International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 12 Issue 4 ǁ April 2024 ǁ PP. 238-257

Research progress and application of sodium alginate grafted copolymer composites

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Abstract

Sodium alginate is one of the few hydrocolloids that can thicken and gel at the same time, so it has many useful properties, including viscosity control, stabilization of suspensions, emulsions and foams, improved freeze-thaw stability, dehydration shrinkage and boiling control, film formation, rheological control, etc.Because of its good gel behavior, biocompatibility, low toxicity and biodegradability, sodium alginate has been widely used.Graft copolymerization is the simplest modification method for natural polymers to produce novel biomaterials with specific properties.Sodium alginate is also good for grafting modification because its reactive groups contain hydroxyl and carboxyl groups.So far, it has been proved that the sodium alginate composite nanomaterials generated by graft polymerization have great potential in biomedical, packaging, environmental and other fields.Here, we review the recent development of sodium alginate grafted polymerized nanomaterials.

Keywords **：** *Grafting Chemical method Chemical enzymatic Radiation method*

Date of Submission: 02-04-2024 Date of acceptance: 14-04-2024

I. Introduce

Sodium alginate (SA) is a kind of natural straight-chain, negative polysaccharide, which is mostly extracted from brown algae[1]. Chemically, it is a block copolymer[2, 3] composed of -D-manniturонic acid (M) and -1-gulonic acid (G) in different proportions, mainly due to different sources of sodium alginate extraction, growth and standing conditions[2, 4]. Sodium alginate chains are arranged as homopolymer sequences (MMM or GGG) or alternate sequences (MGMG)[5]. As far as the gelatability[6] of sodium alginate is concerned, the stronger its gelatability is, the harder the hydrogel formed will be, indicating the higher the content of G segment. However, the gel formed also has the characteristics of fragile.On the contrary, when the content of m-segment is higher, the hydrogel formed by it has the characteristics of good elasticity and soft colloid, etc., but it also has the disadvantage of weak mechanical ability.Therefore, hydrogels with different characteristics can be prepared by adjusting the content ratio of m-segment and G-segment in sodium alginate, and can be converted to isomerism when necessary.Sodium alginate is soluble in water, insoluble in most organic solvents, soluble in alkaline solution, and has good stability when pH 6~11. In recent years, sodium alginate has been used in more and more fields, such as food engineering, pharmacy, tissue engineering, environmental remediation, etc[7-11]. The wide application of sodium alginate is mainly due to its several important properties, such as good biocompatibility and degradation, low cost, low toxicity, low immunogenicity and high adhesion[11-18]. In this paper, the research progress of sodium alginate grafted composites in recent years is reviewed.

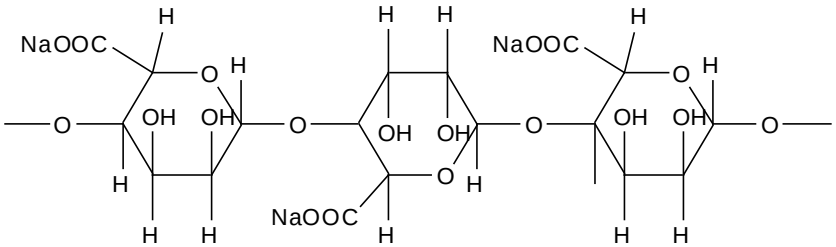

Fig. 1. Structure of sodium alginate.

Graft copolymerization is an important modification method of natural polymers to produce new biomaterials with specific properties and has received considerable attention[19, 20]. Usually the reaction on the macromolecular chain through chemical bond to the appropriate branch chain or functional side group, the product formed is called graft copolymer.The principle of grafting is mainly that active graft points are formed at the main chain (non-terminal group), and then the monomer is grafted to the polymer through free radical, anion or cation addition (or ring-opening) polymerization at the active point[21-24]. The grafts can be classified into radical type and ionic type. On the one hand, free radical grafting can initiate the reaction of main chain macromolecule free radicals through peroxide initiator, light radiation, etc., and then polymerize the monomer to be grafted to form graft chain under the action of free radicals[25-28]. On the other hand, a free radical graft can initiate polymerization by taking advantage of an existing active group on the backbone or by forming an active group on the backbone.

The products produced by polymerization of this reaction were composed of different and mixed homopolymer[5, 29].The products synthesized by radical grafting polymerization were composed of many homopolymers. Ionic graft [30]is also divided into two categories, one is cationic[31, 32] graft polymerization and anion[33] graft polymerization.The methods of anionic graft polymerization are divided into two types: main chain initiation and main chain coupling. Grafting methods of sodium alginate have been developed in recent years. According to their reaction principles, they can be divided into chemical grafting[34], chemical enzymatic grafting[35] and radiation grafting[36].

Chemical grafting methods include ugI reaction method[37, 38], carbonized diamine method[39, 40], free radical polymerization method[15, 41 42]and so on. However, there are still many disadvantages of these methods, for example, the grafting of long-chain alkane derivatives is toxic and the yield is less;Ugi reaction method is exothermic reaction, but there are many byproducts.The carbonized diamine method has a fast reaction rate and is easy to form amide bond or ester bond.The free radical polymerization method can complete the reaction by three steps: bond initiation, bond growth and bond termination, which can reduce the generation of side reactions, but is easy to cause waste.Chemoenzymatic method is the combination of chemical method and enzymatic method. Radiation grafting method, which requires radiation chemical reactions such as ultraviolet light[43, 44] or microwave [45, 46]to generate active groups for cross-linking, is an environmentally friendly green technology.

Table 1. In recent years, the following monomers can be grafted with sodium alginate

The serial number	Species	Examples	References
1	Alkane	Bromododecane, bromooctadecane etc.	47-49
2	Cyclodextrin class	β- cyclodextrin, α - cyclodextrin etc.	50-57
3	Alkene	Acrylic acid, acrylamide etc.	58-76
4	Amino acids	Cysteine, arginine etc.	77-83
5	Alcohols	Ethylene glycol, cholesterin etc.	84-91
6	Esters	Polyurethane etc.	92-96

The monomer used in the reaction shall generally have the following characteristics:

I . Contains functional groups that can be grafted, such as double bonds.

ii.The boiling point is higher than the polymer melting point or viscosity flow temperatureT_f.

iii.Contain carboxyl group, anhydride group, epoxy group, ester group, hydroxyl group and other functional groups.

iv.good thermal stability, in the processing temperature range of monomer does not decompose, no isomerization reaction.

v.No destructive effect on the initiator.

Initiators[97], also known as free radical initiators, can be used to initiate free radical polymerization and copolymerization of alkenes and dienes monomers, as well as crosslinking curing of unsaturated polyesters and crosslinking of polymers.In general, the polymerization temperature of free radical initiators is between 40℃ and 69℃. Initiators can be divided into three types[98-102]: azo initiators, organic peroxyinitiators and inorganic peroxyinitiators.The activity of initiator is related to the length of half-life.The shorter the half-life is, the higher

the initiator activity is. But if the half-life is too short, it is easy to cause explosion. However, too long half-life and too long polymerization time will lead to poor graft efficiency. Take 60℃as standard, highly reactive, $t_{1/2} < 1h$; moderate activity, $1h < t_{1/2} < 6h$;low activity, $t_{1/2} > 6h$. It is very important to select suitable initiators for different types of polymerization. Azo initiators are suitable for bulk polymerization, suspension polymerization and solution polymerization. They are characterized by high decomposition rate and high activity.Organic peroxide initiators do not have too many restrictions on the type of reaction, but after being heated to a certain temperature, they will decompose and produce oxygen-containing free radicals, which are unstable and easy to decompose.Inorganic peroxide initiators are water-soluble initiators, characterized by low temperature polymerization, can reduce chain transfer, branching side reactions, improve the performance of polymerization.

