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Sabyasachi Behera & Prakash A. Mahanwar

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Superabsorbent polymers in agriculture and other applications: a review

Sabyasachi Behera and Prakash A. Mahanwar

Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, India

ABSTRACT

Superabsorbent polymers are a class of polymeric materials that have the ability to absorb and retain a large amount of water and aqueous solutions. **They are composed of three-dimensional polymeric networks that do not dissolve in water but swell considerably in aqueous medium**. The synthetic superabsorbent polymers are replacing the natural ones because of their high absorption capacity, availability of wide varieties of raw materials and longer durability. Due to their hydrophilic, non-toxic, biodegradable, and biocompatible properties, they are the most desirable products **for various applications such as drug delivery, agriculture, bioremediation, fire fighting, biosensors, food industries, thermal energy storage, and tissue engineering**. This article reviews the literature concerned with the classification of superabsorbent polymers, their manufacturing processes, their properties, and the factors affecting them and their applications. **Agriculture is one of the growing sectors due to the requirement of food to meet the growing demands of the expanding global population. The technology of controlled or sustained release of agrochemicals and superabsorbents is a boon to the agricultural sector. The review elaborates the literature related to the drug delivery and agricultural application of the hydrogels in detail.**

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Superabsorbents; swelling capacity; cross-linking; stimuli-responsive; agriculture

1. Introduction

Superabsorbent polymers are hydrophilic polymer networks that have the potential to absorb and hold a large amount of water and aqueous solutions in their network.[1] They are basically polyelectrolytes with a three-dimensional cross-linked structure, the polymer chains are linked to each other through cross-linking.[2,3] They are water-absorbing polymers, they can be natural or synthetic.[2] Some of the natural polymers used for preparing SAP are chitosan, alginate, collagen, dextran, cellulose, chitin, etc. and some synthetic polymers such as acrylic acid, methacrylic acid, polyethylene glycol, vinyl acetate, polyvinyl alcohol, and various acrylates.[4–9] These polymers exhibit a degree of flexibility similar to that of a tissue due to their large water content, for which they have found application in tissue engineering.[10] The superabsorbent polymers have a wide range of applications because of their high water-absorbing capacity, biodegradability[11], and low cost. The capability of the hydrogels to absorb water is because of the hydrophilic functionalities attached to the polymeric backbone, and dissolution of the gel is prevented by introduction of cross-linker into the gel. The synthetic hydrogels have replaced the natural ones as they have high durability, high gel strength, and absorption capacity. They are prepared by bulk, solution, inverse suspension polymerization or polymerization by irradiation techniques. They are found applicable in various fields like drug delivery, agriculture, bioremediation, fire-fighting, biosensors, food industries, thermal energy storage, and tissue engineering. The hydrogels have a characteristic to respond to a wide range of external stimuli including pH[12], temperature[13], enzymes[14], solvent compositions[15], light[16,17] and electric fluids.[18]

2. Historical background

The synthesis of the first water-absorbent polymer was in 1938 by polymerizing acrylic acid with divinylbenzene in aqueous medium by W. Kern.[19] In `the late 1950s, the first generation of hydrogels was prepared which were based on hydroxyalkyl methacrylate and related monomers, were used for developing contact lenses. First, cross-linked potassium acrylate was synthesized by irradiating the aqueous monomer solution, was practically used as a water immobilizing agent in fire-fighting applications.[20] In the 1970s, the first commercial superabsorbent polymer was developed at the Northern Regional Research Laboratory of the the US Department of Agriculture, which was produced by hydrolyzing starch-graft-polyacrylonitrile. Japan

CONTACT Prakash A. Mahanwar pa.mahanwar@ictmumbai.edu.in Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, India

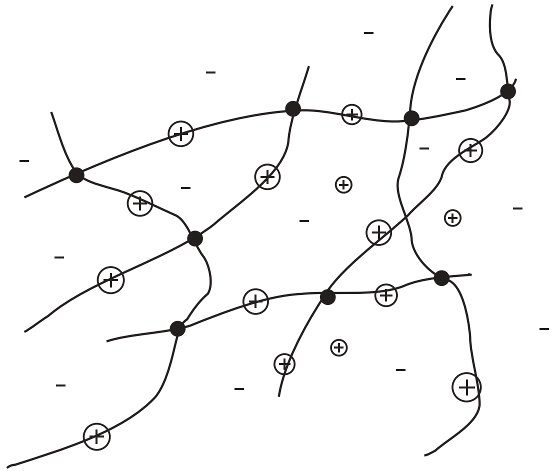

Figure 1. Cationic hydrogel.[16]

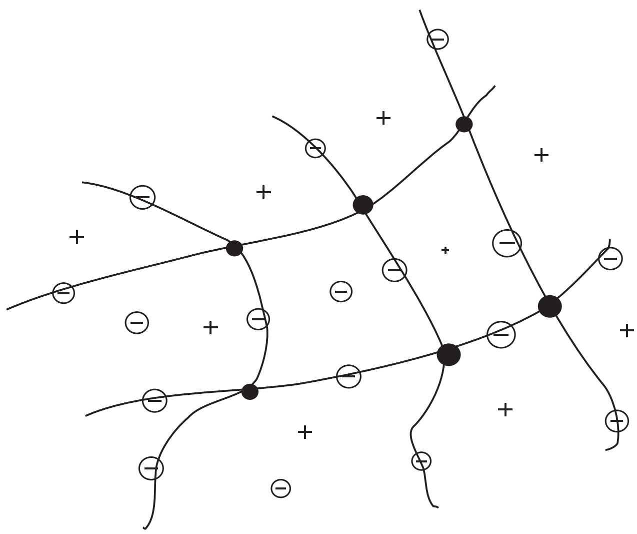

Figure 2. Anionic hydrogel.[16]

commercialized SAP for use in feminine napkins in 1978. France and Germany developed SAP to use in baby diapers in 1980. Gradually, the SAP was used by the US, Europe, and many Asian countries. SAP substituted the bulky cellulose fluff which was unable to retain a large amount of liquid under pressure. This is how SAP introduced a great revolution in personal healthcare industries.

