

PERP Program – New Report Alert

April 2004

Nexant's ChemSystems Process Evaluation/Research Planning program has published a new report, *Super Absorbent Polymers (SAP) (03/04S3)*.

Introduction

Superabsorbent polymers (SAPs) are a unique group of materials that can absorb over a hundred times their weight in liquids and do not easily release the absorbed fluids under pressure. Superabsorbents were first developed by the United States Department of Agriculture in the late 1960s.

Early commercial versions first emerged in the United States in the early 1970s in the form of starch/acrylonitrile/acrylamide based polymers that were called "superslurpers." The applications for these products were originally focused in the agriculture/horticulture markets where they were used as hydrogels to retain moisture in the surrounding soil during growing and transportation. Subsequently, cross-linked polyacrylates and modified cellulose ethers were also commercialized along with starch-grafted cross-linked polyacrylates. However, limited commercial success was obtained with these early polymers.

Superabsorbent polymer-filled diapers were introduced into the Japanese market in 1982 by Unicharm, in 1983 by KAO, and in 1985 by Procter & Gamble. The SAP products utilized were based on cross-linked polyacrylates that had high moisture absorption characteristics. The polymer technology for the production of SAPs was developed by several Japanese chemical companies, notably Nippon Shokubai and Sanyo Chemical. By 1985, the worldwide use of SAPs was an estimated 12,000 metric tons, two thirds in Japan.

Following the phenomenal success of superabsorbents in the overseas baby diaper market, both Kimberly Clark and Procter & Gamble introduced diapers containing SAP into the U.S. market in 1986. These two companies now dominate the U.S. market for personal care products containing SAPs and possess technical capability in SAP production to relate product specifications to process modifications.

The popularity of disposable diapers based on SAPs grew dramatically, leading to explosive growth in SAP demand. In 1990, worldwide demand reached 230,000 metric tons, primarily in the United States, Japan, and Europe.

The original diapers contained considerable wood fluff pulp as an absorbent along with SAPs. These diapers were fairly thick in size and were distributed in large packages that occupied

considerable storage space. The original disposable diapers contained an average of 5-6 grams of SAP per diaper.

The disposable diaper market was nearing maturity in the early 1990s when wood pulp prices surged and disposable diaper producers reformulated diapers to reduce wood fluff pulp and give improved properties. The reformulated diapers were thinner due to the reduction in the amount of wood fluff pulp, which was compensated for by an increase in the average amount of SAP per diaper. The average amount of SAP is now in the range of 10-15 grams per disposable diaper.

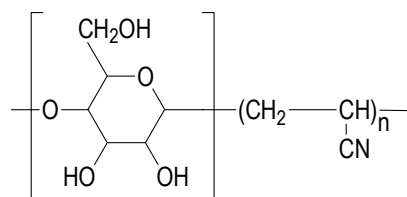
Presently, disposable diapers are the main SAP application and account for 80 to 85 percent of global SAP consumption. Adult incontinence products are the second largest volume application for SAPs because of their high unit concentration. This market has been developing slowly, but is expected to grow further as population average age increases. Feminine hygiene products account for a small share of total SAP consumption. Industrial applications for SAPs have been slow to develop, and account for only a few percent of total global demand. Industrial applications include cable wrap, packaging and liquid waste disposal. Agricultural uses for seed coatings/potting compounds and water retention in arid planting areas rely on SAP's hydrogel properties.

Over the next decade, worldwide SAP demand is forecast to exhibit growth of 3.6 percent per year. This is a result of rising demand for disposable diapers, primarily in countries with rising disposable incomes and low current penetration rates of SAP's. Although smaller markets in comparison to diapers, strong growth is forecast to continue in feminine hygiene products and in incontinence products in developed regions, as a result of efforts to produce slimmer, more efficient products.

There are two primary types of superabsorbent polymers: starch-graft polymers and those based on cross-linked polyacrylates. Although starch-graft polymers were the first developed, these polymers suffer from the disadvantage of salt instability. Polyacrylate polymers initially had difficulty achieving high absorption under load (AUL) characteristics at moderate pressures, as the materials would partially dissolve. However, this problem was solved by partly cross-linking the polyacrylate to provide a networked structure.

