Nexant’s ChemSystems Process Evaluation/Research Planning program has published a new report, *Polyether Polyols (03/04S5)*.

**Introduction**

Two main classes of polyols are used in polyurethane manufacture, polyether polyols and polyester polyols. Polyether polyols provide unusually high hydrolytic stability and good low-temperature flexibility. Their viscosity is relatively low. They are hampered by susceptibility to degradation by light (ultraviolet radiation) and by oxygen when hot. Both antioxidants and UV stabilizers are used to counteract these forms of degradation. Polyester polyols provide superior mechanical properties, such as tensile strength, abrasion, and wear resistance, as well as solvent and oil resistance, to the polyurethanes in which they are used.

Polyether polyols represent a range of products produced by the oxyalkylation of discrete polyfunctional initiators or starters. The resulting polyol products vary considerably depending on the initiator system, product molecular weight, and the oxides utilized for the oxyalkylation. Propylene oxide (PO) and ethylene oxide (EO) are the alkylene oxides (cyclic ethers) most often used in polyether polyols production. The following starters are used industrially to supply the active hydrogens for polyfunctional polyols: glycerin, trimethylolpropane, pentaerythritol, sucrose, sorbitol, water, bisphenol A, ethylenediamine, toluenediamine, ethylene glycol, and propylene glycol.

Table 1 presents the properties and uses of selected polyether polyols. The molecular weight range for polyethers is generally between 180 and 8,000.

<table>
<thead>
<tr>
<th>Starter</th>
<th>Alkylene Oxide</th>
<th>Functionality</th>
<th>Molecular Weight</th>
<th>Hydroxyl Number</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene glycol (PG)</td>
<td>PO</td>
<td>2</td>
<td>2,000</td>
<td>56</td>
<td>Elastomers</td>
</tr>
<tr>
<td>Trimethylolpropane (TMP)</td>
<td>PO – EO</td>
<td>3</td>
<td>4,800</td>
<td>35</td>
<td>Flexible molded foam</td>
</tr>
<tr>
<td>PG – TMP</td>
<td>PO – EO</td>
<td>2.78</td>
<td>3,180</td>
<td>49</td>
<td>Flexible slabstock foam</td>
</tr>
<tr>
<td>TMP</td>
<td>PO</td>
<td>3</td>
<td>306</td>
<td>550</td>
<td>Rigid foam</td>
</tr>
<tr>
<td>Sucrose – PG – water</td>
<td>PO</td>
<td>5.8</td>
<td>856</td>
<td>380</td>
<td>Rigid foam</td>
</tr>
</tbody>
</table>

EO = ethylene oxide; PO = propylene oxide
The growth in demand for polyether polyols is largely a function of growth in polyurethane foam usage. Flexible and semi-rigid foams constitute the major portion of the cellular demand for polyethers. In addition to the dominance of the cellular market by the flexible foams, another factor is the higher proportion of polyol (about 69 weight percent) in flexible foam formulations, compared to about 35 percent polyol in rigid foam formulations. Rigid foams have been growing at higher rates than flexible foams, due to increased utilization of rigid urethane in insulation and structural applications.

Polyols are relatively mature products, and consumption in the developed world is expected to follow growth in gross domestic product (GDP) closely. In the developing world, demand growth will be higher, with increasing per capita consumption as disposable income increases. Growth rates in the developing world are anticipated to be 1.5 to 2.0 times GDP growth.

Global demand growth is forecast to be 4.1 percent per year for the 2000-2005 period and 4.5 percent per year for 2005-2010. East Asia will have the largest increase in demand, growing at 8.3 percent per year for 2000-2005 and 7.6 percent per year for 2005-2010.

The report provides supply and demand estimates for the United States, Western Europe, and East Asia through 2010.

**Polyurethanes**

Polyurethanes result from the reaction of polyols with isocyanates. During reaction of the isocyanate and polyol, low-boiling liquids or water can be introduced and vaporized by the heat given off by the curing reaction to yield a thermoset material with a foamed, cellular structure. Alternatively, inert gases can be introduced for foam formation. Polyurethanes are also used in coatings, adhesives, sealants, and elastomers (collectively referred to as CASE applications); thermoplastic resins; and fibers.

