

Superabsorbent Polymers

By

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Superabsorbent polymers (SAPs) represent a special polymeric materials which can appear in a gel state as a result of absorbing huge amounts of water and aqueous solutions [1]. There are some requirements for polymeric material to quantify as a SAP, such as:

- 1- Dry polymeric substances must absorb twenty times or more of their original weights from water, saline, or physiological solutions.
- 2- The swollen hydrogels must kept their initial shapes.
- 3- The resulting hydrogel should have enough physical integrity to resist flow as well as incorporation with the adjoining particles [2].
- 4- Retain the absorbed solutions under some pressure [3].

SAPs can absorb deionized water up to 100,000% (1000 g/g) while absorption capacities for the ordinary hydrogels is not exceeds 100% (1g/g). This ultrahigh absorption capacity makes SAPs ideal for many absorbing applications like disposable diapers, holding soil moisture, adults incontinence pads, medicine for drug delivery systems, bandages to absorb surgical fluids, and controlled release medium [2]. Also, these high water contents, give the resultant hydrogels a flexibility level comparable to that of the natural tissue.

SAPs, consist generally from polymeric chains network which are cross-linked to overcome the dissolution tendency and to support water diffusion into the network; there are ionic functional groups available along the chains [4]. SAPs can hold over the absorbed solutions under some pressure due to their loosely cross-linked structures as well as their hydrophilic nature, where the hydrophilic groups are hydrated in an aqueous environment, thus creating a hydrogel structure [5].

The desired lineaments of SAPs involve high capacities of swelling, high rates of swelling, highest durability during storage, as well as good gel strength. Indeed, SAPs cannot fulfill all the desired features, therefore the reaction variables must be optimized to obtain a suitable balance among properties. For instance, hygienic hydrogels should have highest absorption rate, as well as lowest both residual monomer content and re-wetting, while an agricultural hydrogel must have higher AUL and lowest sensitivity to salinity [7].

Some of the resultant hydrogels responds to the external stimuli, like pH, heat, electric field, as well as chemical environments. Such responsive hydrogels (called "intelligent" or "smart" hydrogels) attracted an increased attention in many areas like the pharmacy, biotechnology, drug delivery systems, separation processes and agriculture [6].

Types of Superabsorbent Polymers

SAPs can be classified with different point of view (Figure 1).

1- According to their morphological structures, SAPs can be classified as powders, particles, fibers, spherical, emulsions and membranes. These morphological structures were designed to satisfy the various applications needs.

For instance, sanitary napkins and diapers can be formed by putting the powder product in a multi-layers sheet, while for deodorant application, spherical products and particle can be used. Antistatic electric fibers were manufactured from fiber forms, while membranes utilized in anti-fost sheets. For soaking and painting, an emulsion forms can be used.

2- Based on their resources, SAPs can be categorized to:

a- Natural macromolecules such as polysaccharide-based and polypeptide-based materials.

Polysaccharide-Based SAPs such as cellulose, starch, chitin, chitosan and natural gums (xanthan, guar, and alginates) can prepared by either

direct cross-linking of polysaccharide or by graft copolymerization reaction of vinyl monomer(s) upon the polysaccharide in the existence of the cross-linker agent [9].