II. Grafting

Although sodium alginate is more and more widely used in food, medicine and environment, its application is greatly restricted due to its strong hydrophilicity, poor mechanical properties and poor stability.Therefore, grafting modification of sodium alginate has become a hot topic in recent years.

2.1 Chemical grafting

In recent years, the chemical grafting by radical mediated binding with sodium alginate has been more popular, and the initiator system has been widely used in radical grafting.Potassium persulfate[103], ammonium persulfate system[86] and ammonium cerium nitrate[104] are widely used as inorganic peroxide initiators for sodium alginate grafting. Ghasemzadeh et al.[105] prepared super absorbable hydrogel-Silver nanocomposite based on PVA and sodium alginate using acrylamide monomer and free radical polymerization.The reaction was carried out under normal atmospheric conditions using ammonium persulfate as an initiator and methylene diacrylamide (MBA) as a cross-linking agent. Composite nanomaterials exhibit excellent antibacterial properties and can be used in biological systems, wound dressings, catalysis and water purification. Jalababu et al.[106] using ammonium persulfate (APS) as an initiator, functionalized phenylalanine was grafted onto the sodium alginate skeleton by radical polymerization.It is shown that the polymer network hydrogel material can be used in medicine for slow release drug delivery. Zhao et al.[107] chose the grafting reaction induced by free radicals, with ammonium persulfate as initiator, and with N, N '- methylene two acrylamide as crosslinking agent will polyacrylic acid copolymer - methyl acryloyl base oxygen ethyl trimethyl ammonium chloride grafted to the main chain of the sodium alginate, was prepared with a pH sensitive at the same time, swelling of amphoteric water gel material, the material can also adsorption of cationic and anionic dyes. Pentlavalli et al.[108] using APS as initiator and TEMED as promoter, the grafting of N- isopropyl acrylamide to sodium alginate was accomplished by simple radical polymerization.The prepared graft copolymers showed excellent thermal response and showed thermal response behavior at 32°C.The equilibrium swelling of copolymers also clearly demonstrated the temperature response characteristics of hydrogels.Model experiments showed that 70% of the hydrogels were biodegradable after one week.Due to its excellent thermal responsiveness, compatibility and biodegradability, the material has potential applications in drug delivery and bone tissue engineering. Kulkarni et al.[109] using ammonium persulfate as initiator, they grafted polyacrylamide to the main chain of sodium alginate by free radical polymerization, and the amide bond of polyacrylamide was converted into carboxylic acid to obtain a polyanionic electroresponse copolymer.Giri et al.[110] prepared polyacrylamide grafted sodium alginate interpenetrating network microspheres under alkali environment by ionizing gelation method and covalent cross-linking method.The reaction was carried out in nitrogen environment with glutaraldehyde as the reaction crosslinking agent and APS as the initiator.The network microspheres were prepared to encapsulate diclofenac sodium, and the encapsulation rate could be as high as 96.45%.It is shown that the drug release increases with the increase of pH value.The results show that the composite can be used as a matrix material for IPN microbeads with sustained release of diclofenac sodium.Kolya et al.[103] using potassium persulfate($K_2S_2O_8$) as initiator, they successfully prepared graft copolymer based on the mixture of sodium alginate and N, N-dimethylacrylamide and acrylic acid in aqueous medium.The excellent antibacterial activity of the polymer against gram-negative and gram-positive bacteria was verified by AGAR well diffusion method.The excellent antibacterial activity of the polymer against gram-negative and gram-positive bacteria was verified by AGAR well diffusion method.It is shown that the nanomaterial can be prepared with controllable size and can be used as an antibacterial agent. Sun et al.[111] prepared sodium alginate – poly-acrylonitrile copolymer using potassium persulfate as initiator.The suitable dosage ratio was selected. When the mass ratio of sodium alginate grafted acrylonitrile/ polyethylene glycol was 3:2, the fiber morphology was the best, and the surface of the fiber was compact and smooth.When the amount of acrylonitrile increases, the hydrophobicity of the material increases.

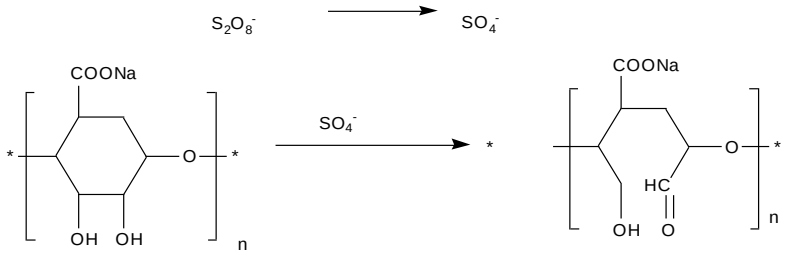

Fig. 2. Mechanism of sodium alginate persulfate oxidation.

The REDOX initiator system has both oxidization and reducibility, and produces free radicals through REDOX reaction to initiate monomer polymerization.Redox-induced grafting because in the presence of a REDOX system, grafting can be performed under mild conditions with minimal side effects.Sand et al.[112]used potassium bromate /thiourea as REDOX initiator for free radical polymerization and graft acrylamide onto alginate to prepare graft copolymer of alginate and acrylamide.In this paper, quantitative acrylamide, thiourea and sulfuric acid solutions were added to the reactor at a constant temperature, nitrogen atmosphere was maintained to protect the reaction, then potassium deoxybromate solution was added to initiate the reaction, and finally the reaction was stopped by letting air into the reactor.The polymer product is washed with methanol.The synthesized graft copolymers showed better swelling, resistance to biodegradation, and metal ion absorption than alginate, which can be explained by the enhancement of these properties shown by graft copolymers.The polymer can be used as superabsorbent and flocculant to remove impurities in coal mine wastewater. Işıklan et al.[104] using ceric ammonium nitrate as REDOX initiator, they prepared sodium alginate grafted with itaconic acid in aqueous solution.The grafting reaction was carried out under nitrogen and terminated with phenol.The stability of grafted polymer was improved compared with that of sodium alginate. Liu et al.[113] using potassium distearate (III) as an oxidation initiator (in this paper, potassium distearate (III) -sodium alginate as a REDOX initiator), they successfully grafted methyl methacrylate onto sodium alginate. The reaction was conducted under nitrogen under mild conditions, and the resulting product was washed with methanol.With potassium distearate (III) as the initiator, the graft polymer showed better solubility and graft efficiency than the cerium ion initiator. In the Ganguly et.al[114] past studies, to free radical oxidation reduction reaction triggered by Michael type, potassium persulfate and sodium hydrogen sulfite as REDOX initiator, N, N - methylene double acrylamide as crosslinking agent, methyl acrylic acid grafted to the sodium alginate scaffold, and use the faculties of HNT as filler, get half the in-situ polymerization of crosslinking network hydrogel.The hydrogel material has the characteristics of drug sustained release, and the drug release characteristics can be adjusted by adjusting the content of the filler and the pH of the medium, the material can be used as a good choice for the controlled release platform.

