

CHEMSYSTEMS PERP PROGRAM

# Polyoxymethylene (POM; Polyacetal)

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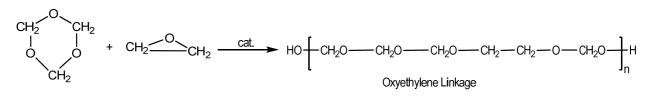
#### INTRODUCTION

Acetal polymers, also known as polyoxymethylene (POM) or polyacetal are formaldehyde-based thermoplastics that have been commercially available for 40 years. Polyformaldehyde itself (i.e., the homopolymer of polyacetal) is a thermally unstable material that decomposes on heating to yield formaldehyde gas. Two methods of stabilizing polyformaldehyde for use as an engineering polymer were developed and introduced by DuPont in 1959 and Celanese in 1962.

DuPont's route for polyacetal yields a homopolymer through the esterification of polyformaldehyde with acetic acid to give a polyformaldehyde-acetic anhydride copolymer.

$$HO - \left[CH_2O - \right]_n H + 2CH_3CO_2H \longrightarrow CH_3CO_2 - \left[CH_2O - CH_2O - \right]_n COCH_3 + 2H_2O$$

The Celanese route for the production of polyacetal yields a more stable copolymer product via the reaction of trioxane, a cyclic trimer of formaldehyde, and a cyclic ether (e.g., ethylene oxide as shown below; or 1,3-dioxalane –  $(CH_2)_2O_2CH_2$ ):



The improved thermal and chemical stability of the copolymer versus the homopolymer is a result of randomly distributed oxyethylene groups. These groups offer stability to oxidative, thermal, and alkaline attack. The raw copolymer is hydrolyzed to an oxyethylene end cap to provide thermally stable polyacetal copolymer.

In this PERP report, Nexant discusses the commercial and developing processes to manufacture polyacetal. Detailed economic analyses comparing the different commercial technologies in use are presented, along with pro-forma economics illustrating the direction of copolymer process technology. Commercial applications, regional demand and a global capacity listing are also provided.

#### COMMERCIAL TECHNOLOGY

Polyacetal Homopolymer

Polyacetal homopolymer (for example, DELRIN, produced commercially by DuPont) is a polyoxymethylene material produced by polymerization of formaldehyde. The formaldehyde, which is supplied to the polymerizer as a vapor, must have a purity of greater than 99.9 weight percent in order to achieve polymer molecular weights in the commercially desired range (20 000 or greater). Water, methanol, and formic acid, present in commercial formaldehyde, act

as chain-transfer agents that lower the polymer molecular weight and must therefore be removed. Conceptual process flow diagrams are provided.

Polyacetal Copolymer

Due to its improved thermal stability, the copolymer has become the preferred form. The commercially significant polyacetal copolymers (for example, CELCON, produced by Ticona (the plastics division of Celanese Corporation)) are addition polymers of formaldehyde and a relatively small amount of a comonomer.

Polyacetal copolymer is produced by a bulk polymerization process. A strong Lewis acid serves as the polymerization catalyst and a chain-transfer agent is added to control molecular weight. Boron trifluoride is the Lewis acid most commonly used today as a catalyst. It is important to remove any water or methanol, as water yields no stable end-groups, and methanol yields only one stable end-group. Hence, as in the homopolymer process, it is important that concentration of water in the streams supplied to the reactor be held to a minimum. Conceptual process flow diagrams are provided.

#### DEVELOPING TECHNOLOGY

It is widely recognized that the copolymer processes currently in commercial operation include additional steps in order to deactivate the catalyst and stabilize the acetal resin. Recent patents discuss a simplified process that significantly reduces the capital costs and operating steps required to produce polyacetal resins. Simply stated, the process uses a strong protic acid to catalyze the polymerization reaction, instead of a Lewis acid. The copolymer acetal resin is then transferred directly from the polymerization reactor directly into a twin screw extruder for finishing. No deactivation steps are required, and removal of formaldehyde or excess monomer is accomplished by drawing a vacuum on the material as it is transferred and as it is being finished.

It does not appear that such a simplified process will work in the production of homopolymer acetal resins, as there are no copolymer units to block depolymerization of the polymer chains. Consequently, homopolymer polyacetal producers have worked to improve the throughput of their processes, most likely by improving the on-stream factors for their polymerizers by reducing polymer fouling of the top heads and vapor lines.

