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Review article

Polyaspartic acid based superabsorbent polymers

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ABSTRACT

Superabsorbent polymers are widely used in many applications such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, drug delivery systems, absorbent pads and other biomedical applications. Most of these superabsorbents are non-biodegradable and thus increasing burden on the earth. Polymer scientist and chemists are looking for environmental friendly solutions. Polyaspartic acid polymers have been reported to possess biodegradable properties. These polymers have been developed mainly as polyelectrolyte. However, this review compiles the work carried on developing polyaspartic acid based superabsorbent polymers. The review covers synthetic methodology, characterization of these polymers by different techniques, different types of polymer prepared using polyaspartic polymers which include co-polymers, grafted polymers, interpenetrating and semi-interpenetrating polymers are covered. The biodegradability studies carried out on the superabsorbent polymers are also discussed.

Contents

Abbreviations: SAPs, superabsorbent polymers; PSI, polysuccinimide; PASP, polyaspartic acid; PASP-Na, polyaspartic acid sodium salt; DAB, diaminobutane; DMF, dimethylformamide; DDA-PASP-Na, sodium dodecylamine modified polyaspartic acid; MW, molecular weight; IPN, interpenetrating polymers; PNIPAAm, poly N-isopropylacrylamide; Semi-IPN, semi-interpenetrating polymers; CYS, cystamine.

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1. Introduction: absorbing, hydrogels & superabsorbent polymers

Polyaspartic acid (PASP) is a representative product in new-era of green chemistry. Polyaspartic acid (PASP), a poly (amino acid), is a promising water-soluble and biodegradable polymer. Its biodegradability makes it particularly valuable from the point of view of environmental acceptability and waste disposal. PASP is used widely as mineral scale inhibitor [such as $CaSO_4$, $BaSO_4$, $CaCO_3$ and $Ca_3(PO_4)_2$] in water treatment applications and as dispersing agents in detergents, paints and papermaking processes. Some studies indicate that as a scale inhibitor, the scale inhibiting capability of PASP is poorer than that of phosphorus-containing inhibitor [1].

Polyaspartic acid polymers fall under the category of water soluble polymers with the property of biodegradability in comparison to other conventional water soluble polymers. Water soluble polymers, such as poly(vinyl alcohol), poly(ethylene glycol), and poly(acrylic acid), are widely used in cosmetics, paper additives, dispersants, and detergent builders, but they are hardly recovered or collected after use. Of concern is the diffusion and accumulation of such non-biodegradable water-soluble polymers in the earth's environment after their release. Polymers with carboxylic acid groups are one of the most important water-soluble polymers; e.g., poly (acrylic acid) has been use as detergent builders scale inhibitors and flocculants and is directly released into the earth's environment. However, they are hardly biodegradable, except for their oligomers, which will possibly produce much damage to the environment [2–4].

Other applications include use of PASP as hydrogel materials. The hydrogel materials have been worked upon to prepare superabsorbent polymers. These superabsorbent polymers (SAP) can absorb large amount of water and the waste is hardly removed even under pressure because of its excellent water absorbing properties, SAPs have an unlimited number of applications. Hydrophilic networks that are responsive to some molecules, such as glucose or antigens can be used as biosensors as well as in drug systems, disposable sanitary products (for example, diapers, incontinence articles, feminine hygiene products, airlaids and absorbent dressings), and in controlled release of drugs. Superabsorbent polymers have the ability to sense environmental changes, like changes of pH, temperature, etc. [5,6]. In the field of medicine these have found applications in the area of drug delivery systems [7], wound closure, healing products [7], scaffolds in tissue engineering and surgical implant devices [8–12].

To qualify as a superabsorbent, a dry material should spontaneously imbibe about twenty times or more of its own weight of aqueous fluid. Moreover, the swollen material should retain its original shape, i.e. a swollen bead is still recognizable as a bead, a swollen fiber as a fiber, and a swollen film as a film [13]. The 'hydrogel' resulting from the transformation of the dry superabsorbent must have sufficient physical integrity to resist flow and fusion with neighboring particles. When exposed to an excess of water, true superabsorbent hydrogel particles swell to their equilibrium volume and do not dissolve. This phenomenon is due to the electrostatic repulsion between the charges on the polymer chains and the difference in osmotic pressure between the inside and outside of the gels. The superabsorbent polymers (SAP) are categorized as hydrogels which can absorb aqueous solutions via hydrogen bonding with the water molecules. The important properties of superabsorbent polymers are the swelling capacity and the elastic modulus of the swollen cross-linked hydrogel. These two properties of the swollen cross-linked hydrogel are related to the cross-link density of the network modulus which means that swelling capacity decreases with increasing crosslink density.

These ultrahigh absorbing materials can imbibe de-ionized water as high as 1000–100,000% (10–1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g). Visual and schematic illustrations of an acrylic – based anionic superabsorbent hydrogel in the dry and water swollen states are given in Fig. 1 below [13].

The hygroscopic materials are usually categorized into two main classes based on the major mechanisms of water absorption, i.e., chemical and physical absorptions. Chemical absorbers (e.g., metal hydrides) catch water via chemical reaction converting their entire nature. Physical absorbers imbibe water via four main mechanisms;

(i) reversible changes of their crystal structure (e.g., silica gel and anhydrous inorganic salts);
(ii) physical entrapment of water via capillary forces in their macro-porous structure (e.g., soft polyurethane sponge);
(iii) a combination of the mechanism (ii) and hydration of functional groups (e.g., tissue paper);
(iv) the mechanism which may be anticipated by combination of mechanisms of (ii) and (iii) and essentially dissolution and thermodynamically favored expansion of the macromolecular chains limited by cross-linkages.