

Effectively Using MPDiol[®] Glycol To Make Unsaturated Polyester Resins

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Introduction: The history of the unsaturated polyester resin (UPR) industry is one of continual improvement. This growth has led to annual production of more than two million tonnes of UPR used to manufacture a broad range of products around the world. Each year improved resins are introduced to meet the diverse and changing needs of the composite industry. These resins are typically made by reaction of a glycol or mixture of glycols with an aromatic acid (e.g. isophthalic acid or phthalic anhydride) and maleic anhydride (MA). Newer resin types are made by reaction of dicyclopentadiene (DCPD), instead of an aromatic acid, with MA and glycols. The unsaturated polymers are then diluted with styrene to adjust the viscosity and form the final resin composition.

The choice of glycol and aromatic acid used in making UPRs strongly influences the final composite properties. Ortho resins (from phthalic anhydride), the industry workhorse, are used in a wide variety of applications. Iso resins are used where more demanding performance, especially corrosion resistance (CR), is required. While propylene glycol (PG) is the main glycol used in producing UPRs, other glycols used include neopentyl glycol (NPG), ethylene glycol (EG) and diethylene glycol (DEG). MPDiol[®] glycol¹ (2-methyl-1,3-propanediol) is now widely available and has a demonstrated ability to make better UPRs with improvements in CR, thermal and mechanical properties. This paper provides a comparison of resins made from MPDiol glycol versus industry standard ortho and iso resins along with data describing strategies to maximize the performance of the finished resin when using MPDiol glycol.

Reactivity and Properties of MPDiol Glycol

MPDiol glycol can be used to make UPRs in one- or two-stage reactions. It brings to polyester production a variety of advantages including improvements in processing and final polymeric properties. Although there are some similarities to all the other glycols commonly used to make UPRs (i.e. PG, EG, DEG, NPG), it is not exactly like any of them. Therefore, to get the most from MPDiol glycol, the reaction protocols and stoichiometries should be modified accordingly.

MPDiol glycol's reactivity makes it easy to build high molecular weight polymers, which improves CR and mechanical performance. The higher boiling point of MPDiol glycol (Table 1) and its greater inherent reactivity results in reactions being about four times faster than those run with PG. When this high-reactivity glycol is used in combination with phthalic anhydride (one-stage reaction, see Appendix, Prep 1 & 2) or isophthalic acid (two-stage reaction, see Appendix, Prep 3 & 4), the use of a catalyst is unnecessary. Since terephthalic acid (two-stage reaction, Appendix, Prep 5 & 6) has low solubility in most glycols, and reacts slowly even with MPDiol glycol, the use of a catalyst such as FASCAT[®] 4100 or 9100² is advised. When using MPDiol glycol, the best quality resins are produced when certain preparation techniques or stoichiometric guidelines are followed. These will be explained later.

MPDiol glycol's unique structure gives polymers with greater ductility, which is observed in the improved tensile strength and elongation of the UPR. The "side-chain" methyl group of MPDiol glycol, when spaced along the UPR backbone inhibits formation of crystalline segments and forms a more styrene-soluble material. Even when the exceptionally crystalline terephthalic acid is used, MPDiol glycol's unique properties when properly utilized generate a clear, styrene soluble UPR.

Figure 1. MPDiol glycol has a single pendant methyl group along the glycol backbone.

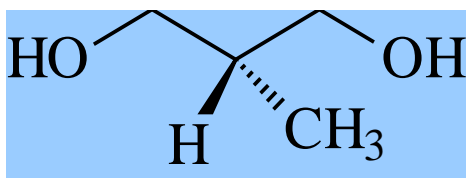


Table 1. MPDiol Glycol Typical properties

Physical State	Liquid
Boiling Point	212°C
Viscosity (@ 20°C)	174 mPa·s
Solubility in Water	100 %
Refractive Index (@ 20°C)	1.445
Density (@ 20°C)	1.01 g/cm ³

There is a problem commonly encountered in making UPRs, when using glycols that have two primary hydroxyls. In the final stage of UPR reactions, an elevated temperature cook is used to drive the acid number of the reactants lower (typically to 20 or less) and convert maleate to fumarate. Also during this final stage, further condensation reactions occur driving up the molecular weight of the polymer, which produces a resin with higher viscosity. The high reactivity of the primary glycols makes it difficult to achieve a high percentage conversion of maleate to fumarate functionality because the condensation reaction occurs simultaneously at a competitive rate. High fumarate content is essential to obtain the best possible resin reactivity and properties (i.e. strength and HDT). However, the fumarate content is often compromised in reactions to control MW build (resin viscosity). Using diprimary glycols to form a UPR will typically produce a resin with only 75 - 85% conversion of maleate to fumarate, with the expected loss in properties. This loss in properties is sometimes acceptable, but never desirable.

