M² Polymer Technologies, Inc.
P.O. Box 365
West Dundee, IL 60118   USA
Phone: 847-836-1393 Fax: 847-836-6483
www.m2polymer.com

View the entire lecture & demonstration at: http://www.youtube.com/watch?v=RMO6srwL2pQ

Hello. This is Martin Matushek from M2 Polymer Technologies.   We are experts in super absorbent polymer chemistry. We sell most of our products for industrial and environmental waste applications.

The first patent for SAP was issued in 1962 to the US Dept of Agriculture for use as water conservation in soil. The product used starch as the basis for the polymer and then grafted acrylamide and acrylonitrile monomers along the chain with crosslinking agents. Starch is made of repeating units of the sugar, glucose, and there are a lot of places to add things and to crosslink these polymer chains so they become and absorbent. SAP technology has changed a lot from that time.

The basic idea behind any of these is to first crosslink polymer chains and then to partially neutralize some of the acid functions to create a diffusion gradient. It is this diffusion gradient that actually draws water molecules into the network of polymer chains and then hydrogen bonding holds the water tightly in place.

Current superabsorbent technology no longer uses starch to form the main polymer chains. SAPs today typically use acrylic acid or acrylamide as the base monomers to form the polymer chains then they add crosslinking agents to bridge these chains and then they partially neutralize the acid groups to create the diffusion gradient.

First…. What is a polymer? A polymer is a large molecule made up of repeating, smaller molecules called “monomers.” Most common plastics are polymers but there are also many natural substances that are polymers – starch, collagen and insulin (a protein made of amino acid monomers) are all examples of “polymers.”

To understand super absorbents, it helps to start by understanding the acrylic acid monomer (Show structure) CH2=CH-COOH

Super absorbents are a ”petrochemical” which means that the basic starting material for these comes from a barrel of crude oil or from natural gas. The original starting material to make the acrylic acid monomer is propylene: CH2=CHCH3

It takes take 1 mole of propylene and 1.5 moles of Oxygen to form acrylic acid:

CH2=CHCH3   + 1.5 O2   --→   CH2=CHCOOH (Acrylic Acid) + H_2O

The acrylic acid molecule has two interesting reactive areas that we will talk about later. They are (1) an unsaturated alkene group C=C and (2) the carboxylic acid group (-COOH).

CH2=CH-COOH is polymerized by removing two hydrogen protons to create a free radical:

~CH2-CH~ (-COOH)
The free radical monomer reacts with others to create a repeating chain of polyacrylate polymer that look like this:

```
~ CH2 – CH – CH2 – CH – CH2 – CH ~
        |           |           |
        COOH        COOH        COOH
```

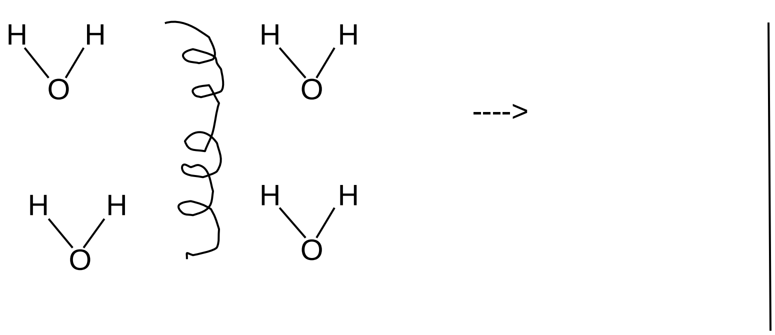
One of the first big commercial uses of polyacrylates was in laundry detergents. These –COOH groups bind with metal ions like Calcium and Magnesium. For that reason, polyacrylates were used in laundry detergents to replace phosphates that were causing algae pollution in lakes & streams. Phosphates and Polyacrylates both bind the Calcium and Magnesium metals in water and this allows detergent surfactants to work better and to get clothes cleaner.

Using this acid group (-COOH) we can neutralize this part of the chain to form Sodium Polyacrylate (-COO-Na)… and the basis of the diffusion gradient that a superabsorbent polymer needs.

Polyacrylates are also used as thickening agents or rheology modifiers. The reason is for their hydrogen bonding interaction with water molecules.

