

PERP Program – Reducing Costs in PET Manufacture

New Report Alert

September 2005

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Reducing Costs in PET Manufacture (04/05S7)***. To view the table of contents or order this report, please click on the link below:

http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Conventional Technology

Polyethylene terephthalate (PET) may be produced from ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). High purity is required of all raw materials. In either case, the first step of the reaction is the formation of a prepolymer, bis-hydroxyethyl terephthalate (bis-HET). Subsequent polymerization of this material (with the removal of ethylene glycol) forms the polymeric polyethylene terephthalate. The extent of polymerization (apparent from the molecular weight of the polymer) is a function of the polymerization conditions and significantly affects the properties of the resin that is produced. As the polymer grows in length, both molecular weight and viscosity of the reacting mass increase; thus intrinsic viscosity (IV) is frequently used as a measure of polymer molecular weight. When very high molecular weights are desired, as is the case for bottle-grade PET resins, the polymerization may be carried out in stages, with different reaction conditions being utilized in each stage.

When starting with terephthalic acid (TPA), the first step in the polymerization sequence is an esterification of 1 mole of acid with 2 moles of glycol. Water is liberated in the process. Also, the esterification reaction is faster and requires less catalyst. The main drawbacks of the esterification scheme are that TPA is less soluble than DMT in glycol and that purification of TPA is more difficult than purification of DMT.

The major breakthrough in the technology of this reaction involved operating at pressures above atmospheric and temperatures greater than the normal boiling point of glycol, to achieve shorter reaction times. Molar glycol to TPA ratios of 1.1:1 to 2:1 are used (presumably some polymerization occurs accounting for a molar ratio of less than 2.0:1). Reaction temperatures range from 258°C to about 263°C. Pressures are below 25 psig, and the water of reaction is removed from the system through a reflux column. Industrial use of these high temperatures and superatmospheric pressures is now almost universal.

The second step in the polymerization sequence is the polycondensation of bis-hydroxyethyl terephthalate with liberation of ethylene glycol for recycle.

When the polymer is to be used for fiber, its molecular weight should be between 14,000 and 20,000. The reaction temperature must be above the melting point of the polymer (260-265°C) and below the temperature at which decomposition occurs too rapidly (300°C), so that temperatures between 275°C and 290°C are favored for polycondensation. The removal of glycol vapors (under vacuum) drives the equilibrium toward polycondensation. The partial pressure of glycol over the polymer melt must be reduced to less than 6 mmHg if useful molecular weights are to be obtained. Because the diffusion rate of by-product ethylene glycol from the molten polymer is rate limiting near the end of the reaction, the ethylene glycol must be separated as quickly as possible. This is accomplished by high vacuum and by mixing the melt so as to continuously expose a large amount of surface. The time of the reaction is at least two hours at 290°C, depending upon the type of reactor used.

Both the high temperature (required to keep the polymer in a molten state) and the high viscosity of the polymer may cause degradation. Triphenyl phosphite is the preferred stabilizer.

Many catalysts have been developed that are effective during the polycondensation as well as during the initial esterification or transesterification. Of these, antimony compounds, such as trioxide or triacetate, are the most common.

Melt-phase polymerization is typically carried to an IV of about 0.60-0.65. The polymer is then converted to a solid particle and crystallized to minimize tackiness in any downstream solid-state polymerization used to raise IV and molecular weight further.

IPT (Invista Performance Technologies) NG3™

INVISTA's (formerly DuPont's) NG3™ process is a departure from conventional polyester technology and is built around the use of a rotoformer in place of conventional polymerization reactors. Rather than relying on the melt plant to produce an intermediate with a high IV (typically around 0.6-0.65), NG3™ produces a low IV intermediate and then carries out most of the polymerization in the solid state. The novel feature of the technology is the formation of pastilles, a form of polymer solid particle that can be further polymerized in a conventional solid-state polymerization plant. The pastilles are formed from low molecular weight polymer (degree of polymerization 20-30, 0.23-0.28 IV), and have a unique crystalline structure that aids further processing.

Another feature offered by NG3™ is the pre-polymerizer. This reactive distillation column is designed to increase the degree of polymerization using a closed loop, nitrogen circulation system and allow elimination of the vacuum system that is integral to conventional technology.

