

Modification of PET

Using MPDiol® Glycol

Introduction

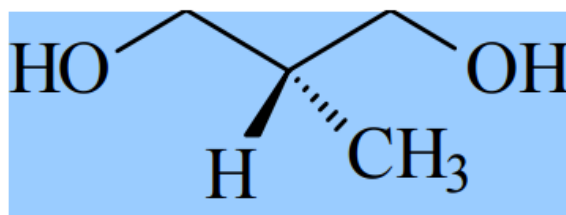
Glycol modification of PET through copolymerization with 2-methyl-1,3-propanediol (sold by Lyondell Chemical Company as “MPDiol® glycol,” hereinafter also referred to as “MPDiol” or “MPD”) is an attractive technique to improve the processability and to differentiate the properties of polyethylene terephthalate (PET). Results show that modification leads to innovative low- melt/high-shrink, optically clear PET copolymers with soft-hand and enhanced dyeability.

Copolymerization of PET using MPDiol glycol can result in significant property enhancements without sacrificing the desirable attributes of the PET homopolymer. Its branched structure imparts flexibility into the polymer backbone. MPDiol glycol lowers the glass transition and melting temperature of PET and decreases the crystallization temperature and rate. These shifts enhance orientation processing, leading to faster elongation rates and higher elongations in films, containers and fiber applications.

In several respects, glycol modification using MPDiol glycol achieves advantages similar to acid modification with isophthalic acid. Moreover, since the molar sensitivity of these effects is equivalent for both comonomers and the molecular weight of MPDiol glycol is approximately one- half that of isophthalic acid, MPDiol glycol can be a more efficient option for performance enhancements.

Physical Properties

The physical properties of MPDiol glycol are shown below. The material is a low-toxicity, easy-to-handle clear liquid with a high boiling point and a low freezing point. It is miscible with ethylene glycol (EG). It can be mixed with EG and purified terephthalic acid (PTA) or dimethyl terephthalate (DMT) to form a stable, feed-mix slurry.



CAS Number	216
Molecular Weight	90.1g/m
Melting Point	< -60°C
Boiling Point	213 °C
Density (20°C)	8.47 lb/gal (1.02 g/cc)
Viscosity (20°C)	174 cP
Vapor Pressure @ 100°C	4.3 mm

Melt-Phase Polymerization

MPDiol glycol readily copolymerizes in both PTA- and DMT-based reactions. Conventional PET catalysts, stabilizers and other additives are used under typical batch or continuous polymerization reaction temperatures and pressures. A batch reactivity comparison between MPDiol glycol-co-PET and purified isophthalic acid-modified PET at two levels of comonomer substitution is found on the chart on the next page. Purified isophthalic acid (PIA) is commonly used to chemically modify PET to improve its processability and properties. The intrinsic viscosity (I. V.) of these copolymers is 0.6 dl/g. It is noteworthy that MPDiol glycol more efficiently incorporates into the copolymer.

During the production of MPDiol glycol-co-PET, pure EG recovery from the low-pressure melt polycondensation step is slightly complicated because the relative volatility (α) between MPDiol glycol and EG is low (EG/MPDiol glycol, $\alpha=1.8$). (This issue is similar to that presented by other glycol co-products used in PET polymerizations, such as diethylene glycol (DEG.)) For the continuous polymerization (CP) process (although a batch process is also used), there are several ways to address the situation. While it is theoretically possible to selectively remove EG from the system, maintaining high EG purity may increase the demand on the distillation equipment in terms of the size of the recovery column (diameter, number of theoretical stages) or its energy requirements (reflux ratio).

