Making High Performance Unsaturated Polyester Resins With 2-Methyl-1,3-Propanediol

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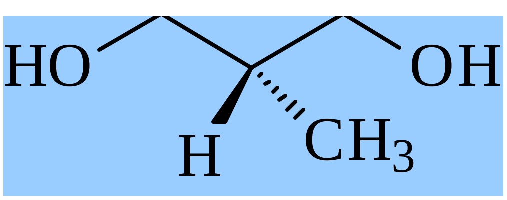
Abstract: Unsaturated polyester resins (UPR's) have been made by reaction of 2-methyl-1,3-propanediol (MPDiol) with all three of the common aromatic acids, ortho-, iso-, and terephthalic acid. The use of this unique glycol allows production of polymers with improved strength and elongation and better caustic corrosion resistance than the resins more routinely made from propylene glycol (PG). Additionally, formation of a UPR by reacting MPDiol and cheap, readily available, recycled PET (polyethylene terephthalate) and maleic anhydride produces a polymer with exceptional performance to price ratio.

Introduction: Unsaturated Polyester Resins (UPR's) are the most commonly used thermoset resins in the world. There are approximately 2.2 billion kilos/year of UPR used around the globe in the manufacture of a wide assortment of products including sinks, shower stalls, pipes, tanks, gratings, and high performance components for boats, buses, trucks, trailers and automobiles. These versatile resins are composed of a family of materials that are made from aromatic acids (isophthalic, terephthalic, and phthalic anhydride), reacted with a glycol (typically propylene glycol) or mixture of glycols, and maleic anhydride. The polymer thus generated is diluted with styrene monomer to adjust the viscosity and form the final resin composition.

The Ortho resins (made from phthalic anhydride) are the most inexpensive class of resin and are used when the structural and corrosion requirements of the part are low. The Iso resins have very good structural and corrosion properties but with their relatively high cost are used only in demanding applications. The Terephthalic resins are currently made in small volumes and are considered a specialty resin. A major reason for the limited availability of Terephthalic resins is the difficulty in making these resins from terephthalic acid (TPA) and propylene glycol (PG). Even though PG is the predominant glycol used in producing all types of UPR's other glycols are used including neopentyl glycol (NPG), diethylene glycol (DEG), and ethylene glycol (EG). Each of these glycols when used in production of a polyester resin makes a contribution to the final set of polymer characteristics, including HDT, water uptake, strength, weatherability, etc.

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



A glycol that has become available recently is MPDiol® glycol (2-Methyl-1,3-propanediol). It brings to polyester production a variety of advantages including both improvements in processing and in final polymeric properties. MPDiol contains two very reactive primary hydroxyls. (See Figure 1) It is therefore inherently more reactive than the industry standard glycol, propylene glycol (PG) which has one primary and one secondary hydroxyl. The "side-chain" methyl group of MPDiol when spaced along a polyester polymer backbone inhibits formation of crystalline segments and a more styrene soluble material is realized. Even when the exceptionally crystalline material terephthalic acid is used in the formulation, the unique properties of MPDiol generate a clear styrene soluble UPR. The structure and reactivity of MPDiol also have a positive impact on the molecular weight and distance between crosslinking points of the polyester polymers formed when the UPR is made. These improved polymers routinely have greater tensile strength and elongation to failure values than similar UPR's made with PG or NPG. Table 1 summarizes the glycol's physical properties.

Table 1. Typical properties for MPDiol.

