

Superabsorbent Polymers

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Superabsorbent Polymers

Introduction

Superabsorbent polymers (SAPs) are materials that have the ability to absorb and retain large volumes of water and aqueous solutions. This makes them ideal for use in water absorbing applications such as baby nappies and adults incontinence pads to absorbent medical dressings and controlled release medium.

Early superabsorbents were made from chemically modified starch and cellulose and other polymers like poly(vinyl alcohol) PVA, poly(ethylene oxide) PEO all of which are hydrophilic and have a high affinity for water. When lightly cross-linked, chemically or physically, these polymers became water-swellaable but not water-soluble.

Today's superabsorbent polymers are made from partially neutralised, lightly cross-linked poly(acrylic acid), which has been proven to give the best performance versus cost ratio. The polymers are manufactured at low solids levels for both quality and economic reasons, and are dried and milled in to granular white solids. In water they swell to a rubbery gel that in some cases can be up to 99wt% water.

1. Mechanisms of swelling in superabsorbent polymers

Before discussing the synthesis of superabsorbent polymers it is first necessary to understand the reasons why they swell. There are several mechanisms to the process of swelling, all of which contribute to the final *swelling capacity* (or centrifuge retention capacity *CRC* – which is the amount of 0.9 wt% saline solution that a SAP can retain under free swelling conditions when surface water has been removed in a centrifuge).

Figure 1

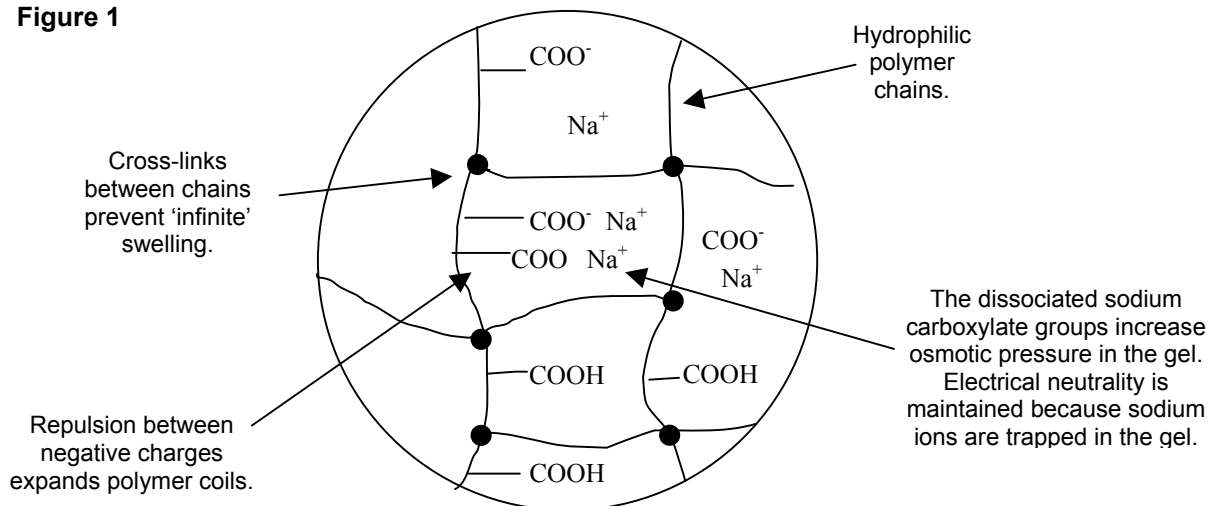
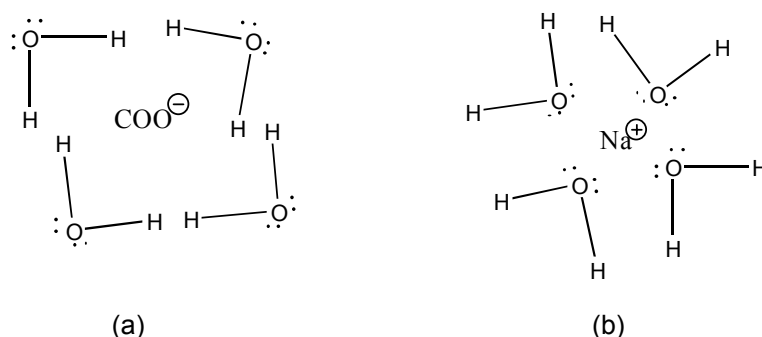


Figure 1 is a diagrammatic representation of part of the polymer network. The polymer backbone in SAP is hydrophilic i.e. 'water loving' because it contains water loving carboxylic acid groups ($-\text{COOH}$). When water is added to SAP there is a polymer/solvent interaction; hydration¹ and the formation of hydrogen bonds are two of these interactions.