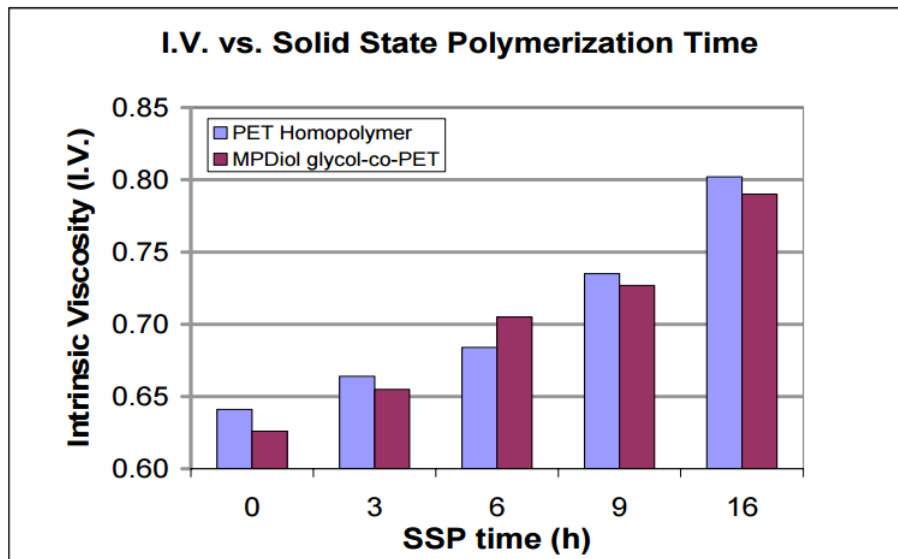
A case study was conducted using 10 mole percent MPDiol glycol-co-PET to determine the capital requirements for distillation capacity to specified glycol composition, purity and recovery rates. There was no impact of MPDiol glycol on water separation in the drying column. For the heavies column, we found that typical glycol recovery units could recover from 50 to 90 percent of the EG at 98 to 99 wt. percent purity without distillation column upgrades. Higher purity EG (>99.8 percent) could require equipment upgrades. If the goal is to recover pure glycol (EG/MPDiol glycol), this can be accomplished at full capacity without upgrades in systems designed for typical EG recovery. This stream can be recycled into the MPDiol glycol-co-PET process or segregated for other applications.

	3 mole %*		10 mole %*	
	PIA	<u>MPDiol Glycol</u>	PIA	<u>MPDiol Glycol</u>
Esterification Time (min)	235	260	220	265
Polycondensation Time (min)	220	195	220	215
Total Batch Time (min)	455	455	440	480
Comonomer Incorporations (mole %*)	4	4	10	12
*mole % comonomer substitution				
- PIA for PTA				
- MPDiol glycol for EG				

Solid-State Polymerization

While PET melt properties are not compromised by low levels of MPDiol glycol substitution, it is generally recognized that solid-state polymerization following melt polymerization is effective at increasing the polymer molecular weight and improving melt processing and material properties. The following section demonstrates the compatibility of MPDiol glycol-co-PET with standard solid-state polymerization technology.

Melt-phase MPDiol glycol-co-PET and PET homopolymer chip compositions were solid-state polymerized at temperatures and times that are typical for PET homopolymer to determine the kinetics. A typical rate profile is shown below for seven mole percent MPDiol glycol-co-PET at T=215o C. Note that the copolymer and homopolymer behave similarly. Overall, we find that the conditions and kinetics for solid-state polymerization kinetics of MPDiol glycol-co-PET are equivalent to PET homopolymer, at least for MPDiol glycol substitution levels (for EG) of 10 mole percent.