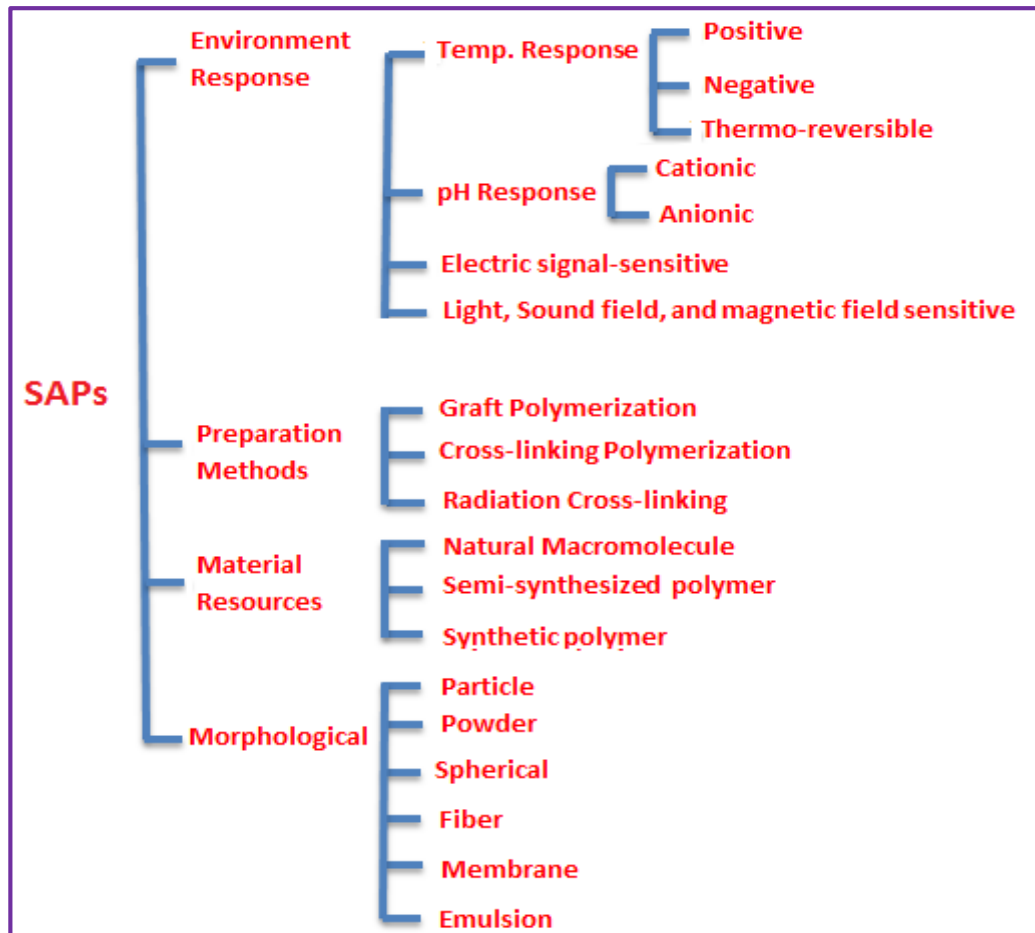


Figure 1:Types of SAPs depended on different point of view [8].

b- Semi-synthesized polymer

c-Synthesized polymers such as petrochemical-based.

As compared with their artificial counterparts, natural-based SAPs possess some advantages like biodegradability(thus escaping the environment from pollution), biocompatibility, their natural source, non-toxic materials, as well as low cost [1].Furthermore, petrochemical-based SAPs have faced some problems such as increasing of global oil price and pollution concerns. The disadvantage of the natural polymers is the low solubility in water, thus, they are modified chemically to soluble

derivatives, such as carboxymethyl starch (CMS) and carboxymethyl cellulose (CMC) [10].

3- Based on preparation method types, SAPs can be divided to cross-linking polymerization, radiation cross-linking, graft polymerization, and networks formation of water-soluble polymer [11].

4- Based on the probability of existence of electrical charges upon the cross-linked chains and types of this charge, SAPs may be grouped into:

a- Non-ionic polymers: They absorb water and aqueous fluids via a mixing effect due to the hydrophilic groups. Water molecules are solvated through hydrogen bonds results in a swollen, soft gel [12].

b- Ionic polymers: They contain anionic and cationic polymers. The presence of charges along the backbone greatly increases swelling due to the strong backbone ion-dipole interaction and due to the enhancement of the osmotic pressure in the gel because of the solvation of the counter-ions.

c- Ampholytic (amphoteric) includes both basic and acidic groups.

d- Polybetaines(zwitterionic) contain both cationic and anionic groups in every repeating unit [4].Photo-chromic hydrogels, recently were prepared with 2800 g/g WAC.

Design Considerations

A SAP material involves two processes; swelling and cross-linking.