3. Classification

SAPs may be divided into 2 groups on the basis of their original source –

- Natural – They are polysaccharide-based (such as cellulose, starch, alginate, and agarose)[21–24] and polypeptide based (such as gelatin, collagen)[25]

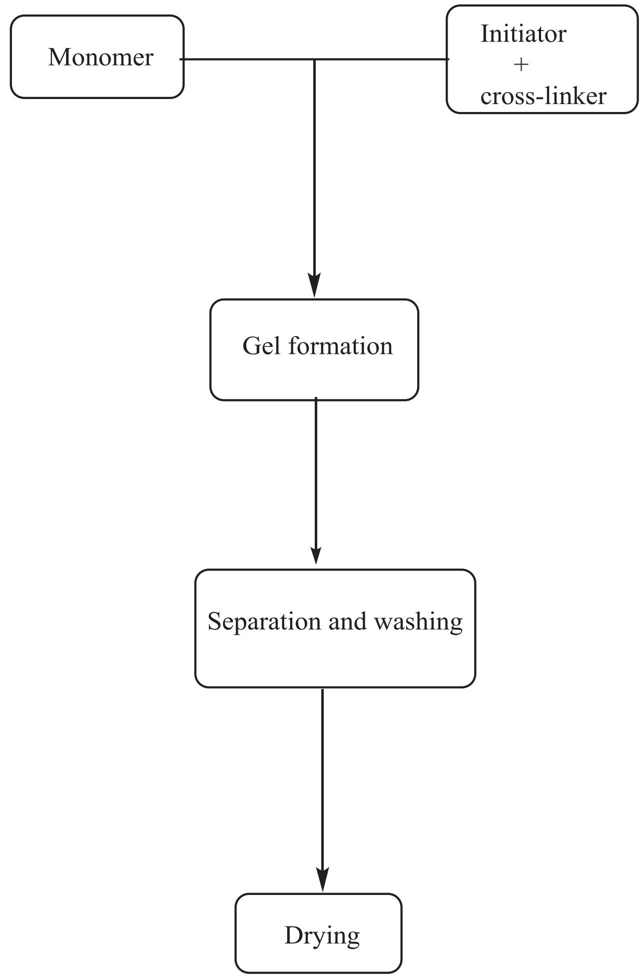

Figure 3. Solution polymerization block diagram.[2]

- Synthetic – They are petrochemical-based (such as polyacrylic acid, methacrylic acid, vinyl acetate, polyethylene glycol)[26–28]

The synthetic ones have higher hydrophobicity and mechanical strength as compared to the natural ones. Better mechanical strength of the synthetic SAPs increases their shelf life or durability, so they are more preferable.[2]

SAPs may be classified into 4 groups on the basis of presence or absence of electric charge located in the cross-linked chains –

- Ionic (anionic and cationic)
- Non-ionic
- Amphoteric electrolyte (both acidic and basic groups)
- Zwitterionic (both anionic and cationic groups in each repeating unit)

Most of the commercial SAPs are anionic.[1]

Based on the polymeric composition, SAPs can be divided into three types –

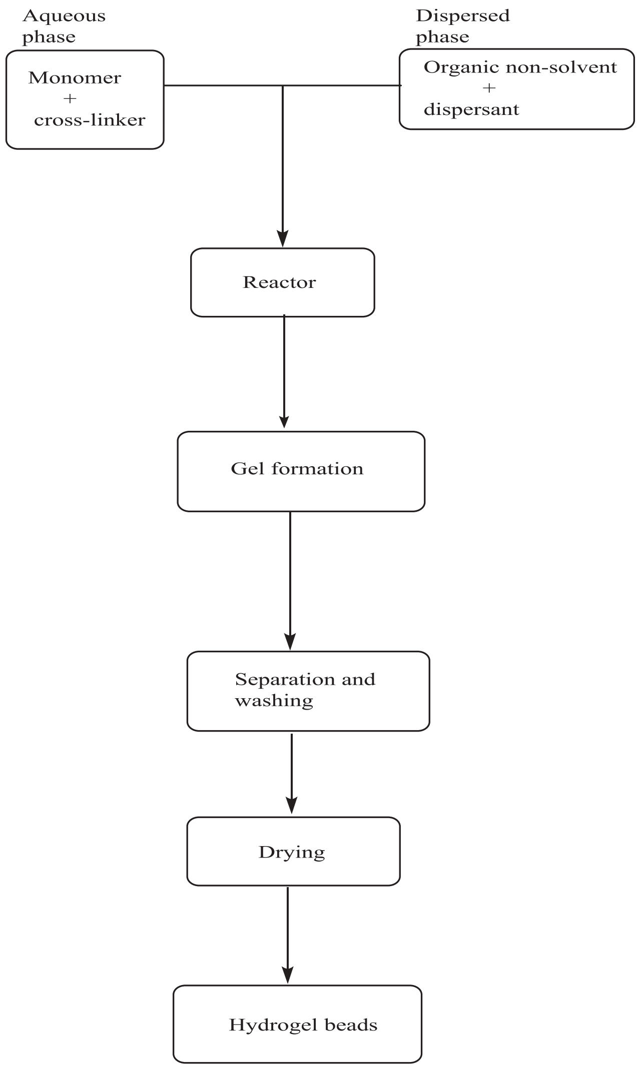

Figure 4. Inverse-suspension polymerization block diagram.[2]

Homopolymeric – the polymeric network is made from a single species of monomer.

- **Copolymeric – the polymeric network is composed of two or more different monomer species with at least one hydrophilic component**
- **Multipolymer interpenetrating polymeric hydrogel – they are made of two independently cross-linked synthetic and/or natural polymers, contained in a network form.**

Based on configuration, that is physical structure and chemical composition, hydrogels can be of three types –
Amorphous
Semicrystalline
Crystalline
Based on type of cross-linking, hydrogels can be of two types, chemically cross-linked that have permanent cross-linking sites, and physically cross-linked that have temporary cross-linking sites.