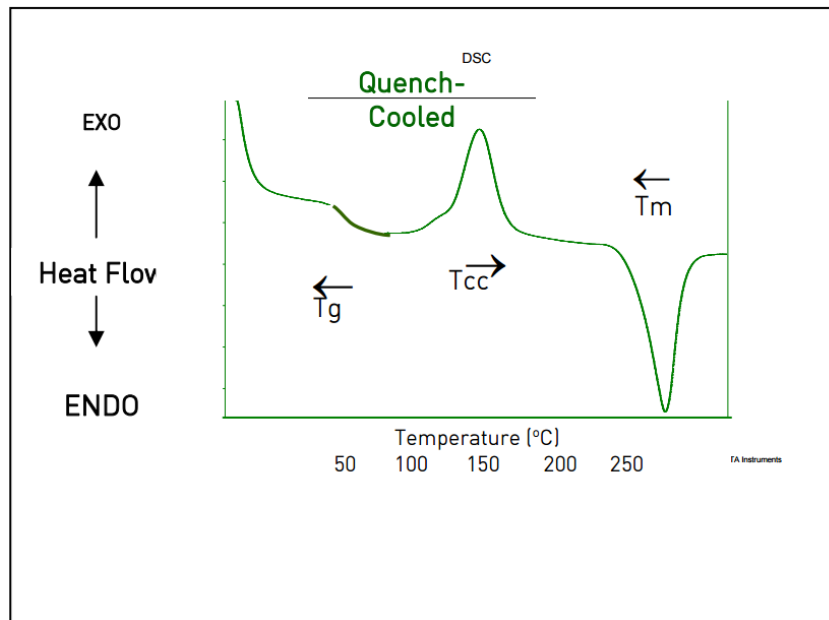


Resin properties

Thermal Transitions

The effects of MPDiol glycol on thermal transitions are illustrated on the differential scanning calorimetry (DSC) scan below.

MPDiol glycol lowers the glass transition temperature (T_g) relative to the PET homopolymer. Less thermal energy is required for molecular motion, because of MPDiol glycol's secondary methyl group, which both promotes main chain bond rotation and behaves like a chain end. This increases the amorphous phase-free volume.

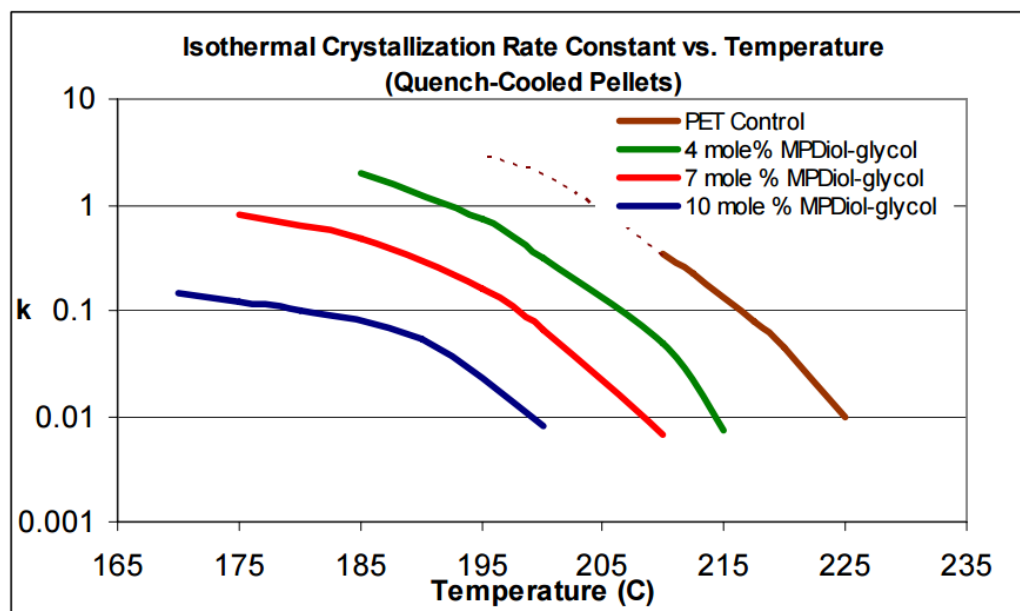


When MPDiol glycol-co-PET is quenched from the melt below its T_g and reheated, it raises the cold crystallization temperature (T_{cc}). More energy is required to sort through the polymer segments, reject MPDiol glycol, and nucleate homogeneous crystallization and growth. The MPDiol glycol-containing segments are excluded into the amorphous phase, leading to lower crystallinity, thinner lamellae, and depressed melting temperatures (T_m). We see that the molar sensitivity to comonomer substitutions between MPDiol glycol and PIA are similar. Since the molecular weight of MPDiol glycol is 55 percent of PIA, significant reduction of raw material consumption is possible via MPDiol glycol substitution.