1. Swelling Process

Swelling behavior is affected by several factors, such as:

1-Interaction nature: There are four prime forces affect the swelling capacities for the ionic hydrogels: interactions between polymer and solvent, ionic interaction, elastic interaction, as well as electrostatic repulsion. The most important one of these forces is the ionic interaction because of the presence of the mobile ions like K^+ and Na^+ within the SAP structure.

2-Polarity: Generally, for natural polymers there is a one-to-one correlation between the number of polar groups and the number of water molecules adsorbed [14].

3-Elastic retroactive force: Swelling tendency will stop at an equilibrium point when the swelling force is balanced by the retroactive force, which is developed as the chains between the cross-links become increasingly elongated [15].

4-Type and degree of cross-linking: The cross-linker varies the polymeric chain length. Smaller chains have more polymer ends, therefore do not contribute to water absorption, while longer chains have more network space and thus increase swelling.

According to Flory equation (Equation 1), for a given polymer-solvent system the equilibrium swelling (S_e) is a function of the cross-link density

$$S_e^{5/3} = B M_c / (1-2M_c /M_w).....(1)$$

Where: B represents a constant for a given polymer-solvent system, M_w is the weight average molecular weight of the similar uncross-linked polymer, M_c is the average molecular weight per cross-link.

5- Solvent properties: Since the swelling involves diffusion of the solvent molecules within the gel network structure, the concentration of the solvent has announced effect according to the Fick's diffusion equation [15]:

$$\partial c / \partial t = \nabla (D \nabla c).....(2)$$

Where D is the diffusion coefficient and c is the solvent concentration.

6-Morphological properties (porosity, particle size): the smaller the average grain sizes, the larger the swelling.

7- Conditions of the swelling environment such as pH, temperature, ionic strength as well as the counter ion and its valance [16].

The mechanism of the swelling process contains the following actions: solvent molecules penetrate the polymeric networks structures. Simultaneously, the molecular chains among the cross-linked points expanding, therefore reducing their enthalpy values. This new molecular network structure has an elastic contractive forces which increases the contraction tendencies of the networks (Figure 2).

Unless these two opposed forces get their balance state, expansion and contraction tendencies cannot reach their equilibrium also. So, the osmotic pressure will be the driving force behind the swelling expansion, while the elastic force within the network is responsible of the gel contraction [11].

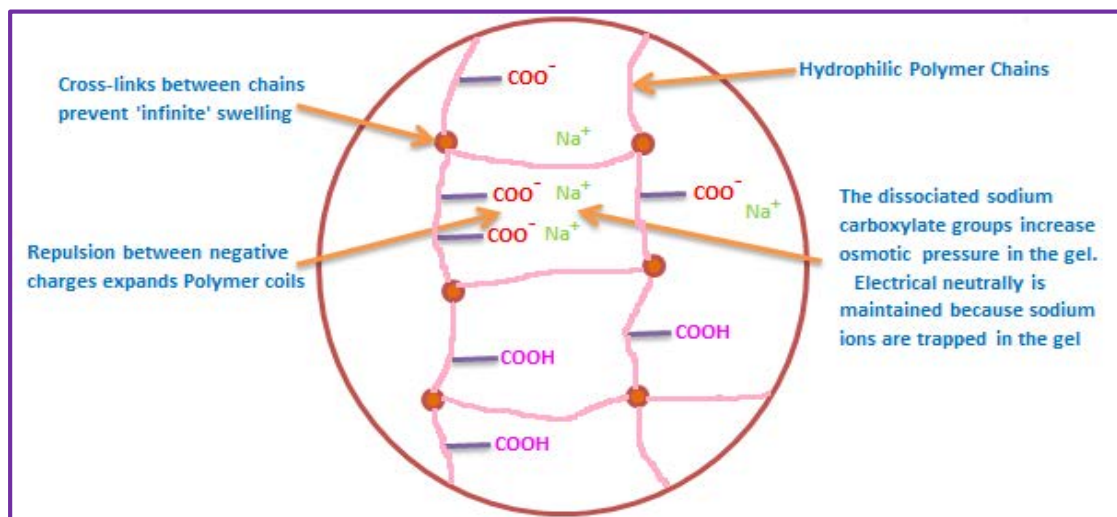


Figure 2: Mechanism of swelling in SAPs [14]

If water is added to the SAP particles, a water /polymer interaction will arise due to the (Mixing Effects), which consists of effects of both hydration (solvation) and the formation of hydrogen bonds.

