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Review Article

Polyaspartic Acid - A Versatile Green Chemical

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Abstract

It is one of the most common scale inhibitor. The polyacrylate is nontoxic and environmentally benign, but it is not biodegradable. Polyaspartate a biodegradeable polymer possess similar properties to the polyacrylates and is used as an antiscalant, adispersant and superabsorber. In this article we review, methods of synthesis of polyaspartate and its hydrogels. Applications of polyaspartate and its hydrogels of are described. Biodegradability with respect to methods of preparation and variation in molecular weight of the polyaspartate is reviewed.

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Introduction

When water is heated in a boiler, soluble salt present in the water are precipitated out and start forming the scale. Various antiscalants have been developed for the prevention of the scale. Antiscalants prevent scale formation entirely or permit the scale to be deposited in such a way that it is easily removed by the fluid flowing along the pipe or heat transfer surface. Antiscalants complex with the cations present in water to prevent formation of the insoluble inorganic solids. The polyacrylate is one of the most common scale inhibitors. The polyacrylate is a polyanion. Polyelectrolytes are polymers with bound positive or negative charges ,are also called macroions or polyions , can be polyanions or polycations, are generally water soluble polymers if their structure is linear. Polymeric antiscalants are generally low molecular weight polymers. Polymeric dispersants consist of higher molecular weight fractions. Dispersants do not stop the formation of scale, but instead are able to keep the scale particles suspended in the bulk fluid by imparting a negative charge to the particles. The polyacrylate comprises 5% of many laundry detergent formulations because of its dispersant properties. A crosslinked form of the sodium salt of polyacrylic acid is used as a super absorbant material in diapers and other personal hygiene products. Crosslinked polyacrylate has a great affinity for water, but is unable to dissolve and swell in aqueous solution. Because of the presence of the charged groups on the polymer chain of a polyelectrolyte, the polymer will be highly expanded in aqueous solution.The polyacrylate is nontoxic and environmentally benign, **but it is not biodegradable**. It is widely used for many applications and it poses an environmental problem from a landfill perspective. When polyacrylate is used as an antiscalant or a dispersant, it becomes part of waste water. The polyacrylate is nonvolatile and not biodegradable, so the only way to remove it from the water is to precipitate it as an insoluble sludge. The sludge must then be land filled. Thus polyacrylate leaves its carbon foot print[1,2].

Therefore there was need to develop chemical agents which possesses properties of polyacrylate and are biodegradable. Polyaspartate has similar properties to the polyacrylates and so it can be used as a dispersant, or an antiscalant, or a superabsorber. **Polyaspartate is biodegradeable.** The polyaspartate increases the nutrient level in plants by keeping fertilizer available for an extended period of time [3]. In this article we review the methods of synthesis , applications and biodegradability of polyaspartate and its hydrogel.

Synthesis

Poly(aspartate)s are condensation polymers of aspartic acid. They are synthetic poly(amide)s that are structural and functional analogues of biomineralization controlling proteins. Their synthesis has been reviewed in several articles [4-6]. The three main methods for the industrial production of poly(aspartic acid) are [5-9] , thermal condensation of aspartic acid, catalyzed polymerization of aspartic acid, and thermal polymerization of maleic acid and ammonium hydroxide. In the thermal condensation process, the aspartic acid is first converted to poly(succinimide) by heating the acid to a temperature above 180^{o}C. Then poly(succinimide) is transformed into poly(aspartic acid) by alkaline hydrolysis. The yield is high, nearing complete conversion. Use of a catalyst lowers the condensation temperature and enables shorter reaction times. An alternative way to produce poly(succinimide) by thermal polymerization of maleic acid and ammonium hydroxide. The structure, chemical characteristics, and properties of a poly(aspartate) depend on the method of preparation [5]. Several other similar methods of preparation of poly(aspartate) have been reported in the literature. [10-31].

A new original method of synthesis polyaspartic acid is presented by thermal polymerization of maleic acid derivatives under microwave irradiation [32]. The reaction required following steps: maleic anhydride is hydrolised in water to give maleic acid (step 1), then it is converted into ammonium derivatives by addition of ammonium hydroxide (step2). The stage 1 and 2 require temperature of 100°C. In this way, ammonium salt or/ and amide of maleic acid is obtained. The cyclic product, namely anhydro-poly(aspartic acid) (step3) is formed. The temperature of polymerization is raised gradually in order to achieve high yield of polycondensation. Water from the reaction is removed by means of distillation. Finally, linear polyaspartic acid is obtained after hydrolysis of the cyclic form at room temperature (step 4). The hydrolysis of the anhydro-poly(aspartic acid) leads to poly(aspartates) containing peptide bonds. The preparation of poly(aspartic acid) from maleic anhydride and ammonia through in a two steps reaction has also been reported [33].