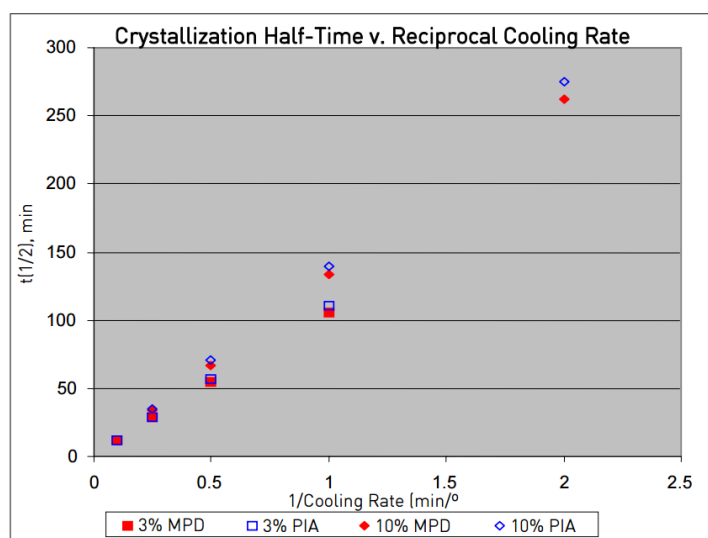
Heat at 5°C/min	3 mole % PIA	10 mole % PIA	3 mole % MPD	10 mole % MPD
T _g (°C)	73	72	73	71
T _{cc} (°C)	122	131	123	132
ΔH _{cc} (J/g)	34.2	31.7	33.4	31.6
T _m (°C)	248	232	248	230
ΔH _m (J/g)	40.7	29.8	40.6	33.4
% Crystalline (as-polymerized)	7.7	2.3	8.4	2.1
Cool at 5°C/min				
T _c (°C)	188	154	187	145
ΔH _c (J/g)	43.3	31.4	51.8	23.1
% Crystalline	51.2	37.1	61.3	27.3

Crystallization

It is well known that the presence of random branching drastically changes the crystallization behavior of linear polymers. MPDiol glycol modification of PET leads to reduced crystallization rates. The sensitivity is shown in the graph below.



On a molar basis, the sensitivity of non-isothermal crystallization kinetics is equivalent between MPDiol glycol and PIA.



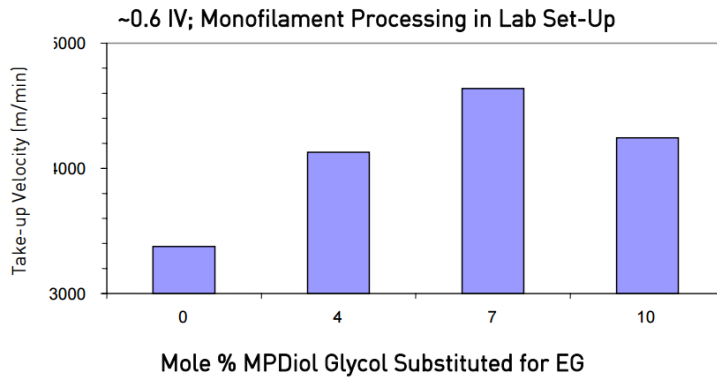
Fiber Properties

Fiber Spinnability

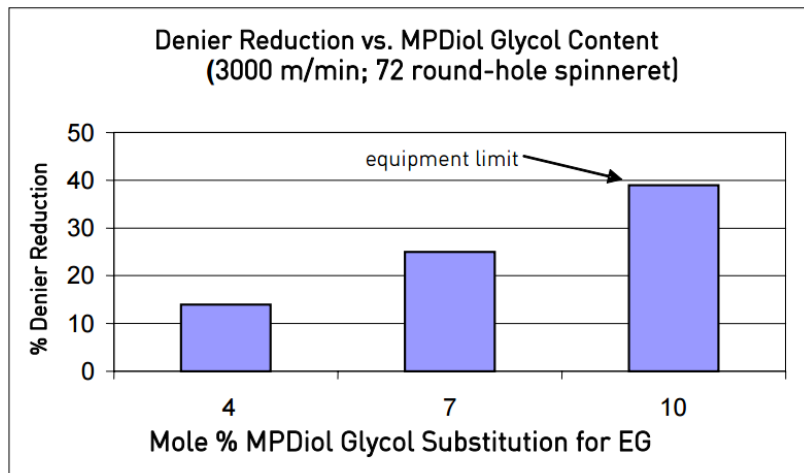
The lower crystallization rate of MPDiol glycol-co-PET relative to the homopolymer reduces the tendency of stress-induced crystallization during fiber spinning. As a result, higher spinning