The hydration is the interaction between solute ions and solvent molecules, i.e. Na⁺ and COO⁻ ions attract the polar water molecules (Figure 3).

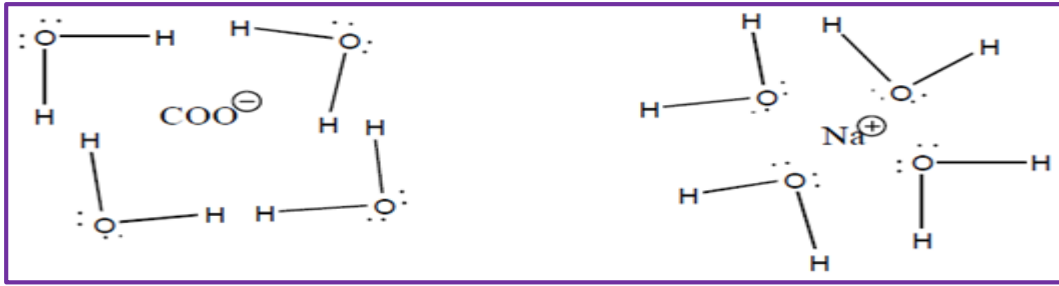


Figure 3: The hydration (solvation) effect [2]

Hydrogen bond (H-bond) which is an electrostatic interaction among molecules, arises in molecules which possess hydrogen atoms connected to atoms with low electronegative like N, F, and O (Figure 4).

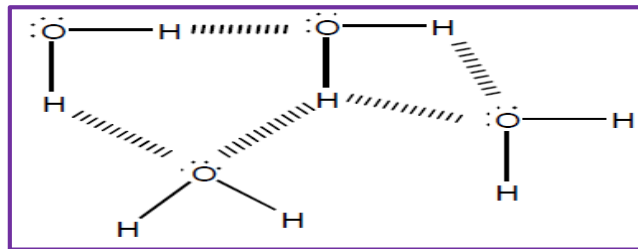


Figure 4: Hydrogen Bonds [2]

These effects creates a cellular structure within the SAP network which can store water molecules.

2. Cross-linking process

Cross-links between polymer chains result in a 3D network; makes SAPs insoluble in water by preventing the polymer to swells to infinity; preventing dissolving. Such behavior arises the elastic retraction forces of the polymeric network. These forces are associated by a reduction of entropy of the chains, since these chains become stiffer from their initial coiled state as shown in Figure 5.

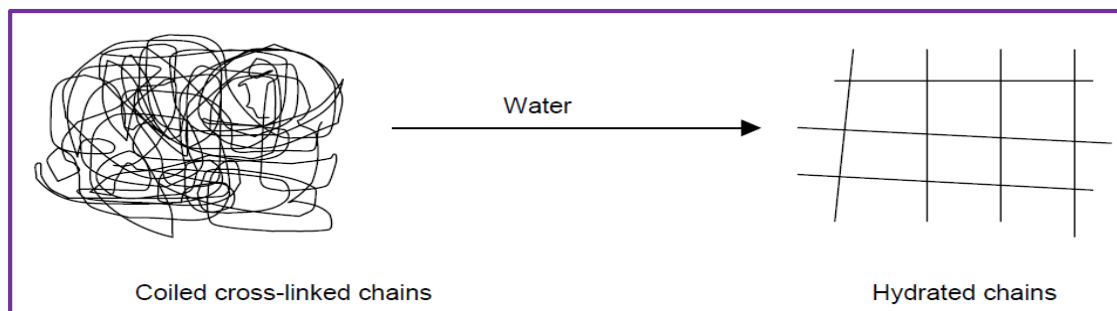


Figure 5: Elastic retraction effect of the network in SAPs [2]

Now, there is an equilibrium between the retraction forces and the chains tendency to swell to infinite dilution. Cross-linking level possess a direct influence on both the swelling capacity range and the gel strength [2].

