

PERP Program – New Report Alert

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Nexant's ChemSystems Process Evaluation/Research Planning program has published a new report, *Thermoplastic Copolyester and Copolyamide Elastomers (02/03S9)*.

This report covers two families of thermoplastic elastomers, loosely called copolyester elastomers (COPE) and copolyamide elastomers (COPA).

COPE was first introduced in 1972 by DuPont (HYTREL), and its demand has been driven by the replacement of thermoset rubbers in transportation applications. Among thermoplastic elastomers, COPE is only surpassed by COPA in price and performance, and thus must generally combine property advantages with lower molding costs in order to replace thermoset rubbers or other thermoplastic elastomers (TPEs).

COPE offers a number of outstanding properties:

- Very good flex crack resistance
- Mechanical properties, such as tensile and tear strength, fatigue resistance and abrasion resistance, which approach thermosets
- Outstanding chemical resistance, especially in applications where fuel or oil resistance is important
- Excellent flexibility at room and low temperatures, approximately -45°C to as high as 140°C (for high hardness grades)
- Outstanding resistance to stress relaxation and creep
- High vapor transmission rate
- Good tactile feel
- High impact strength, even at low temperatures

COPE resins are easy to process, and can be blow molded, injection molded, extrusion coated, calendered, rotational molded, and processed in other extrusion processes (tubing and cast film). They can be further machined by conventional cutting, tapping, or finishing techniques when necessary. COPE resins also feature good adhesion to many other materials including ABS, PBT, PC, paint, glues, and metals. Weatherability and flame resistance can be easily improved with suitable additive packages.

The COPE materials consist of alternating hard and soft segments. Changing the soft block concentration and molecular weight leads to a range of products with different properties, of which softness is perhaps the best indicator.

The COPA elastomers are among the highest cost and highest performing of the thermoplastic elastomers. Only a few silicone and fluoropolymer elastomer grades are higher in price and performance. Due to their high cost, COPA resins are still low-volume materials, and tend to find use in specific applications where less expensive materials will not suffice.

Copolyamide elastomer “PEBAX” was introduced by Atochem (now AtoFina) in 1981. By varying the nature and length of the hard and soft blocks, a wide range of hardnesses can be achieved. Altering the polyether/polyamide weight relationship also changes selected properties such as flexibility.

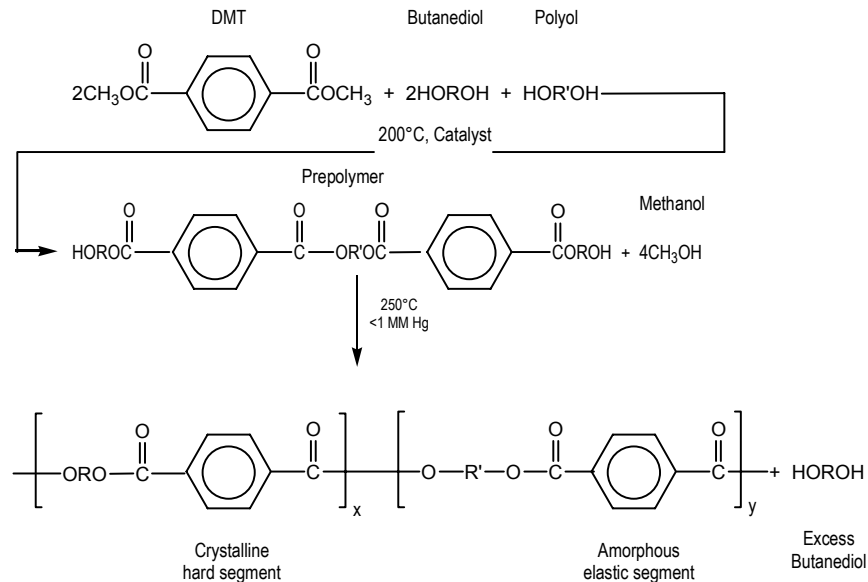
Key physical properties possessed by COPAs include:

- Good chemical resistance
- Wide range of flexibility, which is particularly beneficial in cases where overmolding techniques will be utilized
- High mechanical strength and toughness
- Outstanding low temperature impact strength and flexibility
- Very good dynamic characteristics (recovery)
- Good thermal stability and abrasion resistance
- Low density

These resins are typically fabricated as for COPEs and can also be used in powder coating processes.