1.1. Hydration

This is the interaction of ions of a solute with molecules of a solvent i.e. COO^- and Na^+ ions attract the polar water molecules (figure 2).

Figure 2

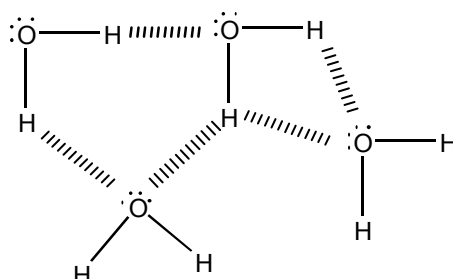


1.2. Hydrogen Bonds

Hydrogen bonds are electrostatic interactions between molecules, occurring in molecules that have hydrogen atoms attached to small electronegative atoms such as N, F and O. The hydrogen atoms are attracted to the non-bonding electron pairs (lone pairs) on other neighbouring electronegative atoms (figure 3)

In water the electronegative atom is oxygen which pulls the hydrogen's electrons towards itself setting up a dipole in the molecule. The positive hydrogen atoms are attracted to the oxygen lone pairs on other water molecules. Oxygen has two lone pairs of electrons and each is capable of hydrogen bonding to two other water molecules.

Figure 3



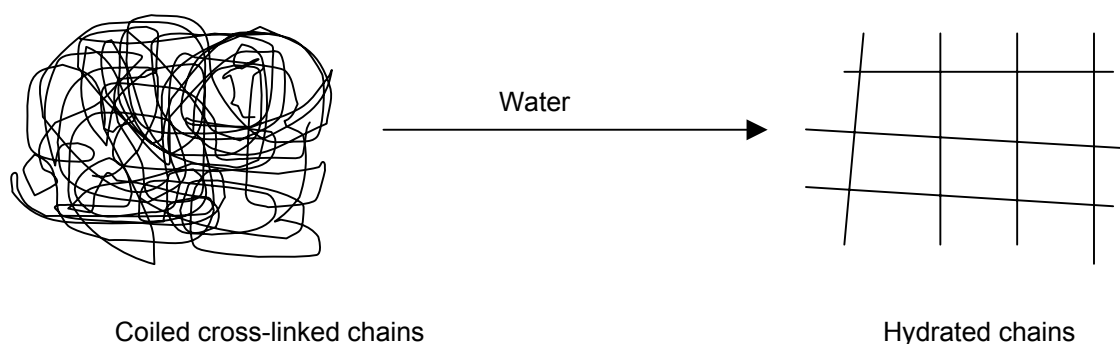
¹ 'Hydration' if water is the solvent and 'Solvation' for other solvents

These effects decrease the energy and increase the entropy of the system. Due to the hydrophilic nature of SAP the polymer chains have a tendency to disperse in a given amount of water (i.e. they are trying to dissolve in the water), which leads to a higher number of configurations for the system and also increases entropy.

1.3. Why doesn't SAP dissolve in water?

Cross-links between polymer chains form a three-dimensional network and prevent the polymer swelling to infinity i.e. dissolving. This is due to the elastic retraction forces of the network, and is accompanied by a decrease in entropy of the chains, as they become stiffer from their originally coiled state (figure 4).

Figure 4



There is a balance now between the forces of retraction and the tendency for the chains to swell to infinite dilution. The degree of cross-linking has a direct effect on the level of swelling of the polymer and the strength of the network i.e. Increased cross-link density = decreased swelling capacity = increased gel strength. Cross-linking is discussed in more detail later.