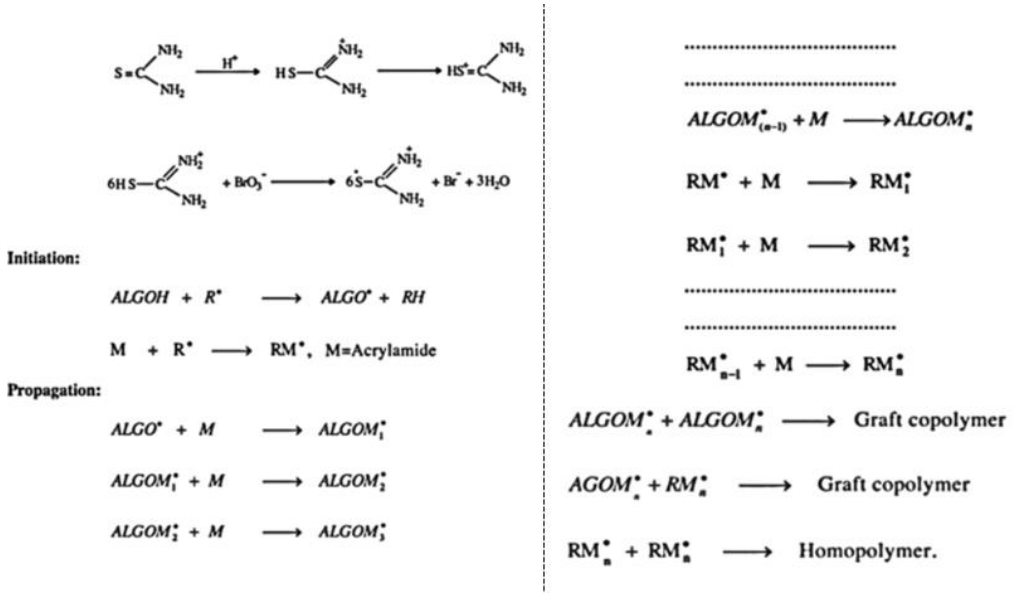

Fig. 3. Graft acrylamide onto sodium alginate by potassium bromate/thiourea.[112]

Diisobutyronitrile peroxide and benzoyl peroxide are more popular when organic peroxides are used as initiators. Işıklan et al. [115]successfully grafted itaconic acid containing a polar functional group onto sodium alginate using benzoyl peroxide (BPO) as an initiator in an atmosphere of N_2.SEM photographs show that the new material is similar to sponge structure and has good adsorption capacity.It was shown that with the increase of polymerization temperature and BPO dosage, graft yield (GY %) and graft efficiency (GE %) first increased and then decreased.It is proved that the graft efficiency and graft yield do not increase with the increase of dosage and time. Salisu et al.[116]using BPO as initiator, methyl methacrylate was grafted with sodium alginate.The reaction was carried out under nitrogen, the products were precipitated by methanol and filtered by acetone.The product graft rate can be as high as 212%.

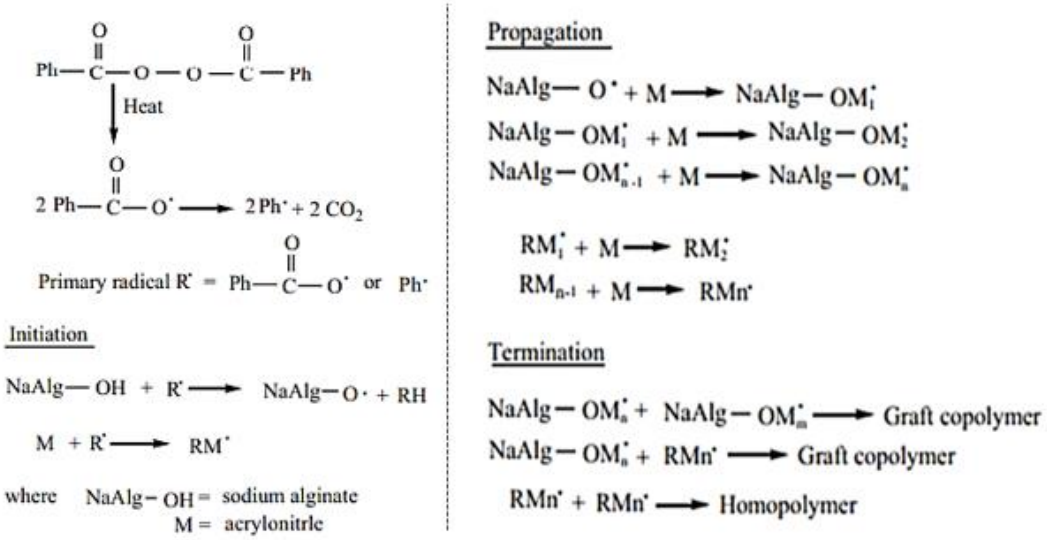

Fig. 4. Mechanism of methyl methacrylate grafting to sodium alginate by BPO.[116]

Most surface initiators of the azo family are similar to azo diisobutyronitrile (AIBN) in structure, but slightly different in structure and dynamics, and can be used to synthesize block copolymers.Azo-containing prepolymers are synthesized by condensing small azo compounds with functional polymers[117] and then by partial decomposition of the polymerized azo compounds or other similar reactions.When these prepolymers decompose in the presence of another monomer, new copolymers can be obtained[118].Işıklan et al.[119] chose azodiisobutyronitrile as the initiator to prepare the graft copolymer of sodium alginate and N- vinyl -2-pyrrolidone. In the reaction, N- vinyl -2- pyrrolidone was mixed with sodium alginate, the reaction temperature was adjusted to 70℃, and the reaction was bubbled with nitrogen for 30min.The acetone solution of AIBN was then added to the mixture, and the volume of the mixture was added to 100ml with ultrapure water. Nitrogen supply and condensation reflux were maintained during the reaction.After the reaction, hydroquinone was used to terminate the reaction, acetone was used for precipitation, filtration and separation, ethanol extraction was used to remove homopolymer, pure graft copolymer was grafted, and finally dried to constant weight under a vacuum of 40°C.The results show that the graft copolymer can be used as drug sustained release agent.

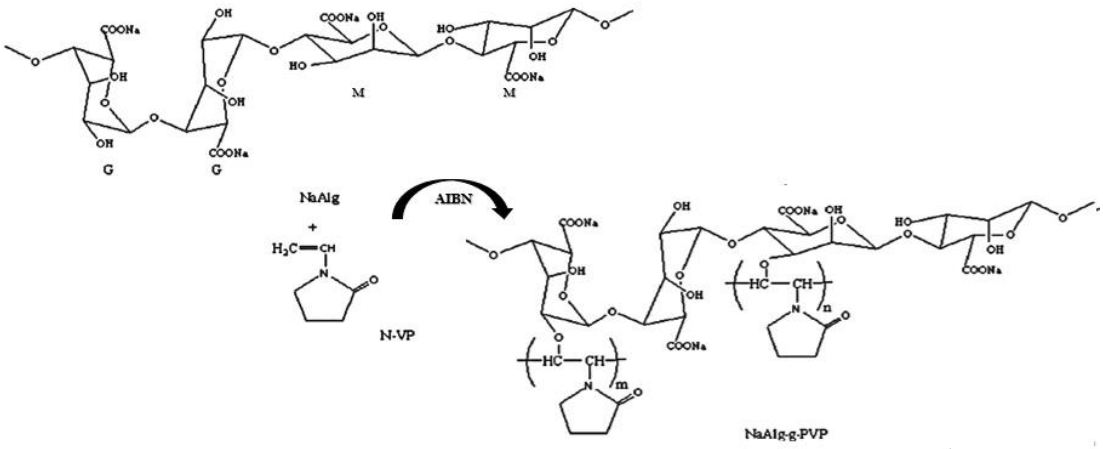

Fig. 5. Mechanism of N- vinyl -2- pyrrolidone grafting sodium alginate induced by azo – isobutyronitrile.[119]

Reversible addition-broken chain transfer (RAFT) is a controlled radical polymer-ization technique that is popular in the synthesis of functional polymers.It can provide synthetic pathways for functional polymers, thus providing stimulation and biological reactions. Kumar et al.[120] synthesized the polymer by grafting it onto the alginate backbone using a reversible additive -- RAFT method, resulting in a self-assembling nanoparticle copolymer in the presence of calcium ions.Firstly, the cations of the fusion body with high molecular weight alginate were converted into tetrabutyl ammonium groups, so that the polymer could be dissolved in DMSO.The RAFT process sensitizes the hydroxyl portion of alginate.Then the copolymers were grafted with polyethylene glycol methyl methacrylate, and the nanocomb graft copolymers were finally obtained.The nano-grafted polymer broadens the application of sodium alginate in various organic and water-soluble media, and has a good encapsulation efficiency for lipophilic drugs.

