Research Status of Polyvinyl Alcohol-Based Chelating Materials

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Abstract. This paper reviewed the research status of polyvinyl alcohol (PVA)-based chelating materials. The preparation methods of PVA chelating materials was introduced including graft copolymerization, blending precipitation, interpenetrating network crosslinking and mechanical melting. The adsorption characteristics of PVA chelating materials were analyzed while the development was proposed.

1. PVA

PVA[1-2] is a kind of polyhydroxy strong hydrogen bond polymer with excellent performance and wide application. The source of PVA is rich because it can be synthesized by non-oil route. With the advancement of technology and the rapid development of materials science, PVA has been processed into a matrix material in the fields of medical treatment, adsorption, high barrier flame retardant, water solubility and degradability. The properties of PVA matrix materials are closely related to their processing methods. Acetylation, etherification and grafting are the general chemical modification methods, meanwhile, blending precipitation[3], radiation grafting[4] and Interpenetrating cross-linking[5] have also been frequently applied. PVA has strong polarity, excellent heat resistance, antistatic property, chemical solvent resistance, and good ion exchange, complexation, chelation, and physical adsorption[6-8]. It also works as a load body for light, oxygen catalyst and immobilized cell[9-10] and can also be blended with a variety of organic and inorganic materials to change its structural interface to improve its specific function[11-14]. PVA foam[15-16] is a pure white polar polymer with a three-dimensional interpenetrating through-hole structure. It can be made into many types of products such as block and thick plate. Therefore, PVA is a high-performance polymer matrix material.

2. Chelating materials

The chelate is a complex with a cyclic structure influenced by metal atom or ion acts. Due to its cyclic structure, it is of outstanding thermodynamic and thermal stability properties and widely used in water pollution chemistry, analytical chemistry, marine chemistry, radiochemistry, medicine, organic synthesis and biochemical treatment. The chelate forms a chelate ring with the same metal ion through two or more ligands. Oxygen and nitrogen are most common coordinating atoms followed by sulfur, phosphorus, arsenic and so on. The chelating agent itself or combining with other materials have excellent functions because of various structures. Most of which have linear and branched structures besides cyclic structures such as porphyrins and crown ethers. Organic chelating agents are Commonly used such as aminocarboxylate complexing agents (NTA, EDTA and DTPA, etc.),
dithizone, 8-hydroxyquinoline, phenanthroline, sodium potassium tartrate, ammonium citrate; inorganic chelating agents includes Phosphates and quaternary ammonium salts.

3. PVA-based chelating materials

PVA-based chelating materials are widely recognized for people’s enthusiasm for environment-friendly, easy-to-process and rapidly biodegradable polymer materials. The preparation of chelate and high polymer by different methods is a great material design idea and the use of advanced technology to achieve more diverse functional chelation materials is the common means. The PVA-based chelating material is grafted with a PVA backbone as a matrix material, interpenetrating entanglement, surface modification or composite to enhance its properties and structure. There are extensive applications in matrix material selection, synthesis preparation methods, processing and microstructure adjustment [17-19], etc. PVA chelating materials not only have the main characteristics of PVA but also have the key functions of chelating materials. They are simple in synthesis, strong in chelation, high in selectivity, good in stability, easy to elute, and relying on electrostatic action for heavy metal ions which accounts for its excellent performance.

4. PVA-based chelating material preparation method

There are mainly two ways to prepare PVA-based chelating materials depending on the structure and properties. One method is to introduce a chelating group into a polymer skeleton matrix by a macromolecularization method such as a graft reaction. The chelating material matrix is cheap and easy to obtain, and the type, the number of side groups and the matrix on the substrate are introduced by a chemical reaction. The distribution can be artificially controlled and regulated, and the function selectivity is higher; The other method is to prepare a polymerizable monomer having a chelating group, and then polymerize and form by homopolymerization, copolymerization, ring-opening polymerization and polycondensation. The general preparation method is divided as follows:

4.1 Graft copolymerization

Graft copolymerization is a method to form a branched copolymer by attaching branched group to a main chain of polymer. The main chain and the branch itself may be either a homopolymer or a copolymer. The grafting means mainly involve the chain transfer reaction and the radiation grafting method.

Jinman Tong [20] used PVA as raw materials to synthesize spherical crosslinked PVA particles by suspension polymerization. The activated grafting method was used to introduce amino acid functional groups on the surface of the particles to synthesize a polymer chelating agent-containing amino acid epoxidized crosslinked PVA.

