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Superabsorbent Polymers and Superabsorbent Polymer Composites

Suda Kiatkamjornwong*

Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Phyathai Road, Wangmai, Pathumwan, Bangkok 10330, Thailand.

* Corresponding author, E-mail: ksuda@sc.chula.ac.th

ABSTRACT: This article briefly describes the general aspects and cross-linking polymerization of superabsorbent polymers (SAPs) and superabsorbent polymer composites (SAPCs). Research and development of SAPs has become very active after the Northern Region Laboratory of the United States Department of Agriculture invented the first SAP, used as a soil conditioner. Based on the advancements in organic/inorganic syntheses, SAPs are produced and used in a wide range of applications for fluid absorption. The rapid growing nanotechnology has led to more explorations of SAPs and SAPCs for applications in biomedical, biotechnology and advanced technologies. Examples of research work of SAPs and SAPCs published in refereed, reviewed articles are introduced.

KEYWORDS: Superabsorbent polymers; Superabsorbent polymer composites; Water absorption capacity; Cross-linking reaction; Ionic functional groups.

INTRODUCTION

Superabsorbent polymers (SAPs) or hydrogels are loosely cross-linked, three-dimensional networks of flexible polymer chains that carry dissociated, ionic functional groups. They are basically the materials that can absorb fluids of greater than 15 times their own dried weight, either under load or without load, such as water, electrolyte solution, synthetic urine, brines, biological fluids such as urine sweat, and blood. They are polymers which are characterized by hydrophilicity containing carboxylic acid, carboxamide, hydroxyl, amine, imide groups and so on, insoluble in water, and are cross-linked polyelectrolytes. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving by solvation of water molecules via hydrogen bonds, increasing the entropy of the network to make the SAPs swell tremendously. The factors that supply absorbing power to polymers are osmotic pressure, based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure. Not only are they of high fluid absorbing capacity, but the absorbed fluid is hard to release, as they merely immobilize the fluid by entrapment rather than by holding it in the structure

SAPs possess a number of attributes that make them attractive in many different applications. SAPs have supplanted much of the traditional absorbents in infant diapers and have made significant improvements in the performance of feminine hygiene products and adult incontinence products as a result of superior water-absorbing properties. Because of their excellent characteristics, SAPs are widely used in many fields, such as agriculture, horticulture, sanitary goods, and medicine. The basic property of water absorption has suggested the use of SAPs in many other applications, including paper towels, surgical sponges, meat trays, disposable mats for outside doorways and in bathrooms, household pet litter, bandages and wound dressings. The ability of the swollen gels to release the water to the surroundings as vapor has also been used in various ways, for example, as humidity-controlling products or as soil conditioners. SAPs may also be used to release water-soluble substances from within the network structure into the surroundings as a solution. For example, pharmaceuticals and fertilizers may be incorporated into SAPs to yield controlled release products. Another characteristic of the swollen polymer is its rubbery nature, which has been used to control the consistency of products as diverse cosmetics or concrete or to contribute a soft, yet dry, feel to a product like hot or cold packs for sore muscles. The soft, rubbery nature may also be employed to impact sealing properties to products that are in contact with water or aqueous solutions, for example, underground wires and cables. Since they are widely applied not only in the fields of personal care products, bio-sorbent, bio-material, pharmaceutical, drug delivery systems, but also in agriculture, forestation, industrial, construction, communication industries, and environmental applications, SAPs provide ways for water management for both wanted or unwanted water depending on its particular purpose. Therefore, water absorption capacity (WAC) is the most important characteristics of SAPs and SAPCs. This can be measured by volumetric, gravimetric, spectroscopic and microwave methods.

SYNTHESIS TECHNIQUES

From a material resource point of view, SAPs can also be divided into natural macromolecules, semi-synthetic polymers, and synthetic polymers. From a preparation point of view, they can be synthesized by graft polymerization, cross-linking polymerization, networks formation of water-soluble polymer and radiation cross-linking, etc. There are many types of SAPs presently in the market. Mostly, they are lightly cross-linked copolymers of acrylate and acrylic acid, and grafted starch-acrylic acid polymers prepared by inverse suspension, emulsion polymerization, and solution polymerization. The polymerization techniques have been described[1].