4. Preparation techniques

SAPs can be prepared by three techniques –

- ***Bulk polymerization*** – In this technique, a small quantity of cross-linker is added in the formulation, polymerization is initiated chemically, by radiation, or by UV catalysts. The initiator to be chosen depends on the type of monomer and solvents used. The polymerized product may be produced in various forms such as films, membranes, rods, particles, and emulsions. It is the simplest technique which involves only monomer and monomer-soluble initiators. Due to high monomer concentration, the rate and degree of polymerization is high. With the gradual conversion, the viscosity of the reaction increases which produces heat during polymerization **that** can be kept away by controlling reaction at low conversions. A homogeneous hydrogel is glassy and transparent which is hard but when submerged in water, the glassy hydrogel swells to become soft and flexible.[2] The advantage of this method is that it produces a high molecular weight polymer with high purity.[10]
- ***Solution polymerization*** – The solution copolymerization or free radical initiated polymerization of acrylic acid and its salts with acrylamide and a cross-linking agent is mostly used in producing superabsorbents. The polymerization is initiated by thermal (such as ammonium persulfate[29–33] and potassium persulfate[34–40]), UV-irradiation[41–45] or by a redox initiator system[46,47] Neutralization technique plays a key role in here, in polyacrylates, the carboxylic acid groups are partially neutralized before (pre-neutralization) or after (post-neutralization) the polymerization. Neutralization is carried out using aqueous solutions of sodium or potassium hydroxide.[48] The advantage of this method over bulk polymerization is the presence of the solvent helps in controlling viscosity as well as promotes proper heat transfer, i.e. acts as a heat sink[49,50] Solution polymerization of acrylic acid and its salts with a water soluble cross-linking agent, which is a fast exothermic reaction leads to the formation of gel-like elastic product. The reaction product is washed with distilled water or ethanol to remove unreacted monomers, oligomers, cross-linking agent, initiator, and other impurities. The formation

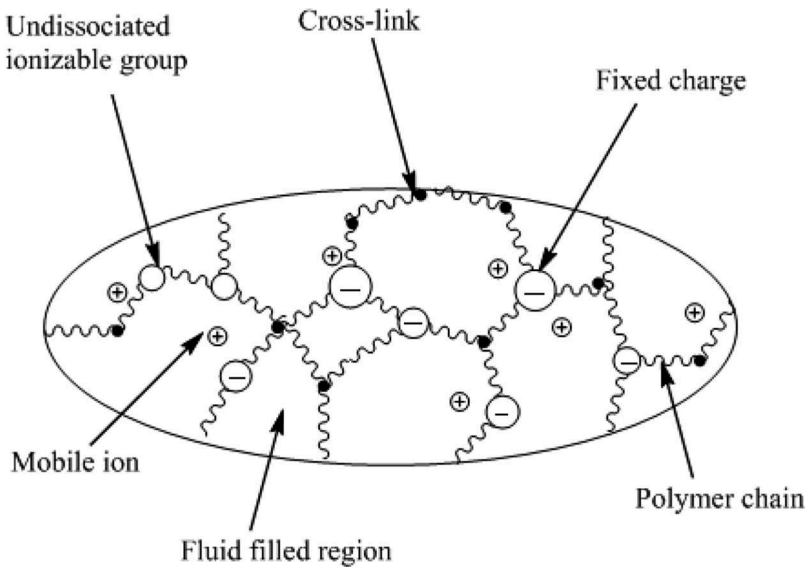

Figure 5. Structure of a hydrogel.[3]

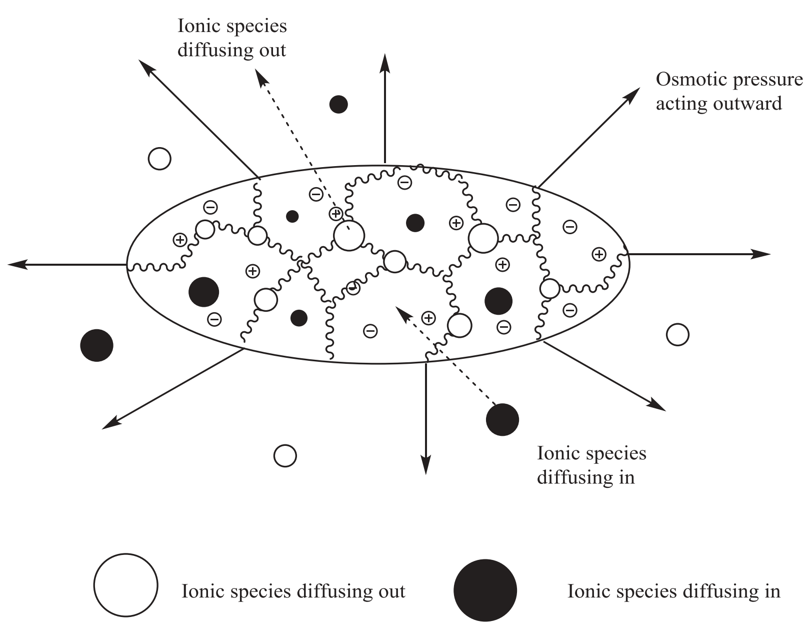

Figure 6. Swelling of hydrogel.[3]

of the heterogeneous hydrogel and phase separation occurs when the volume of water during polymerization exceeds the water content corresponding to the equilibrium swelling, this process is called microsyneresis.[51] The gel formed is dried, pulverized and sieved to achieve particular particle size. This technique has some demerits like handling of the rubbery solid product, irregular particle size distribution and lack of reaction control, but has some merits like it is an economical and a faster method for production of SAPs.[1] The solvents used for solution polymerization are water, ethanol, and their mixture.[2]

- ***Inverse suspension polymerization*** – Inverse-suspension polymerization technique is used to produce spherical SAP beads with particle size ranging from 1 micron to 1 mm, which is an advantage that one gets direct powder or beads, which reduces the effort of grinding. It is a water-in-oil process which is different than the most common oil-in-water process that is why it is called inverse-suspension. This technique involves two phases, one is aqueous phase and another is organic phase. The organic phase consists of a solvent and a stabilizer while the aqueous phase consists of the monomer, cross-linker, and initiator.[52] The micro-particles produced are washed

