Proceedings of the 7th International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/2027.39412

Applications of Polymeric Surfactants in the Papermaking Industry: Retention, Drainage, and Paper Strengthening

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Abstract. Polymeric surfactants are a kind of functional material with the dual characteristics of high-molecular-weight and low-molecular surfactant. The hydrophilic groups and hydrophobic groups in their molecular structure enable them to be directed at the phase interface to form a dense and stable interfacial membrane. This article systematically reviews the core applications of polymer surfactants in the paper industry, focusing on the two directions of retention and filtration systems and paper enhancement technology. The mechanism of the role of spherical polyelectrolyte brushes, cationic polyacrylamide/bentonite systems, super-branched cationic polyacrylamide, etc. in assisted retention and auxiliary filtration, as well as the performance of polyvinyl alcohol, chitosan-grafted polydimethylsiloxane, etc. in paper enhancement and functionalisation were analysed. Research shows that polymer surfactants can significantly improve the retention rate of paper, improve the filtration performance, and enhance the physical strength of paper through mechanisms such as charge neutralisation, bridge flocculation and spatial resistance. Driven by the concept of green chemistry, fluorine-free and plastic-free coatings and natural polymer-modified products are becoming important development directions in this field.

Keywords: Polymeric surfactant, Papermaking auxiliary, Retention and filtration, Paper reinforcement, Surface glueing

1. Introduction

Interface chemistry is widely used in the papermaking industry, from the dispersion of fibres in water to the retention of fine particles on the net, and finally to the laying and curing of paints on paper. There is interface chemistry in every link, and the application of surfactants in the paper industry is extremely important. The papermaking process puts forward several typical requirements for aids: the dispersion stability of fibres and fillers in water directly affects the uniformity and forming quality of paper pages; the retention rate of fine groups determines the utilisation rate of raw materials and white water load; the flocculation control of the wet system is related to the operation efficiency of the paper machine and the cleanliness of the net; the uniformity of the paper surface coating affects the printing suitability and blocking performance; the interaction between the auxiliary and the fibre fundamentally determines the effect of enhancement, gluing and functionalisation.

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DOI: 10.54254/2755-2721/2027.39412

Although traditional low-molecular surfactants can effectively reduce surface tension, they have limitations in the wet papermaking environment. For example, chromatographic separation is easy to occur when compounding with polymers, and the adsorption layer is thin and the stability is insufficient. The emergence of polymeric surfactants solves this problem. Polymer surfactants usually refer to amphiphilic polymers with a relative molecular mass of more than 2000. Their molecular chains contain both hydrophilic and hydrophobic groups, which retain the directional arrangement of surfactants at the interface. At the same time, they have the unique viscosity, film formation and rheological adjustability of polymers.

Compared with low-molecular surfactants, polymeric surfactants are not dominant in reducing interfacial tension, and the micellarisation behaviour is not obvious. However, polymeric surfactants are outstanding in terms of dispersion, flocculation and solubility. When the dosage is large, they can also have strong emulsification, foam stabilisation, thickening and adhesion. First of all, polymeric surfactants can be adsorbed at the interface to form a dense protective film to stabilise the dispersion system. It can also reduce the surface potential of particles and eliminate electrostatic repulsion by anion groups; the unique structure of polymeric surfactants can use the long chain structure to bridge between multiple particles to accelerate solid-liquid separation; form a three-dimensional barrier on the surface of the particle through the hydrophobic chain section to prevent aggregation; cooperate with the help of molecular chain entanglement and hydrophobic Use the viscosity of the regulated system to improve the performance of the coating and glueing process. It is these characteristics that make it find a unique value positioning in the field of papermaking.

This article aims to systematically sort out the current situation and mechanism of polymer surfactants in the paper industry, combine specific research cases, analyse the advantages and challenges, and look forward to the future development direction.