In a dry state, a polyacrylate is curled up like a pigs tail:

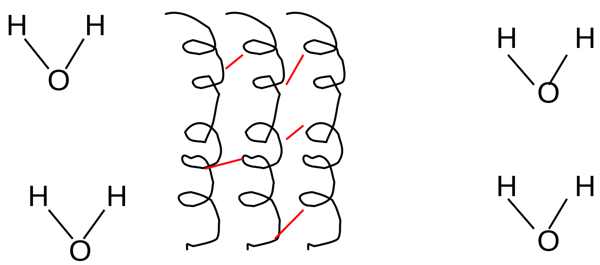
However, once surrounded by water molecules, the interaction between H and O on the chains and from the water molecules causes these chains straighten out like strands of spaghetti:

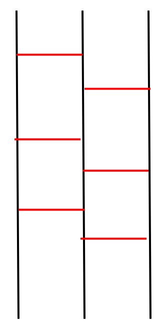


Once straightened out, these polymer strands exert greater resistance in fluid flow thereby thickening the fluid.

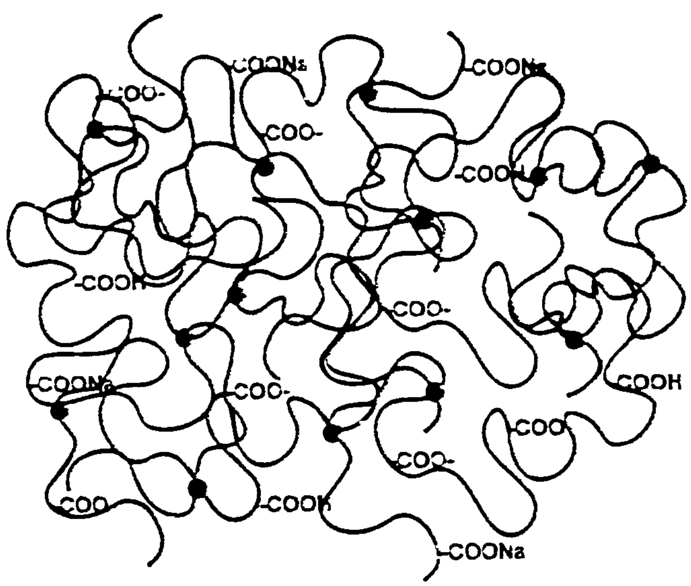
A special crosslinked acrylate called a “Carbomer” is widely used as a thickener in cosmetics and personal care products. As little at 1/4th of 1% forms a perfectly clear gel like this hair gel. (DEMO).

The basic idea in designing a superabsorbent polymer is to build small crosslinking bonds between the polymer strands so that they are kept linked as they straighten out.





Adding more and more chains and then partially neutralizing the –COOH acid groups, you get something that looks like this:



This then forms a kind of a “cage” where water molecules are drawn inside and then held in place there through Hydrogen bonding. It only takes a very small amount of crosslinking agent – typically only ¼ - ½% by weight to accomplish this!

(DEMO) This is a 4mm sphere of SAP. In it’s dry state it is 99% polymer and about 1% water moisture. After soaking, this same sphere swells about 30X its original size and its mass balance is now 99% water and 1% polymer! No chemical changes …. Just a lot of water pulled into the matrix of polymer chains!

(DEMO) This little toy is called a Hoberman sphere and it expands many times its size – like these SAP Spheres do when soaked in water. These SAP Spheres (as we call them) take water into the matrix of polymer chains because of a diffusion gradient that is caused by the neutralization of many of the carboxylic acid (-COOH) groups along the backbone. These chains want to uncurl – but can’t fully – because they are constrained by the small crosslinking molecules.

A final demonstration shows what the choice of crosslinking agent can do to a superabsorbent polymer. The amount of crosslinking agent used it typically very small – only ¼ to ½% by weight.

A crosslinking agent is a small molecule or monomer that has dual binding functionality on at least two sites. A common example of a crosslinking agent would be something like Methylene-bis-acryamide (MBA):

```
          O             O
          ||            ||
CH2=CH-C-NH-CH-NH-C-CH=CH2
```

Note the symmetry in the molecule and the two highly reactive alkene groups on each end!

(DEMO) By varying the choice of crosslinking agent we can change the properties of the superabsorbent. This sample of Waste Lock® 770 will solidify the 100 mls of water in 30-45 seconds whereas a second sample – MediSAP 715 – solidifies the water in under 10 seconds! A third sample actually expands in volume as it absorbs and looks like snow (We sell this as “Snow SAP.”)

All three chemicals are polyacrylate superabsorbent polymers but offer different and unique properties based on the crosslinking agent.

For more information, please visit us on-line at www.m2polymer.com