

# Producing UPRs with 2-Methyl-1,3-Propanediol

The history of the unsaturated polyester resin (UPR) industry is one of continual improvement. Each year improved resins are introduced to meet the diverse and changing needs of the composite industry. MPDiol® 1 glycol (2-methyl-1,3-propanediol) has demonstrated an ability to make UPRs with improvements in both corrosion resistance (CR) and mechanical properties. A comparison of resins made using MPDiol® glycol as a replacement for other glycols in typical resins made from common aromatic acids (ortho and iso) will be presented.

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**M**ore than two million tonnes / year of UPR are used worldwide in the manufacture of a broad range of products. These versatile resins are typically made by reacting glycols with an aromatic acid (e.g. isophthalic acid or phthalic anhydride) and maleic anhydride. They are then diluted with styrene to adjust viscosity and form the final resin composition.

The choice of glycol and aromatic acid used in making a polyester strongly influences final composite properties. Ortho resins (from phthalic anhydride), the industry workhorses, are used in a wide variety of applications. Iso resins are used where more demanding performance (especially CR) is required. While PG (propylene glycol) is the main glycol used in producing all types of UPR, other glycols used include neopentyl glycol (NPG),

diethylene glycol (DEG), and ethylene glycol (EG). MPDiol glycol® is now widely available and when used correctly can be a cost effective way to improve UPR properties.

### Reactivity and properties of MPDiol® glycol

MPDiol® glycol (2-methyl-1,3-propanediol) 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.

MPDiol® glycol's reactivity makes it possible to build polymer molecular weight, thereby improving corrosion resistance and mechanical performance. Its higher boiling point (Table 1) and the greater reactivity of the system result in reactions run with MPDiol® glycol 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) or isophthalic acid (two-stage reaction) the use of a catalyst is unnecessary.



Unsaturated polyester resins are used in a large number of applications.

Since terephthalic acid (two-stage reaction) has low solubility in most glycols, and reacts slowly even with MPDiol® glycol, the use of a catalyst such as FASCAT 4100 or 9100<sup>2</sup> is advised.

MPDiol® glycol's unique structure produces 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 a more styrene-soluble material is realized (fig.1). Even when the exceptionally crystalline terephthalic acid is used, MPDiol® glycol's unique properties generate a clear, styrene soluble UPR.

A common problem encountered in making UPRs, when using glycols with two primary hydroxyls, is that the high reactivity of

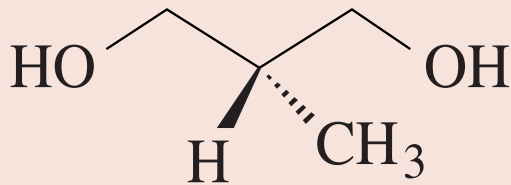


Fig. 1. MPDiol® glycol has a single pendant methyl group along the glycol backbone.

Table 1. MPDiol® glycol: typical properties

Physical state	Liquid
Boiling point	213°C
Viscosity (at 20°C)	178 mPa.s
Solubility in water	100 %
Refractive index (at 20°C)	1.445

these glycols makes it difficult to achieve high conversion of maleate to fumarate functionality. The fumarate is necessary to obtain optimum resin reactivity and properties, but 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 to 85% conversion of maleate to fumarate, with the expected loss in properties. This loss in properties is sometimes acceptable, but never desirable.

We have developed several methods to eliminate these problems when using diprimary glycols, so that high fumarate content can be achieved and the polymeric molecular weight can be controlled. One of the easiest is adjusting the reaction conditions so that a small portion of the required glycol addition is delayed until the final stage of the cook. Conversion yields of maleate to fumarate of 94 to 98% are now routinely obtained, giving typical final polymer properties of acid number  $\approx 20$  Mn = 2000 – 2500 and Pd = 2 – 3. This provides a finished UPR with a very workable viscosity and excellent properties.

Table 2 shows data from trials where MPDiol® glycol is used as a substitute for PG in typical ortho and iso resins and compared to these industry-standard UPRs. Both ortho resins were made as one-stage reactions, standard for this type of chemistry. The iso resins were made using standard two-stage conditions. (Only selected resins from the series made are shown here.)

#### Procedure for UPR casting and corrosion testing

All resins were cured with 1% Luperox DDM-9<sup>2</sup> 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. Tensile and flexural tests were run according to ASTM standards. 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.

The samples were then removed and flexural tests run to determine the percentage of the initial property retained.

MPDiol® glycol (2-methyl-1,3-propanediol) 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® glycol 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 a potential eight-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. ■

Table 2: Data from trials

Property	Standard Ortho	Modified Iso	Modified Iso	Standard Iso
PA(IPA)/MA/MPD/PG	1.0/1.0/.../2.1	1.0/1.0/2.1/...	0.8/1.2/2.1/...	1.0/1.0/.../2.1
Fumarate %	98	97	96	96
Molecular Weight (vs p-styrene)				
M <sub>n</sub>	1600	1872	2902	2300
M <sub>w</sub>	5170	5465	6913	10248
PD	3.23	2.92	2.38	4.45
Viscosity @ 40-5% SM (cP)	250 (40)	285 (40)	350 (45)	400 (45)
Tensile strength (Kpsi)	7.8	11.5	11.2	12.1
Tensile modulus (Kpsi)	625	615	525	550
Tensile elongation (%)	1.4	2.8	3.4	2.9
Flexural strength (Kpsi)	17.8	22.2	21	24.7
Flexural modulus (Kpsi)	625	600	540	580
HDT (°C)	95	85	111	110
Barcol Hardness	45	42	45	47
Boiling H <sub>2</sub> O (% retention)	6	22	88	75
Boiling HCl (% retention)	6	61	78	82
Boiling KOH (% retention)	6	72	87	39

1 MPDiol® glycol is a registered trademark of Lyondell Chemical Company.  
2 Luperox DMM-9, Fascat 4100 and 9100 are products of AtoFina.