In 1999, Rohm and Haas Company’s researchers reported, lightly cross-linked, high molecular weight sodium polyaspartates with superabsorbing, and electrolyte-responsiveness properties [34]. They used ethylene glycol diglycidylether as a cross-linker. To enhance the swelling capacity, several hydrophilic polymers such as starch, ethyl cellulose, carrageenan, β-cyclodextrin, and CMC have been incorporated into the hydrogels (after or before the hydrolysis step) to attain modified super absorbing polymer (SAP) composites [35-38]. For the crosslinking of polyaspartic acid , various methods have been introduced , including chemical and radiation processes. To prepare SAP researchers have also used difunctional amine , amino acid , or their polymeric analogs as the chemical crosslinker. Polyethylene glycol diglycidylether (PEG-diepoxide) with different molecular weights has also been employed to synthesize biodegradable poly(aspartic acid) hydrogels with super-swelling behaviour [39]. Method of producing super – absorbing polymeric network of polyaspartate from crosslinked polysuccimide using an organic base containing at least two primary amine groups have been reported [40]. A method of preparing super absorbent polymer by reacting polysuccinimide (dissolved in organic solvent) with crosslinker and reacting polysuccinimide in situ with net or a solution of alkali metal hydroxide has also been reported [41]. A water insoluble polyamino acid cross linked gels have been prepared with the absorbing capacity of 20 times the weight of 1% NaCl solution [42] . Gamma –irradiation to prepare the biodegradable super – absorbent hydrogel (36-38) has also been applied

Applications:

Several new environmentally acceptable scale-inhibitors compared with conventional antiscalants are known [43-58]. Polyaspartic acid an environmentally benign agent for the dissolution of calcium salt deposits. The chelating power of polyaspartic acid with calcium is investigated by performing the potentiometric titration against polyaspartic acid solutions. It is found that polyaspartic acid is fully deprotonated at pH 7. The titration curves are successfully modeled by assuming that four aspartyl residues from an actual polyaspartic acid molecule consist of a hypothetical molecule (denoted as H_4L) that has four distinct acid moieties (four dissociation constants). The resulting dissociation constants and calcium-binding constants for polyaspartic acid at pHs (10, 7, 5, and 3.5) show that polyaspartic acid replaces interfacial water to react with calcite at high pH (≥7) and the dissolution of calcite can be described by a surface adsorption and complexation mechanism. At low pH (≤5), surface adsorption of polyaspartic acid on calcite surface still plays an important role, and both acidic species attacks (H^+ and H_nL^{n-4}, n = 1,2,3,4, attacking carbonate sites) and chelant attacks (L^{4-} and H_nL^{n-4}, n = 1,2, attacking calcium sites) affect the calcite dissolution. The dissolution of calcite in acidic polyaspartic acid solutions represents the most complicated case [59].

Another investigates the use of sodium polyaspartate, a nontoxic, biodegradable polycarboxylic sequestrant is for removing calcium phosphate deposit consisting of hydroxyapatite (HAP) and brushite or dicalcium phosphate dihydrate (DCPD) from stainless steel surfaces. Cleaning studies show that the use of sodium polyaspartate under alkaline conditions significantly enhances the removal rates when compared to deionized water. In acidic solutions, sodium polyaspartate concentrations below 300 ppm inhibit removal of HAP/DCPD deposits whereas higher concentrations increase the removal rate. Comparative cleaning studies at alkaline pHs show that sodium polyaspartate cleans the surface at a rate comparable to sodium citrate but slower than in ethylenediaminetetraacetic acid. Supplementary dissolution experiments show that sodium polyaspartate enhances the HAP/DCPD dissolution rate while inhibiting the release of Ca^{2+}. On the basis of these findings, it is concluded that sodium polyaspartate improves the HAP/DCPD dissolution and cleaning rates by Ca^{2+} sequestration [60].