Physical State	**Liquid**
Melting Point	**- 60 °C**
Boiling Point	**213 °C**
Density (@ 20 °C)	**1.02 g/cc**
Viscosity (@ 20 °C)	**178 mPa·s**
Flash Point	**>110 °C**
Solubility in Water	**100 %**
Vapor Pressure (@ 100 °C)	**4.3mm Hg**
Refractive Index (@ 20 °C)	**1.445**

MPDiol can be used to make unsaturated polyester resins in one stage or two stage reactions similar to the way other glycols would be used. Appropriate adjustments must be made to initial charge ratios based on molecular weight differences between glycols, and adjustments in the processing conditions must be made to account for the high reactivity of MPDiol. The relatively high reactivity of Phthalic Anhydride (1 stage reaction) and Isophthalic Acid (2 stage reaction) make the use of a catalyst unnecessary. Because Terephthalic Acid (2 stage reaction) has very low solubility in most glycols and therefore tends to be much slower reacting even with MPDiol at elevated temperatures, the use of a catalyst such as an organo tin oxide like FASCAT 4100 or 9100 is recommended.

Results and Discussion: An overview of the synthesis and properties of the UPR's made with MPDiol are given for the three different classes of resin (Ortho, Iso, and Tere). Properties of commercially available Ortho and Iso resins are provided as a standard of comparison for these resins. A typical reactor set up for running these types of reactions can be seen in Figure 2.

Synthesis and Properties of an Ortho Resin
The synthesis of Ortho resins from MPDiol is straightforward, and is done via a typical one pot one stage reaction, which requires no added catalyst. The high reactivity of MPDiol, makes it possible to drive the reaction with the second acid group on phthalic anhydride (PA). The end result of the increased reactivity is that a higher molecular weight polyester polymer is formed than would normally be made by reaction of PA and PG. The average molecular weight (M_n) observed in a series of runs with MPDiol was 2000-2400 with a polydispersity of about 3.0. A typical Ortho resin made with PA/PG would have a M_n of about 2000 or less with a broader polydispersity (>4). Molecular weight of a polymer is a major factor in determining the thermal-mechanical properties of a resin. Therefore, a series of Ortho resins made with MPDiol demonstrated exceptional properties. The caustic corrosion resistance of these finished resins is also dramatically improved. (Notice the excellent caustic corrosion performance observed for the Iso and Tere resins made with MPDiol.) The mechanical properties of a typical MPDiol modified Ortho resin are shown in Table 2 and compared to a commercial UPR.

Figure 2. Typical reactor set up.

Table 2. Comparative Properties of a Standard (Commercial) Ortho Resin and a Modified Ortho Resin (made with MPDiol replacing PG).

Property	MPD Modified Ortho	Standard Ortho
PA/MA/MPD/PG	**0.8/1.2/1.6/0.5**	**0.8/1.2/--/2.1**
Tensile Strength (MPa)	76	55
Tensile Modulus (MPa)	3725	4000
Tensile Elongation (%)	3.5	1.2
Flexural Strength (MPa)	138	110
Flexural Modulus (MPa)	3725	4410
HDT (^{o}C)	110	110
Water boil (% retention)	61	55
KOH boil (% retention)	61	25
HCl boil (% retention)	52	50
Viscosity at 45% styrene (cps)	400	200

Synthesis and Properties of an Iso Resin

The preparation of the Iso resin is a very straightforward one pot two stage reaction. With the relatively high reactivity of the Isophthalic acid and the MPDiol in the reaction, it is not necessary to add a catalyst. The resin produced has low color and good cure reactivity. The thermal and mechanical properties of the polymer are as expected, see Table 2. Once again the average molecular weight (M_n) observed in a series of runs was about 2000-2500 with a polydispersity of 3.0. The greater length of the MPDiol molecule versus PG molecule produces a polyester polymer of greater ductility which expresses itself as an improvement in tensile elongation and a reduction in HDT. The polymer corrosion resistance in water and acid are essentially unchanged by the presence of MPDiol. However, the caustic corrosion resistance of the UPR is markedly improved.

Table 3. Comparative Properties of a Standard (Commercial) Iso Resin and a Modified Iso Resin (made with MPDiol replacing PG).