Several methods have been developed to overcome these problems when using diprimary glycols^{3,4}, so that high fumarate content can be achieved and the polymeric molecular weight can be controlled. A method that is generally applicable is slowing the rate of the condensation reaction relative to the maleate-fumarate isomerization. This is easily accomplished by using only 70 - 80% of the required amount of MPDiol glycol during the first half of the reaction. During the second half of the reaction, PG is added in a quantity equal to the 20 - 30% of MPDiol glycol not used earlier. This PG addition should occur at the same time as the MA addition. Because the PG has one primary and one secondary hydroxyl group, it reacts relatively slowly in condensation reactions, thereby stopping the build-up of molecular weight at the end of the reaction, while allowing the isomerization to complete, and dropping the acid number to about 20. This type of procedure is described in detail in Appendix A, Preps 1, 3, and 5.

Another method that successfully forms high fumarate resins when using diprimary glycols is increasing the rate of isomerization while holding the rate of condensation constant. This can be accomplished by adjusting the stoichiometry so that the cook is under an acid-rich condition (based on excess MA) using only 70 - 80% of the required amount of MPDiol during the first stage of the reaction. In the second stage of the cook, the MA (and no additional glycol) is added and allowed to react for several hours near 200°C. With about three or four hours left until reaction completion, the necessary amount of MPDiol glycol (20 - 30% of stoichiometric) is added and thoroughly reacted. Following the MA addition, several things are accomplished in this reaction during the acid-rich cook. The MA caps the initially formed hydroxypolymer, and in this hot, acid-rich environment, is isomerized rapidly and completely to fumarate. Because the MA addition moves the reaction away from balanced stoichiometry, condensation reactions to advance the polymer molecular weight are dramatically slowed. This type of procedure is described in detail in Appendix A, Preps 2, 4 and 6.

Using either of these two processes, conversion yields of maleate to fumarate of 94 - 98% are now routinely obtained, giving typical final polymer properties with an acid number \approx 20, $M_n = 2000 - 3000$, and Polydispersity = 2 - 3. This provides a finished UPR with a very workable viscosity and excellent properties. The properties of these polymer systems are shown in Appendix B.

Procedure for UPR casting and Corrosion Testing

The resins were cured with 1% Luperox[®] DDM-9 peroxide (MEKP) and 0.2% Cobalt Naphthenate (6% CoNap solution in mineral spirits) overnight under ambient conditions, followed by a postcure for five hours at 100°C. The physical properties of the cured thermosetting polymers were determined using ASTM test methods. Tensile strength, modulus and elongation are determined using ASTM D-638, Type 1. Flexural strength and flexural modulus: ASTM D-790. DTUL: ASTM D-648. Short term environmental testing was performed by placing flexural test specimens in a sealed tube with the indicated solvent for one week at 100°C. Following the high temperature exposure the samples were removed and flexural tests were run to determine the percentage of initial flexural strength the sample retained.

Conclusions: MPDiol glycol has unique characteristics that make it very useful in the synthesis of all types of UPR chemistry. The following advantages are observed when using MPDiol in UPR production:

Increased Production Rates: Because both hydroxyl groups of MPDiol glycol are primary, it has an inherently high reactivity. Its high boiling point (30°C > PG) makes it possible to run reactions hotter, providing at least a four-fold increase in reaction rates.

Improved Styrene Solubility: The unique molecular structure of MPDiol glycol produces a polyester with reduced crystallinity and therefore increased styrene solubility. This is particularly evident in polyesters containing high proportions of terephthalate segments.

Improved Corrosion Performance: Use of MPDiol glycol as the main glycol in a polyester produces a UPR that shows better corrosion resistance versus similar polymers using PG, EG or DEG. Significant improvements are routinely observed in caustic corrosion resistance.

Improved Mechanical Performance: UPRs made with MPDiol glycol have greater ductility and better mechanical performance than similar polymers produced with PG. In conjunction with their excellent corrosion performance, this results in UPRs that routinely retain a very high percentage of their initial properties following environmental exposure.