1.4. Swelling in ionic polymers

For ionic polymers there is another solvent/polymer interaction beyond simple mixing. The neutralised chains contain charges that repel each other (figure1). Overall electrical neutrality is maintained as the negative carboxylate groups are balanced by the positive sodium ions. Upon contact with water the sodium ions are hydrated (figure 2b) which reduces their attraction to the carboxylate ions (due to the high dielectric constant of water). This allows the sodium ions to move freely within the network, which contributes to the osmotic pressure within the gel. The mobile positive sodium ions however, cannot leave the gel because they are still weakly attracted to the negative carboxylate ions along the polymer backbone and so behave like they are trapped by a semi-permeable membrane. So the driving force for swelling is the difference between the osmotic pressure inside and outside the gel. Increasing the level of sodium outside of the gel will lower the osmotic pressure and reduce the swelling capacity of the gel. The maximum swelling of the gel will occur in deionised water.

1.5. Testing fluid for superabsorbent polymers

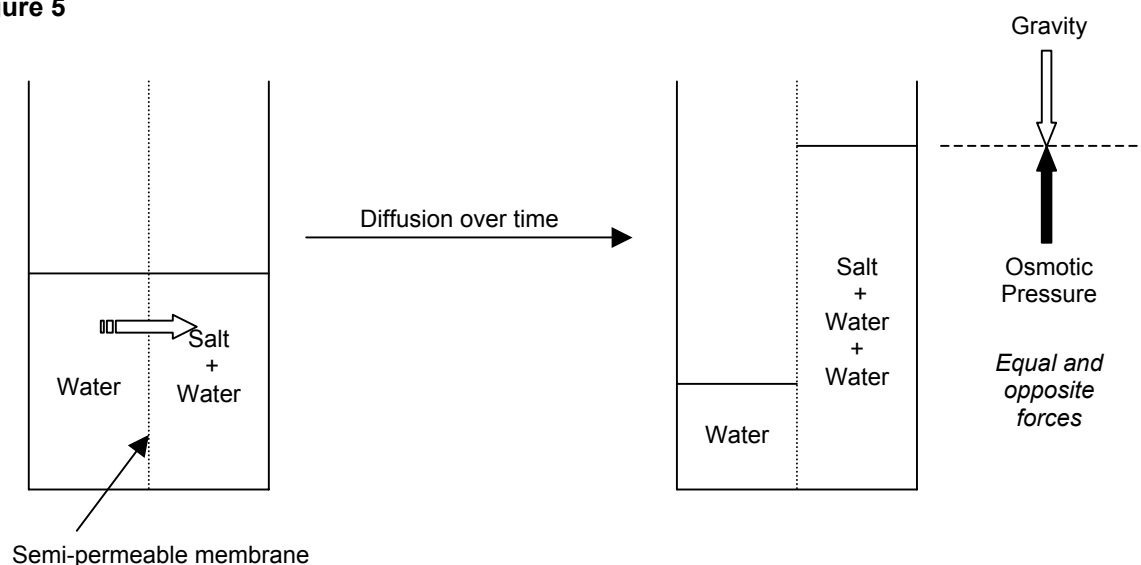
Body fluids such as urine contain ions including sodium, which reduce the swelling capacity of a superabsorbent compared to pure water. In order to more closely simulate the real life application of SAP i.e. in a diaper, superabsorbents are normally tested in a saline solution. This simulates the effects of ion concentration on swelling capacity in application. For more information on the industry standard test methods for superabsorbents refer to the EDANA (European Disposables and Nonwovens Association) web site at <http://www.edana.org/index.cfm>

1.6. Osmosis and osmotic pressure

What is osmosis and osmotic pressure?

Osmosis can be demonstrated by a simple experiment (figure 5).

Figure 5



In the above example the two solutions are separated by a semi-permeable membrane, which allows the passage of water but not salts. Hence the only way for the solutions to equilibrate i.e. have all of the salt in all of the water is for the water to travel through the membrane. Hence an *osmotic pressure* is set up in the solution, which is the pressure that would need to be exerted on it to prevent the passage of distilled water across the membrane.

If we compare SAP to the above example, the force of gravity, which prevents all of the water moving across the membrane, is analogous to the cross-linking in the polymer preventing it from dissolving (or infinitely swelling). Because osmotic pressure is a force it can be overcome by an equal and opposite force and if the SAP was squeezed hard enough it would not swell at all, however this force would need to be large.