The sodium acrylate and starch-graft polymers account for virtually all of the commercial volume of super absorbent polymers, and are the focus of this report. Although other chemistries, such as polyacrylamide, poly (ethylene oxide), poly (vinyl alcohol), polysuccinimides, and hydrolyzed polyacrylonitrile polymers have been explored, these chemistries have yet to gain widespread commercial acceptance. Thus, sodium acrylates are expected to remain the commercially preferred SAP material.

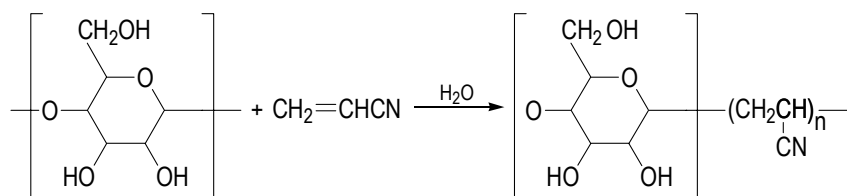
Starch-grafted polymers were originally developed by the United States Department of Agriculture and patents were licensed to General Mills Inc. among others. This polymer is prepared by graft-polymerizing acrylonitrile onto a starch substrate to give the type of structure shown:



Polyacrylonitrile Starch Graft Polymer

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The polymerization reaction is as follows:



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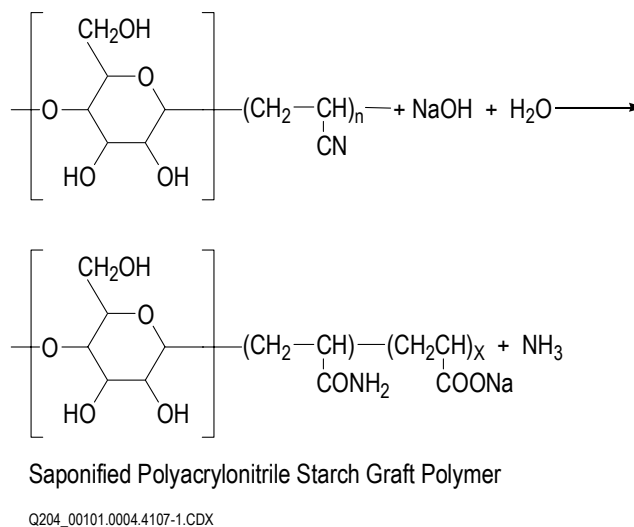
Ammonium ceric nitrate has been used as an initiator with 0.1 mole cerium ions in one normal nitric acid. Optimal results are obtained when starch is gelatinized by heating in water at 80°C for an hour prior to the reaction, which occurs at around 30°C and atmospheric pressure. Gelatinization breaks down the starch chains giving increased reactivity with the acrylonitrile and a higher molecular weight product.

Saponification of the graft polymer with an alkali yields a final product with nitrile, amide, and carboxyl functionalities. The reaction is shown on the next page.

The saponification reaction takes place at 95°C and atmospheric pressure with a ratio of alkali to acrylonitrile of 0.6-0.8 to 1 for saponification. Washing with water removes excess salts produced during saponification. Acrylonitrile was used originally; acrylic acid monomer, which is nontoxic, is now preferred.

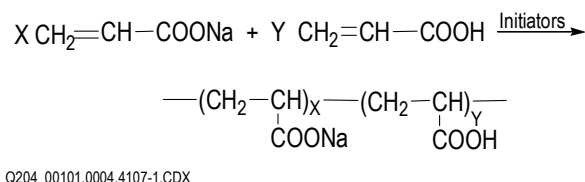
After this reaction, drying and pulverization give a white powder.

Several starch sources have been mentioned including corn, potato, and rice starches and fluff pulp. A variety of cross-linking agents and catalysts likewise have been mentioned in the literature.



Typical patents on polyacrylate SAPs involve the copolymerization of acrylic acid, sodium acrylate, and a cross-linking agent to provide a minimally cross-linked polymer containing carboxyl and sodium carboxylate groups.