APPENDIX A

Detailed Resin Preparations

Prep 1- Procedure for the Synthesis of an Ortho Resin from MPDiol Glycol and PG

Reactor charge

Phthalic Anhydride (PA)	296 g	2 moles
2-Methyl-1,3-propanediol (MPDiol glycol)	360 g	4 moles
Maleic Anhydride (MA)	294 g	3 moles
Propylene glycol (PG)	95 g	1.25 moles

Reactor

Two liter resin reactor, heating mantle, temperature controller, mechanical agitation, steam heated reflux condenser, nitrogen bubbling.

Procedure

1. Add MPDiol glycol, (MPD)PA, MA and PG to the reactor.
 2. Heat at 190 - 200°C for 10 hours (until equivalent amount of water is collected) and until the final acid number has reached 20 – 30.
 3. Add 150 mg of inhibitor (hydroquinone).
 4. Cool to 140°C.
 5. Discharge and blend the resin with 600 g of cold styrene containing about 150 mg of t-butyl hydroquinone.
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Prep 2 - Procedure for the Synthesis of an Ortho Resin with MPDiol Glycol

Reactor charge

PA	592 g	4 moles
MPDiol glycol-1st	648 g	7.2 moles
MA	470 g	4.8 moles
MPDiol glycol-2nd	184 g	2.04 moles

Reactor

Two liter resin reactor, heating mantle, temperature controller, mechanical agitation, steam heated reflux condenser, nitrogen bubbling.

Procedure

1. Add MPDiol glycol-1st, PA and MA to the reactor.
2. Heat with good stirring at 190 - 200°C for 6 hours with a slow stream of N₂ sparging the reactor. An equivalent amount of water is collected.
3. Add MPDiol glycol-2nd and heat for 5 hours until equivalent amount of water is collected and acid number has reached 20-25.
4. Add 300 mg of inhibitor (hydroquinone).
5. Cool to 140°C.
6. Discharge and blend 600 grams of resin with 400 grams of cold styrene containing about 150 mg of butyl hydroquinone.

Prep 3 - Procedure for the Synthesis of an Iso Resin with MPDiol Glycol and PG

First Stage Charge

Isophthalic Acid (IPA)	332 g	2 moles
MPDiol glycol	360 g	4 moles

Second Stage Charge

MA	294 g	3 moles
PG	95 g	1.25 moles

Reactor

Two liter resin reactor, heating mantle, temperature controller, mechanical agitation, steam heated reflux condenser, nitrogen bubbling.

Procedure

First Stage:

1. Add MPDiol glycol and IPA to the reactor.
2. Heat at 190°C for 6 hours (until equivalent amount of water is collected).
3. Cool mixture to about 120°C.

Second Stage:

4. Add MA & PG.
5. Heat at 200°C for about 10 hours (collect approximately 50 ml. of water) until the final acid number has reached 20.
6. Add 150 mg of inhibitor (hydroquinone).
7. Cool to 140°C.
8. Discharge and blend the resin with 600 g of cold styrene containing about 150 mg of t-butyl hydroquinone.

Prep 4 - Procedure for the Synthesis of an Iso Resin with MPDiol Glycol

First stage charge

IPA	664 g	4 moles
MPDiol glycol-1 st	648 g	7.2 moles

Second stage charge

MA	470 g	4.8 moles
MPDiol glycol-2 nd	184 g	2.04 moles

Reactor

Two liter resin reactor, heating mantle, temperature controller, mechanical agitation, steam heated reflux condenser, nitrogen bubbling.

Procedure

First stage

1. Add MPDiol glycol-1st and IPA to the reactor.
2. Heat with good stirring at 190 - 200°C for six hours with a slow stream of N₂ sparging the reactor. An equivalent amount of water is collected.
3. Cool mixture to about 120°C.

Second stage

4. Add MA and heat at 200°C for about six hours with a slow stream of N₂ sparging the reactor.
5. Add MPDiol glycol-2nd and heat at 200°C for five hours with N₂ sparge until an equivalent amount of water is collected, and the final acid number has reached 20-25.
6. Add 300 mg of inhibitor (hydroquinone).
7. Cool to 140°C. Discharge and blend 550 grams of resin with 450 g of cold styrene containing about 150 mg of butyl hydroquinone.