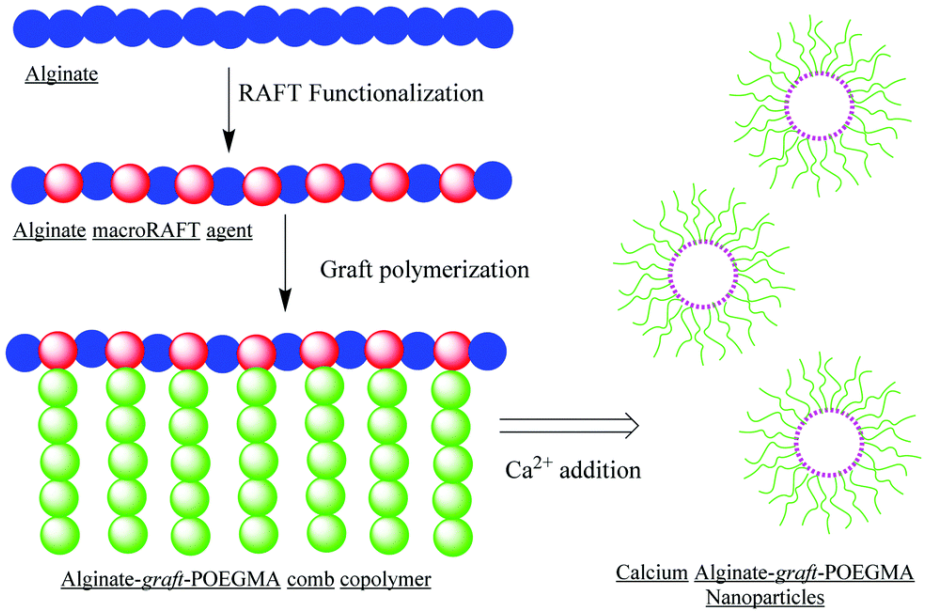

Fig. 6. The polymer was grafted onto alginate skeleton by RAFT method and self-assembled into nanoparticles via calcium mediation.[120]

In the present study, grafting of sodium alginate by using the reaction of schiff base between amino and aldehyde groups has made some progress.Since sodium alginate contains active carboxyl and hydroxyl groups, carboxyl/hydroxyl groups can be carboxyl/hydroxyaldehyde groups by oxidative pathway, and then compounds with amino groups can be grafted onto sodium alginate to achieve the Schiff base reaction. The oxidant usually chooses sodium periodate, potassium permanganate and so on[121-125]. Li et al.[122] proposed that sodium alginate be oxidized with sodium periodate at room temperature for 8 hours, quenched with ethylene glycol after the

reaction is complete, and precipitated with ethanol. The resulting product is dialyzed for 7 days, and gentamicin sulfate is then grafted onto sodium alginate through the Schiff base reaction.The graft polymerized multilayer membrane showed long-term inhibition of bacterial infection and biofilm, and had good application potential in the strict control of antibiotic delivery and the inhibition of the development of drug-resistant bacteria. For example Gao et al.[126] after dissolving sodium alginate in ethanol, the sodium alginate was oxidized with sodium periodate and the reaction was carried out in a dark environment for 6 hours. The product was then quenched with ethylene glycol and washed with ethanol.In water, the oxidized sodium alginate was grafted with poly ((2-dimethylamino) ethyl methacrylate) in a Schiff base reaction.The product is still washed in ethanol and the graft polymerized product can be used for oral protein delivery.

It should be noted here that since sodium alginate is a photosensitive substance, all reactions should be conducted in a dark environment to avoid the photooxidation of sodium alginate, which would affect the process of the reaction[127].In addition, the hydroxyl groups of C-2 and C-3 in alginate oxidized by sodium periodate will crack the carbon-carbon bond and form two aldehyde functional groups[56]. The aldehyde group obtained from the oxidation reaction reacts simultaneously with the adjacent unoxidized residues (hydroxyl) to form cyclic hemiacetal.But hemiacetal is not stable and can be converted into aldehyde group under acid environment[128, 129](Fig. 7).

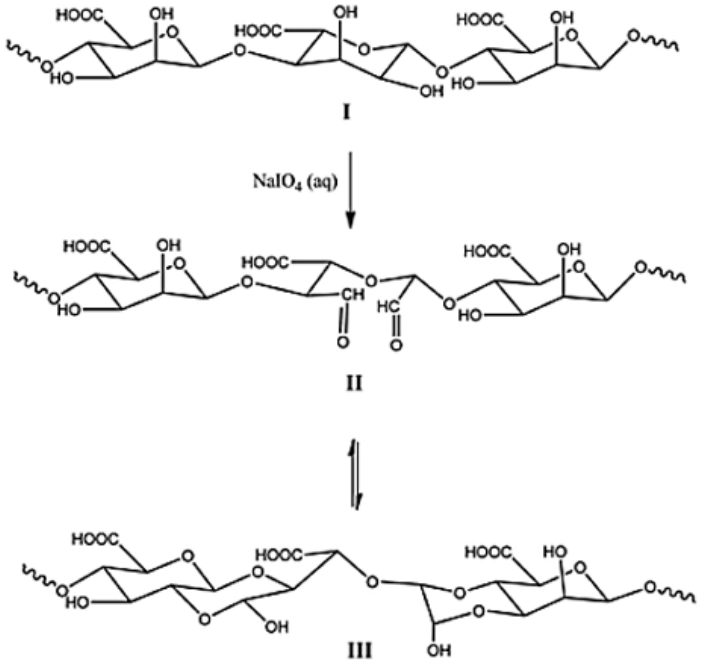

Fig. 7. Sodium alginate was oxidized by sodium periodate, after which hemiacetal was formed between the molecules.[129]