Bulk polymerization

Bulk polymerization is the simplest technique which involves only monomer and monomer-soluble initiators. High rate of polymerization and degree of polymerization occur because of the high concentration of monomer. However, the viscosity of reaction increases markedly with the conversion which generates the heat during polymerization. These problems can be avoided by controlling the reaction at low conversions. The advantage of bulk polymerization is that it produces high molecular weight polymer with high purity. Polyacrylate SAPs are prepared by this technique.

Solution polymerization/cross-linking

In solution co-polymerization/cross-linking reactions, the ionic or neutral monomers are mixed with the multifunctional cross-linking agent. The polymerization is initiated thermally, by UV-irradiation, or by a redox initiator system. The presence of solvent serving as a heat sink is the major advantage of the solution polymerization over the bulk polymerization. The prepared SAPs need to be washed with distilled water to remove the unreacted monomers, oligomers, cross-linking agent, the initiator, the soluble and extractable polymer, and other impurities. Phase separation occurs and the heterogeneous SAP is formed when the amount of water during polymerization is more than the water content corresponding to the equilibrium swelling. The best example is preparation of poly(2-hydroxy ethyl methacrylate) SAPs from hydroxyl ethyl methacrylate, using ethylene glycol dimethacrylate as a cross-linking agent. Using this method, a great variety of hydrogels has been synthesized. The SAPs can be made pH-sensitive or temperature-sensitive by incorporating methacrylic acid or *N*-isopropyl acrylamide as monomers.

Suspension polymerization or inverse suspension polymerization

Suspension polymerization is a method to prepare spherical SAP microparticles with size range of 1 µm to 1 mm. In suspension polymerization, the monomer solution is dispersed in the non-solvent forming fine monomer droplets, which are stabilized by the addition of stabilizer. The polymerization is initiated by radicals from thermal decomposition of an initiator. The newly formed microparticles are then washed to remove unreacted monomers, cross-linking agent, and initiator. Some SAPs microparticles of poly(hydroxy ethyl methacrylate) have been prepared by this method. Recently, the inverse suspension technique has been widely used for polyacrylamide-based SAPs because of its easy removal and management of the hazardous, residual acrylamide monomer in the polymer.

Polymerization by irradiation

Ionizing high energy radiation, like gamma rays[2] and electron beams[3], has been used as an initiator to prepare the SAPs of unsaturated compounds. The irradiation of aqueous polymer solution results in the formation of radicals on the polymer chains. Also, radiolysis of water molecules results in the formation of hydroxyl radicals, which also attack the polymer chains, resulting in the formation of macroradicals. Recombination of the macroradicals on different chains results in the formation of covalent bonds, so finally a cross-linked structure is formed. Examples of polymers cross-linked by the radiation method are poly(vinyl alcohol), poly(ethylene glycol) and poly(acrylic acid). The major advantage of the radiation initiation over the chemical initiation is the production of relatively pure and initiator-free SAPs.

Cross-linking in Superabsorbent Polymers

There are two main types of cross-linking, bulk and surface cross-linking in most advanced SAPs, especially those used in diapers and napkins. The difference between the surface cross-linking and bulk cross-linking is shown below. Network formation is caused by post-polymerization cross-linking or curing in the case of using a UV source[1]. A bi-functional or multi-functional monomer is first mixed with the pre-formed polymer chains and a coupling reaction between the cross-linker and the functional groups on the pre-formed polymer is triggered by low temperature mixing, followed by heating. Ionic cross-linking and covalent cross-linking are the two different types of post-polymerization cross-linking[4].