speeds (increased production speeds), finer denier filaments, and filaments with higher elongations are accessible.

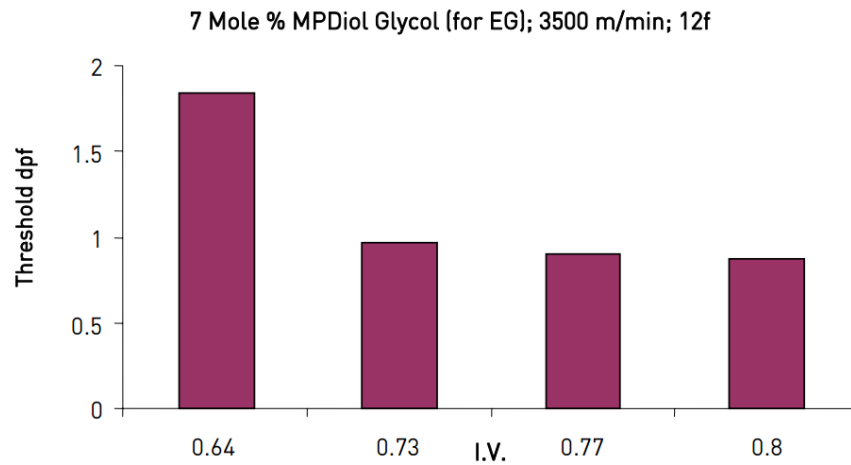
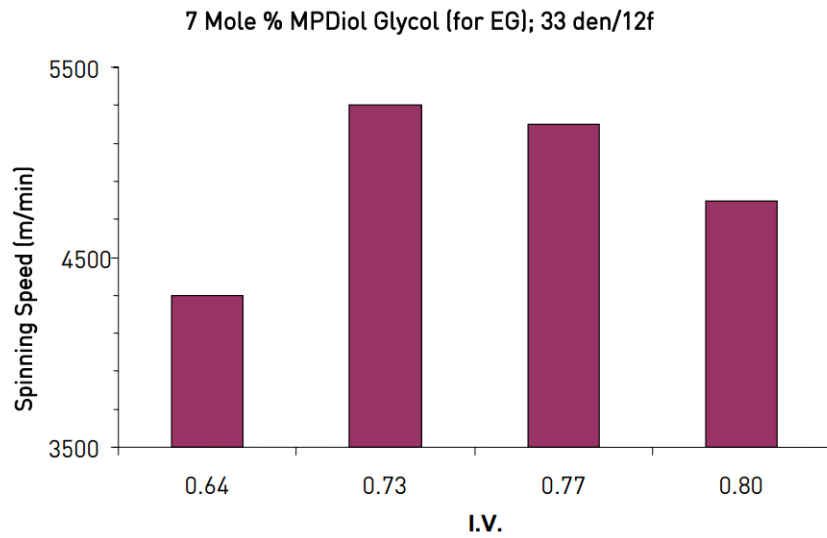
An example of the effect of MPDiol glycol substitution on spinning speed is shown for monofilaments in the graph below. In these trials, the extrusion mass throughput was constant. Therefore, filament denier also decreased with increasing take-up velocity. We observed that maximum spinning speed, prior to fracture, increases until the MPDiol glycol reaches a concentration of seven mole percent. Then, it decreases slightly with increasing MPDiol glycol content. At this substitution level, the slower development of crystallinity initially allows for the greatest draw-down and highest spinning speed before reaching the critical stress for spin-line fracture to occur. At some concentration of MPDiol glycol (above seven mole percent), the crystallization rate is insufficient to provide the deformation strengthening needed to further increase the draw-down without fracture.