1.7. Summary

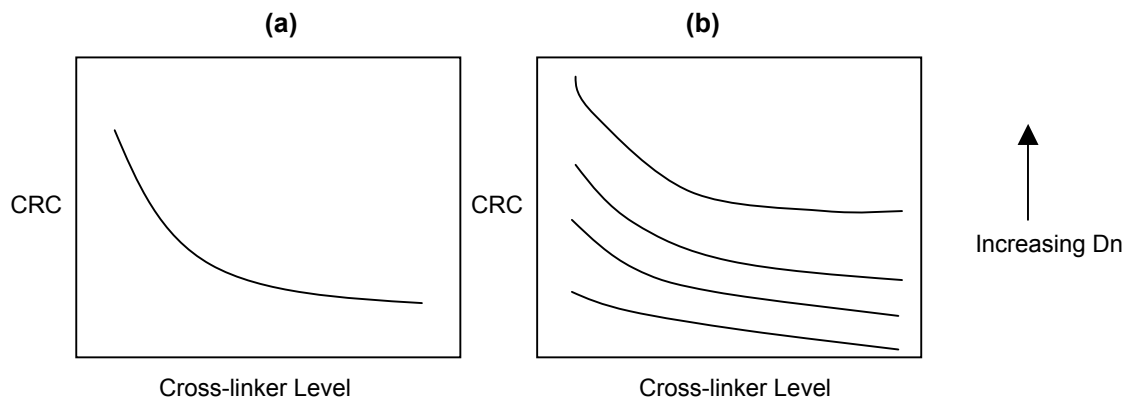
We know that neutralising the polymer chains increased the osmotic pressure of the SAP and hence the swelling capacity. We also know that the swelling capacity is restricted by the degree of cross-linking within the network, hence the resultant swelling capacity is a combined effect of the two.

2. Swelling capacity in SAP – Effects of Cross-linking and Neutralisation

2.1. Effect of cross-linking on swelling capacity

For a fixed degree of neutralisation (Dn) the capacity of a superabsorbent polymer decreases with increasing ratio of cross-linker (when swollen in saline solution).

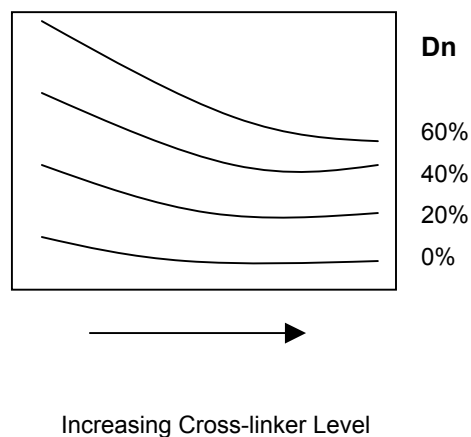
Figure 6



When the Dn is changed the curves show similar trends but the slopes change. The higher the Dn the steeper the curve.

When the polymers are in deionised water there is a large difference in the CRC from 0% to 20% Dn but this difference is less pronounced as Dn increases (figure 7)

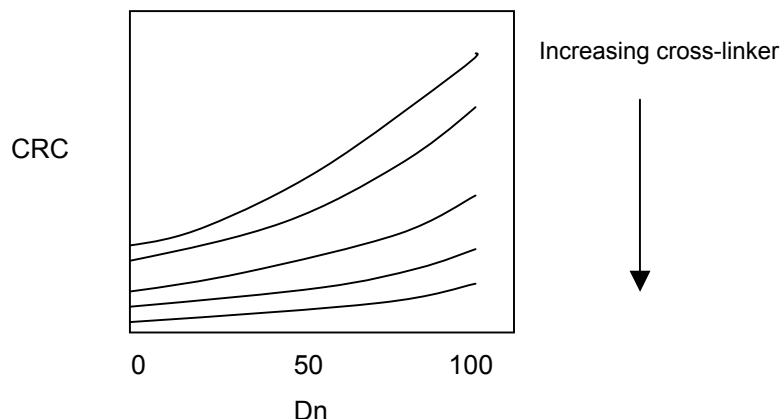
Figure 7



2.2. Effect of neutralisation on swelling capacity

If the level of cross-linker is fixed and swelling is carried out in salt solution the degree of swelling increases with the degree of neutralisation (figure 8)