Property **IPA/MA/MPD/PG**	MPD Modified Iso **1.0/1.0/2.1/---**	Std Iso/PG **1.0/1.0/---/2.1**
Tensile Strength (MPa)	86	76
Tensile Modulus (MPa)	3650	3800
Tensile Elongation (%)	4.2	2.5
Flexural Strength (MPa)	152	138
Flexural Modulus (MPa)	3930	3800
HDT (^{o}C)	91	106
Water boil (% retention)	80	85
KOH boil (% retention)	88	50
HCl boil (% retention)	75	80
Viscosity at 45% styrene (cps)	350	300

Synthesis and Properties of a Terephthalate Resin
When using MPDiol, preparation of the terephthalate resin is a remarkably easy one pot two stage reaction. Terephthalic acid (TPA) is a very insoluble and non reactive material. Even when using a reactive glycol like MPDiol and taking advantage of its high boiling point, best results are obtained by using a small amount (approximately 100 ppm) of catalyst in the reaction. This esterification can be completed with no catalyst present, but addition of an organo tin oxide catalyst (e.g. FASCAT 4100 or 9100) is the most efficient method to complete the reaction. The finished resin is a low color material with high curing reactivity. The thermal and mechanical properties of the polymer are excellent yielding a resin with properties that are comparable to those of an Iso type resin, see Table 3. The corrosion resistance of this polymer in water, acid, and caustic are excellent. Table 4 provides properties for two Terephthalate polymers made with different ratios of TPA and Maleic Anhydride.

Table 4. Comparative Properties of two Terephthalate Resins made with MPDiol replacing most of the PG and having different ratios of TPA/MA.

Property	**Terephthalate***	**Terephthalate**
TPA/MA/MPD/PG	**0.8/1.2/1.6/0.5**	**1.0/1.0/1.6/0.5**
Tensile Strength (MPa)	64	89
Tensile Modulus (MPa)	3240	3790
Tensile Elongation (%)	3.7	4.0
Flexural Strength (MPa)	132	152
Flexural Modulus (MPa)	3310	3860
HDT (^{o}C)	120	99
Water boil (% retention)	93	68
KOH boil (% retention)	93	93
HCl boil (% retention)	85	79
Viscosity at 45% styrene (cps)	650	500

* Material described in reaction procedure

Synthesis and Properties of a UPR made from post consumer recycled PET

The combinations of MPDiol, Terephthalate, and Maleic Anhydride that produce unsaturated polyester resins, make polymers that demonstrate excellent thermal, mechanical, and corrosion properties. One of the very cheapest sources of the terephthalate moiety that can be used in making a UPR is post consumer scrap PET, available as recycled PET. The reaction of MPDiol with PET is a straight forward transesterification reaction that breaks down (digests) the high molecular weight PET polymer to make a very low molecular weight terephthalate diester of MPDiol and EG groups. The lowest molecular weight terephthalate product is made when an equimolar ratio of MPDiol and EG is achieved. Reaction of this Stage 1 digestion product with maleic anhydride followed by dilution with styrene forms an unsaturated polyester resin. The properties of a typical UPR of this type are shown in Table 5. The UPR resin labeled as Terephthalate A is a polymer that was made with an equimolar mixture of MPDiol and EG. The thermal and mechanical properties of this resin looked very good and comparable to the resins shown in Tables 3 and 4. The corrosion data however seems to show an unexpectedly large loss particularly in caustic corrosion resistance.

The data in Table 5 labeled Terephthalate B was obtained from a resin made in a multistage process. The Terephthalate diester of MPDiol was first made by reaction of 2 equivalents of

MPDiol with 1 equivalent of dimethylterephthalate. This Terephthalate Diol was then used in reaction with PET to form the "Stage 1-type" product. The advantages to this more complex procedure are that the ratio of MPDiol to EG is altered in this way to a 3/1 ratio. And from a processing standpoint, the use of a higher molecular weight Terephthalate Diol versus MPDiol directly, means a larger volume of liquid is used in reaction with the solid PET and the first stage reaction is easier. The properties of the finished product, Terephthalate B, are excellent across the board. The thermal, mechanical, and corrosion properties of Terephthalate B compare very well with those obtained from the Terephthalate and Iso resins found in Tables 3 and 4. Therefore, the combination of Terephthalate and MPDiol forms polymers with excellent thermal and mechanical properties over a fairly wide range, but in order to maximize the corrosion properties of a Terephthalate resin, MPDiol must be the predominant glycol in the mixture.