INVISTA claims the following advantages:

- Installed cost reduction for the melt plant
- Large, single-train melt plant with capacity in excess of 1150 tons per day offering substantial economy of scale advantages
- Reduced overall energy consumption
- Enhanced product quality, with reduced acetaldehyde

Developing Technology

- Eastman *IntegRex* Process

Eastman recently announced an innovation in the polyester chain called *IntegRex*, that promises savings compared to conventional *para*-xylene to polyester resin technology. Eastman says it will build a 350,000 metric ton integrated PET manufacturing facility using this new technology at its existing site in Columbia, SC. Eastman's existing purified terephthalic acid facilities will be retrofitted using additional elements of *IntegRex* to supply intermediates for the expansion. The company expects to receive patents on more than 100 process and product innovations surrounding the technology. Information released by Eastman suggests that the innovation allows for multiple process variations, process optimization that results in reduction of energy, labor, process steps and equipment, and elimination of the solid-stating process.

The improvements that Nexant believes may be part of *IntegRex* include:

- The use of aqueous TA solution with EG in the polyester plant eliminating TA drying and solidifying equipment in the TA plant and the slurry mix equipment in the polyester plant.
- Direct coupling of the water distillation in the CTA oxidation section to the reactor. This provides for a lower cost removal of the water produced in the CTA reaction and lower waste treatment costs (removal of the acetic acid contained in the water).
- Hydrogenation of 4-CBA and color impurities after esterification in the polyester plant instead of in the TA plant.
- Use of higher CHDM (1,4-cyclohexanedimethanol) content comonomer polyester which enables higher IV attainable in the melt phase and possible elimination of polyester solid-stating.

- Eastman Pipe Reactor

Eastman Chemical has filed a recent patent application that describes a novel pipe reactor design for either esterification or polycondensation or both. It is unclear if the reactor design characterized in the patent is part of the overall *IntegRex* design.

The Eastman patent claims that there are numerous cost and operation related simplifications because of the pipe reactor design:

- Because the reactors are pipe with flexible orientation and layout, the plant can be designed for limited space conditions, such as areas that have interferences from other piping, columns, etc.
- The pipe reactors do not require level or pressure control.
- In a large part (or totally), pumps, reactor agitators, reactor screws (horizontal agitators), and associated seal systems are eliminated
- The pipe reactors can be welded without gaskets, which reduces emissions out of the reactor and air leakage into the reactor, improving product quality
- The fabrication time for the traditional long-lead items is eliminated or greatly decreased, shortening the overall project schedule

The patent claims that the pipe reactor design can be used to produce lower IV polyester or PET resin with IV in the range of 0.75, sufficient for carbonated drink applications, without the need for additional solid-stating.

- M&G EasyUp Process – Improved Solid-Stating

M&G has developed an SSP technology improvement called EasyUp that it claims simplifies the process and the plant layout, lowering both the capital cost and the operating cost.

The EasyUp process takes place in a special gas atmosphere which allows the use of smaller sized equipment. The reaction itself takes place in a horizontal kiln type reactor which guarantees a perfect plug flow (equivalent to 500 CSTR in series vs. 10 CSTR in series of standard technology). Overall, the streamlined process requires half the equipment utilized in standard technology.

- Inventa-Fischer Elimination of Solid-Stating

Inventa-Fischer (a subsidiary of Uhde GmbH since 2004) offers what they claim is the latest proven technology based on its innovative 2-reactor technology for the polyester polycondensation.

The two-reactor technology used in the plant can be adapted to the production of all polyesters (PET, PBT, PTT, PEN) and their co-polymers, and is said to offer significant financial advantages over the more conventional 4-reactor technology. The unique technology is characterized by the so-called Espree tower reactor, which combines the esterification and pre-polymerization stages in one reactor devoid of mechanical agitation. A new surface active process and constructional elements within the Espree tower ensure an efficient short term reaction and enable the maintenance of a gentle temperature and pressure profile. The material then passes to the Discage finishing reactor, which handles the required medium and high-viscosity polymer without further solid stating.

The advantages of 2-reactor technology as outlined by Inventa-Fischer are the lower capital investment compared with 4-reactor plants, lower maintenance costs, lower energy consumption, and reduced temperature profile. An 80 thousand metric tons per year plant using the process was successfully started up in late 2003.

- Zimmer Elimination of Solid Stating

Zimmer is developing a process called the Direct High IV Process (DHI) that eliminates solid stating (SSP) and the production of melt chips. The design uses the conventional Zimmer front end (melt) design.

The DHI design features an acetaldehyde scavenger injection downstream of the finishing reactor. There are a number of commercially available FDA approved acetaldehyde scavengers.

The design includes a granulation system with an underwater pelletizer that uses the latent heat in the chips directly following chips formation to promote crystallization. The process can produce bottle resin chips similar to conventional chips when the plant is designed to produce chips rather than direct to perform (or both). The chips are spherical and are claimed to be highly uniform with a reduced amount of dusting and dust losses.