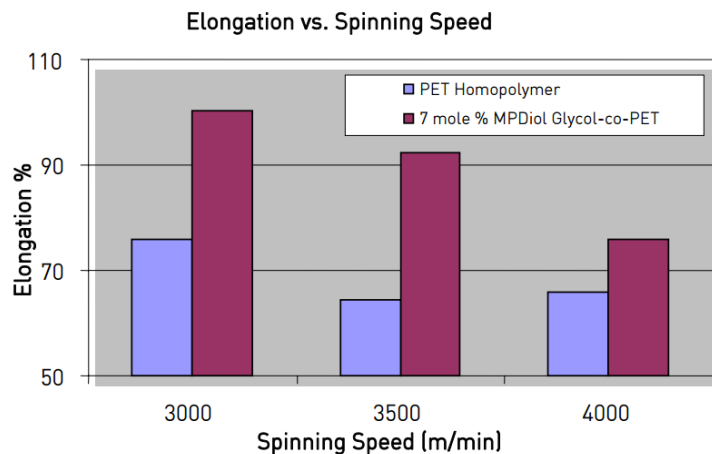
In another trial, copolymers were melt-spun at 3000 m/min through a 72 round-hole spinneret. The mass throughput rate was incrementally decreased, resulting in finer denier partially oriented yarn (POY). Relative spinnability is defined as the finest denier (lowest mass throughput rate) that could be sustained. The results for these tests are shown below. Spinnability was superior to the PET homopolymer control. It is interesting that in these experiments, the spinnability of the 10 mole percent MPDiol glycol-co-PET was better than the seven mole percent MPDiol glycol-co-PET. Moreover, the ultimate denier reduction was not observed for the 10 mole percent MPDiol glycol-co-PET material due to winder equipment limitations.