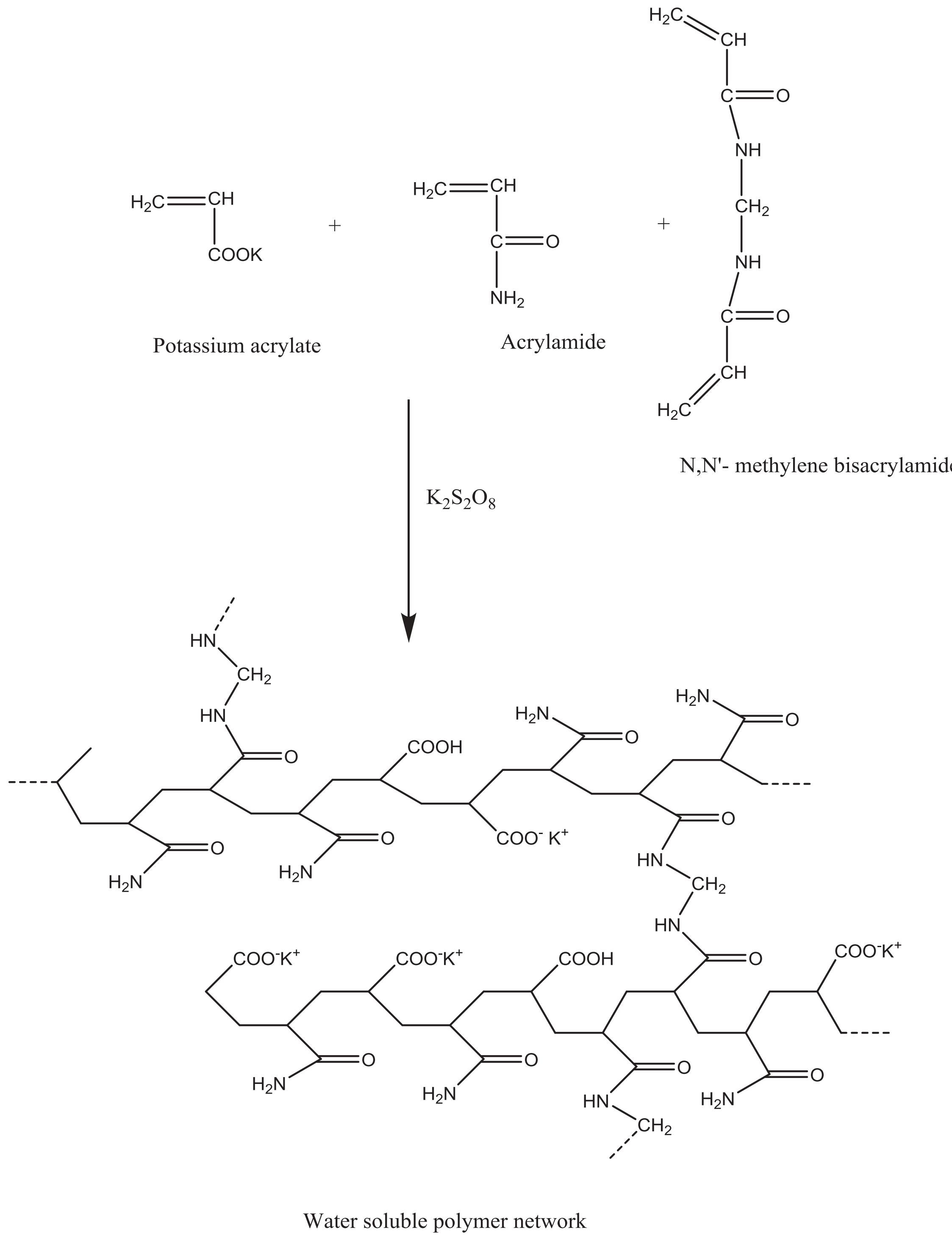

Figure 7. Mechanism of cross-linking of poly(potassium acrylate-co-acrylamide) hydrogel.[1]

to remove the unreacted monomers, cross-linker, and the initiator. The micro-particles are removed by filtration or centrifugation from the organic phase, and then dried to form a free-flowing powder. Poly (hydroxyl methacrylate) is formed by this technique[53,54] The particle shape of the polymer depends on the viscosity of the monomer phase and the particle size depends on the hydrophilic – lipophilic balance of the suspending agent, usually a low HLB value of the suspending agent that is an oil-soluble suspending agent is employed like Span 60[55] and Span 80[56,57] Particles size also depends on the type of suspending agent, agitation speed and rotor design.

- ***Radiation polymerization*** – Ionizing high energy radiation like gamma rays[58–60] and electron

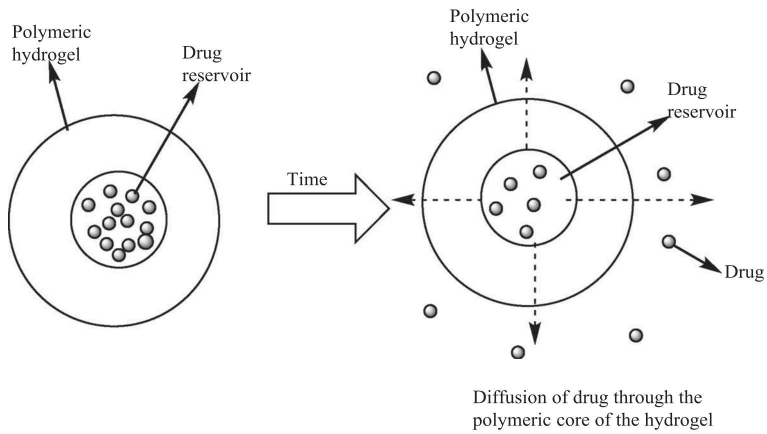

Figure 8. Control release of drug through reservoir system.[83]