Chweinsberg et al. [61], of Henkel Surface Technologies, Germany has reported inhibition and dispersion results of $CaSO_4$ and $CaCO_3$ scales performed with poly-(aspartic acid)s of varying mean molecular weight, molecular weight distribution, degree of branching, and purity. Quan et. al. [62] conducted static and dynamic experiments to test the scale inhibition performance of a polyaspartic acid inhibitor and found that scale inhibition, exceeding 90%, with only 3 mg/L polyaspartic acid in a 600 mg/L hardness solution at temperatures below 60^{o}C. With a higher hardness solution of 800 mg/L, the scale inhibition reached 90% with 6 and 12 mg/L polyaspartic acid at 30 and 60 ^{o} C, respectively. The modified poly(aspartic acid)s, such as poly(aspartic acid-co-aminocarboxylic acid) , alkylamine modified poly(aspartic acid) and crosslinked poly(aspartic acid) showed 3 times higher calcium-ion chelating ability, hygroscopicity and water absorption than that of poly(acrylic acid) with a M_w of 14000. The maximum swelling of poly(aspartic acid) hydrogel prepared by the γ-irradiation of homopoly(as-partic acid) was 3400 g-deionized water/g-dry hydrogel [57].

Only the type of amide linkage affects the calcium ion chelating ability. Poly(α-aspartic acid) showed a higher calcium ion chelating ability than poly(β-aspartic acid) and poly(α,β-aspartic acid) [64]. Based on the viewpoint of global environmental problems, it is required to free from conventional one-way type society of mass production, mass consumption, and mass disposal, and to be looked forward to establishing the recycling system which loads less materials to the environment. Water-soluble materials which are particularly difficult to be recovered after use should be substituted to the biodegradable polymer materials which can be decomposed in natural environments. [65]. Currently, the most promising green scale inhibitors are based on poly(aspartic acid). However, field operation data are very limited, and widespread use of poly(aspartic acid) scale inhibitors awaits field operation experience [63,66].

Thermal polyaspartate is a nutrient absorption enhancer in agricultural applications. Recent investigations have shown that certain variations of polyaspartate enhance the uptake, and therefore the effectiveness, of foliar and soil insecticides, as well as pre-emergence and post-emergence herbicides. The practicality of such benefits was demonstrated successfully in greenhouse and field tests. The polyaspartate is compatible with most common insecticides and herbicides and also can be tank-mixed and applied with conventional sprayers [66,67]. The possibility of reducing the moisture content in diesel fuel by using a hydrophilic polymer, thermal polyaspartate ion, which is simply and cheaply synthesized, was investigated. It was shown that when thermal polyaspartate is added in a given amount to a given volume of diesel fuel, the moisture content decreases significantly [68,69] Water-insoluble polyaspartyl polymers were synthesized by using water as medium instead of organic medium. Taking Ca^{2+} as a reference, the binding of several heavy-metal ions, including Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+}, Cu^{2+}, and Mn^{2+}, by polyaspartyl polymers was studied. The experimental results revealed that polyaspartate is an excellent binding agent for the investigated heavy-metal ions. These cation ions were bound to polyaspartate polymer by the same mechanism as Pb^{2+}, which can be explained by ion exchange model. Since polyaspartate has a protein-resembling structure that is sensitive to trace heavy metal, it was used to remove some trace heavy-metal elements in Chinese herbal medicines. It was found that polyaspartate material was an effective agent for the removal of Pb^{2+}, Cd^{2+}, and Hg^{2+} ions from glycyrrhizin, angelica, and gynostemma pentaphyllum [70]. The maximum swelling of poly(aspartic acid) hydrogel prepared by the γ-irradiation of homopoly(as-partic acid) was 3400 g-deionized water/g-dry hydrogel [57]. A group of researchers at the University of Crete in Greece have devoted efforts toward developing environmentally friendly antiscalant additives [43-48]. Nakato et al [71] also reported that the calcium-ion chelating ability of the PASP was affected only by the type of amide linkage. Gao et al [75] studied the scale inhibition and biodegradation properties of a polyaspartic acid prepared from poly(succinimide) by thermal condensation. A solution containing 400 mg/L Ca2þ and 800 mg/L HCO_3^- was dosed with varying concentrations of PASP and held for 10 h at 80 ^{o} C. The percentage scale inhibition varied from 88% at a polyaspartic acid dosage of 2mg/L to full inhibition at a polyaspartic acid dosage of 6 mg/L.