The pores with large surface distribution of the polymer chelating agent have a large specific surface area and can chelate heavy metal ions to form a stable chelate compound, especially for Pb$^{2+}$. Chen XiaoJuan [21] successfully prepared spherical crosslinked PVA particles by suspension polymerization and studied the influencing factors such as PVA content, surfactant dosage, glutaraldehyde dosage, reaction temperature and oil-water ratio. The spherical PVA surface introduces amino acid functional groups by activated grafting which have good adsorption effects on Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$. The method of bulk polymerization, emulsion polymerization or suspension polymerization can fully contact the PVA matrix and the chelating group, and the product has high crosslinking degree. The disadvantage is that the post-treatment is complex and a large number of three wastes are produced.

An excellent PVA-based chelating material can also be obtained by the surface modification grafting method. Hao Zhang [22] invented a PVA/PE nanofiber membrane that adsorbs hemoglobin via iminodiacetic acid surface functionalization and Ni$^{2+}$ chelation. The Langmuir model was used to describe the adsorption performance of bovine hemoglobin on Ni$^{2+}$ chelated PVA/PE nanofiber membrane, which provided a feasible reference for large-scale purification of hemoglobin and other proteins. Cheng Cheng [23-24] prepared a modified novel chelate sponge PVA-MA-HH by graft
polymerization and then nucleophilic substitution reaction, which has higher balance adsorption capacity for Cu\textsuperscript{2+}, Ni\textsuperscript{2+} and Cd\textsuperscript{2+}.

Pre-irradiation and radiation grafting is also a preparation technology in recent years. The production equipment is easy to obtain, the processing is simple and environmentally friendly, but the grafting rate of the product is not satisfactory and the performance of PVA chelating materials is difficult to control. Li Zhigang\cite{25} synthesized the amphiphilic graft copolymer with temperature-sensitive branching by pre-irradiation and co-irradiation grafting, PVDF-g-PNIPAAm graft copolymerization with different grafting rate and uniformity is different. Shi Fuxia\cite{26} produced quaternary ammonium salt type strong basic anion exchange fiber PP-g-VP copolymer were grafted by electron beam pre-irradiation. The higher the monomer concentration, the higher the graft ratio, the longer the quaternization time, the higher the conversion rate. The adsorption of ruthenium (VII) on this material quickly reaches the adsorption equilibrium in a weakly acidic medium with a pH of 2.2. Wang Yunlong\cite{27} prepared expanded polytetrafluoroethylene hybrid membrane by radiation grafting. The macroporous structure of PTFE was covered by SEM, and it was covered by neutralization of silver nitrate solution. Both antibacterial properties and long-lasting antibacterial activity are improved.

Graft copolymerization is currently the most mature preparation method in chemical and physical application, and is the easiest method to prepare PVA-based chelating materials. Continuous optimization of solvent selectivity and environmental-friendly solutions are required in subsequent production, as well as adjustment of the structure of the PVA-based chelating material to ensure its properties.

**4.2. blending precipitation**

Blend precipitation refers to a method in which two or more homopolymers or copolymers are physically or chemically combined to change the chemical or physical properties of the substance, including solution blending precipitation, emulsion blending precipitation and Colloidal blending precipitation, etc.

The advantages of blending precipitation are mature technology, low cost and environmental protection. Lu Long\cite{28} prepared EDTA modified magnetic chitosan by coprecipitation method, and chelated and adsorbed Pb\textsuperscript{2+}/Cu\textsuperscript{2+} ions in polluted water, which provided technical support for the repair of heavy metal contaminated water. Zeng Rong\cite{29} prepared chitosan/PVA blend membrane by solution blending according to the complementary characteristics of chitosan and PVA materials. The membrane has a large capacity adsorption for Cu\textsuperscript{2+}, Ni\textsuperscript{2+} and plays an active role in the treatment of water pollution.

The method of blending precipitation needs to control the proportion of the components in the reaction phase and the process parameters, and the PVA-based chelating materials with good performance can be obtained by effectively adjusting the reaction selectivity and material morphology of each phase. Li Meng\cite{30} of Tianjin University synthesized the dendrimer tetraethyl diamine (PETEDA). The active layer was formed by blending PETEDA and PVA, and the PES ultrafiltration membrane was used as the support layer to prepare PETEDA-PVA-PES. The composite membrane has good permeation selectivity to CO\textsubscript{2}/CH\textsubscript{4}. Han Zhu\cite{31} explored that crosslinked PVA nanofibers and crosslinked PVA-PEI nanofibers still exhibit good water stability and porous structure after immersion in water for 72 hours, due to strong chelation between amine groups, The average diameter between hydroxyl groups and Rh\textsuperscript{3+}, RhNP is about 2.5\pm 0.2nm. In addition, the PVA-PEI nanofibers grow uniformly and densely by in-situ reduction. RhNP has more in-situ reduction size and dispersion control than the pre-synthesized RhNP deposited directly thereon. As a result, the novel nanomaterial is fabricated into a non-enzymatic electrochemical sensor and exhibits a higher electrocatalytic activity for H\textsubscript{2}O\textsubscript{2}.

