

PERP Program – New Report Alert

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Nexant's ChemSystems Process Evaluation/Research Planning program has published a report, *Modified Polyphenylene Oxide (MPPO) (02/03S3)*.

The polyphenylene oxides (PPO) are also referred to as polyoxyphenylenes and polyphenylene ethers (PPE). Variations in the configuration of the ether group (e.g. *ortho*, *meta*, or *para*), and in the extent and type of substitution (e.g. alkyl, halo, etc) on the aromatic backbone permit the synthesis of a large number of possible homo- and co-polymers. This report includes modified PPOs which fall into the performance range of the engineering thermoplastics, but excludes lower molecular weight PPO materials and copolymers used as heat transfer fluids, gas absorbents, and gas chromatography reagents.

PPO thermoplastics were commercially introduced by General Electric in 1965 and applied to surgical instruments and appliance parts. Neat PPO was too difficult for molders to process because it required specialized machinery and a drying step. Modified PPO compounds (MPPOs) were introduced shortly thereafter based on the incorporation of high impact polystyrene (HIPS). Subsequently, PPO compounds containing PPO/polyamide, PPO/polyetherimide, and recently, PPO/polypropylene have been introduced.

About seventy-five percent of modified PPO resins are compounded blends of PPO, high impact polystyrene (containing 8-10 percent rubber), and additives. PPO and polystyrene are miscible in all proportions so compounding these materials is relatively straightforward. The rubber particles from HIPS are uniformly distributed throughout the new polymer matrix. Most of the remainder of modified PPO resins contain polyamide 6 or 6,6. PPO compounds modified with other resins are small in volume.

PPO and polystyrene/HIPS form compatible blends and typically have intermediate property values, except for impact strength which is elevated. Apparently, the ductile PPO matrix is toughened more effectively by rubber than is the brittle polystyrene. However, the rubber particles which optimize MPPO blend performance are smaller than those typically found in HIPS, so special grades of HIPS are preferred. The figure below illustrates the melding of desirable properties in blending PPO with HIPS.

Properties of PPO/HIPS Blends



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Some modified PPO grades also contain a fire retardant, glass, and mineral fillers, or are further modified with additional elastomer. Typically, PPO content ranges from 20 to 80 percent. The ability to vary the PPO content, and to incorporate a variety of other additives permits the production of MPPO materials with a wide range of performance and processability. The properties of the individual polyblends are determined mainly by the PPO:HIPS ratio and by the presence and amount of key additives (e.g. flame retardants and reinforcing agents).

The addition of HIPS to PPO produces an alloy with a broad property profile, excellent flame resistance, and moderate cost. At the lower end of the performance spectrum are cost-effective alternatives to flame-resistant grades of ABS and at the higher end are alternatives to polycarbonate and nylon resins. However, the mechanical properties of PPO/HIPS are less favorable than those of straight polycarbonate or PC/ABS materials. Thus, PC/ABS materials have become strong competitors to modified PPO polymers.

Key physical, mechanical, and electrical properties for selected grades of PPO/HIPS, PPO/Polyamide, and PPO/Polypropylene are summarized in the report.

The notched Izod impact strength (room temperature) of modified PPO varies from 2.3 to 10.0 footpounds per inch, a range that encompasses many engineering polymers, although not polycarbonates. These impact strength values are insensitive to changes in relative humidity, but, as with other engineering plastics, impact strength declines with decrease in temperature. Unlike other engineering plastics, however, modified PPO resins retain more of their original toughness at low temperatures.

The highly aromatic nature of the polymer results in very low water absorption; the aromatic ether linkage of the polymer backbone is highly resistant to hydrolysis. The products are largely unaffected by hot and cold water, detergents, and dilute aqueous acids and bases.

PPO/Polyamide blends combine the dimensional stability, low water absorption and heat resistance of PPO with the chemical resistance and flow of polyamides (polyamide 6 and 6/6 are typically used). Blends of PPO and polypropylene combine the dimensional stability, low water absorption and heat resistance of PPO with the ductility (toughness), chemical resistance, and low water absorption of polypropylene. PPO/PP blends also offer improved recyclability, because they can be reground together with other polypropylene-based resins. This point is particularly important to the automotive industry.



Extensive information is provided in the report concerning interpolymer competition among engineering thermoplastics, both neat and glass-filled varieties.

Most commercially significant PPO resin is produced through the oxidative coupling of 2,6-xylenol in the presence of oxygen. The reaction is represented by the following equation:



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The monomer yields a linear polymer, since the position *para* to the hydroxy group is the only available active site. Other PPO resins can be produced containing one or more other comonomers, and, indeed, materials containing 5-10 percent 2,3,6-trimethylphenol have been commercialized.

The exothermic polymerization reaction takes place in a liquid-phase stirred reactor in the presence of a toluene solvent, a copper-halide-amine catalyst system, and oxygen sparged into the reaction mixture. The reactor operates batchwise at 25-35°C, and at atmospheric pressure.

Reactor effluent is treated for catalyst inactivation, then phase separated. The organic phase is water washed and again separated. Following antisolvent precipitation, wet PPO is recovered, washed, separated, and dried.

Compounding of PPO with other polymers and additives is now typically performed in highlyautomated lines incorporating twin-screw extruders to provide excellent mixing action. In the cases of PPO/polyamide and PPO/polypropylene blends, compatibilizers are added to improve the compatibility and dispersion of PPO in the blend. PPO end-capped with functionalized maleic anhydride can be used to react with the polyamide or polypropylene polymer, producing a compatibilizing block copolymer in-situ.

Economic estimates are provided on a current U.S. Gulf Coast basis for 50/50 blends of PPO with HIPS, polyamide 6,6, and thermoplastic olefins (TPO). Transfer prices are developed for 2,6-xylenol and PPO. Sensitivities to phenol and methanol prices, as well as blend production capacities, are presented. The effect of transfer prices versus market for non-PPO blend components is also evaluated.



This report also presents global demand for modified PPO projected through 2007, categorized by major end use applications and also by region (United States, Western Europe, Japan, rest of world). MPPO global capacity by producer is given for 2002.

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