Flexible polyurethane foam (FPF) is used as cushioning for a wide variety of consumer and commercial products, including furniture, carpet cushion, transportation, bedding, packaging, and textile backing. FPF cushions upholstered furniture, office chairs, stadium seating, and auditorium seating, providing support, comfort, resiliency, and durability. FPF underlayment improves the comfort and lifespan of carpeting by absorbing much of the energy from traffic and thus protecting the carpet face which allows the carpet to look better longer. Additional benefits are sound deadening and thermal insulation.
Rigid polyurethane foam (RPF) is used primarily in building construction as insulation for roof and wall panels, insulated windows and doors, and air barrier sealants. Polyurethane foams have one of the highest insulating values per inch of thickness, making it possible to have thinner walls and lower profile roofs while maximizing efficiency, increasing space utilization, and reducing heating/cooling costs. In addition to thermal insulation, RPF also provides sound deadening benefits. RPF applied on-site acts as a sealant by expanding to fill gaps around window frames, plumbing pipes, and electrical outlets, cutting air infiltration and saving energy.

Polyurethane coatings improve the appearance and lifespan of products and their components. Polyurethane coatings on car exteriors give a high gloss finish with improved color retention, and scratch- and corrosion-resistance. Polyurethane coatings are also used to glaze windshields and windows, increasing strength and providing fog resistance. Other types of polyurethane coatings are used in construction where steelwork and concrete are spray-coated to make them more durable and less costly to maintain. Coatings used in the aerospace industry protect the external parts of aircraft from extreme temperature swings, rust, and pitting.

Polyurethane adhesives and sealants provide strong bonding and tight seals in a variety of applications. Rapid “green strength” is an important advantage of polyurethane adhesives, providing a firm initial bond before fully curing and reducing the need for clamping. Polyurethane adhesives are used in the assembly of shoes, automotive interiors, and textile/packaging laminates. PU adhesives are also used for bonding polyester sheets in land and marine applications, as well as bonding glass to polycarbonate plastics for bulletproof building windows, aircraft windows, and tank and armored car windows. Polyurethane binders are mixed with wood for making engineered wood products such as medium-density fiberboard (MDF) and oriented strand board (OSB). Polyurethane sealants offer shape retention, fast curing, adhesion to bare concrete, and paintability. Their high-strength, water-resistant seals find use in road/airfield/floor repair, plumbing, construction, transportation, window assembly, and other uses.

Polyurethane elastomers are rubber-like materials that can be created with a wide variety of properties and molded into almost any shape. Among the outstanding properties available are resistance to abrasion, impact, shock, temperature, cuts and tears, oil and solvents, most types of chemicals, aging, mold, mildew, and fungus. High load-bearing capacity, light weight, and machinability are additional attributes of polyurethane elastomers.
Polyols for Polyurethane Foams

Polyols of interest for polyurethane foams generally are based on starters with a functionality (active hydrogen content) of three or higher. Flexible foams usually employ tri-functional polyols, while higher-functional polyols are principally used in the production of rigid foams.

The trifunctional polyether polyols are principally oxyalkylene adducts of glycerine, trimethylolpropane (TMP), and 1,2,6-hexanetriol; the glycerine and TMP products dominate. Although TMP is more expensive than glycerine, the differential between the prices of comparable molecular weight polyols based on these materials is slight due to the high average product molecular weight.

The overall equation for production of the glycerine adduct of PO is:

\[
\begin{align*}
&\text{CH}_2\text{OH} + n \text{CH}_2\text{H}_2\text{C}=\text{CH}\text{CH}_3 \\
&\text{CHOH} \rightarrow \text{CH}_2(\text{OC}_3\text{H}_6)^a\text{OH} + \text{CH}_2(\text{OC}_3\text{H}_6)^b\text{OH} + \text{CH}_2(\text{OC}_3\text{H}_6)^c\text{OH}
\end{align*}
\]

where \(a + b + c = n\).

Reaction conditions are 120 to 140°C and 30 to 40 psig. The catalyst (KOH) concentration is 0.2-1.0 wt percent based on the total reaction mixture. Yields are approximately 92 percent.