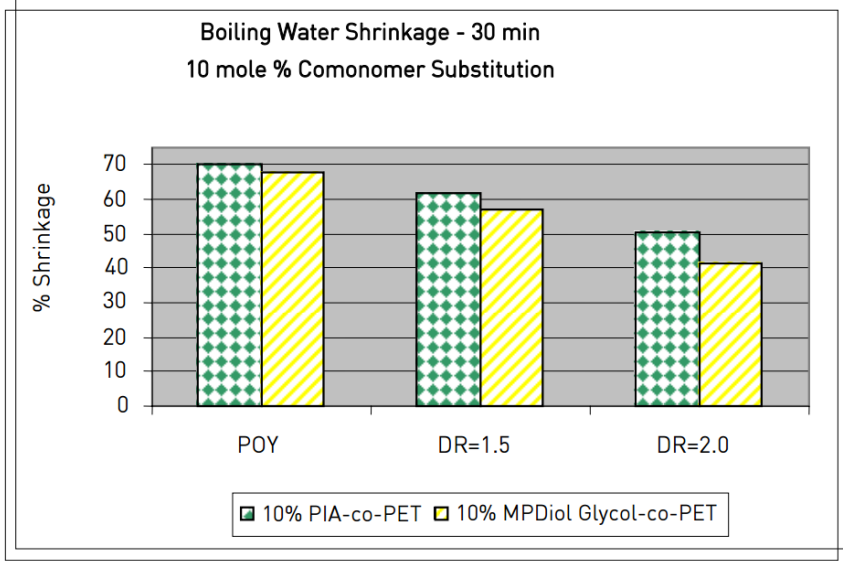
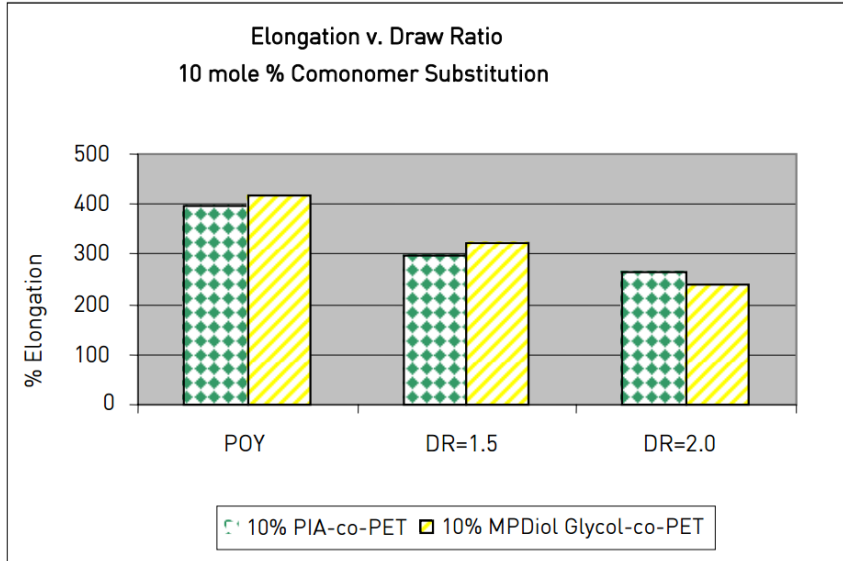
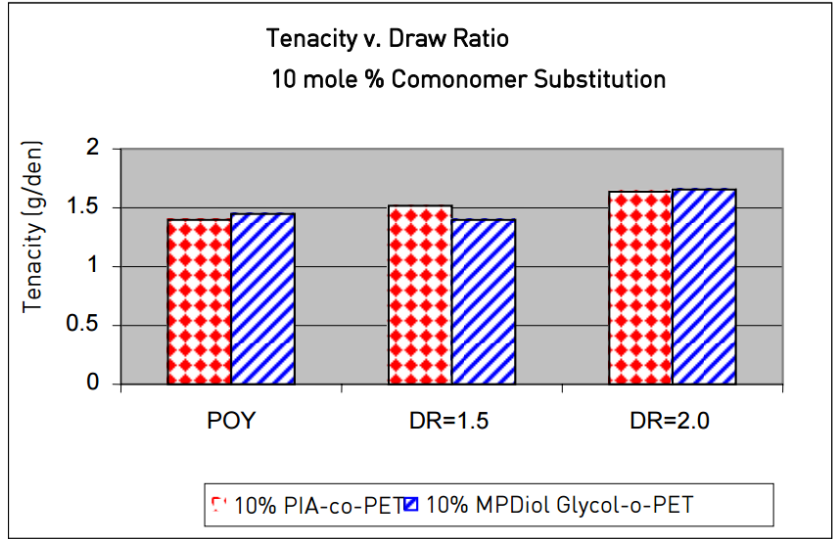
Molecular weight increase via solid state polymerization is an option for improving fiber spinnability. While the spinnability advantages of MPDiol glycol-co-PET can be obtained with conventional melt-phase intrinsic viscosities, the test data indicates the potential to reach higher performance at the higher molecular weights generated from solid state polymerization. An example of this advantage is illustrated below for seven mole percent MPDiol glycol-co-PET at different I.V. values. We also see the impact of increasing I.V. on the ability to spin finer filaments.



Another processability advantage derived from low levels of MPDiol glycol substitution is known as “wind-up speed suppression.” Wind-up speed suppression leads to yarns, which, when spun at high spinning speeds, exhibit properties of yarns spun at lower spinning speeds. MPDiol glycol-co-PET provides this advantage over PET homopolymer because the latter, when melt spun above a certain speed (typically about 3500 m/min), tends to crystallize in the spin line. This limits the mechanical properties, such as percent elongation at higher spinning speeds. MPDiol glycol delays the onset of stress-induced crystallization to higher levels of stress (higher spinning speeds). Therefore, higher elongation values are obtained.



On a molar basis, the tenacity, elongation and boiling water shrinkage of MPDiol glycol-co-PET and PIA-co-PET are comparable. This behavior is illustrated on the next three charts for spun-drawn yarns (244d/72f) at 10 mole percent comonomer substitutions.

