Application Data

MPDiol® Glycol

Use in Producing Unsaturated Polyester Resins

General

MPDiol glycol (2-methyl-1,3-propanediol) can be used in production of UPRs with phthalic anhydride, isophthalic acid and terephthalic acid. The unique structure and reactivity of MPDiol glycol makes it particularly useful in combination with terephthalate-type starting materials. Use of MPDiol glycol as the primary source of glycol in making unsaturated polyester resins provides improvements in caustic corrosion resistance and mechanical performance (strength and elongation) compared to typical ortho, iso or terephthalate resins.

Key Features and Benefits

Increased Production Rates: Because both hydroxyl groups of this glycol are primary, it has an inherently high reactivity. The high boiling point (30oC > 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 glycol molecule produces an unsaturated 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 glycol as the predominant glycol in a polyester resin produces a UPR that demonstrates better corrosion resistance than similar polymers made with propylene glycol (PG), ethylene glycol (EG) or diethylene glycol (DEG). Large improvements are routinely observed in caustic corrosion resistance.

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

Structure and Properties

MPDiol glycol contains two very reactive primary hydroxyls (See Figure 1). It is, therefore, inherently ore reactive than the industry standard glycol, PG, which has one primary and one secondary hydroxyl. The “side-chain” methyl group of MPDiol glycol 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 terephthalic acid is used in the formulation, the unique properties of MPDiol glycol generate a clear styrene soluble UPR. The structure and reactivity of MPDiol glycol 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 neopentyl glycol (NPG). Table 1 summarizes the glycol's physical properties.

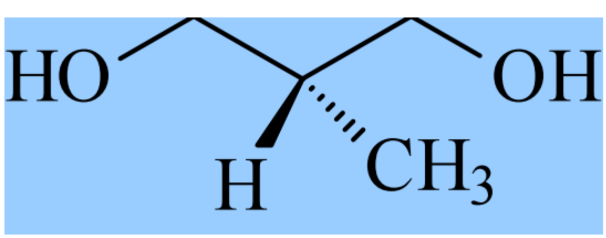

Figure 1 MPDiol glycol has a single pendant methyl group along the glycol backbone.

Typical Properties

Physical state	liquid
Melting point	- 54^{o}C
Boiling point	212^{o}C @ 760 mm Hg
Density	1.01 g/cm^{3} @ 20^{o}C
Viscosity (@ 20^{o}C)	178 mPa·s (178 cP)
Flash point	127^{o}C (closed cup)
Solubility in water	100 %
Vapor pressure (@ 100^{o}C)	4.3mm Hg (0.083 psi)
Refractive index (@ 20^{o}C)	1.445

UPR Synthesis and Properties

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. MPDiol glycol's reactivity makes it possible to build polymer molecular weight, thereby improving corrosion resistance and mechanical performance. The reactivity of phthalic anhydride (one-stage reaction) and isophthalic acid (two-stage reaction) make the use of a catalyst unnecessary. Because terephthalic acid (two-stage reaction) has very low solubility in most glycols and therefore tends to be much slower reacting even with MPDiol glycol at elevated temperatures, the use of a catalyst such as an organotin oxide like FASCAT 4100 or 9100, a product of AtoFina, is recommended.

Typical reaction procedures and the properties of the resultant UPRs made with MPDiol glycol are given below. Properties of a commercially available resin are provided as a standard for comparison with these resins. A typical reactor set up for this set of reactions can be seen here.

Ortho (GP) Resins – Synthesis and Properties

The synthesis of ortho resins from MPDiol glycol is straightforward and is done via a typical one pot, one-stage reaction. No catalyst is required in this reaction. The high reactivity of MPDiol glycol, particularly in comparison to PG, makes it possible to drive the reaction with the second acid group on phthalic anhydride (PA). This produces a higher molecular weight polyester polymer than would typically be made by reaction between PA and PG. Polymer molecular weight, to a large extent, controls the thermal and mechanical properties of the resin. Therefore, ortho resins made with MPDiol glycol have significantly improved thermal and mechanical properties, rivaling those of standard "iso type" resins. The corrosion resistance of the MPDiol glycol-based resins in water and acid environments shows some small improvement from the level of a typical PG-based ortho resin, but the caustic corrosion resistance is dramatically improved. The detailed procedure for synthesis of an orthophthalate UPR with MPDiol glycol and the resultant properties of the cured resin can be viewed in a separate document (2239).