a) Bulk or core/bulk cross-linking: Such a cross-linking of the polymer normally takes place during the polymerization stage of the monomer to form a network in which a cross-linking agent is actually a co-monomer with a higher functionality than the main monomer. The reactivity ratio of the cross-linker and the monomer is very important. If the reactivity ratio of the cross-linker is higher than that of the monomer, it will react at low monomer conversion. On the other hand, if the reactivity ratio of the cross-linker is lower than that of the monomer, it will react at a high monomer conversion. Extractable product contains low molecular weight polymer chains that are not incorporated in the polymer network and can be readily extracted in excess liquid. The degree of soluble polymer is important in determining the optimum cross-linking level, since too low a cross-linking level gives high WAC with low strength and high extractable product, while too high a cross-linking level induces low extractable product with non-tacky gel and having low WAC. To obtain an acceptable level for most SAP users, a balance is required with a small amount of extractable, high gel strength and high WAC.

b) Surface cross-linking: This type of surface cross-linking is a new process that improves the absorption against a pressure profile of the polymer gel, such as for feminine napkins. For the surface cross-linking reaction, surface treatment is necessary. Because high swelling capacity is obtained, but poor absorption against pressure occurs due to low elastic gel strength, caused by the low core cross-linking level. Swollen particles are easily deformed and clump together under load. The liquid supplying voids are closed. When the swelling under load is increased, the capacity under load is decreased. Therefore, gel blocking happens, so post-treatment is necessary to solve this problem This takes place during the final stages of SAP manufacture, and can be used to tune the desired properties of the SAP. Surface treatment is also a necessary step to provide better SAP products. A compound having at least two functional groups, capable of reacting with the carboxylate groups on the polymer backbone, such as polyhydric alcohol (monopropylene glycol), diglycidyl ethers (ethylene glycol diglycidyl ether), or quaternary amines, is usually used as a cross-linking agent. The cross-linking agent can be incorporated to the SAP by dissolving it into a solution containing water and a swelling suppressant solvent. Generally, the cross-linking reaction of the coated SAP particles can be performed by heating the polymer for a predetermined time. The amount of the cross-linking agent and heating time can be varied to give SAPs products with different swelling properties, such as absorption against pressure and saline flow conductivity. By the surface treatment, a highly cross-linked shell results with increased rigidity and a lower level of cross-linking core. The shell is of finite thickness, which can be fully controlled by adjusting the coating solvents and particle size of SAPs. The harder surface prevents gel blocking or fish eyes and allows liquid to flow freely to the SAP particles for fluid absorption.

Particle size and particle size distribution (PSD) are one of the important parameters for performance quality of the final products. Generally particle size and PSD have a direct effect on a free swell rate of the SAPs, where the small particle size can absorb faster than the larger particle size. The PSD controls the extent of fluid absorption; inter-particle voids resulting from a broad PSD hold unabsorbed water, which may cause problems with the products. Therefore, controls in polymerization technique, optimization of grinding machine and particle size classification are the keys to success in industrial production of diapers or napkins.

Many kinds of SAPs have been commercialized since the hydrolyzed starch-polyacrylonitrile graft copolymer; the super slurper was first developed by the Northern Regional Laboratory of the United States Department of Agriculture in 1961[4]. Since then tremendous amounts of research and development have been made in an attempt to modify SAPs structure and morphology to enhance WAC, gel strength and absorption rate. New types of SAPs and superabsorbent polymer composites (SAPCs) are emerging for more advanced applications, especially in the nanotechnology field. A well-known example of SAP is an acrylate family which is widely used in many industrial applications especially in personal care products.