Copolyester elastomers are composed of polyether segments, such as poly(alkylene oxide), alternating with polyester segments, such as poly(alkylene terephthalates). The polyether segments are amorphous elastic segments that provide flexibility by virtue of their low glass transition temperature. The polyester segments are hard by virtue of their crystallizability, which gives the material good performance under environmental extremes. Most commercial products, such as DuPont’s HYTREL, are based on dimethyl terephthalate (DMT) and polytetramethylene ether glycol (PTMEG).

COPE is made by typical melt polymerization procedures. First, a prepolymer is prepared by reacting an ester, such as dimethyl terephthalate, with a poly(alkylene oxide), such as polytetramethylene ether glycol, and an excess of a short-chain diol, such as 1,4-butanediol. The reaction takes place in the presence of titanate catalyst, with evolution of methanol. The prepolymer is driven to a molecular weight of 25-30 thousand by distilling off some of the excess original short-chain diol at 250°C and a pressure less than 1 mm Hg absolute. The reaction sequence is as follows, where ORO is 1,4-butanediol and OR’O is PTMEG:

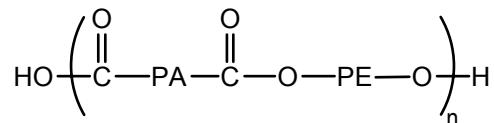


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Other dicarboxylic acids such as isophthalic acid, phthalic acid, and naphthalenic di-acids are sometimes used, and 1,6-hexanediol can substitute for some of the 1,4-butanediol. Other polyols are also sometimes utilized, such as polybutylene adipate glycol and polypropylene glycol.

Small amounts of branching agents such as trimellitic anhydride, trimesic acid, and oxypropylated triols can be added to provide long chain branching and improve the reaction rate, but potentially at the expense of physical properties such as elongation, tensile strength and tear resistance.

The copolyamide elastomers (COPA) can be prepared by reacting a dicarboxylic polyamide with a poly(oxyalkylene) glycol, employing a catalyst to achieve a homogeneous phase. The general formula for the polyether block amide is shown below, where PA represents the polyamide block and PE represents the polyether block:



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Various nylons that can be employed as the polyamide segment include nylon 6, nylon 11, nylon 12, nylon 6/6, nylon 6/11, and nylon 6/12. For the polyether diol segment, polyethylene glycol, polypropylene glycol, and PTMEG can be employed. A typical catalyst is tetrabutylorthotitanate. The polymerization conditions are such that the reactants are maintained in a fluid state. Typical conditions are 200-300°C (392-572 °F) at 0.5-2.0 mm Hg of pressure.

The proportion of polyglycol to total block polymer can vary from 50-85 percent. If the amount of polyoxyalkylene glycol is in the 5-50 percent range, the resulting block copolymers are moldable and/or extrudable substantially nonelastomeric products which can be formed into a variety of form-stable shaped articles, fibers, and filaments.

Block copolymers having a polyoxyalkylene content of between 15-30 percent are form-stable and possess a certain softness without containing a plasticizing additive. Block copolymers with a polyoxyalkylene content between 30 and 50 percent, are soft to very soft, yet non-elastomeric.

If the amount of polyoxyalkylene glycol is between 50 and 85 percent, the resulting block copolymers are elastomers having physical and mechanical properties similar to those of natural or synthetic rubber. Diacidic couplers, such as adipic, isophthalic, azelic, sebacic, and dodecanedioic acid can be used to tailor the melting point of the resulting material.

Economics were developed for COPEs containing three different soft (amorphous) segments, PTMEG, butanediol adipate, and poly(propylene oxide) glycol, and for a COPA grade containing PTMEG as the soft segment.

Most participants are integrated into at least some of their soft segment production, which also permits a COPE or COPA producer to keep certain aspects of their formulations proprietary. Some producers are also integrated into DMT production. An additional set of economics illustrates the benefits of feedstock integration.

The commercial portion of the report presents global demand for COPE by application and by region, with forecasts to 2007. The largest COPE demand continues to be for transportation applications. Global COPA demand by region is likewise forecast to 2007. COPA is used predominantly for ski boots and high-end sportswear.

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