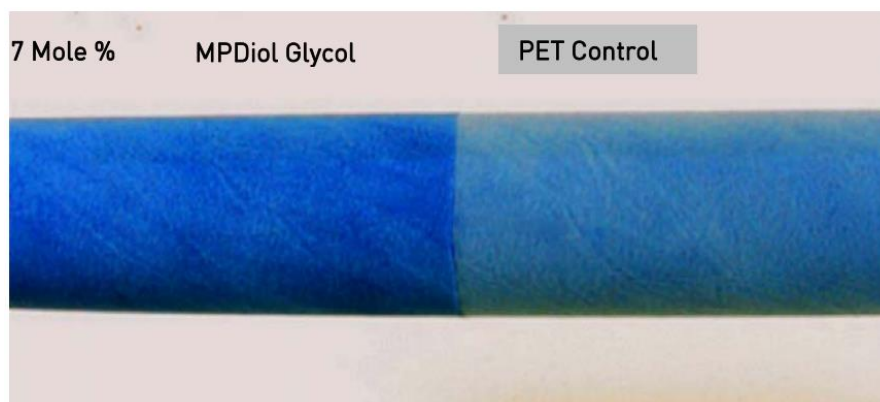


Dyeability

Enhanced disperse dyeability is a key advantage of MPDiol glycol-co-PET. MPDiol glycol-co-PET fabrics can be dispersed-dyed at atmospheric boil conditions to achieve the same color strength as fabrics produced from PET homopolymer, which are dyed under high-temperature/high-pressure conditions. If dyed under equal conditions, for example, at boil, MPDiol glycol-co-PET produces deeper shades using the same dye-bath concentration. Also, equivalent color strengths can be obtained using less dye stuff for MPDiol glycol-co-PET than for PET homopolymer. Moreover, efficient dye uptake occurs in the absence of dye carriers. The use of MPDiol glycol to improve dyeability is generally advantageous with respect to costs associated with dyestuff, carriers, energy consumption and environmental control.

An illustration of the enhanced disperse dyeability of MPDiol glycol-co-PET vs. PET homopolymer is pictured below. In this test, a knit yarn sock with both yarns knitted in different sections, was dyed in a “competitive” condition in a carrier-free, pressure-dyeing process. The dyeing was carried to exhaustion at 130o C. It is evident from the photograph that the seven mole percent MPDiol glycol-co-PET dyes are significantly deeper with a higher rate of dyeability. The Kubelka-Munk (K/S) reflectance values, which are proportional to the colorant concentration in the materials, also validate the greatly enhanced dyeing characteristics associated with a small amount of MPDiol glycol comonomer incorporated. We also observed that MPDiol glycol is more efficient at disperse dye uptake than PIA-modified PET and equal molar substitution levels.

Competitive Pressure Dyebath (130oC) to Exhaustion (No Carrier)



Summary

Chemical modification of PET using MPDiol glycol leads to efficient advantages in fiber conversion and fabric properties. Processing and property advantages have also been observed for film and sheet applications.

MPDiol glycol substitution for EG, on a molar basis, compares equivalently to PIA substitution for PTA with respect to some resin and fiber properties. Due to the difference in molecular weight between the two comonomers, copolymers based on PIA require twice as much material as needed for MPDiol glycol-co-PET. Therefore, MPDiol glycol offers the potential for considerable cost savings based on raw material consumption.

MPDiol glycol is well positioned to participate in the growth of filament applications. The increased spinning speeds that are possible with MPDiol glycol-co-PET have the potential to increase production speeds, to produce finer denier filaments, and to produce filaments with higher elongation. Low-melt/high-shrink properties can benefit thermal bonding efficiencies in the bi-component fibers used in woven and non-woven applications. Moreover, this feature can be exploited in heat extruding to yield high bulk yarns. Self-bulking or self-crimping is also possible.

MPDiol glycol also improves disperse dye uptake in PET. MPDiol glycol allows for more efficient dyeing operations from the standpoint of dyestuff and energy consumption. Overall, MPDiol glycol-substituted PET enables product differentiation through easily made copolymer compositions.

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