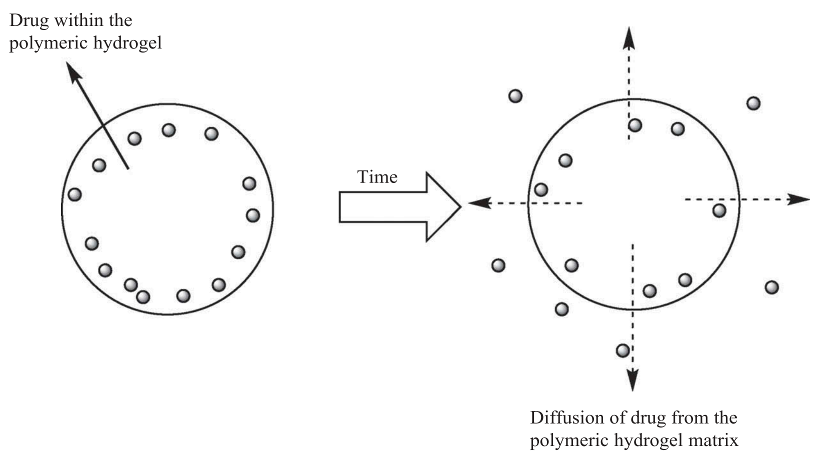

Figure 9. Control release of drug through matrix system.[83]

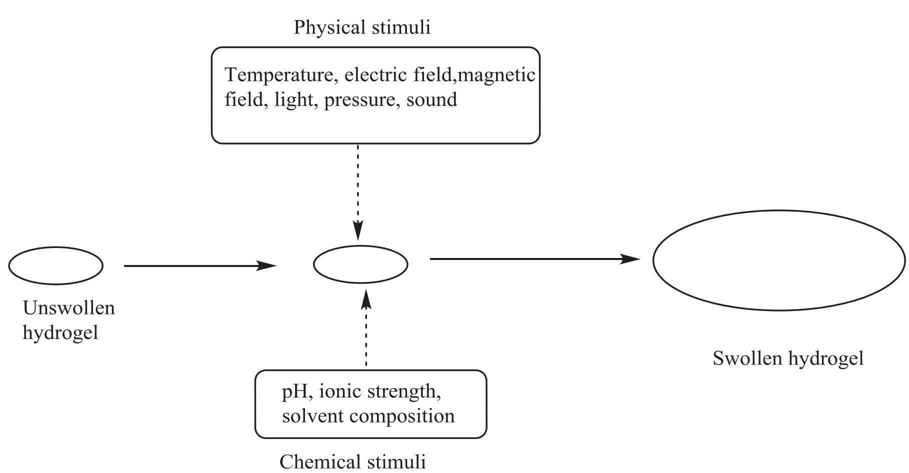

Figure 10. Stimuli responsive hydrogels.[86]

beams[61,62] are used to initiate the polymerization process to produce SAPs of unsaturated compounds. The irradiation of the aqueous polymer solution results in the formation of radicals on the polymer chains. The radiolysis of water molecules leads to the formation of hydroxyl radicals, which attack the polymer chains **to** form macro radicals. These macro radicals recombine to form covalent bonds leading to a cross-linked structure. The advantage of this technique over chemical initiation technique is that

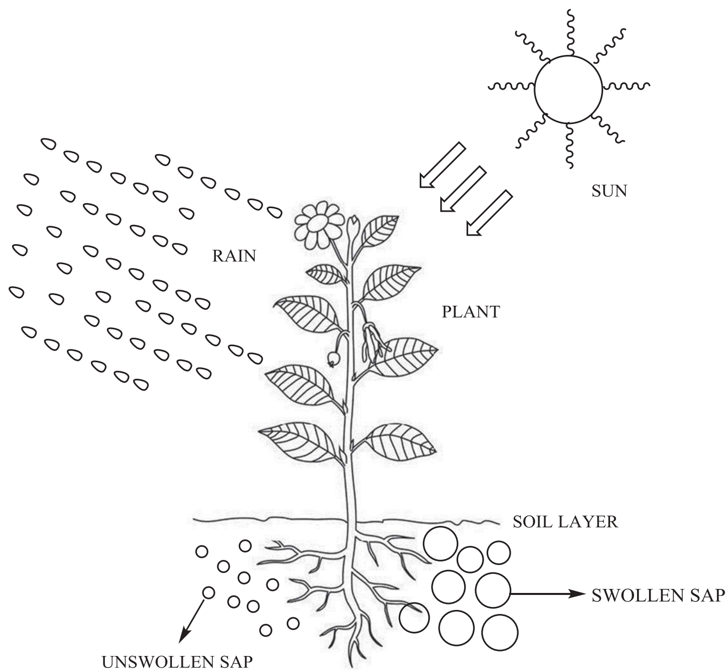

Figure 11. Stimuli responsive hydrogels.[86]

the product obtained is comparatively pure as no chemical initiator is involved in here.

The most common synthetic technique is the free-radical cross-linking copolymerization of acrylamide which is a hydrophilic non-ionic monomer with a small quantity of cross-linking agent, in addition with an ionic co monomer in order to increase its swelling capacity.[28]

5. Properties

Following are the properties of a superabsorbent polymer –

- High water absorption capacity,
- Different water absorbing rate depending on the required application,
- Colorless, odorless and non-toxic,
- High water absorbency under load,
- Low cost,
- Re-swelling capacity,
- Biodegradability,
- Biocompatibility
- Good durability and stability in swelling environment

6. Principle of swelling

The polymeric backbone in SAP is hydrophilic in nature as it contains water-loving carboxylic acid groups (-COOH). Therefore, when water is added to the SAP, there is a polymer-solvent interaction which includes hydration and formation of hydrogen bonds.

Hydration is the interaction of ions of the solute with molecules of the solvent, that is – COO^- and Na^+ or K^+ ions attract the polar water molecules.