Several parameters affected the cross-linking efficiency such as, the steric hindrance in the position of the pendant double bonds, solubility level of the cross-linker in the reactants mixture and ability of the cross-linker to exhibit intermolecular addition reactions [7]. Cross-links formed either by covalent, ionic, or H-bonds.

Covalent cross-links are formed either when the major monomers (e.g., acrylic acid) is copolymerized with a di-, tri-, or tetra – vinyl monomer or by reacting the polymer chains with a di- or tri - functional reagents that reacts with the carboxylic acid groups[17].

The reaction between charged polymer chains and polyvalent ion with opposite charge leads to the ionic cross-linking as shown in Figure 6.

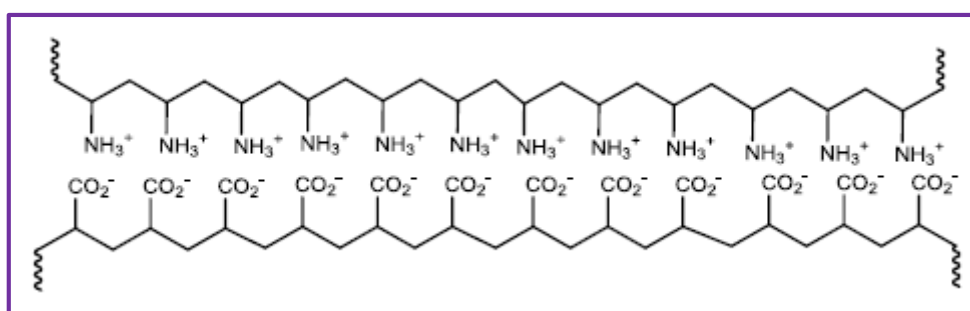


Figure 6: Ionic cross-linking [12]

The creation of H- bonds between segment of one chain with the segment of another chain resulted in the weak chemical cross-linking (Figure 7).

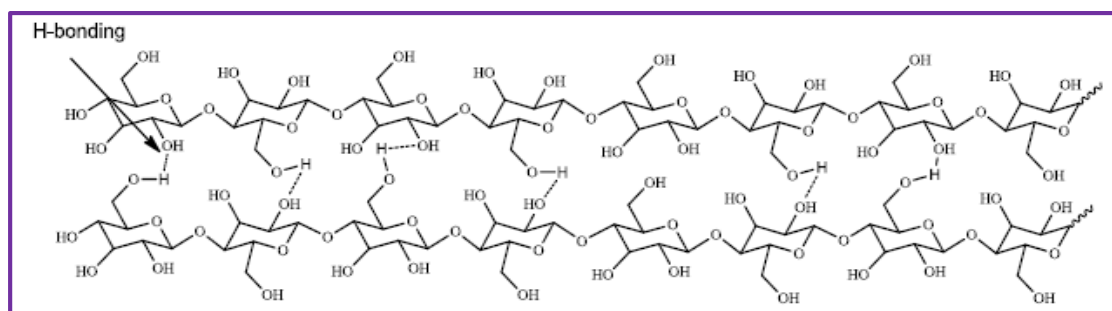


Figure 7: Hydrogen bonds cross-linking [12]

Cross-linking in SAPs, can be classified also into bulk (core) and surface cross-linking. Core cross-linking is usually occurs during the polymerization reaction stage of SAP production [2].

Surface cross-linking of SAP particles can improves both the flow and the absorption against pressure greatly [18]. Particles with surface-cross-linking protected their shapes during the swelling process. This leads to a less densely packed gel bed with air pockets, therefore the fluid can easily flow in high permeability pattern (Figure 8 b).