Prep 5 - Procedure for the Synthesis of Terephthalate Resin with MPDiol Glycol and PG

First Stage Charge

Terephthalic Acid (TPA)	332g	2 moles
MPDiol glycol	360g	4 moles
Catalyst (FASCAT 9100)	0.1 g	150 ppm

Second Stage Charge

MA	294g	3 moles
PG	95g	1.25 moles

Reactor

Two liter resin reactor, heating mantle, temperature controller, mechanical agitation, steam heated reflux condenser, nitrogen bubbling.

Procedure

First Stage:

1. Add MPDiol glycol, TPA and catalyst to the reactor.
2. Heat at 205°C for 10 hours (until equivalent amount of water is collected).
3. Cool mixture to about 120°C.

Second Stage:

4. Add MA & PG.
 5. Heat at 200°C for about 12 hours (collect approximately 50 ml. of water) until the final acid number has reached 20.
 6. Add 150 mg of inhibitor (hydroquinone).
 7. Cool to 140°C.
 8. Discharge and blend the resin with 600 g of cold styrene containing about 150 mg of butyl hydroquinone.
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Prep 6 - Procedure for the Synthesis of Terephthalate Resin with MPDiol Glycol

First stage charge

TPA	664 g	4 moles
MPDiol glycol-1 st	648 g	7.2 moles
Catalyst (FASCAT 9100)	0.2 g	150 ppm

Second stage charge

MA	470 g	4.8 moles
MPDiol glycol-2 nd	184 g	2.04 moles

Reactor

Two liter resin reactor, heating mantle, temperature controller, mechanical agitation, steam heated reflux condenser, nitrogen bubbling.

Procedure

First stage

1. Add MPDiol glycol-1st, TPA, and catalyst to the reactor.
2. Heat with good stirring at 190 - 200°C for six hours with a slow stream of N₂ sparging the reactor. An equivalent amount of water is collected.
3. Cool mixture to about 120°C.

Second stage

4. Add MA and heat at 200°C for about six hours with a slow stream of N₂ sparging the reactor.
5. Add MPDiol glycol-2nd and heat at 200°C for five hours with N₂ sparge until an equivalent amount of water is collected, and the final acid number has reached 20 - 25.
6. Add 300 mg of inhibitor (hydroquinone).
7. Cool to 140°C. Discharge and blend 550 grams of resin with 450 g of cold styrene containing about 150 mg of butyl hydroquinone.

APPENDIX B
Tables of Resin Properties

Table 1 - Properties for an Ortho Resin with MPDiol Glycol and PG

Property	Modified Ortho	Standard Ortho
PA/MA/MPDiol Glycol/PG	0.8/1.2/1.6/0.5	0.8/1.2/--/2.1
Tensile Strength (MPa)	76	55
(Kpsi)	11	8
Tensile Modulus (MPa)	3725	4000
(Kpsi)	540	580
Tensile Elongation (%)	3.5	1.2
Flexural Strength (MPa)	138	110
(Kpsi)	20	16
Flexural Modulus (MPa)	3725	4410
(Kpsi)	540	640
HDT (°C)	110	110
(°F)	230	230
Water boil (% retention)	61	55
KOH boil (% retention)	61	25
HCl boil (% retention)	52	50
Viscosity at 45% styrene (cP)	400	200

Table 2 - Properties for an Ortho Resin with MPDiol Glycol

Property	Standard Ortho	Modified Ortho 1	Modified Ortho 2	Modified Ortho 3
PA/MA/MPDiol Glycol /PG	1.0/1.0/---/2.1	1.0/1.0/2.1/---	0.9/1.1/2.1/---	0.8/1.2/2.1/---
Fumarate %	98	97	98	97
Molecular Weight				
M _n	1600	1872	2036	1874
M _w	5170	5465	6767	6210
PD	3.23	2.92	3.32	3.31
Viscosity @ 40% SM (cP)	250	285	300	325
Tensile Strength (kpsi)	7.8	11.5	10.9	9.7
Tensile Modulus (kpsi)	625	615	565	550
Tensile Elongation (%)	1.4	2.8	2.7	2.2
Flexural Strength (kpsi)	17.8	22.2	21.9	20.8
Flexural Modulus (kpsi)	625	600	580	575
HDT (°C)	95	85	88	104
Barcol Hardness	45	42	48	43
Boiling H ₂ O (% retention)	6	22	25	21
Boiling HCl (% retention)	6	61	51	45
Boiling KOH (% retention)	6	72	58	49