Polyacrylate superabsorbent polymers are one of the largest families of the polymer. They are prepared by free-radical initiated polymerization of acrylic acid and its salts with a cross-linker in aqueous solution or as suspension drops of aqueous solution in a hydrocarbon solvent. Furthermore, copolymerization of acrylic acid with other hydrophilic vinyl monomers such as acrylamide has expanded widely the applications of SAPs. The types of co-monomer and cross-linker monomer play an important role in designing SAPs properties and applications. Bulk, solution, and suspension polymerizations are the major production processes for polyacrylate SAPs. In addition, polymerization by radiation has also gained much attention for future clean technology production. The monomer and cross-linker concentrations, the initiator type and concentrations, pre-neutralization or post-neutralization of the carboxylic acid groups, the relative reactivities of the monomer pairs and cross-linker polymerization additives, the medium pH, the reaction temperature, in conjunction with the types of initiator, are all significant factors in both polymerization processes. Several initiating sources for a particular monomers and special additives include thermal initiator, redox initiator, and photochemical initiator, such as non-ionizing radiation or ionizing radiation. The types of cross-linking agent modify the final properties of SAPs. Without a cross-linking agent incorporated in the SAPs, soluble polymers are always obtained. Cross-linking polymerization plays a significant role in the properties of superabsorbent polymers. Three principal bonding types, namely, covalent, ionic and physical cross-links are used to bind the polymer chains together. The copolymerizing cross-linkers used in SAPs range from di-functional compounds such as *N, N'*-methylenebisacrylamide or diacrylate esters to tri-functional compounds like 1,1,1-trimethyolpropanetricarylate to tetra-functional compounds such as tetraallyloxyethane. In addition, covalently cross-linked SAPs can also be produced. The preformed polymers with the above-mentioned functional monomers react with the carboxylic acid groups by means of a condensation polymerization. Ionic cross-links are formed in which a polyvalent ion of opposite charge reacts with the charged polymer chains. The cross-linking points are thus formed as a result of charge association of the unlike charges. Physical cross-links are formed by means of hydrogen bonding of segments of one polymer chain with the segments of another polymer chain. This type of cross-link is not quite stable, because it is easily destroyed under heat or pressure.

Although there are a few researchers in the area of SAPs in Thailand, SAPs research work carried out here falls into the categories of redox initiation, radiation initiation and polymerization, either by copolymerization or graft copolymerization as follows. Polysaccharide can be a very good substrate for preparing biodegradable SAPs. Starch and chitosan are the most suitable substrates for graft co-polymerization[5-10] to produce SAPs. Syntheses of SAPs by hydrophilic vinyl monomers by inverse suspension polymerization have been widely carried out[11-12] and by solution polymerization[13-15], via radiation initiation and polymerization[16-22].

SUPERABSORBENT POLYMER COMPOSITES (SAPCS)

Theoretically, there is a wide range of inorganic materials with expandable layers available for utilization for the preparation of SAPCS. In recent years, the study of organic-inorganic nanocomposites has become a very important field. Currently, reinforcing polymers with small amounts of smectite clays has attracted increasing interest, because the derived hetero-structural materials exhibit impressive mechanical, thermal, optical, and other properties that increase their technological values. The organic/inorganic phases are quite different in nature and incompatible, leading to phase separation. Interfacial bonding and adhesion is introduced to avoid phase separation by covalent bonding. Phyllosilicate is an appropriate material to prepare SAPCs. Clays have sandwich types of structure with an octahedral Al sheet and two tetrahedral Si sheets. There are many types of phyllosilicate: kaolinite, montmorillonite, hectrite, saponite and, synthetic mica, etc. The commonly used layered silicate for the preparation of polymer/layered silicate nanocomposites belongs to the same general family of 2:1 layered phyllosilicate. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of aluminium or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers (for example, Al^{3+} is replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} is replaced by Li^{+}) generates negative charges that are counterbalanced by alkali and alkali earth cations situated inside the galleries. In the case of tetrahedrally substituted layered silicates, the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can react interact more readily with these than with octahedrally-substituted material. Therefore, intercalation structures can be produced in SAPCs. The SAPCs find many new applications beyond those of SAPS, such as nanocomposite materials, for example, fabrication of silver or zinc nanoparticles in SAP or SAPC networks. The proven applications are for catalysis, optics, electronics, bio-medicals and quantum-sized domain applications. Some potential application of SAPCs in water treatments have been described[23-26].

FUTURE PROSPECTS

SAPs and SAPCs are very dynamic research areas in polymer sciences due to the advances in polymer syntheses resulting in better WAC, higher gel strength and faster absorption rate, as well as other materials properties for comfort and safety. Nanotechnology will likely play a major role in the production of the higher performance SAPs and SAPCs.

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