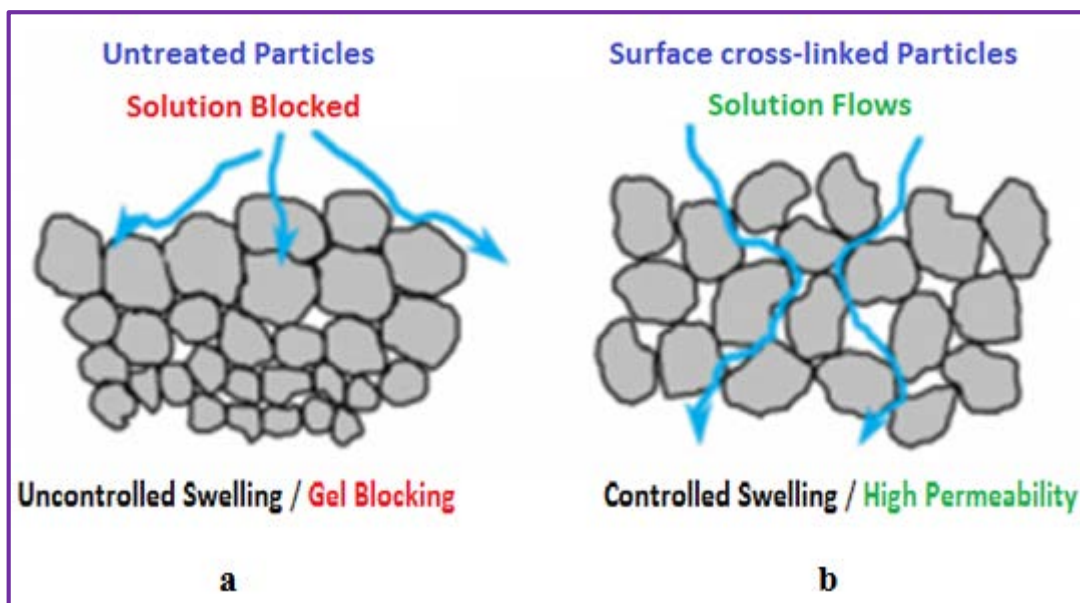


Figure 8: Effect of surface cross-linking on the solution flow [18]

In contrast, SAP with no surface treatment tends to show high swelling capacity but possess poor absorption versus pressure. Unfortunately, this way to improve the swelling capacity by reducing the cross-linking density, usually restricted by the increasing in extractable content of the hydrogel.

Furthermore, the pressure on these untreated particles can cause a "gel blocking" which prevents further liquid penetrating the gel bed.

To obtain cross-linking density in the surface higher than in the bulk (Figure 9), particles subjected to the cross-linking solution, then 'cured' by heating [2].

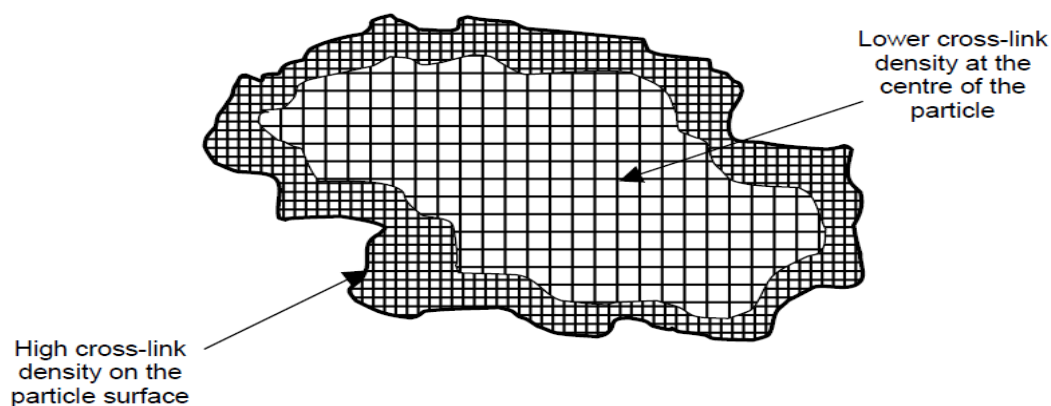


Figure 9: A surface cross-linked superabsorbent particle [2]

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