Figure 8



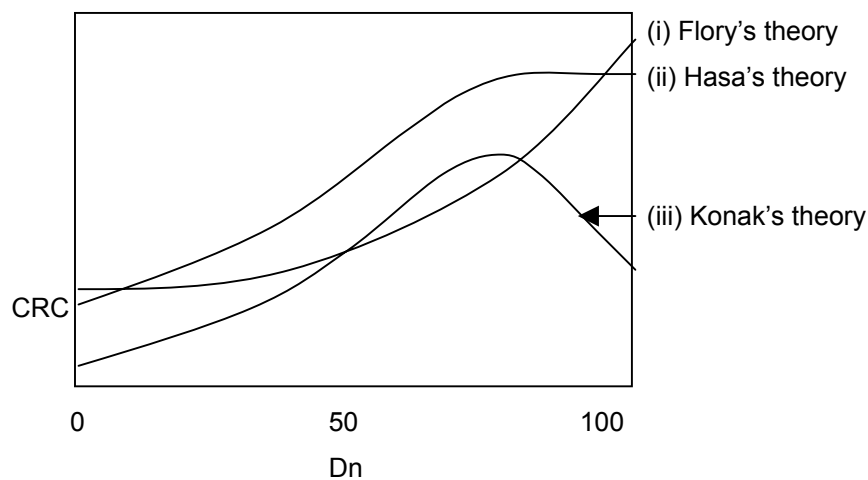
The slopes of the curves now decrease with increasing cross-linker. Certain cross-linkers like TMPTA become less soluble and therefore less efficient at high Dn, hence this would lead to a higher than predicted CRC value.

2.3. Theories on the behaviour of gels at varying Dn and Cross-linker levels

- (i) Flory's Theory – The CRC increases with increasing Dn and decreasing cross-linker level monotonically.
- (ii) Hasa's model – Counter-ion condensation² predicts that Dn reaches a critical value and after this the swelling does not change i.e. a plateau is reached.
- (iii) Konak's model – Predicts a maximum on the CRC versus Dn curve exists and after this the swelling will go back down.

This is demonstrated visually on the chart below (figure 9)

Figure 9



² Counter-ion condensation theory – As the Dn increases past a certain value (75%?) the free ions (Na^+) will condense on the polymer chains i.e. the number of free ions (which contribute to the osmotic pressure) will not increase after a certain value. Hence the swelling ratio after this value will not be as high as predicted.

2.4. Methods of neutralisation in the manufacture of SAP

In the manufacture of most superabsorbent polymers there are two routes that can be taken. The neutralisation stage of the process can be carried out in the monomer solution before the polymerisation (Pre-neutralisation) or on the polyacrylic acid gel (Post-neutralisation).

Pre-neutralisation – This is the easiest from a technical standpoint because the neutralisation of the monomer can take place in the liquid phase (usually with sodium or potassium hydroxide solution). The solubility of some types of cross-linker is affected by the pH of the monomer solution, so this is an important factor to consider when selecting the type of process to manufacture superabsorbents.

Post-neutralisation – Requires the mixing of a solid gel with, normally, a solid neutralising agent such as sodium carbonate or a liquid neutralising agent such as sodium hydroxide. Mixing solids is more difficult than liquids and requires more energy. Harsh mixing conditions can lead to the breaking of polymer chains and the loss in performance of the polymer. Incomplete incorporation of the neutralising agent can also harm performance. These are factors to consider when selecting a pre-neutralised process.

There are advantages and disadvantages with both methods but both can produce good quality SAP's under the right conditions. The choice of method should be accompanied by careful consideration of the after polymerisation work-up, through the processing and drying methods.

3. Cross-linking in superabsorbent polymers

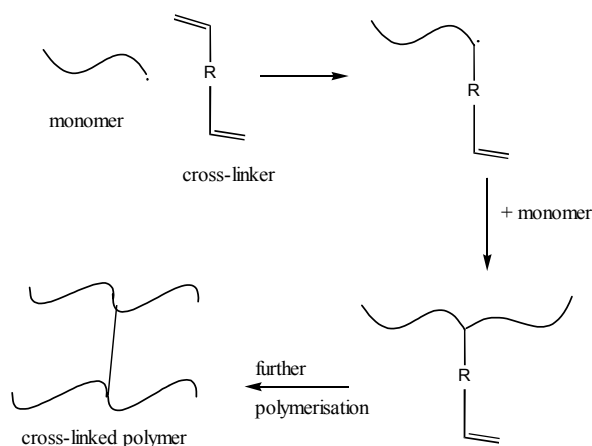
There are two main types of cross-linking in most superabsorbent polymers.