Hydrogen bonds between the polymer molecules and water molecules increase the entropy of the system, which makes them soluble in water, but infinite solubility can be prevented by the introduction of cross-linking.[48]

Most synthetic SAPs are polyelectrolyte gels which contain ionic groups, when immersed in an aqueous medium, these ionic groups dissociate and create an overall charge density along the chains and increase the concentration of mobile ions in the gel. The mobile ions inside the gel contribute to the osmotic pressure within the gel. The main contributors for high water absorbency are difference between the osmotic pressure of swollen gel and the external solution and repulsion between polymer chains caused by ionic groups.[4] Thus, the absorbency of SAPs can be tuned by controlling the ratio of ionic to non-ionic part. For example – acrylamide which is non-ionic can be incorporated into poly (sodium acrylate) in order to control the water absorbency of the polymeric network.[63]

7. Cross-linking in SAP

There are two main types of cross-linking –

- ***Bulk cross-linking*** – it takes place during the polymerization stage in which a cross-linking agent acts as a co-monomer which has a higher functionality than the monomer. For example diacrylates or bisacrylamides are mostly used polyunsaturated cross-linkers.[64–72] The reactivity ratio of the cross-linker and the monomer plays a decisive role. If the reactivity ratio of cross-linker is higher than that of the monomer, it will react at low monomer conversion and vice versa. Low level of cross-linking gives high water absorbency with low gel strength, while high cross-linking level gives high gel strength with low water absorbing capacity.
- ***Surface cross-linking*** – it is a newer technique which enhances the absorption against pressure profile of the polymer gel. Surface treatment is necessary for this process. Low cross-linking level leads to low gel strength with poor absorption against load occurs, swollen particles deform easily and cluster together under load. When swelling under load is increased, the capacity under load is decreased. As a result, gel blocking occurs, so post-treatment is required to resolve this issue. Treatment with polyvalent metal salts or electrophilic polysubstituted compounds can be used for surface cross-linking, coating of the particles is done using glycerin or other polyols.[4] Bifunctional compounds able to react with the carboxylate groups of the polymer backbone like polyhydric alcohol, diglycidyl ether, or quaternary amines are employed as cross-linking agents. By the surface treatment, a highly cross-linked shell results with improved strength and lower core cross-linking level. The harder surface prevents gel blocking or fish eyes and allows free flow of liquid into superabsorbent particles for fluid absorption.[51]

Hydrogels are cross-linked by physical and chemical means. In physically cross-linked hydrogels, physical interactions are present between polymer chains, while in chemically cross-linked hydrogels, covalent bonds are present between polymer chains.[73]

Physical cross-links include entangled chains, hydrogen bonding, hydrophobic interaction and crystallite formation. Physical cross-linking gives reversible hydrogels. Chemical cross-linking is achieved by covalent cross-linking of polymers by using high energy radiation or by free-radical polymerization, they give permanent hydrogels, the hydrogels have good mechanical properties.[74]

8. Factors affecting

The factors affecting the properties of SAPs are as follows:

(1) Type and concentration of monomer, initiator and cross-linking agent
(2) Degree of neutralization
(3) Polymerization technique
(4) Polymerization temperature
(5) Type and concentration of the surfactant used
(6) Stirrer and reactor type and stirring rate
(7) Type of addition of porogen and its type and concentration
(8) Drying technique, temperature and time
(9) Post-treatment or surface cross-linking

9. Applications

Superabsorbent polymers have the following applications –

- ***Hygienic products*** – SAPs are widely used for absorbing water and aqueous solutions for baby diapers, adult incontinence products and feminine hygiene products. This application of SAPs replaces traditional absorbing materials such as cotton, cloth, paper etc., which has some drawbacks like low efficiency, low recyclability, and leakage. Cellulose based hydrogels have been mostly used for this application.[75,76]
- ***Biosensors*** – Because of the highly open structure and large inner surface, the SAPs can hold large amounts of molecules, thus used for biosensing applications to detect chemical and biological analytes.[62] Other characteristics of hydrogels like their tunable viscoelasticity, biocompatibility, odorless or anti-fouling properties and being responsive to external stimuli. Biocompatibility of Polyvinyl alcohol, odorless Polyethylene glycol, and stimuli-responsive acrylates are used in biosensors.[77] They are used in optical biosensors, photonic sensors, electrical and magnetic transducers.[78]
- ***Cosmetics*** – SAPs are used in cosmetic formulations for skin care as they possess good moisturizing properties due to their high water content. Their hydrophilic base creates a matrix to the skin which is efficient in delivering active ingredients into the skin, thermosensitive hydrogels are specially employed for localized, controlled and

continuous delivery of active ingredients.[79] The bioadhesive hydrogels have one advantage over the conventional ones, that is they allow longer residence times on the application site, thereby maintaining a high local concentration of active agent in the surrounding tissues over a longer time. This is advantageous for an active ingredient intended for superficial action and also exerting their action at the deeper layers of the skin. Different hydrogels were formulated using polymers like carrageenan, xanthan gum, guar gum and carbomers (derivative of acrylic acid).[80] A patent shows a combination of different polysaccharides (konjac mannan, xanthan gum, pullalan and carrageenan) to produce a stable, flexible, transparent, and slightly sticky hydrogel which will be used as a cosmetic for skin care.[81]