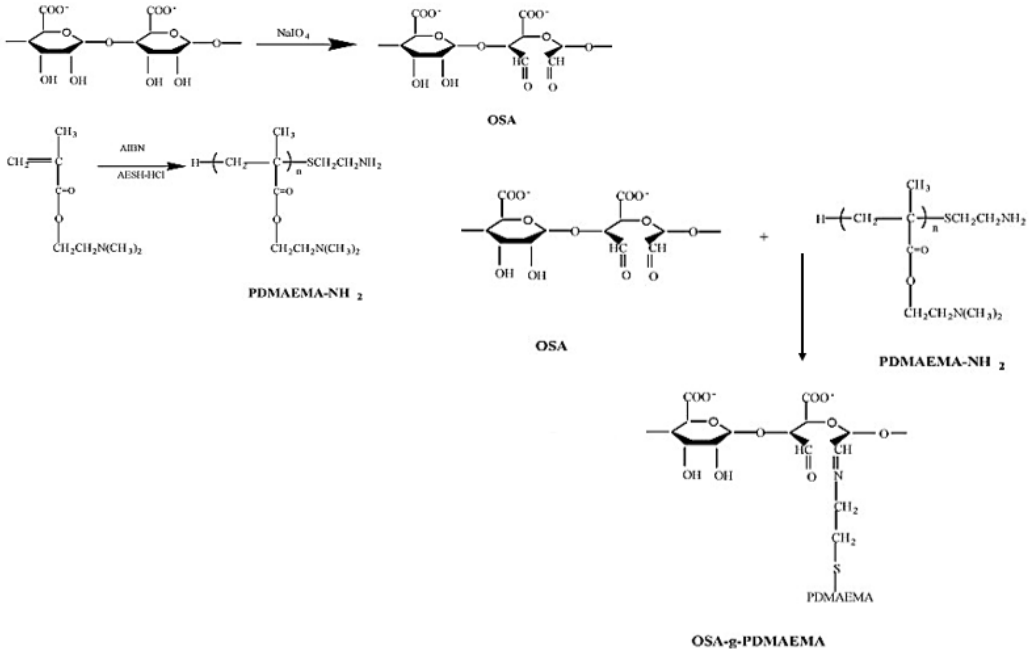

Fig. 8. Mechanism of grafting sodium alginate on Schiff base reaction.[126]

Self-assembly grafting is an effective method for the spontaneous association of numerous units into new molecular systems without external involvement[130]. Shi et al.[131, 132] realized the hydrophobic modification of sodium alginate by directly grafting glycolic acid onto sodium alginate by means of chemical self-assembly.The EDC and NHS protection reactions were added under slightly acidic conditions.Finally, the polymeric products were cross-linked to the hydrogel microspheres with calcium chloride.The graft reaction condition is mild, the cost is low, and the operation is simple.The results show that the polymeric product can be used as drug carrier. Iatridi et al.[66] self-assembled after heating in an aqueous medium and grafted a random copolymer of N-isopropylacrylamide and N-tert-butylacrylamide onto sodium alginate.

The grafted alginate gels showed higher capability in heat induction and heat setting.

Injectable gels for specific applications, such as stem cell transplantation, controlled drug delivery and other fields have the corresponding application prospects. Huang et al.[133] self-assembled a superabsorbent polymer by reverse-suspension of -cyclodextrin, acrylic acid and sodium alginate by grafting the -cyclodextrin and acrylic acid onto sodium alginate chains.Due to the addition of cyclodextrin, the new material has good biodegradability.The excellent water absorption and water retention of the new material make it possible to be used as a water retention agent in the future agricultural field.

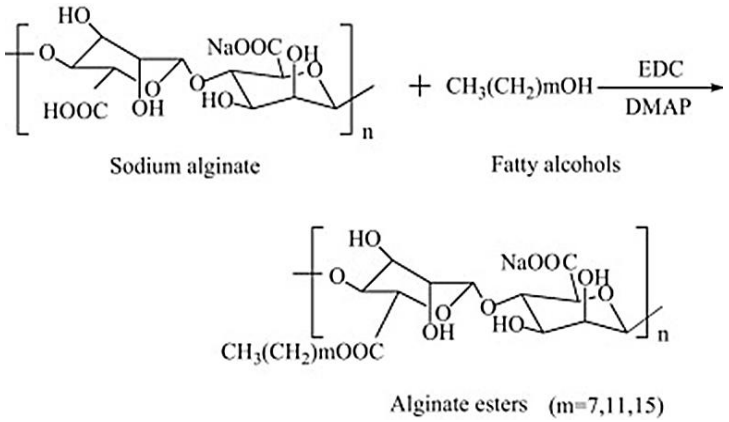

Fig. 9. Synthesis mechanism of alkyl link branched into esterification of sodium alginate by chemical self-assembly method.[84]

Sodium alginate, through oxidation, provides a new reactive group-aldehyde group on the chain and is suitable for chemical graft modification, especially through reductive amination. Omtvedt et al.[54] grafted cyclocarboxylate onto alginate using a three-step method.First step by periodate oxidation of sodium alginate, the second step in the oxidation of sodium alginate, add 4-pentine-1-amine reductive amination, the third step, copper azide-acetylene catalyzed cycloaddition, alginate hydrogel ability successfully to form with cyclodextrin inclusion compound of ability are united in wedlock, and the success of the change in the hydrogel soluble and difficult to soluble in the release of active ingredient.

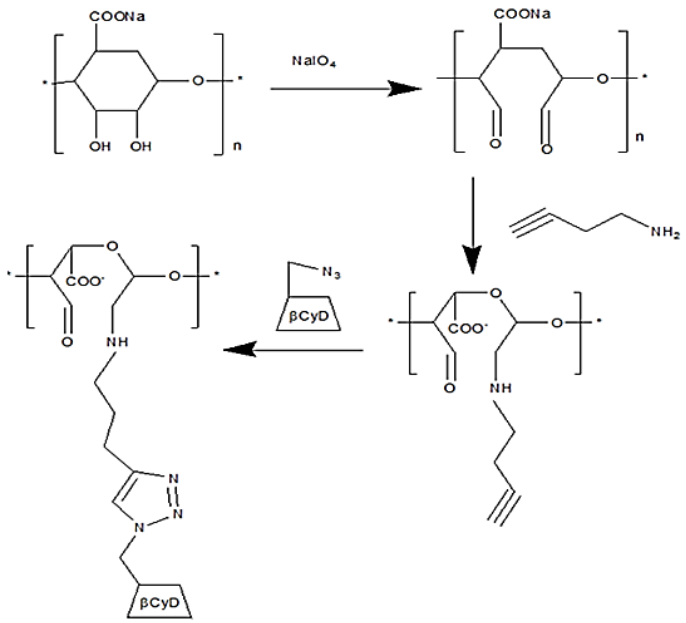

Fig. 10. Mechanism diagram of amine grafting of cyclodextrin to sodium alginate by three-step method.[54]

Because the sodium alginate skeleton contains carboxylic acid group, it is also one of the more common methods to graft sodium alginate through carbimide reaction. The commonly used activating coupling agents are carbimide (EDC) and N-hydroxysuccinimide (NHS).Sodium alginate reacts with EDC to form an unstable intermediate, and then reacts with NHS to form a stable NHS-ester. Soledad Lencina et al. [134]graft copolymer was developed by reacting the carboxyl group of sodium alginate coupled with the amino group on the monomer to obtain the amide bond.The gel materials synthesized by graft copolymer showed good rheological thermal response and biodegradability, and could be used as potential materials for medical hydrogel injection. Chen et al.[135] lended nanofibers based on alginate derivatives and polyethylene glycol were successfully prepared by electrospinning.The nanofibers were firstly grafted with octylamine to the carboxyl group of sodium alginate by the carbonimine method, and then the mixture of alginate derivatives and polyethylene glycol was used to eliminate bubbles. After that, a high-voltage power supply was used to adjust the voltage to 10-20 kV, and then the electrospinning nanofibers were prepared through the injector.Blended nanofibers are good candidates for biomedical applications due to their high drug loading and slow release properties. Li, Liu et al.[136]prepared three kinds of resins with sodium alginate grafted to agarose gel with decreasing graft rate, and the polymer prepared was a kind of resin containing high capacity protein cation exchange chromatography.The graft reaction was facilitated by EDC and NHS in an alkaline environment, and the grafted products are worthy of further development for high performance protein chromatography. Sabri et al.[137] Realized the grafting of sodium alginate on the surface of submicron particles, and the graft copolymers showed strong reversible aggregation/dissociation aggregation properties in aqueous solution.It is shown that 300 nm silicon dioxide particles are first functionally organized with aminosilane coupling agent, and salicylic acid is grafted on submicron silicon dioxide particles.Then functionalized silica particles were grafted to sodium alginate using EDC and NHS as protective agents for the graft reaction.With sodium alginate grafting modification of silica particles, in comparison with previous gathered under acid condition average diameter increased 10 times, and of the modified particles at pH 3.0 settling velocity quickened, and subsidence completely, and the increasing ability of the condensation of the reason may be due to the adjacent sodium alginate modified form intermolecular hydrogen bond between particles.The aggregation reaction process is reversible because the aggregates can break up and disperse again as the pH increases to 7.0.The results show that surface grafting can be used as a potential method to promote particle aggregation and simplify the