- **Bulk or core cross-linking** – Which normally takes place during the polymerisation stage of superabsorbent production.
- **Surface cross-linking** – Which is a newer process that improves the absorption against pressure profile of the polymer.

3.1. Core cross-linking

Cross-linking is the joining of molecules – generally joining two or more macromolecules with a smaller molecule. The most important type in the case of superabsorbents, and the most common, is the covalent cross-link. In SAP manufacture the most common types of cross-linker are organic molecule that contain two or more polymerisable double bonds. These molecules are incorporated into the backbone of the polymer chains as they grow during the polymerisation reaction (figure 10).

Figure 10



Several factors determine the incorporation of the cross-linkers in to the polymer and their distribution along the polymer backbone.

3.1.1.Reactivity Ratios

Reactivity ratios are a measure of the affinity for each of the reaction components to react with each other, i.e. does an acrylic acid molecule prefer to react with one like itself or something else like a cross-linker molecule for example. In the case of SAPs there are two general cases: -

Pre-neutralised polymer – Acrylic acid, sodium acrylate, cross-linker

Post-neutralised polymer – Acrylic acid, cross-linker

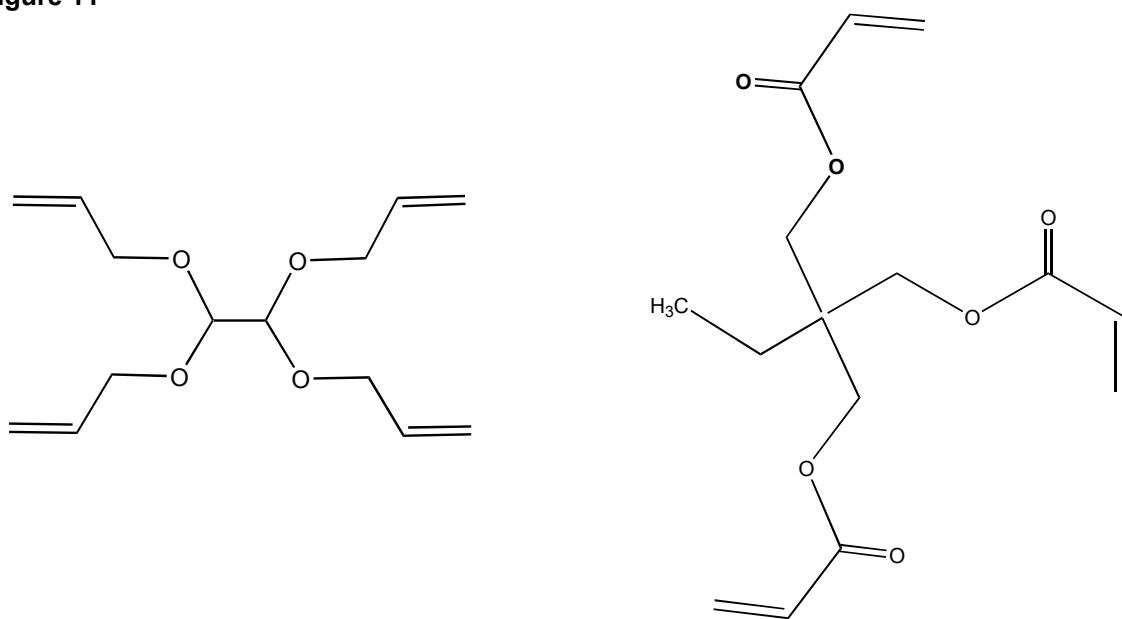
If the cross-linker has a high reactivity ratio then most of it will be consumed in the early stages of the polymerisation and any polymer chains made during the latter stages will be less likely to cross-link and end up as extractable chains. Cross-linkers with low reactivity ratios have the opposite tendency. The choice of cross-linker or mixture of cross-linkers determines the structure of the final polymer network.

3.1.2.Extractables

Generally low molecular weight polymer chains, that are not incorporated in to the polymer network are called the soluble or extractable fraction. These chains can be readily extracted from the polymer when the polymer is swollen in excess liquid, hence the name *extractables*. The degree of soluble polymer is important in determining the optimum cross-linker level and performance of the product. Too little cross-linker and the polymer will have a high swelling capacity, low strength against pressure and a tacky feel due to high extractables, and too much will give low extractables, low tackiness but a low swelling capacity. Using the extractables and swelling capacity data is useful in optimising the quality of the polymer.