- ***Drug delivery systems*** – Biocompatibility, biodegradability, hydrophilicity, and non-toxicity are the properties of hydrogels which make them an appropriate choice for drug delivery applications.[82] The highly porous structure of the SAPs which can be regulated by varying the cross-link density of the gel matrix and type and concentration of the porogen used, this feature allows incorporation of the drug in the gel matrix as well as the delivery of the same at a controlled rate.[83] Polymers such as co-polymer of acrylic acid and acrylamide, biocompatible glucose acrylate-co-methacrylic acid polymer are used for in-vitro release of drugs[84,85] Smart hydrogels are developed which include stimuli-responsive hydrogels which absorb and release the active ingredients depending on various stimuli such as pH, temperature, electric and magnetic field. Stimuli-responsive hydrogels can be synthesized using polymers such as chitosan, gelatin, polyethylene oxide, poly (2-hydroxyethyl methacrylate), ethylene-co-vinyl acetate, poly(N-vinyl pyrrolidone) and poly(N-isopropyl acrylamide).[86]
- ***Agriculture*** – SAPs are used as watersaving materials and soil conditioners in agriculture because of their high water retention properties.[87] SAPs improve porosity in clayey soils as the polymeric particles expand and contract during moisture cycles.[20] The application of SAPs moderated the adverse effect of irrigation deficit regions and drought stress conditions on plant growth.[88] Fertilizers are used in combination with superabsorbents to obtain both controlled or sustained release and water retention properties.[89] This combination of fertilizer and superabsorbent helps improve plant nutrition, depreciate water evaporation losses and reduce the frequent irrigation.[90] SAPs are used in pest management in aquatic and terrestrial regions by control release of pests from SAP granules.[91] Mainly polyacrylate and polyacrylamide based superabsorbents are used for this application.[69] Sodium alginate[92], ethyl cellulose[89], chitosan[90] and various polysaccharides[7] are also used in agriculture and horticulture. Agar and starch-based hydrogels are used for control-release of herbicide and improve soil health as agar and starch act as a soil conditioner and thus enhance plant growth.[93]
- ***Pharmaceuticals*** – Due to high water-containing capacity, biocompatibility, non-toxicity and soft consistency of the hydrogels, they resemble natural living tissues, so used in many pharmaceutical formulations.[94] Swelling characteristics and diffusional behavior of hydrogels make them useful for pharmaceutical applications.[95] Proper material selection, fabrication process, and surface texture are important in designing of hydrogels for control release of pharmaceutical formulations.[96]
- ***Diagnostics*** – Introduction of hydrogel-based reconstructive tumor models in recent years for the investigation of cancer. Hydrogel-based drug delivery systems have improved chemotherapy results and gene therapy efficacy by increasing drug half-life, facilitating controlled release of drugs and decreasing non-targeted exposure. Hydrogels are attractive for localized and targeted therapy due to their sustained localized administration.[97]
- ***Biomedication*** – Hydrophilicity, non-toxicity, biocompatibility, and enhanced diffusivity of hydrogels make them efficient in biomedical application. Polyethylene oxide and polyvinyl pyrrolidone are some of the synthetic polymers, proteins and various polysaccharides are the natural polymers used in bioremediation.[98]
- ***Artificial snow*** – SAPs are swollen in water and spread over a surface and frozen by a cooling system to form artificial snow, the feeling of artificial snow is very close to powder snow.[99] Soft snow is prepared by slightly cross-linking polyacrylate while hard snow is formed by copolymerizing acrylic acid with acrylamide along with an increased amount of cross-linking agent.[42]
- ***Wound dressing*** – Hydrogel-based dressings reduce pain at the wound site through a cooling effect and low adherence to tissue, the high water content of hydrogels makes them useful in the treatment of dry wounds.[100] The tunable mechanical properties of hydrogels allow them to adjust to wounds that are located in different body parts, they absorb and retain wound exudate. The

tight mesh size of hydrogels prevents bacterial infection but allows efficient transport of biomolecules.[101] Natural polymers like chitosan, collagen, dextran, agarose, pectin, pullulan, carrageenan and fibrin and synthetic polymers like polyethylene oxide, polyvinyl pyrrolidone, polyvinyl alcohol, and various polyacrylates are used in this application.[102]

- ***Food industries*** – The tunable properties of micro-hydrogels are used for advanced rheological control, they enable fat reduction in processed-foods. A commercially available microgel called *Simplesse* which is prepared from microparticulate whey protein is used as a fat replacement in foods.[103] Edible polymer-based hydrogels are used in food packaging.[104]
- ***Polymer concrete compositions*** – Polyelectrolyte hydrogel particles are used as internal curing agents in concrete. When the hydrogel particles are added to the concrete, the water stored within the hydrogels promotes the curing reaction as a result of which volumetric shrinkage and crack formation is reduced which increases the shelf-life of concrete.[105] pH-sensitive superabsorbents are used to improve the self-healing and self-healing characteristics of cracks in concrete.[106]
- ***Aqueous gel for fire-fighting*** – Sodium polyacrylate is used as a fire gel, used while performing fire stunts. The fire gel is coated on the surface of an object, fuel is applied on the top of the gel, and fuel is ignited. The fire gel acts as an insulating barrier between the burning fuel and the surface of the object, thus preventing burns and injuries.[107] Superabsorbent hydrogels prepared by mixing bentonite and acrylamide are effective to weaken the activities of various oxygen-containing functional groups in coal gangues, they exhibit both cooling and combustion-control effects, they can also prevent combustion of coal gangues.[108] Water-logged cross-linked acrylic or acrylamide based superabsorbents can be directly spread onto fire thereby reducing the amount of time and water in fire-fighting.[109]
- ***Thermal energy storage*** – Superabsorbent polymer hydrogels absorbed aqueous calcium chloride solutions to act as both thermal and water storage material. **The water content of the calcium chloride solution absorbed superabsorbents was extremely higher as compared to that of zeolites and silica gel**.[110] **A graphene oxide-modified salt hydrate/poly (acrylamide-co-acrylic acid) hydrogels phase change composites were prepared with tunable phase transition behavior. The incorporation of grapheme oxide improved the thermal energy storage capacity of the polymer composite, thereby increasing the thermal stability**.[111]
- ***Tissue engineering*** – Because of the high water content in the superabsorbents, they are generally quite compatible with cells and may enter into specific or non-specific binding with cell receptors.[112] The soft and rubbery hydrogels resemble living tissues, their biocompatibility also makes them suitable for tissue engineering. Hydrogels based on natural polymers like hyaluronic acid, alginate, collagen, gelatin, agar, dextran, etc. and synthetic polymers such as polyoxymethylene, polyethylene glycol, polyvinyl alcohol, polylactic acid, polyacrylamide, and polyhydroxylethyl methacrylate are used[113,114]
- *Water treatment* – Water is one of the most essential substance for humans and other living organisms. There is a serious threat to the ecology as water pollution is gradually increasing; the industries release many toxic chemicals into the water stream. The main contaminants in the polluted water are the heavy-metal ions and dyes. The hydrogels are used for waste-water treatment, they are available in different shapes such as beads, films, and nanocomposites. The hydrogel beads are used to remove heavy-metal ions like Cu^{2+}, Ni^{2+}, and Pb^{2+}. The hydrogel beads are also used for adsorption of dyes like Crystal violet and Congo red. The hydrogels also remove radioactive waste from water.[115]