In addition to glycerine adducts containing 100 percent propylene oxide, adducts are marketed which contain both ethylene and propylene oxides. The distribution of the alkylene oxides in the polymer chain can be either random or blocked.

Polyurethane foams with improved tensile strength and elongation properties can be prepared from EO-PO copolymers. Placing the ethylene oxide at the tail of a polyol chain as an end cap has several advantages. A terminally unsaturated chain (due to the isomerization of PO) has no hydroxyl group at the end, and reaction with an aromatic polyisocyanate produces an unstable polyurethane. If EO is added at the end of the polymer chain, a significant reduction in terminal unsaturation results.

Another advantage of having EO at the tail of a polyol chain relates to the reaction rate of the polyol with an isocyanate for polyurethane production. Primary hydroxyl groups resulting from end
capping react much more rapidly with isocyanates than do the secondary groups that result from the typical base-catalyzed production of straight PO polyols.

Inclusion of higher molecular weight compounds in a flexible polyurethane foam generally improves the foam’s physical and mechanical properties. The use of polyether polyols with molecular weights in excess of 5,000-6,000 is not normally practical because of terminal unsaturation, viscosity, and handling problems.

One of the most successful approaches to the problem of increasing polyol molecular weight has been to include in the polyol solution a polymer which will react with the isocyanate at a rate comparable to the polyol-isocyanate reaction rate. This will result in a foam with integral cross linking and excellent mechanical and physical properties.

**Technology Advancement – Double Metal Cyanide Catalysts**

A key factor in Bayer’s acquisition of the Lyondell polyols business in April 2004 was obtaining the patented IMPACT technology for polyols manufacture using double metal cyanide (DMC) catalysts. These catalysts produce an ultra-pure polyether polyol with low monol content, allowing higher molecular weight products (up to 20,000) compared to conventional potassium hydroxide catalysts (4,000-5,000). Polyurethanes made from IMPACT polyols show improved tensile and tear strength, elongation, and dynamic properties, as well as reduced compression set and hysteresis, all important factors in elastomer applications. IMPACT polyols permit production of elastomers that are both soft and tough, without the use of plasticizers.

Heterogeneous transition metal catalysts known as “double metal cyanide” (DMC) catalysts have several advantages over conventional acid and base catalysts including the ability to make polyols with very narrow molecular weight distributions, very low levels of unsaturation, and low viscosity. An additional advantage is they obviate the need to remove the catalyst, because only small quantities are used.

Bayer announced the first continuous process technology for polyols in May 2000. Bayer’s continuous addition of starter (CAOS) technology, a further development of IMPACT, made it possible to produce uniform products in a continuous process. Contrary to the response of classical potassium hydroxide catalysts, IMPACT DMC catalysts allow the short chains in a mixture of polyols of differing molecular weights to grow more rapidly than longer chains. Thus, products with a uniform molecular weight will form despite the continuous addition of starter. The high activity and selectivity of the DMC catalysts are claimed to result in significant reductions in process energy usage and waste generation.
Economics

Cost of production estimates for base-catalyzed trifunctional polyols for flexible foam and higher-functional polyols for rigid foams are detailed in the report. These results highlight the effects of plant scale, as well as variations in starter consumption and unit cost. Substitution of ethylene oxide for propylene oxide for performance reasons also has the effect of lowering costs due to EO’s relatively lower unit cost.

A broadly applicable means of attaining lower fixed costs is the use of larger processing equipment on a dedicated basis for larger volume polyol products and on a campaign basis for smaller volume polyol products. To obtain the economy of scale offered by larger equipment, the tradeoff is the need for careful production planning and scheduling, as well as the possible need for additional storage for finished polyol products.

Continuous processing can be used to improve productivity in the polyols reaction step, but downstream treating has typically remained a series of batch operations with intervening holding tanks. However, the advent of DMC catalysts may push the industry increasingly to continuous operation.

A speculative cost of production estimate for continuous, DMC-catalyzed polyols process producing a glycerine-based polyol is included in the report based on very limited information. The continuous process appears to give a 4 to 5 cent per pound savings in bottom-line costs versus the closest comparative batch polyol, while offering superior product properties.