2. Structure and properties

2.1. Structural characteristics

Polymer surfactants are composed of two parts: hydrophobic structure and hydrophobic structure. According to the source, they can be divided into two categories: natural polymer surfactants and synthetic polymer surfactants. Natural products include cellulose derivatives, starch derivatives, lignin sulphonates, chitosan, etc., which have excellent viscosity, emulsification, and biodegradability [1]. The synthetic class is prepared by homopolymerisation of amphomophobic monomers, hydrophobic monomer copolymerisation, or polymer chemical reaction. It has a wide selection of monomers and high structural designability [2]. According to the ion type, it can be divided into anionic, cationic, amphotic and non-ionic, among which cationic polymer surfactants and amphoteric polymer surfactants dominate the wet application of papermaking. The reason is that the surface of fibres, fillers and fine fibres in the papermaking wet system is usually negatively charged. Cationic polymer surfactants can be directly anchored to the fibre surface through electrostatic adsorption to achieve effective charge neutralisation and bridge flocculation, thus significantly improving the retention rate and water filtration performance. The type of polymer surfactant carries positive and negative charge groups on the same molecular chain at the same time, with a wider pH adaptation window and stronger anti-electrolyte interference ability, and can maintain stable retention and filtration efficiency in a closed white water system.

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2.2. Interface adsorption

The behaviour of polymeric surfactants on the interface is essentially different from that of low-molecular surfactants. Low-molecular surfactants are adsorbed at the interface in a "monomolecular layer", while high-molecular surfactants tend to form a thicker and denser adsorption layer due to the entanglement between chain segments and the multi-site anchoring effect. The study of spherical polyelectrolyte brush (SPB) provides a model system for understanding this behaviour. Mei et al. found that when anionically functionalised SPB and cationic polyacrylamide (CPAM) are combined, the flocculation efficiency is related to the synergy of SPB's high cationic exchange capacity (CEC) and grafted poly electrolyte chain flexibility [3]. Field-emission scanning electron microscopy and atomic force microscopy. The analysis supports the model of anionic SPB as a "particle bridge" between fibre and calcium carbonate.

2.3. Design of super-branched structure

Because of its three-dimensional structure, super-branched polymers usually show unique properties that are different from linear polymers, such as rich functional end groups, large internal molecular cavities, better solubility, and lower melt viscosity. In the design of flocculants, the superbranched structure provides a new structural design for the functional enhancement of polymer surfactants. Cong synthesised cationic polyacrylamide (BCPAM) with star-shaped branching structure by aqueous free radical polymerisation with tetranetyl alcohol as the branching agent and cerium ammonium nitrate as the initiator, and further used nano-silicon dioxide particles generated by the in situ hydrolysis of ethyl silicate for physical cross-linking to prepare super branched cationic Subpolyacrylamide (SiO_2/BCPAM) [4]. Compared with linear cationic polyacrylamide, this super-branched product has the characteristics of high surface functionality, low ontology and solution viscosity, and small fluid dynamics radius. The study attributes this structural advantage to the multi-arm configuration of super-branched molecules. The branched chain segment can prevent the polymer from adsorbing on the fibre surface in a flat-volt configuration, and at the same time prevent the diffusion of the polymer to the fibre pores, thus reducing the attenuation of charge, which is conducive to maintaining a more stretched configuration on the fibre surface.

3. Applications in papermaking

3.1. Auxiliary retention and auxiliary filtration: mechanism and system

Retention and filtration are the most mature fields of application of polymeric surfactants in the wet part of papermaking. The fine fibres and filler particles in the paper are small in size and large in surface area, and are easily lost in the forming net, which not only causes waste of raw materials, but also increases the load of white water treatment. The function of the retention filter aid is to make these particles aggregate and thus be trapped in the fibre network [5].

Its mechanism of action can be summarised into four levels: Zeta potential charge neutralisation, chimeric structure, bridge flocculation and condensation and flocculation. The research of Mei et al. provided direct microscopic evidence for the "particle bridge" mechanism [3, 6]. They used an anion-functionalised spherical polyelectrolyte brush and CPAM compounding to test the flocculation efficiency through dynamic water filter tanks, and analysed the flocculation structure in combination with FESEM and AFM to confirm the anion SPB acts as a bridge between fibre and $CaCO_3$.