#### PROCESS ECONOMICS

Economics for various plant types and locations are provided, and are discussed in detail. The pricing basis for the economic analysis is for first quarter 2011; economics were prepared for U.S. Gulf Coast, Coastal China (i.e., Shanghai, Zhejiang, or Guangdong), and Inland China (i.e., Shanxi, Shaanxi or Inner Mongolia). Different capital investment location factors are used, reflective of the construction costs in the three locations.

The specific cost of production tables that have been evaluated are as follows:

• Homopolymer polyacetal through a process believed to be representative of DuPont's

- Solution copolymer polyacetal in a process commonly referred to as a solution hydrolysis process because the polyacetal polymer is placed into a solution or slurry prior to undergoing the hydrolysis reaction. The solution hydrolysis process is still in use in older plants, although refinements have been made in operating conditions
- Bulk copolymer polyacetal process, which is similar to the solution process up to the point of exit from the polymerization reactor. Instead of being ground and placed into solution or a slurry, the finely divided polymer falls through a drop shaft and into a compounding extruder. Water is added to serve as a chemical reactant for the hydrolysis reaction
- Simplified bulk copolymer polyacetal process represents the direction of copolymer polyacetal production technology. The simplified bulk process incorporates improvements in the area of comonomer purification, catalyst efficiency (reduced use per pound polymer), more effective stabilizers (formaldehyde scavengers), and catalyst neutralization (as opposed to removal)

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities, and direct and allocated fixed costs. These categories are presented annually by unit consumption and per metric ton. The contribution of depreciation is also included to arrive at a full cost estimate.

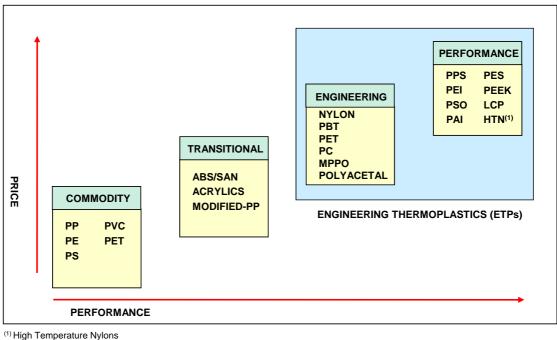
In light of this strong integration with formaldehyde which exists in the industry, the key raw material variable that polyacetal producers' face is methanol pricing. Polyacetal production accounts for only a small fraction of total methanol demand, so polyacetal producers have relatively little leverage in pricing over methanol producers.

To test the effect of alternative methanol pricing, sensitivities are included for the USGC economic analyses. The sensitivities used reflect the approximate range of methanol USGC contract prices which have occurred over the past decade.

#### COMMERCIAL MARKET REVIEW

Polyacetal is only one of a number of engineering thermoplastics (ETPs), as illustrated below.

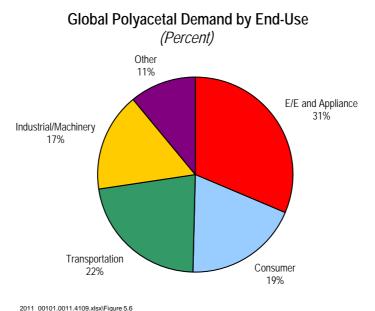




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Although acetal resins compete quite strongly against nylon 6 and 6,6, they do, at times, compete against other materials in the Engineering Thermoplastic family. This is partly a result of the versatility of these materials and partly a result of property deficiencies being overcome by blending, additives, or other techniques.

Polyacetal's versatility and usefulness in small parts is largely responsible for the demand by end-use pattern shown below, where the largest end-use sector is electrical/electronics (E/E) and appliances at 31 percent of the global total. Note that demand is fairly evenly spread among the next three largest end-use markets, a pattern which is unusual in engineering plastics.







Other discussion in the commercial analysis includes a review of polyacetal end-uses, and polyacetal demand for the regions:

- North America
- Western Europe
- China
- Rest of World
- Global Summary

Additionally, a global listing of polyacetal plants is provided, with capacity, location, and polymer type (i.e. homopolymer or copolymer).





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