Zimmer claims a 15-20 percent ISBL capital cost savings for the design.

- Inventa-Fischer Melt to Preform

Inventa-Fischer's Two-Reactor technology can also be designed to produce resin directly to preforms as mentioned previously, which they call Melt to Preform (MTP).

The process claims several cost advantages related to the preform production:

- Lower conversion cost from raw materials to preform

- Lower raw material consumption
- Lower emissions

In addition, there are claims related to preform characteristics and quality, such as less thermal stress, combined quality optimization for polycondensation and injection molding processes, and increased mechanical bottle properties, such as burst strength.

Inventa-Fischer also claims that the MTP process does not require comonomer for the purpose of reducing the melting point, in this case IPA.

- Zimmer Direct to Preform

Zimmer is offering a process called the Direct To Preform (DTP) process that integrates chips and preforms production, eliminating the production of bottle grade chips. As with Zimmer's DHI, the design uses the conventional Zimmer front end (melt) design.

Zimmer calls DTP a logical extension to DHI. The process features direct melt feed to the preform machines (machines that have been modified for melt feed by Husky). In addition, the process allows for simultaneous chips and preforms production.

Zimmer lists several advantages:

- No intermediate chips handling - less contamination
- Lower IV variations, no residual moisture to degrade IV
- Brighter and better color (no risk of oxygen intrusion)
- Chips have lower heat of fusion - reduced energy use in preform machines
- New formulations possible
 - Heavy-metal free catalysts (no SSP capacity penalty)
 - Lower cost recipe (lower IPA content possible)

Economics

Economics have been developed for production of melt-phase and solid-state PET from market price purified terephthalic acid for a typical U.S. Gulf Coast plant location for the estimated year average 2005 raw material prices and unit costs. Isophthalic acid is added at about 2 percent replacing a corresponding amount of PTA to produce a bottle-grade suitable polymer.

The Eastman pipe and Zimmer DHI processes show 0.3-0.4 cents per pound advantage in total cost plus return versus a conventional SSP plant operating on PET chips from a melt-phase plant.

Nexant has estimated an integrated *IntegRex* complex based on process developments disclosed in relevant patents to date and limited disclosures by Voridian/Eastman in the public domain.

The integrated cost of production for a 660 thousand ton per year improved TA plant and a similar sized pipe-reactor PET plant (6 lines) is presented, along with a conventional 660 thousand ton per year PTA plant integrated with a 660 thousand ton per year conventional PET plant (3 lines) and with a non-integrated conventional plant.

This evaluation shows the *IntegRex* integrated plant to have an identifiable advantage over the costs of both the integrated and non-integrated conventional plants. If we had assumed that the pipe-reactor technology could support a larger per line capacity and a resultant three-line PET plant, the *IntegRex* cost advantage would have been even greater.

Commercial Analysis

Supply, demand, and trade are projected for the United States, Western Europe, and Asia Pacific through 2010.

- United States

Polyester has two major outlets in the United States: PET resin for packaging applications, and polyester fiber for textiles. PET resin, or bottle grade, is one of the fastest growing plastics markets and accounts for more than 60 percent of the total polyester production in the United States. It has been growing at double-digit rates worldwide. Polyester fiber is the second largest segment, but it is mature in the United States market. Competition from imported textiles will continue to limit future growth. The third use, film, is also a mature market.

- Western Europe

PET fiber developments in Europe are expected to reflect an ongoing focus on specialties and a move away from commodity textile fibers, with the overall market size remaining fairly flat. The fiber industry in Europe is disadvantaged relative to Asian producers by the high cost of labor and capital. The bottle grade PET sector is expected to continue a high rate of growth, with mineral water replacing carbonated soft drinks as the main growth engine.

- Asia Pacific

The Asia Pacific PET industry is undergoing a period of rapid expansion, and an ongoing concentration of activities in China. The region now accounts for around 80 percent of global PET fiber production, and 40 percent of global PET bottle grade production.

Over-capacity has led to periods of significant oversupply and extremely volatile pricing. Many producers have sought to export a proportion of their output to Western markets, although the cost of freight and duty make this less attractive.

=====
Copyright© by Nexant, Inc. 2005. All Rights Reserved.

Nexant, Inc. (www.nexant.com) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, Nexant/ChemSystems has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant's chemicals and petroleum group has its main offices in White Plains (New York) and London (UK), and satellite offices worldwide.

These reports are for the exclusive use of the purchasing company or its subsidiaries, from Nexant, Inc., 44 South Broadway, 5th Floor, White Plains, New York 10601-4425 U.S.A. For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: <http://www.nexant.com>.