separation process. Conzatti et al.[138] grafted thermally sensitive POLYn-isopropylacrylamide onto sodium alginate by the carbonite diamine method. The addition of polyn-isopropylacrylamide enhanced the surface hydrophobicity of the material, which is expected to be used in wound dressings.

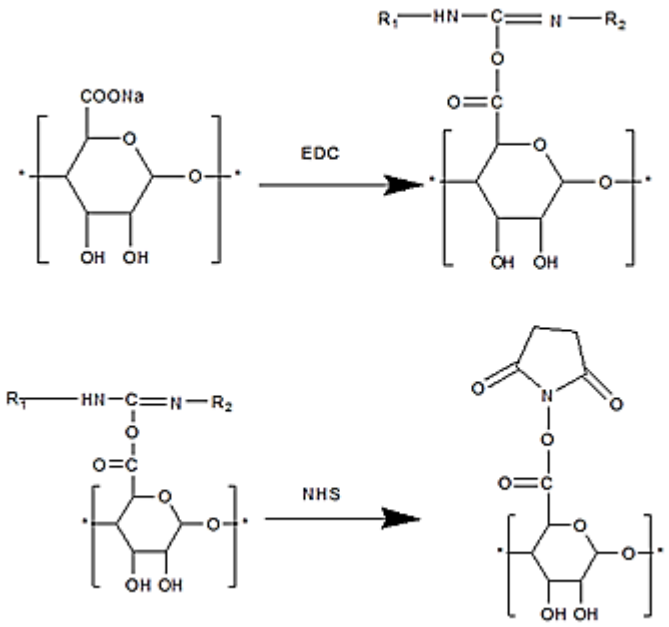

Fig. 11. Mechanism of SODIUM alginate activation by EDC/NHS.[2]

Among all kinds of sodium alginate chemical graft methods, the Ugi four component condensation reaction is a more unique method.It develops specific properties of alginate without the use of a catalyst, while other reactions require a catalyst to activate hydroxyl or carboxyl groups[139]. When choosing Ugi reaction to facilitate sodium alginate grafting, some characteristics of the reaction should be known.The first Ugi reaction chemically modified sodium alginate should maintain the reaction pH at about 3.6 and dilute the polymer concentration to about 2.0%.Then formaldehyde, n-octylamine and cyclohexyl isocyanate were successively added to the solution to complete the four-component condensation reaction of Ugi[140-143]. Zhao et al. [144]Proposed grafting -cyclodextrin onto sodium alginate by Ugi reaction.In addition, azobenzene doped with polyethylene glycol is used as guest molecule.

The reaction is relatively simple, as the quantitative sodium alginate is dissolved in water and the pH is adjusted to 3.6 by HCl solution.Then the graft copolymer was prepared by adding -cyclodextrin and cyclohexyl isocyanate for 24 hours.The mixture was dialyzed and freeze-dried to obtain the final product.The results show that the graft product is aggregated with azo-PEG, and the aggregate can be used as emulsifier carrier to release curcumin under light irradiation.

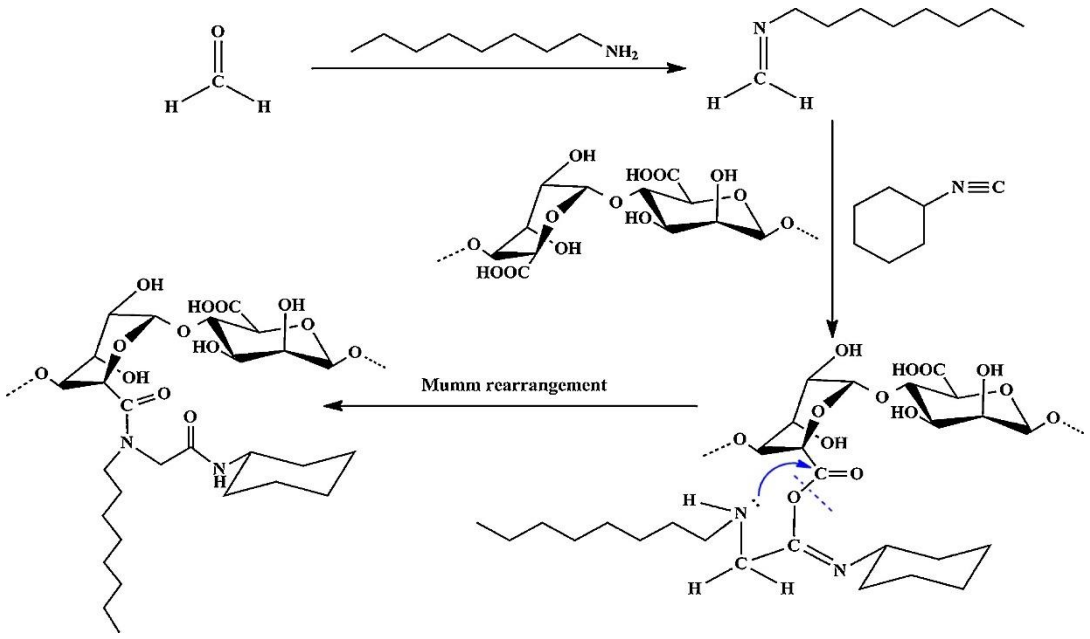

Fig. 12. Ugi reaction promotes the graft synthesis mechanism of sodium alginate.[139]

2.2 Chemoenzymatic grafting

Enzymes are known as green catalysts and are highly specific. Omagari et al.[61] ,Kadokawa et al.[145], Kedzior et al.[146] all used phosphorylase catalysis method to synthesize starch grafted sodium alginate. Due to highly controlled stereoselectivity and regional selectivity of enzyme polymerization catalyzed by phosphorylase, amylose with clear structure has been effectively synthesized and starch grafted sodium alginate composite materials have been obtained. Donati et al. [147]modified sodium alginate by a combination of chemical and enzymatic methods. First, 1-amino-1-deoxygalactose (galactosamine) was injected onto the uronic acid groups in manniturонic acid (M residues) via n-glucoside bonds, using EDC and NHS as the reaction coupling agent.AlgE4 and 6 will be used for the difference isomerization reaction to convert the unsubstituted sodium alginate (segment M) in the modified polymer into (segment G) sequence.The modified alginate polymer obtained by differential isomerism is able to bind calcium by introducing a G-segment sequence.A reliable method for differential isomerization of mannitose aldoglycan after modification is presented in this paper to obtain a material that can be customized selectively modified for its structure and physical properties. Rokstad et al.[148] developed a chemoenzymatic method to prepare alginate beads with high stability and covalent attachment.Sodium alginate (M segment) was partially grafted to methacrylate by photocross-linking, and two enzymatic steps were then introduced alternately and block sequentially by differential isomerization (G segment).Finally, alginate samples containing only methacrylate groups on M residues and sufficient (G segment) alginate samples were prepared to allow gel formation.Alginate beads prepared by chemical enzymatic method and photocrosslinking showed high stability and could be used in protein delivery bioreactor.