Table 3 – Properties of Iso Resins made with MPDiol Glycol and PG

Property	Modified Iso	Std Iso/PG
IPA/MA/MPDiol Glycol/PG	1/1.5/2/0.625	1/1/2.05/
Tensile Strength (MPa)	86	76
(Kpsi)	12.5	11
Tensile Modulus (MPa)	3650	3800
(Kpsi)	525	550
Tensile Elongation (%)	4.2	2.5
Flexural Strength (MPa)	152	138
(Kpsi)	22	20
Flexural Modulus (MPa)	3930	3800
(Kpsi)	570	550
HDT (°C)	91	106
(°F)	196	223
Water boil (% retention)	80	85
KOH boil (% retention)	88	50
HCl boil (% retention)	75	80
Viscosity at 45% styrene (cP)	350	300

Table 4 – Properties of Iso Resins made with MPDiol Glycol

Property	Standard Iso	Modified Iso 1	Modified Iso 2	Modified Iso 3
IPA/MA/MPDiol Glycol/PG	1.0/1.0/---/2.1	1.0/1.0/2.1/---	0.9/1.1/2.1/---	0.8/1.2/2.1/---
Fumarate %	96	95	96	96
Molecular Weight				
M _n	2300	2439	2606	2902
M _w	10248	5278	5981	6913
PD	4.45	2.16	2.30	2.38
Viscosity @ 45% SM (cP)	400	250	360	350
Tensile Strength (kpsi)	12	12.5	11.9	11.2
Tensile Modulus (kpsi)	550	560	530	525
Tensile Elongation (%)	2.9	3.8	3.6	3.4
Flexural Strength (kpsi)	24.6	21.7	22	21
Flexural Modulus (kpsi)	580	560	550	540
HDT (°C)	110	90	99	111
Barcol Hardness	47	45	43	45
Boiling H ₂ O (% retention)	75	69	80	88
Boiling HCl (% retention)	82	70	72	78
Boiling KOH (% retention)	40	77	79	87

Table 5 – Properties of Terephthalate Resins made with MPDiol Glycol and PG

Property	Terephthalate*	Terephthalate
TPA/MA/MPDiol Glycol/PG	0.8/1.2/1.6/0.5	1.0/1.0/1.6/0.5
Tensile Strength (MPa)	64	89
(Kpsi)	9.5	12.5
Tensile Modulus (MPa)	3240	3790
(Kpsi)	470	550
Tensile Elongation (%)	3.7	4.0
Flexural Strength (MPa)	132	152
(Kpsi)	19	22
Flexural Modulus (MPa)	3310	3860
(Kpsi)		
HDT (°C)	120	99
(°F)	248	210
Water boil (% retention)	93	68
KOH boil (% retention)	93	93
HCl boil (% retention)	85	79
Viscosity at 45% styrene (cP)	650	500

* Material described in reaction procedure

Table 6– Properties of Terephthalate Resins made with MPDiol Glycol

Property	Standard Iso	Modified Tere 1	Modified Tere 2	Modified Tere 3
TPA(IPA)/MA/MPDiol Glycol/PG	1.0/1.0/---/2.1	1.0/1.0/2.1/---	0.9/1.1/2.1/---	0.8/1.2/2.1/---
Fumarate %	96	94	94	94
Molecular Weight				
M _n	2300	3180	2950	2830
M _w	10248	13600	7700	8000
PD	4.45	4.27	2.61	2.82
Viscosity @ 45% SM (cP)	400	350	340	320
Tensile Strength (kpsi)	12	11.4	11.3	10.6
Tensile Modulus (kpsi)	550	470	450	460
Tensile Elongation (%)	2.9	4.1	4.1	3.4
Flexural Strength (kpsi)	24.6	20.4	18.4	18.2
Flexural Modulus (kpsi)	580	490	490	490
HDT (°C)	110	100	106	112
Barcol Hardness	47	36	37	38
Boiling H ₂ O (% retention)	75	82	86	89
Boiling HCl (% retention)	82	57	72	83
Boiling KOH (% retention)	40	93	90	93

1. MPDiol glycol is a registered trademark of Lyondell Chemical Company
2. FASCAT 4100 and 9100 and Luperox DMM-9 are registered trademarks of AtoFina
3. US Patent 6,492, 487
4. US Patent 6,555,623