Biodegradability:

The biodegradability of poly(aspartic acid) was reviewed by Thombre and Sarwade in 2005 [6]. The environmental degradation of polymers is a complex process that is influenced by various factors, such as microorganisms, solar radiation, temperature, and moisture cycles. Polymer properties affecting biodegradability are chemical structure,molecular weight, morphology, crystallinity, glass transition, hydrophilicity, and water uptake [57]. For instance, sodium poly- (aspartate) synthesized in the presence of phosphoric acid as a catalyst is 100% biodegradable, whereas the same polymer synthesized without a catalyst is only 70% biodegradable [71]. Although no significant variations in the ratio of α- and β-amide bonds and the stereoregularity for the two polyaspartic acids was observed, the amount of amide protons differed between the polyaspartic acids synthesized in the presence and absence of phosphoric acid. Therefore, it was concluded that the biodegradability of a polyaspartic acid is affected by the structures of branching and irregular end groups in the polyaspartic acid [71-74]. Freedman et al. [74] has reported that a linear poly(amide) backbone is essential for 100% biodegradation. Nakato et al. [72] investigated the relationship among the structure of poly(aspartic acid)s, their biodegradability, and their calcium-ion chelating abilities. Biodegradability was found to be affected by the number of amide protons and the ratio of dicarboxylic acid end groups to dicarboxylic acid and succinimide end groups. It was concluded that the chirality of the aspartic acid unit and the type of amide linkage in the polyaspartic acid scarcely affected the biodegradability of the polymer [6].

The biodegradability tests performed have indicated that *Pedobacter* sp.KP-2 hydrolyzed polyaspartic acid of high molecular weights over 5000, *Sphingomonas* sp. KT-1 hydrolyzed only polyaspartic acids of low molecular weights (<5000), while the cell extract could hydrolyze high-molecular-weights polyaspartic acid to aspartic acid monomer. The polyaspartic acid hydrolase was purified from the cell extract of *Sphingomonas* sp. KT-1 and characterized. The molecular cloning results indicated that the structure of this enzyme is similar to those of PHB depolymerases . The results of NMR and GPC analyses showed that this enzyme hydrolyzed the amide bond between aspartic acid units in polyaspartic acid to yield aspartic acid oligomers(76). Microbial degradation of thermally synthesized poly(aspartic acid) (M_n, 7500; M_w, 20 000; number of branched units/100 monomer units) was completely degraded in natural river water within 15 days at 25 °C [77]. A new polyaspartic acid degrading bacterium (strain KP-2: JCM10638) was isolated together with *Sphingomonas* sp. KT-1 (JCM10459) from river water, and identified as a member of *Pedobacter*. A *Pedobacter* isolate was capable of degrading high-molecular-weight polyaspartic acids polymers of 5000 to 150,000, and a small amount of low-molecular-weight products of 250 to 5000 was accumulated as residues during the growth of the isolate on polyaspartic acids. In contrast, the other isolate *Sphingomonas* sp. KT-1 degraded only low-molecular-weight polyaspartic acids below 5000. A mixed culturing of *Pedobacter* sp. KP-2 with *Sphingomonas* sp. KT-1 resulted in a complete degradation of polyaspartic acid-P1 sample, but a small amount of low molecular weight components was accumulated during the degradation of highly branched polyaspartic acid-P2 and polyaspartic acid-P3 samples [77].

Biodegradabilities of various types of poly(aspartic acid)s such as poly(α-l-aspartic acid), poly(α-d-aspartic acid), poly(β-l-aspartic acid), and poly(α,β-d,l-aspartic acid)s was studied using the OECD 301C method and their calcium ion chelating abilities were measured to understand the relationship between the structure of poly(aspartic acid)s and its properties. Distinct tendencies were found both between the number of amide protons and biodegradability and between the ratio of the dicarboxylic acid end groups to the dicarboxylic acid end group plus succinimide end group and biodegradability. The chirality of the aspartic acid unit and the type of amide linkage in poly(aspartic acid) had no apparent effect on the biodegradability of poly(aspartic acid). The result of repetitive biodegradability analyses for poly-aspartic acid suggested the complete biodegradation is possible. Regarding the calcium ion chelating ability, only the type of amide linkage affected the calcium ion chelating ability. Poly(α-aspartic acid) showed a higher calcium ion chelating ability than poly(β-aspartic acid) and poly(α,β-aspartic acid) [78].

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