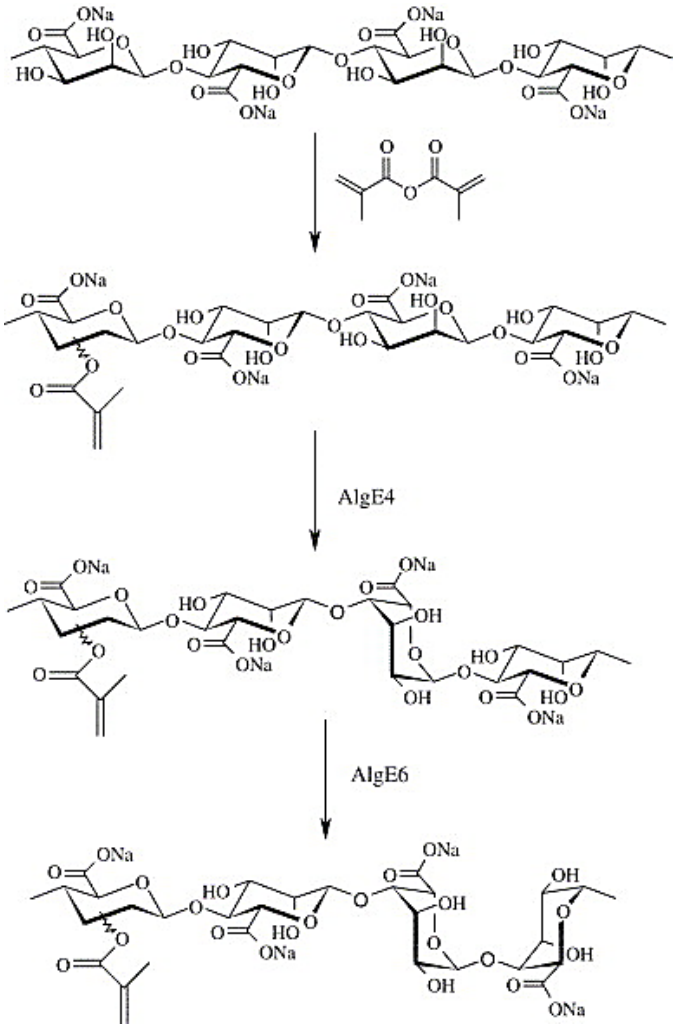

Fig. 13. Mechanism of sodium alginate modified by chemical enzymatic method.[148]

2.3 Radiation grafting

The radiation grafting is performed by irradiation with an appropriate source of radiation in a solvent containing the selected monomer.Common energy sources are high-energy electrons, ultraviolet (UV) and so on[149, 150]. A number of different pathways can be used to introduce the graft chain to the polymer surface. With the help of photoinitiators such as benzophenone (BP), UV energy has been widely used for surface graft polymerization of polymers.

Uv-induced graft polymerization is a powerful technique with low operating costs and the potential to reduce or even avoid adverse effects on bulk polymers.Radiation modification of natural polymers, such as sodium alginate, also solves the problem of product sterilization and can be used to produce pure products that are not contaminated by residual toxic initiators. Akkaya et al.[151] using benzophenone as a photoinitiator, they completed the graft polymerization in two steps under ultraviolet radiation.The first step is to activate sodium alginate under uv light at 254nm. In the second step, glycidyl methacrylate (GMA) was grafted to activated sodium alginate under 365 nm uv light. In this paper, GMA was grafted to sodium alginate, and then the polymer was used as a fixing material. Then the epoxy group and carboxyl group on the material were selectively used to fix urease. The use of secondary composites as models for the development of multi-enzyme systems is expected to have applications in the medical field, as these enzymes are not randomly immobilized and can support the immobilization of two or more enzymes of the desired activity. Taşkın et al.[152] also attached itaconic acid (IA) to a sodium alginate (NaAlg) membrane by using ultraviolet radiation and using benzophenone as an initiator. The grafting reaction was carried out in nitrogen atmosphere, and the membrane material produced by grafting composite had better hydrophilicity. In the Smyth et al. [153] past research, the 4, 4-azo double (4 -cyano pentanoic acid) (ACVA) as azo initiator combined with ultraviolet light, trigger a radical polymerization, the cellulose nanocrystals grafted onto the sodium alginate, graft polymerization composites

greatly improved after sodium alginate dissolved in the water, the mechanical performance is weaker, is expected to be in the future of the corresponding application in biomedical fields.

Microwave radiation will cause the "selective excitation" of polar bonds, resulting in bond fracture, resulting in free radical site formation.However, the carbon-carbon skeleton is relatively non-polar and is not affected by microwave radiation, so the structure of the skeleton can be kept intact, and finally high-quality graft products can be obtained[154]. Akin et al[155] synthesized the copolymer of sodium alginate grafted with N, N-dimethylacrylamide (DMAAm) by azo diisobutyronitrile (AIBN) in aqueous solution while maintaining nitrogen atmosphere and microwave radiation.It can be seen from the SEM figure that the surface morphology of alginate changes to a low porous and nodular structure, which looks like a fiber. Copolymers are expected to be used as biomaterials, especially for controlled drug delivery. Isiklan et al.[156]choose in aqueous solution by microwave radiation will N, N-isopropyl acrylamide (NIPAAm) grafted onto the sodium alginate, grafting reaction with 2450 MHz and 500 W output power of microwave oven in nitrogen atmosphere, and are equipped with a flow of intake system, condensing unit and microwave oven reaction initiator and crosslinking agent, respectively chose azodiisobutyronitrile (AIBN) and glutaraldehyde.The spherical grafted hydrogel was prepared to increase the water content and improve the mechanical properties.Its hydrogel beads are also an ideal drug carrier. Telford et al.[26] grafted isopropylacrylamide onto sodium alginate using microwave radiation, and the reaction was performed using azo diisobutyronitrile as initiator and glutaraldehyde as cross-linking agent. The pH-responsive and thermal responsive materials were prepared. The polymer material at pH7.4 and 37℃ has a good release ability for the drug model, which is similar to the human environment, and has a good prospect in the field of drug delivery in the future.

γ ray radiation grafting is considered as a green method to prepare new materials.It has relatively low requirements for the reaction environment, and can produce corresponding different chemical reactions in the polymer under low temperature and mild conditions, especially chain crosslinking and graft copolymerization, without the involvement of other chemical agents.Shelar-lohar et al.[157] produced graft copolymers of acrylonitrile grafted with sodium alginate by γ ray radiation and modified them to chelate amidoxime-sodium alginate graft copolymer.The reaction was under nitrogen, the sample was irradiated by ^{60}Coγ radiation, the total dose was 15 kGy, and the crude product was washed and settled with methanol.The polymer can be used as an effective adsorbent of cationic dyes. The physical adsorption of the polymer is spontaneous and exothermic, and has good recycling ability. Lencina et al.[158] prepared heat-sensitive aqueous hydrogels by grafting N-isopropylacrylamide onto sodium alginate using low dose ^{60}Coγ radiation.The new hydrogel material showed good swelling behavior at 24℃ and 37℃, and the swelling behavior at 37℃ was better than that at 24℃, and the reaction would not have uncontrollable side reactions, so it could be used in the replacement of scaffold materials and engineering tissues delivered by drugs and growth factors in the future.However, other unwanted radioactive reactions may occur in the process of radiation grafting, and the removal of homopolymers is also an issue that needs to be further studied.