Different preparation methods can obtain PVA-based chelating materials with different properties, and adding different additives is beneficial to the chelating performance. Takashi Kobayashi\cite{32}
immobilized the chelating agent 5-dodecyl salicylaldoxime (LIX860-I) on PVA gel beads for recovery of Cu\(^{2+}\) in an aqueous solution containing copper sulfate (0.4-0.7wt% CuSO\(_4\cdot5\)H\(_2\)O). The chelate equilibrium ability between the Cu\(^{2+}\) and the chelate extractant in the gel beads is substantially the same as the chelate equilibrium ability in the liquid-liquid extraction, and the PVA gel bead performance reaches the desired level. S. Biswas[33] studied the chemical reaction of CrO\(_3\), PVA and sucrose in water to synthesize shape-controlled Cr\(_2\)O\(_3\) ferromagnetic particles. The Cr\(^{3+}\)-PVA chelating material reacts in a separate group in the micelle to produce a Cr\(^{3+}\)-polymer composite with excellent dispersion properties in water under heating.

Blend precipitation has achieved good results in the processing of multi-component high-polymers, and has outstanding performance in improving the functional properties of PVA-based chelating materials. The blending and precipitation can make the PVA-based chelating material process fully contact with the reaction, and the separation and purification are simple, but the mechanical strength of the obtained chelating material needs to be optimized and various additives need to be further studied.

4.3. Interpenetrating network cross-linking

Interpenetrating network cross-linking is a three-dimensional cross-linked interpenetrating network formed by the intertwining, bonding or physical interaction of polymer chemical cross-linking bonds. The internal interpenetrating structure can enhance the mechanical strength of the material. The specific surface area, capacity and strength of the modified PVA-based chelating material are increased as a whole, and the adsorption capacity is also increased.

Porous PVA-based chelating materials having a network interpenetrating structure by physical cross-linking method have satisfactory properties. Li Jianwei[34] made PEG as porogen, nanocellulose (CNFs) as the reinforcing phase, the obtained PVA-based chelating material has a swelling degree of 1000, which is far improved than the pure PVA, and the thermal stability is significantly enhanced. The porous composite PVA material can be used for preservation and logistics protection of packaged products. Su Xiaodi[35] PVA/chitosan composites with stable swelling and interpenetrating network structure (IPN) were prepared by cyclic freeze-thaw method. Different preparation processes have different effects on material properties. Lian Zhe[36] mixed natural polymer sodium alginate (SA) with PVA composite, through the chemical cross-linking method to prepare PVA/SA interpenetrating network materials. With the increase of SA content, the hydrogen bonding between SA and PVA molecules is enhanced, the network becomes loose by compaction, the mesh is enlarged. The material has a complete network structure.

High-polymers with interpenetrating network cross-linking internal structures are a unique kind of functional materials which have shown great potential in industries such as paints, adhesives and gradient sound absorbing materials[37].

4.4. Mechanical melting

Mechanical melting is a method in which a substrate, a monomer, an initiator, and other additives are mixed under a certain condition before heated and melted to graft a monomer onto a matrix material. Zou Mengjiao[38] prepared styrene-butadiene rubber grafted maleic anhydride (SBR-g-MAH) by melt grafting method and added a new type of third monomer to improve the grafting ratio and grafting efficiency of SBR-g-MAH. In the same temperature, the amount of SBR-g-MAH and Si69 increased, and the storage modulus, loss modulus and tan\(^\delta\) all decreased first and then increased.

The mechanism of melt grafting is relatively complicated, and the grafting efficiency and rate are low, which accompanied by serious side reactions. Peng Xianbin[39] used water as a plasticizer and foaming agent to achieve continuous extrusion and foaming of PVA on ordinary single-screw extrusion equipment, and obtained comprehensive control by adjusting water content, mold temperature and screw speed.

The advantage of melt grafting is that it is easy to operate with low cost or no post-treatment of the product. However, the processing of PVA-based chelating materials requires various additives and
structural stability of the molding materials. It is more difficult to control.