Isophthalate Resins – Synthesis and Properties

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 glycol in the reaction, it is not necessary to add a catalyst. The resin is a low-color, high-reactivity material. The thermal and mechanical properties of the polymer are as expected. The greater length of the MPDiol glycol 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 not significantly changed by the presence of MPDiol glycol. However, the caustic corrosion resistance of the UPR is markedly improved. The detailed procedure for synthesis of an isophthalate UPR with MPDiol glycol and the resultant properties of the cured resin can be viewed in a separate document (2238).

Terephthalate Resins – Synthesis and Properties

When using MPDiol glycol, preparation of the terephthalate resin is a remarkably easy one-pot, two-stage reaction. Terephthalic acid (TPA) is an insoluble and non-reactive material. Even when using a reactive glycol like MPDiol glycol 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. An organotin oxide catalyst, like FASCAT 4100 or 9100 from AtoFina, has proven to be very effective. The finished resin is a low-color, high-reactivity material. 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. The corrosion resistance of this polymer in water, acid and caustic are excellent. The detailed procedure for synthesis of a terephthalate UPR with MPDiol glycol and the resultant properties of the cured resin can be viewed in a separate document (2240).

PET Recycle Resins – Synthesis and Properties

PET (polyethyleneterephthalate) reclaimed from recycle streams is a very economical source of starting materials for production of UPRs. This type of resin usually has properties (thermal, mechanical and corrosion) that place it in the low performance category along with the “ortho- type” resins. Reaction between PET and MPDiol glycol can produce a UPR in a typical two-stage reaction that has properties which are significantly better than the usual PET resin. The first stage of reaction which involves digestion of the PET ester in MPDiol glycol, technically a transesterification, requires a catalyst (e.g. zinc acetate). Reaction with maleic anhydride and addition of styrene produces a finished resin with low color and high reactivity. The thermal and mechanical properties of the polymer are excellent. The corrosion resistance of this polymer in water and acid are very good. The caustic corrosion resistance of the polymer is reduced, because of the relatively high ethylene glycol content in the polymer. The detailed procedure for synthesis of an UPR from PET and MPDiol glycol and the resultant properties of the cured resin can be viewed in a separate document (2241).

Comparison of Glycols in UPR Production – Reactivity and Properties

A series of reactions were run to determine the relative reactivity of MPDiol glycol versus PG with terephthalic acid or isophthalic acid. The result of the comparison is shown in Figure 2 (see next page). The higher boiling point of MPDiol glycol and the greater inherent reactivity of this glycol with two primary hydroxyl groups result in MPDiol glycol-based reactions actually run about four times faster as those run with PG.

A problem that can be encountered with MPDiol glycol and other diprimary glycols (e.g. EG, DEG, or NPG) is the effect their high reactivity has on the final stage (last four hours) of reaction that forms the finished unsaturated polyester polymer. As the resin cook is concluding, it is normal to heat the reaction to 200-210oC 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 reactions are proceeding, the polymer will increase in molecular weight, which will adversely affect 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 diprimary glycol with its high reactivity tends to favor molecular weight build (and therefore higher resin viscosity). Use of MPDiol glycol (or one of the other 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. In some instances, this loss in properties is acceptable, but it is never desirable.