Table 5. Comparative Properties of two Terephthalate Resins made from reaction of PET and MPDiol having different ratios of MPDiol/EG.

Property	**Terephthalate A**	**Terephthalate B**
"TPA"/MA/MPD/EG/PG	**0.8/1.2/0.8/0.8/0.5**	**0.8/1.2/1.2/0.4/0.5**
Tensile Strength (MPa)	74	70
Tensile Modulus (MPa)	3275	3275
Tensile Elongation (%)	2.9	3.0
Flexural Strength (MPa)	145	138
Flexural Modulus (MPa)	3585	3450
HDT (^{o}C)	117	117
Water boil (% retention)	73	93
KOH boil (% retention)	12	93
HCl boil (% retention)	67	72
Viscosity at 45% styrene (cps)	250	600

Procedure for UPR casting and Corrosion Testing

All the resins made and studied (Tables 2-5) were cured with 1% DDM-9 (MEKP) and 0.2% CoNap (6% solution in mineral spirits) overnight under ambient conditions, followed by a postcure for 5 hours at 100^{o}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^{o}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.

Comparison of Glycols in UPR production - Reactivity and Properties

A series of reactions were run to determine the relative reactivity of MPDiol versus PG with terephthalic acid or isophthalic acid. The result of the comparison is shown in Figure 3. The higher boiling point of MPDiol and the greater inherent reactivity of the system result in reactions run with MPDiol being about 4 times as fast as those run with PG. A comparison was also made to evaluate the reaction of different glycols reacting with terephthalic acid. The reaction of PG with TPA is quite slow as previously discussed. The resin produced on completion was also relatively cloudy. Cloudy resins are a problem that we believe is due to the difficulties associated with dissolving a material that is "crystalline" or somewhat crystalline in a styrene solvent. The terephthalate moiety is known to be particularly problematic in this regard and it takes a special glycol to overcome this problem. Reaction with NPG, EG and DEG also produced problems with resin cloudiness. The product of NPG and TPA was so crystalline it would not dissolve at all in styrene. Additionally the EG and DEG based UPR's had relatively high moisture absorption. A qualitative comparison of these systems can be seen in Figure 4.

Figure 3. Comparative reaction rate of PG and MPDiol with Isophthalic and Terephthalic Acid

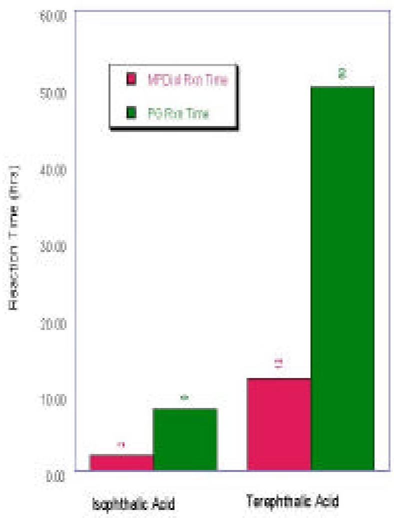
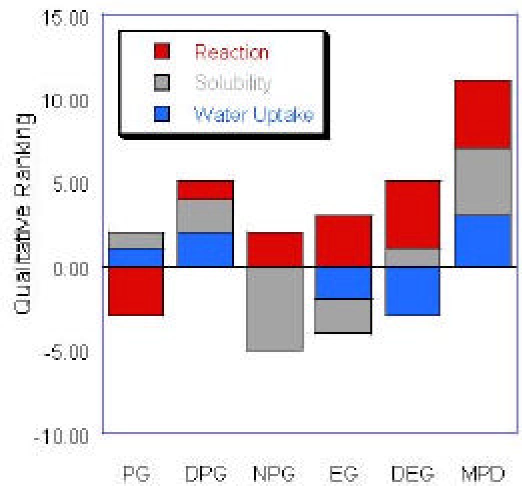


Figure 4. Comparison of TPA-glycols reaction; reaction rate, polymer solubility in styrene, and water absorption of UPR.