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CPAM is a representative product. The compounding system of CPAM and inorganic particles shows a synergistic effect. Perng and others constructed a dual chemical retention system with two cationic polyacrylamides, colloidal silicon dioxide, and spheroidal anionic polymer particles, and experimentally observed the feasibility of nano-silk mica as a substitute for commercial particles [7]. The results showed that the first-way retention rate of nano-silk mica for fine particles and chemicals It can reach 76.9–80.9%, and the greyness retention rate is between 16–24%. Based on the above research, it can be seen that the effectiveness of polymer surfactants in assisted retention and filtration cannot be summarised by a single mechanism, but is the result of the superposition of charge neutralisation, bridge flocculation and particle coordination: CPAM provides cationic anchor positioning points, and inorganic particles or SPBs act as "bridges" to jointly build three-dimensional flocculation. Network, so as to realise the efficient interception of fine grouping and the significant reduction of water filtration resistance. Asselman and Garnier studied the role of anionic particles in the polyacrylamide-montmorillonite flocculation aid system, which laid the foundation for understanding the two-component synergistic mechanism of the system [6].

3.2. Paper enhancement: hydrogen bonding and cross-linking

Improving paper strength is another important application direction of polymeric surfactants. The natural binding force between cellulose fibres is limited, and enhancing the inter-fibre binding through polymeric auxiliaries is a major direction of papermaking chemistry [8].

Water-soluble polyvinyl alcohol (PVA) can form dense hydrogen bonds with cellulose fibres because of the hydroxyl group on its molecular chain. Xu et al. used aldehyde and glutaraldehyde as cross-linking agents to improve the wet strength of paper in the presence of fully hydrolysed PVA as a co-reactant [9]. Although the use of dual-functional aldehyde alone can improve the wet strength, it will reduce the folding resistance; the introduction of PVA not only improves the wet strength, but also improves the dry strength and folding resistance. The reaction between glutaraldehyde and PVA promotes the formation of cross-linking between fibres and improves the wet strength under the premise of flexibility. Among a variety of Lewis acid catalysts, $Zn(NO_3)_2$ has been proven to be the most effective. Aditya Nair et al. reported an economical, plastic-free and fluorine-free coating method, which uses a copolymer of polyvinyl alcohol and chitosan grafted polydimethylsiloxane copolymer to treat paper substrates [1]. The resulting coated paper shows good water-repellent performance, and the Cobb60 value is as low as about 20 ± 2.1 G/m2, the water contact angle is as high as 119 ± 6.3°, and the Kit rating is 7.6/12 [1].

3.3. Surface modification and functional coating

The application of polymeric surfactants in paper surface modification is developing from glue enhancement to functionalisation. Polymer latex containing hydrolysable emulsifiers is used in paper coatings. Itoh and others examined the adsorption behaviour of polystyrene latex containing alkali-containing hydrolysable cationic emulsifier on sodium carbonate pretreated filter paper. The hydrolysis of the emulsifier and the adsorption of the latex on the paper are carried out at the same time, which can quickly and efficiently fix or coat polystyrene on the paper at room temperature, and the polymer is desorbed after rinsing. Rarely, the polymer-coated paper surface has acquired water-repellent and quick-drying properties [10].

The follow-up research of Itoh et al. further used poly (styrene-co-butyl methacrylate) and poly(styrene-co-butyl acrylate) latex as dispersants and adhesives for water-based carbon black paints, which proves that latex containing hydrolysable emulsifiers has higher adhesion than latex

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containing non-hydrolysemulsifiers [11]. In addition, the preparation of polycationic grafted cellulose fibre provides new ideas for the design of retention aids and enhancers. By dissolving cationic polyacrylamide in water and adding it to the cellulose fibre suspension at alkaline pH, CPAM forms a micron-level uniform film on the surface of the fibre through electrostatic adsorption, and the resulting graft fibre can be used. To enhance the retention of negatively charged fillers, fibres and pigments without changing the original performance of the paper [12].

4. Challenge and optimisation

Although the application of polymeric surfactants in papermaking has achieved remarkable results, it still faces multiple challenges in industrial practice.