4.5. other methods
The application of new technologies born the development of new materials. Qi Junmei[40] used three kinds of 3D printing technologies such as stereolithography (SLA), fused deposition (FDM) and selective laser sintering (SLS) to produce polymer materials. Zhang Yun[41] designed and synthesized a series of new spherical solid phase adsorbent materials based on the advantages of solid phase adsorbent and liquid phase extractant. Macroporous reticulated polyvinyl alcohol beads (MR-PVA) and contain a large amount of hydroxyl, carboxyl and amino groups. The adsorption capacity of Zn\(^{2+}\) for new PVA/EDTA composite pellet resin is greater than that of other biosorbents. Li Xiaoli[42] studied the effect of new adsorbent to adsorb and pure heavy metals based on dynamic fixed bed. The introduction of CS in immobilized ionic polymerized PVA-based composites not only enhanced the mechanical strength, chemical and thermodynamic stability of PVA/CS, but also increased adsorption capacity. The method of preparing repeated thawing-high low temperature and super-zero gas foaming can also improve the performance of PVA chelating materials.

5. PVA chelate material adsorption type
PVA chelating materials have good adsorption for 17 kinds of metal ions such as Fe\(^{3+}\), Cr\(^{3+}\), Pb\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\), Hg\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), etc. The adsorption types and capacities of the materials are different from preparation methods. In order to remove different types of wastes in water, Yang Lan[43] prepared multifunctional multi-walled carbon nanotubes (MWCNTs)/nano Fe\(_3\)O\(_4\)-PVA microspheres by esterification reaction. Sanju Francis[44] γ-irradiated EDTA and PVA aqueous solutions with different ratios under Co-60 source to form PVA-EDTA hydrogel. The thermal stability of PVA chelating materials was characterized by TGA, and PVA chelating materials were found the chelating efficiency of medium EDTA is about 10% of pure EDTA in solution. Quan Feng[45] used electrospinning technology to prepare a film composed of PVA/PA6-Cu\(^{2+}\) composite nanofibers, and immobilized catalase (CAT) on PVA/PA6-Cu\(^{2+}\) nanofiber membrane. The PVA chelate material Thermal stability and storage stability are significantly improved.

PVA chelating materials have a wide range of applications in membrane separation and analytical chemistry by utilizing the properties of adsorbing different metal ions. Jing Zhu[46] prepared a hydrophilic fiber PVA/PE nanofiber membrane with a certain fiber size by melt extrusion to recover protein lysozyme, and adsorbed lysozyme 199 mg/g under optimal conditions. The iminodiacetic acid (IDA) on the PVA/PE chelating material is covalently linked to the cyanuric acid activated membrane surface, and the chelation performance is enhanced.

PVA Chelating Materials are of great significance for the combination of coenzymes, cofactors and enzymes in the field of bioengineering and metal chelation reactions. Because a large number of hydroxyl groups in the PVA chain are easily linked to various functional groups through esterification and acetalization (ketone) reaction, materials with different properties and functions are obtained, and their applications involve polymer chemical, textile, metallurgy, construction. In the fields of medicine, environmental protection, cosmetics, automotive glass and oilfield chemistry, the newly developed monomer and side chain-based products and applications with strong chelation adsorption are still expanding, and the adsorption types of PVA chelating materials will still increase.

6. Prospect
High-performance polymer materials are developing rapidly with the increasing demand for society. PVA chelating materials show unique performance in separation science and have good development prospects. With the research progress of blending modification, copolymer grafting, interpenetrating network cross-linking, mechanical melting and functional preparation of new technologies, PVA chelate materials have outstanding biodegradability, broad-spectrum antibacterial properties, strong polarity. Performance such as enhanced recombination and high selectivity will be extended to a wider range of industries. As a high-adsorption material, it has strong selectivity for various heavy metal
ions in water. It not only has excellent environmental adsorption performance, but also has wide application space. It is widely used in medical and health, food packaging, metallurgy and marine chemistry industries. The pursuit of PVA chelating materials with excellent properties is a requirement of social development. The chemical reaction and physical processing methods of graft copolymerization, blend precipitation, interpenetrating network crosslinking and mechanical melting listed in the paper are still the main preparations of PVA chelating materials. At the same time, new equipment and technologies will be applied to change the structure of the matrix material and the properties of the side chain groups to obtain higher performance PVA chelating materials. The efficient application of new equipment and new technologies such as 3D printing will be expected in the future. Create greater value in the development of new materials, the promotion of renewable resources and the promotion of economic and social development.

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