A problem that is observed with MPDiol is the high reactivity of this di-primary glycol in the last hours (final stage) of reaction to form the finished unsaturated polyester polymer. As the resin cook is concluding it is normal to heat the reaction to 200-210^{o}C for several hours, in order to obtain a low acid number (typically about 20), and isomerize the maleate to fumarate (it is desirable to obtain 90-95% or higher fumarate conversion). As these two reactions are proceeding, the polymer will increase in molecular weight, which of course will adversely effect the finished resin viscosity. Therefore, producing a resin with the highest possible fumarate content, while obtaining a suitably low acid number, and a polymer molecular weight that generates a workable resin viscosity is tricky at best and normally leads to compromise in reaction conditions and polymer properties. The use of a di-primary glycol whether MPDiol or DEG or NPG produces additional problems in the final stage of reaction, because the high reactivity of the glycol tends to favor molecular weight build (and therefore higher resin viscosity). Use of MPDiol (or one of the other di-primary glycols) to form a UPR, will typically produce a resin with only 75 to 85% conversion of maleate to fumarate, with the expected loss in properties. In some instances this loss in properties is acceptable, but it is never desirable. We have developed several methods to reduce or eliminate these problems when using di-primary glycols, so that high fumarate content can be achieved and the polymeric molecular weight can be controlled. One of the easiest is adjusting the glycol stoichiometry so that a small amount of PG can be introduced into the reaction. The lower reactivity of the PG slows down molecular weight build in stage 2, and makes it possible to increase fumarate conversion. Conversion yields of maleate to fumarate of 94-98% are now routinely obtained, with acid numbers of approximately 20 for the finished polymer, and molecular weights (M_n) = 2000-2500 with a polydispersity of between 2 and 3, which provides a finished UPR with a very workable viscosity.

Conclusions: MPDiol (2-methyl-1,3-propanediol) is a glycol with unique characteristics that make it very useful in synthesis of Ortho-, Iso-, and Terephthalate based Unsaturated Polyester Resins. The following advantages are observed when using MPDiol in making a UPR.

Increased Production Rates: Because both hydroxyl groups of MPDiol are primary, it has an inherently high reactivity. The high boiling point (30 ^{o}C > PG) makes it possible to run reactions hotter, providing a potential eight fold increase in reaction (esterification) rates.

Improved Styrene Solubility: The unique structure of the MPDiol molecule produces a polyester polymer with reduced crystallinity and therefore increased styrene solubility. This reduction in crystallinity is particularly noticed in polyester systems that contain high proportions of terephthalate segments, which are typically highly crystalline.

Improved Corrosion Performance: The use of MPDiol as the predominant glycol in a polyester resin, produces a UPR that demonstrates better corrosion resistance than similar polymers made with PG, EG, or DEG. Large improvements are routinely observed in caustic corrosion resistance

Improved Mechanical Performance: The UPR's made with MPDiol demonstrate better. mechanical performance (strength and elongation to failure) than similar polymers made with PG. Combined with the excellent corrosion resistance of these polymers, these UPR's routinely retain a very high percentage of their initial properties following environmental exposure.

MPDiol® glycol is a registered trademark of the Lyondell Chemical Company.

Biographies

Lau Yang is a senior research fellow at Lyondell Chemical's Newtown Square, PA research center. Dr. Yang received his Ph.D. in Chemistry from University of Chicago in 1974. His current interests are thermoset resins and composites.

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