The performance of high-efficiency products is highly sensitive to parameters such as molecular weight distribution, charge density, and hydrophilic and hydrophobic chain segment ratio. Although the retention and filtration effect of super-branched cationic polyacrylamide is better than that of linear analogues, Cong's research also pointed out that the application research of super-branched polymers in the papermaking industry has just begun, and there is a lack of research on the effects of molecular structure, molecular configuration, molecular weight, molecular weight distribution, etc. of super-branched polymers [4]. A systematic study on the influence of fruit, as well as a systematic study on the influence of slurry properties, other chemical additives, manufacturing conditions, etc., on the enhancement effect. The quantitative correlation between the controllable synthesis of molecular structure and performance still needs to be deepened. Organotellurium-mediated emulsion polymerisation (TERP) technology provides a new way for the precise control of the structure of superbranched polymers. By copolymerising vinyl telluride and acrylate under aquauric emulsion conditions, superbranched poly (butyl acrylate) with a branching structure can be synthesised. Its molecular weight, dispersion, branching number, and branching length can be accurately controlled by adjusting the amount of chain transfer agent, branching monomer and monomer [2].

The fluctuation of pH value, the accumulation of electrolytes, and the existence of soluble colloidal substances in the wet environment of papermaking may interfere with the interface adsorption and flocculation behaviour of the auxiliary. The dynamic behaviour study of CPAM/bentonite system shows that the parameters related to the first-run retention rate and white water cycle are important factors affecting the dynamics of the wet part [5]. The synergistic or antagonistic effect between the auxiliaries makes the formula design more complicated.

Some synthesised polymeric surfactants have poor biodegradability and accumulate in the environment for a long time. The restrictions on PFAS in paper packaging are pushing the industry to find alternatives. The latex system containing a hydrolysable emulsifier represents a beneficial attempt to reduce surfactant residue [13].

5. Prospects

The future development direction of polymer surfactants in the paper industry can be summarised as "high efficiency, environmental protection and intelligence".

In terms of high efficiency, the focus is on the development of special products that are resistant to high shear and acid and alkali, which are suitable for the harsh working conditions of high-speed paper machines and closed white water systems. Because of its unique solution conformation and rich functional end groups, the super-branched structure shows the potential to surpass linear polymers in the field of flocculation and enhancement. Cong's research shows that when the amount of super-branched cationic polyacrylamide (SiO_2/BCPAM) is 0.5% (dry pulp), the break resistance

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index, tear index, and tensile index of the paper page increase by 23.59%, 12.44% and 25.47%, respectively compared with the blank sample, and the paper is filtered. The performance and the retention rate of the first journey increase with the increase in usage. An in-depth study of the structural relationship of super branched polymers in the complex environment of papermaking wet parts will provide a theoretical basis for the development of special aussiliaries to meet the needs of high-end paper.

In terms of environmental protection, the research and development of fully biodegradable products is the core direction. The chemical modification and performance optimisation of chitosan-based, cellulose-based and sugar derivative-based surfactants will continue to deepen. The latex system containing hydrolysable emulsifier can achieve high-efficiency coating at room temperature, and the amount of polymer deattachment is extremely small, which provides new ideas for green coating technology [13].

In terms of intelligence, auxiliaries with dynamic response to external stimuli such as temperature and pH will realise the precise regulation of the papermaking process. The "synchronous hydrolysis-adsorption" mechanism of hydrolysable emulsifier lax provides inspiration for intelligent responsive coating design [5].

From a broader perspective, the development trajectory of polymer surfactants in papermaking reflects the paradigm shift of the paper industry from "experience formula" to "molecular design". When the molecular structure of the auxiliary can be rationally designed to match the specific fibre surface and process conditions, the development of paper chemicals has taken a key step from a skill to a science.

6. Conclusion

With their unique hydrophobic-hydrophobic molecular structure, polymeric surfactants play an irreplaceable role in the paper industry, such as retention and filtration, paper enhancement, and surface functionalisation. The cationic polymer surfactant represented by CPAM is still the core of the retention and filtration system, and the new molecular structures such as super-branched structures and spherical polyelectrolyte brushes are promoting the development of auxiliary performance to a higher level. PVA and its cross-linking system continue to be effective in the field of paper enhancement, and the lax system containing hydrolysable emulsifiers provides a new path for green coating technology. At present, the main challenges include the precise regulation of the structure-performance relationship, the stability of efficiency in complex wet environments, and the biodegradability of synthetic aids. The future development direction should focus on the three dimensions of high efficiency, environmental protection, and intelligence, promote polymer surfactants from empirical formulas to molecular design, and provide key material support for the green upgrading of the paper industry.

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