10. Superabsorbent polymers in controlled drug delivery

The hydrogels are extensively employed in drug delivery applications because of their physical properties. Basically smart or intelligent hydrogels are studied for drug delivery applications.[17] The highly porous structure of hydrogels can be tuned by controlling the cross-link density of the gel matrix and their response to the aqueous environment in which they are surrounded by. The drug release rate relies on the diffusion coefficient of small or macromolecule through the polymeric gel network. The entrapped drug is protected by the hydrogel and is released in response to environmental stimuli such as temperature, pH, electrical and magnetic fields, solvent composition, light, ions, etc. A lot of research has been done on hydrogels for drug delivery because they decrease the usual problems related to drug dosage and render stable and compatible drug release.[116]

Drugs can be loaded into hydrogels by two methods,

(1) The hydrogel monomer is mixed with drug, initiator, with or without cross-linker, allowed to polymerize, trapping the drug within the polymer matrix. This is called in-situ loading, in which the hydrogel network formation and drug encapsulation is achieved simultaneously. The drug release will be determined by diffusion, swelling, and reversible drug-polymer interactions.
(2) A preformed hydrogel is allowed to swell to equilibrium in the drug solution, the drug is absorbed in the polymer gel matrix, and then the drug-loaded hydrogel is dried. This is called post-loading. Drug release will be determined by diffusion and gel swelling and drug-polymer interactions.

The post-loading method has advantages over the in-situ loading method because the polymerization parameters and conditions may have adverse effects on drug properties and difficulties may arise while purifying the device after loading.[117] The device geometry also has a significant effect on drug release kinetics, the delivery device can be of different shapes such as thin film, sphere, cylinder, and irregular solid.[118]

Stimuli-responsive hydrogels are designed in such a way that they exhibit changes in their swelling behavior, network structure, permeability, and strength according to stimuli. These hydrogels are sensitive to various stimuli such as temperature[15,119], pH[37,120,121], magnetic field[122], and electric field.[123]

11. Superabsorbent polymers in agriculture

One of the important parts of agriculture is the irrigation process which helps in the growth of plants and crops by providing nutrients to the soil. Irrigation processes are very expensive in water-scarce areas, so to solve this problem, superabsorbent hydrogels have become an attractive alternative. They reduce the cost along with the continuous irrigation characteristic of this process. The high swelling capacity and retaining the ability of aqueous solutions of SAP hydrogels helps to maintain the moisture content of the soil.[124] SAP hydrogels are used in agriculture because they reduce water consumption in irrigation, irrigation cost, reduce plants and crops death, stabilize fertilizers in the soil, prevent leaching out of active ingredients to the groundwater, and enhance plant growth.[125]

11.1. SAP hydrogel as water retaining agent

The superabsorbents reduce water consumption, as they have high water absorbing and retaining ability, thereby maintaining moisture in the soil. SAP granules are mixed with the soil in given amounts. After soil watering, the granules absorb water by swelling and release it slowly as the soil dries off via diffusion. Irrigation water loss and evaporation losses are avoided in this way. As the SAP absorb water, they swell up and expand, as a result, the porosity of soil increases rendering a better oxygen supply to the roots. Polyacrylate based SAPs were used as a soil conditioner to promote plant growth in drought-prone areas. Concerning the low degradation rates of polyacrylate based SAPs and the release of toxic chemicals in their slow degradation, new environmental-friendly bio-based SAPs based on cellulose and starch were developed which can be degraded by microbial organisms.[126] Incorporation of porogen increases porosity which results in the enhancement of seed germination and growth rate of seedling, root growth and reduction in soil erosion due to less soil compaction. More porosity means more oxygen available to the roots of the plants.[127]

11.2. SAPs as nutrient carrier

Nitrogen is an essential nutrient for plants, so nitrogen fertilizers are employed in agricultural applications. The most commonly used nitrogen fertilizer is urea as it has high nitrogen content (46%). Due to surface run-off, leaching, and vapourization, the plant uptake, as well as the efficiency of it, decreases, these nutrient losses can be reduced by the use of slow-release fertilizers. Other than reducing nutrient losses, the slow-release fertilizers have many advantages such as a sustained or controlled supply of nutrients for a long period of time, the increase in efficiency of fertilizer, reduction in the frequency of application, reduction in ill-effects of over-dosage and toxicity. The fertilizer can be incorporated inside a hydrogel by two methods –

- *In-situ method*, in which the fertilizer is added to the reaction mixture and polymerized in-situ,
- *Post-loading method* – The dry gel is swollen in the fertilizer solution until it reaches swelling equilibrium, then the gel is dried and the device is obtained.

The in-situ method has drawbacks such as the entrapped compound may affect the polymerization process as well as the polymer network structure.

The post-loading method also has demerits like the loaded compound accumulate on the surface during drying of the hydrogel which leads to a ”burst effect” and the loading of the compound may be affected if it influences the water absorbency.[128]

12. Conclusion

Superabsorbent polymers are those which have the potential to hold a huge quantity of water or biological fluids and release certain amounts depending on their environment. The properties of superabsorbents are enhanced by incorporating organic and inorganic fillers (such as phyllosilicates which include kaolinite, montmorillonite, hectrite, saponite and synthetic mica) to form superabsorbent polymer composites. The rapid growth in nanotechnology has led to exploration of SAP composites for applications in biotechnology and biomedical technologies. The hydrogels have also found applications in dye sorption, water purification, and heavy metal ions separation. Recently, these polymeric networks have been tailored and designed to fulfil the needs of different applications, both natural and synthetic polymers have been modified to form smart hydrogels which are responsive to pH, temperature, light and ionic fluids. New ideas to design or recreate hydrogels with improved mechanical properties, superporous and comb-type rafted hydrogels with fast response time, self-assembling hydrogels from hybrid graft copolymers and from genetically engineered triblock copolymers are just a few examples of hydrogel biomaterials with a smart future.

ORCID

Sabyasachi Behera http://orcid.org/0000-0002-5893-3300
Prakash A. Mahanwar http://orcid.org/0000-0002-7594-4044

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