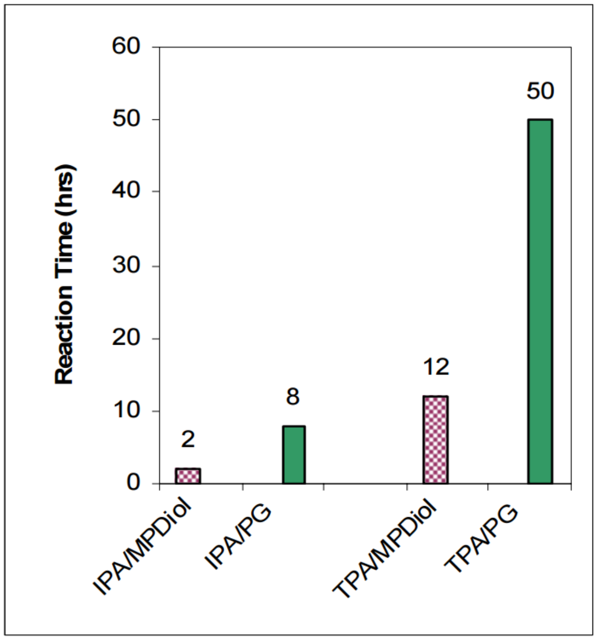

Figure 2. Comparative reaction rates of PG and MPDiol glycol with isophthalic and terephthalic acid

We have developed several methods to reduce or eliminate these problems when using diprimary glycols (1), 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 molecular weight build in stage two, 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 number average molecular weights (Mn) = 2000-2500 with a polydispersity of between two and three which provides a finished UPR with a very workable viscosity and excellent properties.

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 of TPA 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 that adds up some of the positive and negative aspects of these glycols in reaction with TPA to form an UPR can be seen in Figure 3 (next page). Based on clarity, quality, and ease of production, MPDiol glycol is clearly the best glycol to use in combination with TPA to form an unsaturated polyester resin.

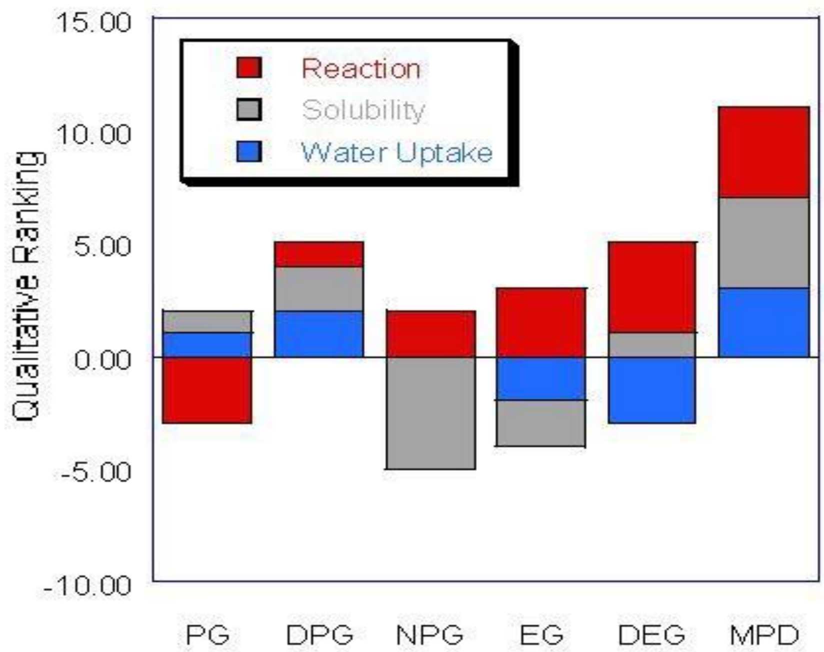

Figure 3 Comparison of TPA-glycol reactions incorporating factors for reaction rates, polymer solubility in styrene and water absorption of UPR.

Summary

MPDiol glycol (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 glycol in making a UPR.

Increased Production Rates: Because both hydroxyl groups of MPDiol glycol are primary, it has an inherently high reactivity. The high boiling point (30oC > 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 glycol 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 glycol 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: UPRs made with MPDiol glycol 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 UPRs routinely retain a very high percentage of their initial properties following environmental exposure.

1) US patent **6,492,487**, Process for making reactive unsaturated polyester resins from 2-methyl-1, 3-propanediol, **Yang; Lau S.; Baylis; Edmund; Gosset; Patrice**

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