
SYNOXOL™ BEPD / g	-	-	-	-	234.8	236.5	238.1	241.5	82.8	161.0
Propylene Glycol (PG) / g	162.0	122.4	82.2	-	148.7	112.2	75.4	-	157.3	152.8
Mono Ethylene Glycol (MEG) / g	-	33.3	67.1	136.2	-	30.5	61.5	124.7	-	-
Isophthalic acid (PIA) / g	368.4	371.1	374.0	379.8	338.2	340.5	342.8	347.7	357.8	347.7
Maleic Anhydride (MA) / g	265.8	267.7	269.8	273.9	243.9	245.6	247.3	250.7	258.1	250.8
Total charge / g	1129	1130	1130	1133	1118	1119	1120	1121	1125	1122
Reaction water / g	129	130	130	133	118	119	120	121	125	122
Theoretical properties at acid value = 18 mgKOH g^{-1}										
Hydroxyl number / mgKOH g^{-1}	44	45	45	46	40	41	41	42	42	42
Hydroxyl excess / %	8	8	8	8	8	8	8	8	8	8
Molecular weight (M_n) / Da	1200	1200	1200	1200	1200	1250	1200	1200	1200	1200
Molecular weight (M_w) / Da	1600	1600	1600	1600	1900	1500	1600	1600	1600	1600
Polydispersity	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Functionality	1.3	1.3	1.3	1.2	1.4	1.4	1.4	1.3	1.3	1.4
Practical data										
Acid value / mgKOH g^{-1}	16.8	17.3	15.7	17.4	19.1	18.1	17.8	19.8	20	18
Hydroxyl number / mgKOH g^{-1}	41.5	43.5	43.4	44	40	40.8	39.9	40.5	42	42
Molecular weight (M_n) / Da	1900	2000	2100	2100	2000	1900	1900	2100	1900	2100
Molecular weight (M_w) / Da	4400	5000	5100	4900	4700	4500	4400	4800	4800	4800
Polydispersity	2.3	2.5	2.5	2.3	2.3	2.3	2.3	2.3	2.3	2.3
T_g (onset) / °C	20	20	19	18	19	15	11	11	18	19

UPR formulations

Table 4 - Summary of diol content as a percentage of diols present

Resins	A	B	C	D	E	F	G	H	I	J
NPG / mol%	60	60	60	60	30	30	30	30	50	40
SYNOXOL™ BEPD / mol%	0	0	0	0	30	30	30	30	10	20
PG / mol %	40	30	20	0	40	30	20	0	40	40
MEG / mol%	0	10	20	40	0	10	20	40	0	0

Gelcoat formulation

	Weight %
Polyester, 60 % in styrene	63.2
Thixotropic additive, HDK N20 [5]	5.20
Talc, Finntalc M05	5.20
Styrene	6.20
TiO_2, Kemira 650	15.60
BYK 501 [6]	0.21
Grind for 20 min at 2000 rpm at T = max. 45° C	
Styrene	7.30
Promoter, Co-octoate 10%	0.12
Co-promoter, DMAA (Dimethylacetoacetamide)	0.1
Inhibitor, THQ 10%	0.07
Mix properly and add 2% MEK-Peroxide-50 as initiator just shortly before use.	

[5] Wacker Chemical
[6] BYK-Chemie