The basic reaction chemistry is shown in the following:

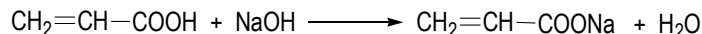


Cross-linking during polymerization is important in that it yields a networked polymer, which will not dissolve in water, and can absorb and retain water under low load.

A typical cross-linking agent is trimethylolpropane triacrylate in concentrations of 0.05 mol percent relative to the monomer. Cross-linking is also possible with ethylene glycol diglycidyl ether which reacts with carboxyl groups on the polymer molecules to crosslink them.

Controlling molecular weight of the polymer product is important in order to balance performance versus yield. Low molecular weight species are extractable, whereas high molecular weight species require a longer polymerization time. Commercial superabsorbent polymers typically contain between 5 and 20 percent extractables.

To carry out the polymerization, an acrylic acid solution is neutralized with sodium hydroxide to a level of 65-80 mol percent to provide a pH compatible with human skin:



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Thereafter, the polymerization is carried out at 30-45 weight percent of the monomers in aqueous solution at 75°C and atmospheric pressure. A typical initiator for the acrylic polymer polymerization is 2,2,1-azo-bis-(2-amidinopropane) dihydrochloride.

After the reaction, the material is removed, dried, ground to a fine powder, and treated with additional curing agent. The additional curing step is designed to yield a superabsorbent particle with a cross-linked “shell”. The purpose of the shell is to better control swelling of the superabsorbent particle. There is a tendency of superabsorbent particles to form clumps when aqueous liquids are added, thereby reducing the diffusion of additional liquid through the partially swollen mass. Surface cross-linking of the particles controls surface swelling, thus reducing clumping.

Economics and Market Outlook

Cost of production estimates are presented for sodium polyacrylate SAPs, both without and with starch grafting. While significantly lower cost is attained by the starch-graft SAPs, they are not preferred by end-users due to inferior performance characteristics. The impact of back integration is also assessed.

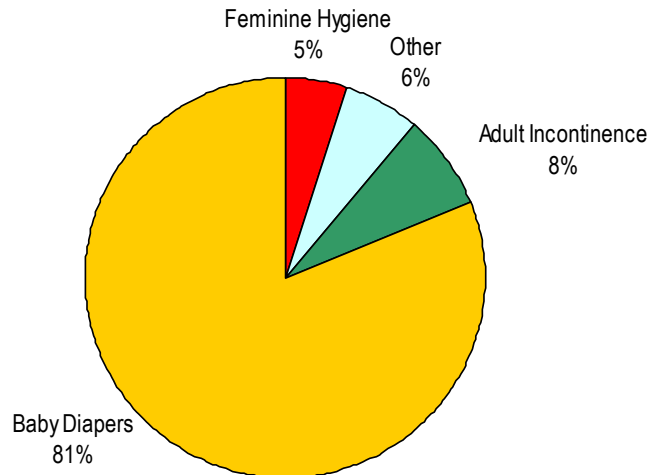
The report describes the various end products that take advantage of SAPs high absorbency. These include personal care products, as well as agricultural/horticultural, industrial, and miscellaneous other uses.

Global demand by end use is provided for 2000-2008. A regional demand breakdown is also given for the same time period, along with the historical and predicted global supply/demand balance.

Global demand for SAP totaled an estimated 1.05 million tons in 2003; demand growth for 2003-2008 is forecast to average 3.6 percent per year. Baby diapers will be the lowest growth market as a result of the maturity of this application in developed regions. All other applications are forecast to have above-average growth.

Globally, baby diapers account for an estimated 81 percent of SAP demand as shown in Figure 1. Adult incontinence is the next largest sub-segment (8 percent), followed by other applications (6 percent) and then feminine hygiene (5 percent).

Figure 1
Global SAP End-Use Pattern, 2003
(percent)



Total = 1.05 Million Tons

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On a regional basis, rapid growth in developing regions will result in an increasing share of SAP demand occurring in developing countries.

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