

Nylon 6 and Nylon 6,6

Process Technology, Production Costs, Regional Supply/Demand Forecasts, and Economic Comparison of Alternative Production Routes are presented.

PERP07/08S6

Report Abstract

April 2009

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INTRODUCTION

Polyamides or nylons are the first engineering plastics and still represent the biggest and most important class of these types of material. The development of polyamide began with the first publications describing polycondensation which is the basic principle of nylon synthesis in 1929. The development of nylon production continued with the synthesis of poly (hexamethylene adipamide), the original “nylon” which was conducted by Wallace H. Carothers in a DuPont Laboratory in 1935. This invention resulted in the first patent for the production of synthetic polyamides in 1937 and the subsequent commercial production of nylon 6,6 for toothbrush filaments by DuPont in 1938. In 1941, DuPont introduced the first moldable nylon grades. The other commercially important polyamide, nylon 6 based on caprolactam was first produced at IG Farbenindustrie in Germany by P. Schlack in 1938 and the patent for nylon 6 was subsequently issued in 1941. Although the large markets of polyamides were traditionally for fiber applications, the use of polyamides as plastics grew gradually since the 1950s.

Polyamides comprise a wide range of materials, depending on the monomers employed. Commonly used products are designated as nylon 6; 6,6; 6,12; 11 and 12 with the nomenclature designating the number of carbon atoms that separate the repeating amide group. Nylon 6 and nylon 6,6 continue to be the most popular types among polyamide commercial products, still accounting for more than 90 percent of nylon used in the global market.

Two basic reactions are used to synthesize polyamide engineering polymers: (1) polycondensation of a dibasic acid and a diamine or (2) polymerization of an amino acid or lactam. The most widely used nylon polymers are semicrystalline products with molecular weight of 10-40 thousand and chemical structures in which amide linkages connect aliphatic chain segments.

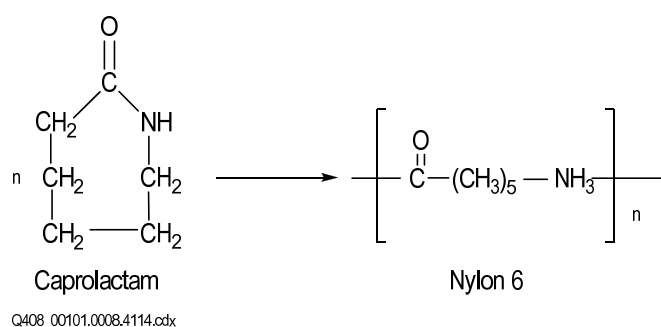
Polyamides are a versatile family of thermoplastics that have a broad range of properties ranging from relative flexibility to significant stiffness, strength, and toughness. Major properties such as resistance to chemicals, toughness, thermal stability, good appearance, and good processability are key considerations that make nylon suitable for engineering plastics applications. Traditionally, the majority of nylon produced was used in the fiber application. This consumption trend has changed substantially over the past decade with increasing proportion of nylon going into the engineering thermoplastics market. This is due to the fact that nylons have particular utility in performing mechanical duties that traditionally relied on metal parts.

In terms of properties, nylon 6 and nylon 6,6 appear to be comparatively similar although nylon 6 has better toughness and processability. On the other hand, nylon 6,6 has superior mechanical properties and higher heat resistance. For engineering plastics, both nylon 6 and nylon 6,6 can be used over an extensive range of applications including automotive, consumer, industrial, electrical and electronics segments. Overall, automotive applications have been the major driver for this positive growth in recent years in the trend towards replacing metal parts with plastics, in order to reduce weight and costs as well as meet vehicle emission standards.

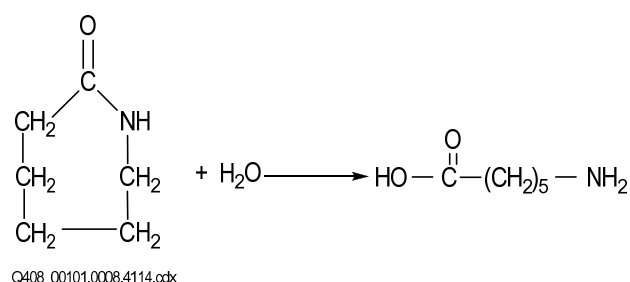
Market outlook for nylon 6 and nylon 6,6 varies extensively depending on domestic demand and current market conditions in each country. Overall, developed markets of North America and Europe will experience sluggish growth over the foreseeable future as a result of the global economic downturn and movement of several manufacturing activities into lower-cost base countries. One of Japan's very mature markets (automotive industry) will likely suffer low growth over the next coming years due to saturated market conditions and steady erosion of the Japanese manufacturing base. China is expected to be one of the fastest growing countries for ETP nylon, largely driven by phenomenal growth in the automotive and electrical/electronics markets.