Trivedi et al.[159] using cerium ammonium nitrate as a photoinitiator, grafted methyl acrylate onto part of the sodium salt carboxymethylated sodium alginate.The photograft copolymerization reaction was carried out in a photochemical reactor. The sodium alginate carboxymethylated was first stirred continuously at 55℃ under nitrogen flow, and then stood at room temperature for 20 minutes after one hour.A solution of cerium ammonium nitrate of a certain concentration is added to the reaction flask, which is then rinsed with purified nitrogen and then purified methyl acrylate is added and assembled with a leach-well containing 125W medium-pressure mercury lamp.The grafting process keeps the temperature in the range of 15-45℃.After the graft reaction, the irradiated sample solution was carefully removed and the rough graft copolymer was separated by centrifugation.The product was repeatedly washed and purified with 95% methanol, and finally washed with pure methanol.After vacuum drying of the original graft copolymer at 40℃, soxhlet extraction was used to remove the homopolymer, and the final product was still dried to constant weight at 40℃ vacuum drying.After being treated with hydroxylamine in alkaline medium, the graft copolymers obtained have potential applications as adsorbents for metal ion adsorption.

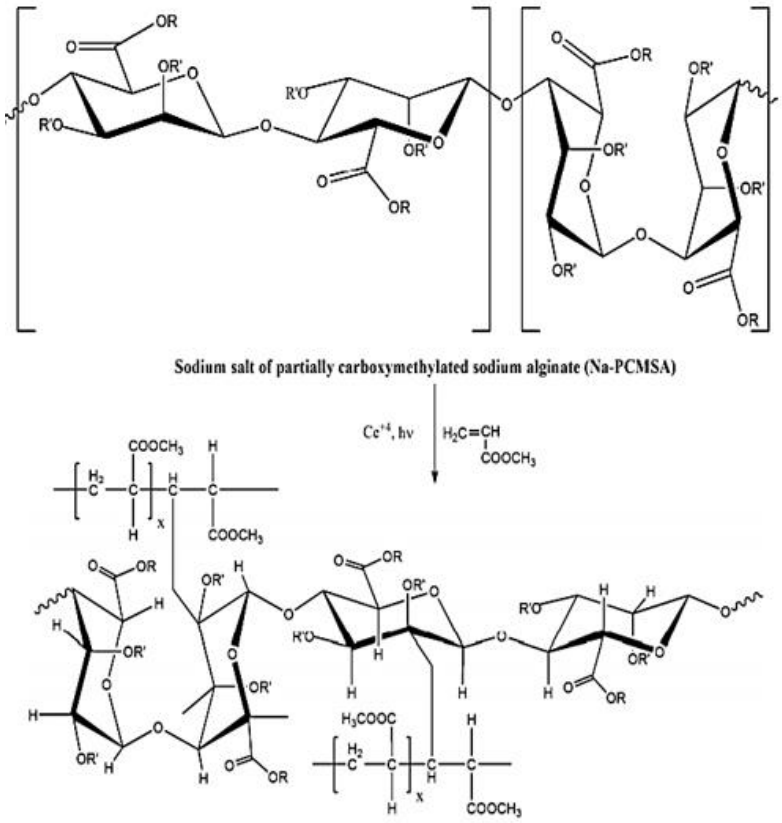

Fig. 14. Mechanism of photoconductive sodium alginate grafting[159]

2.4 Ionic grafting

Ionic graft polymerization is easier to control the structure of the product than free radical polymerization, and there are fewer heterogeneous substances. Active anion polymerization is also more efficient than free radical polymerization, because the tendency of spontaneous chain termination is much lower in anionic systems. Gao et al.[160, 161] using functionalized polyisobutylene as a macromolecular initiator, they completed the grafting of tetrahydrofuran (THF) onto sodium alginate.Sodium alginate is dissolved in dichloromethane and acylated with decyl chloride and trimethylamine.Brominated polyisobutene and silver perchlorate were added into dichloromethane solution for cationic ring-opening polymerization with tetra-hydrofuran.Finally, the graft polymerization of acylated sodium alginate with the polymer chain in the above steps was completed in dichloromethane.The graft polymer was combined with silver nanoparticles, and the composite showed good antibacterial activity and anti-protein adsorption. This novel graft copolymer is expected to have a good application prospect in biomedical field.

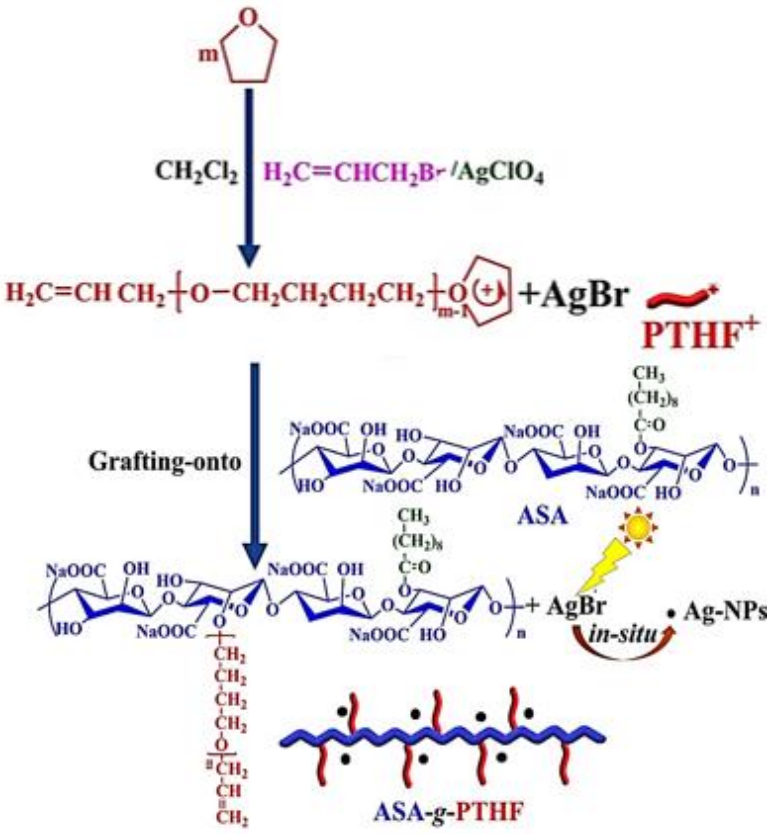

Fig. 15. The synthesis process of ionic ring-opening polymerization of sodium alginate.[160]

III. Results and Prospects

In this chapter, we discuss the development of novel materials by grafting and polymerization of sodium alginate.So far, alginate grafted polymeric materials have been developed in various forms, such as beads, matrix blocks, foams, fibers, sponges, particles and nanoparticles.The methods of graft polymerization to produce products and their applications under each method are described.Although many advances have been made in the field of sodium alginate grafted polymerized new materials and scientific achievements, some of the achievements still lack commercial applications. Therefore, in the following research, not only should more potential pathways of alginate graft polymerization be found, but also the practical applications of sodium alginate graft copolymerization in various fields must be paid attention to.

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