3.1.3.Some common types of cross-linker

Figure 11



(a) Tetraallylethoxy ethane

(b) 1,1,1-Trimethylolpropanetricrylate (TMPTA)

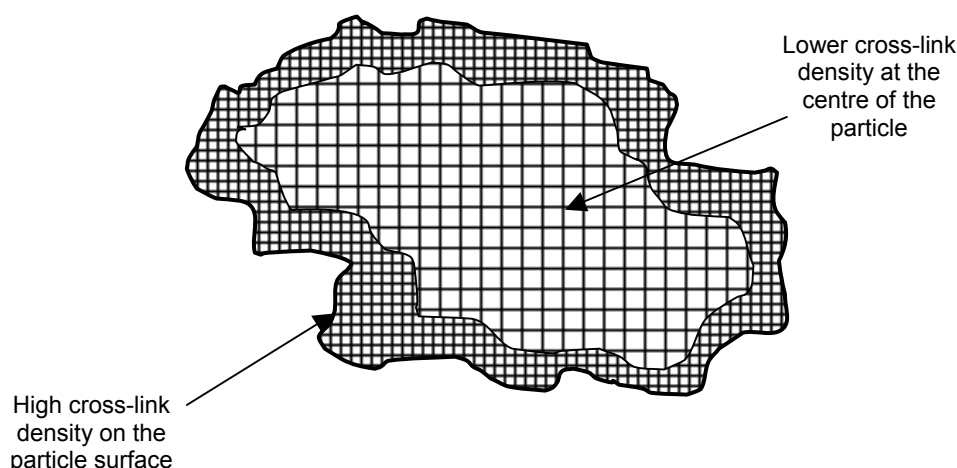
3.2. Surface cross-linking of superabsorbent polymers

Historically it is known that SAPs with no surface treatment and low internal cross-linking tend to show high swelling capacities but poor absorption against pressure. Improving the swelling capacity of SAP by decreasing the core cross-linking, i.e. decreasing the cross-linking density, is limited by the accompanying increase in extractable polymer content of the gel. Likewise the increase in capacity would lead to a decrease in the uptake of liquid when the SAP was under load, for example a baby sitting on its diaper³. This means that when a pressure is applied on the SAP, liquid is not absorbed effectively in these areas. Moreover the pressure on the semi-swollen gel can cause a blockage in the area⁴ preventing further liquid entering the gel bed and being absorbed by dry SAP underneath. This phenomenon is called gel blocking and causes diapers to leak. Hence increasing the swelling capacity using conventional means (lowering core cross-linker) leads to an overall decrease in capacity under load.

Improving the absorption against pressure and the swelling rate of a SAP can be achieved by cross-linking the surface of the particles. Post cross-linking is normally performed on the dried, milled and sized SAP as the final stage of the process. A cross-linking solution is applied to the particles, which are then 'cured' normally through heating. The chemicals that perform the cross-linking usually have at least two functional groups capable of reacting with the carboxyl groups on the polymer backbone for example polyhydric alcohols such as glycerine.

The result of this process is an increase in the density of cross-linking on the surface of the particles giving what can be described as a core-shell particle. The core of the particle is the lightly cross-linked polymer and the shell represents the higher cross-linking density on the surface. This is visually described in figure 12.

Figure 12 – A surface cross-linked superabsorbent particle



³ This is due to lower elastic gel strength in the gel.

⁴ Void spaces and channels between particles, which would normally supply liquid by to the rest of the SAP granules, are closed off due to the deformation of the gel particles.

Manipulation of the surface coating on SAP particles is one of the key steps in tailoring the properties of the product. With a good quality base polymer (i.e. low extractable, low residual and desired capacity) different types of coating solution and cross-linker can be applied to give the polymer many different performance characteristics.

4. Summary

SAP is now a mature product that has quickly progressed from specialty chemical to special commodity. It has revolutionised the baby diaper and adult incontinence industries over the last 30 years and is now a material that is used by millions of people every day.

Reference:

Buchholz , FL (Editor) & Graham, AT - Modern Superabsorbent Polymer Technology
John Wiley & Sons, November 1997, 0471194115