CHEMISTRY

Nylon 6 is the linear addition polymer of caprolactam (6-amino-caproic acid). The polymerization process for nylon 6 can be batch or continuous, however, the state-of-the-art process for its manufacture is continuous polymerization. Three reversible reactions, hydrolysis, polycondensation, and polyaddition are the main steps in nylon 6 production. The overall reaction is illustrated as follows:

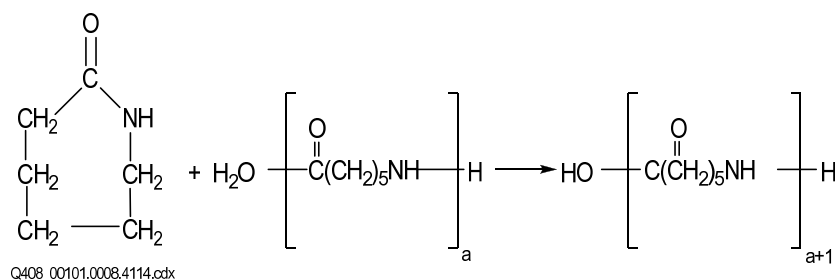


The first step is a hydrolysis reaction to open the caprolactam ring, forming ϵ -aminocaproic acid:



This reaction proceeds in molten caprolactam in the presence of a small weight percent water. Although the reaction will proceed with only caprolactam and water present, a material such as phosphoric acid is added at low concentration to act as a chain stabilizer and help achieve the desired final viscosity (molecular weight).

Polyaddition is the reaction which is mainly responsible for the growth of the linear polymer chains. It is the most important reaction as soon as a certain amount of end groups has been made available by the hydrolysis of caprolactam. Thus, final polymerization occurs by the following caprolactam addition reaction:



The polymer dissolves in the unreacted caprolactam. The polymer end groups affect the stability and final molecular weight of the polyamide. Organic acids (such as acetic acid) can be added as chain stabilizers. Monofunctional organic amines can also be added.

The linear polymer chain formed in the polyaddition reaction can further increase its molecular weight via a polycondensation reaction. The reactive end groups polycondensate forming linear chain molecules and byproduct water. Thus, two linear chain molecules condense producing a longer chain molecule with higher molecular weight. In other words, the polycondensation is regarded as the most important reaction in the last phase of nylon 6 formation in which the distribution of polymer chain lengths is adjusted. Caprolactam can also be polymerized in-situ in a mold. A typical procedure uses the sodium salt of caprolactam as a catalyst. A brief discussion of the raw materials – caprolactam, additives, initiators, catalysts, and chain stabilizers and additional ingredients used during production of nylon 6 is given.

- **Nylon 6,6 chemistry and raw materials are also discussed.**

PRODUCTION PROCESSES

Nylon 6 Batch & Continuous Processes

Commercially, the ring-opening polymerization of caprolactam to nylon 6 can be accomplished by both hydrolytic and anionic mechanisms. However, nylon 6 is produced almost exclusively by hydrolytic polymerization of caprolactam because it is easier to control and better adapted for large-scale operation. The polymerization process for nylon via the hydrolytic mechanism can be batch or continuous. The hydrolytic process for nylon 6 contains the following steps: caprolactam and additives addition, hydrolysis, addition, condensation, pelletizing, leaching/extraction of monomers, drying, and packaging.

- Process flow diagrams and process descriptions for both the batch and continuous process are given in the report.

Nylon 6,6 Batch Process

- A batch nylon 6,6 process is described in this section and illustrated with a process flow diagram.

Nylon 6,6 Continuous Process

To solve the limitations inherent in the batch process, the continuous polymerization process was developed. The main steps of the continuous process include salt preparation, and polymerization. Solid phase polymerization is an additional step used to increase molecular weight of the polymer without damaging properties of the polymer.

A conceptual process design for the Salt Preparation process is schematically illustrated, coupled with a brief description.

The concentrated nylon salt solution is pumped from storage into the first-stage polymerization reactor, and this is schematically illustrated along with a brief description.

A brief description of solid-phase polymerization (SPP) is given.

CURRENT COMMERCIAL TECHNOLOGIES

This section reviews the technical features of modern commercial processes offered by the major licensors of polyamide technology. In the polyamide market, most producers have developed their own technology know-how and the advantage stay with the developers. DuPont, for instance, has developed its own proprietary technology. The basic production steps in manufacturing nylon have not changed significantly through the years and several technology holders generally hold similar production features for most commercially produced nylon: nylon 6 and nylon 6,6. Manufacturing technology, however, has improved from year to year in terms of production efficiency, reduction in utility requirement, special features in reactor design to improve quality and to minimize raw material. Major commercial licensors for polymer production process includes Zimmer AG and Uhde Inventa-Fischer.

- **Lurgi Zimmer GmbH process flow diagram and process description are given.**
- **Uhde Inventa-Fischer process is described along with schematic illustrations.**

TECHNOLOGY DEVELOPMENTS

Nylon 6 and nylon 6,6 have been commercially produced for almost seventy years. The technology for producing nylon today is considered to be mature. However, every one of the many steps used in nylon production has been the subject of numerous improvements over the years and important developments are constantly being made with respect to process and equipment design and catalysts improvements.

The technology developments for nylon 6 continuous productions have been focused on further process advancements and cost reduction if a way can be found to avoid the lactam wash extraction step.

Other trends in technology can be characterized as evolutionary – there does not appear to be a revolutionary advance on the horizon. Areas where design improvements are being sought with the existing continuous processes are improvements in energy utilization, improvements in quality, increases in scale, and further improvements in capital utilization. The advances in technology and engineering of polyamide products will lead to the development of differentiated new products, offering valuable solutions in existing and new markets.

Most commercial improvements and developments for nylon production are generally treated as confidential information. This technology section reviews recent published patents on process improvements, new production technologies, new methods of recycling raw materials, and many more. However, it is not known if these patents will be effectively applied in a commercial scale production or not.

PRODUCT AND END-USE

Resins and Compounds

The usefulness of nylons rests upon their combination of properties and their susceptibility to modification. The key properties of nylon include resistance to oil and solvents, toughness, fatigue and abrasion resistance, low friction and creep resistance, high tensile strength, thermal stability, fire resistance, drawability, good appearance and good processability.

- Resins properties and additives and fillers are discussed; recycling, storage, and compounding are mentioned in brief.

Fabrication Methods

Processability is another advantage that nylon has over thermosets and other engineering plastics. Nylon can be processed via a variety of techniques including injection molding, extrusion, blow molding, monomer casting, solution coating, fluidized-bed or electrostatic coating, or forming. The large proportion of nylon is processed by injection molding, extrusion and blow molding.

- Injection Molding and Extrusion are briefly discussed; Blow Molding, Rotomolding, Reaction Injection Molding, Assembly Techniques are also mentioned in brief.

Nylon Major Markets

Polyamide 6 and 6,6 are highly versatile materials that are consumed in a host of applications including fibers, films, and molded articles. This section in the report focuses only on the technical, or engineering polymer applications of polyamide 6 and 6,6.

- Automotive, electronics and electrical, consumer & other applications are briefly discussed; new developments in Nylon 6 and 6,6 products are mentioned in brief.

ECONOMIC ANALYSIS

Costs of production estimates for the following have been developed:

- Production of Nylon 6 via batch process
- Production of Nylon 6,6 via batch process
- Production of Nylon 6 via continuous process
- Production of Nylon 6,6 via continuous process

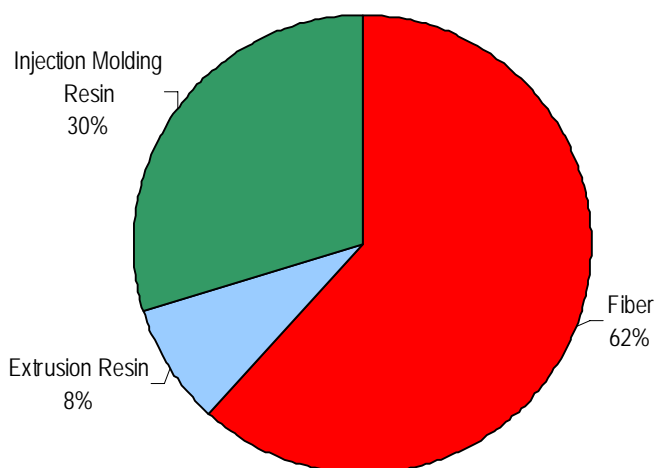
In the petrochemical industry, feedstock integration is an important consideration in assessing the competitive position of participants in a given value chain. This is true, even though there is still a high-value added component to compounded nylon resin selling prices. With a number of alternative routes to caprolactam and HMDA production under development, an understanding of the potential impact of alternative pricing for these raw materials is important.

To test the effect of alternative caprolactam or HMDA prices on nylon 6 and nylon 6,6 production costs, sensitivities have been prepared that looked at these raw materials at alternative prices. Also, a sensitivity analysis was performed to test the impact of larger sized lines on the economics of continuous units.

MARKET ANALYSIS

Nylon was introduced to the market in the 1940s as the first synthetic fiber. From the 1950s onwards, nylon demand for resin has steadily grown accounting for 38 percent of the global demand for nylon nowadays (as shown in the Figure below). Among most types of polyamide, approximately 85-90 percent of nylon in the global market are nylon 6 and nylon 6,6.

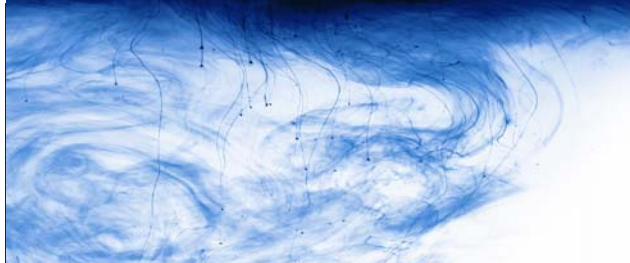
Global Nylon Consumption by End-Use
(6.7 million tons)



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- Supply and demand for North America, Europe Japan, and China are discussed.
- Nylon 6 and Nylon 6,6 engineering thermoplastics demand by end use for 2005-2007, estimate for 2008 and forecast to 2012 is given for each of the regions above.

Production capacity for individual plants are given for each region cited above (tables list company, location, capacity and type of nylon produced).



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