Study on Synthesis and Modification of Polyepoxysuccinic Acid

Leng Manxi, Lu Xingyu, Feng Wenrong, Wang Xinping, Fu Weiqiang, Y ang Zeyu, Wang Haoqi

College of engineering, Southwest Petroleum University, Nanchong Key Laboratory of Robot Engineering and Intelligent Manufacturing, Nanchong Sichuan 637000, China

ABSTRACT. This article reviews the recent experimental studies of polyepoxysuccinic acid and its derivatives as water treatment agents, and briefly summarizes the synthesis and modification of polyepoxysuccinic acid and its derivatives as scale inhibitors. Based on this, combined with the modification history of polyepoxysuccinic acid, it puts forward its views on the optimization of its performance, and focuses on the explanation of the polyepoxysuccinic acid scale inhibitors during the synthesis process. Performance of scale agents. Finally, with the concept of green chemistry as the core, some problems that polyepoxysuccinic acid and its derivatives will face in the future preparation and research are put forward, which provides a reference for the molecular structure changes and the introduction of functional groups in subsequent derivatives research.

KEYWORDS: Polyepoxysuccinic acid, Derivative, Water treatment agent, Comonomer, Green chemistry

1. Introduction

PESA was first born in the US Bates Laboratory and belongs to the green scale inhibitor[1]. The "green" water treatment agent is the development direction of water treatment agent in the 21st century. Polyepoxysuccinic acid, as a green scale inhibitor, is characterized by the absence of N and P elements, and will not cause the problem of eutrophication of water bodies in long-term use. In addition, polyepoxysuccinic acid has good biodegradability and has good alkali resistance.

Prior to this, water treatment agents have successively experienced inorganic scale inhibitors, natural polymer scale inhibitors and phosphorus-containing polymer scale inhibitors [2]. Traditional natural polymer scale inhibitors have problems such as high cost and large drug usage in actual use, and phosphorus-containing polymers have poor scale inhibitory effects on calcium phosphate, zinc scale, and iron oxide precipitation, and are easy to hydrolyze [3]. Polyepoxysuccinic acid thus stands out and plays a role in changing the water treatment agent. However, the defects of polyepoxysuccinic acid itself are also obvious, the functional group is single, and the scope of application is extremely limited. Therefore, many researchers have begun experimental research on the modification of polyepoxysuccinic acid.

2. Synthesis of Polyepoxysuccinic Acid

2.1 One-Step Synthesis

Xiong Rongchun et al. [4] used maleic anhydride as a raw material, and used sodium hydroxide to create an alkaline environment, so that maleic anhydride was hydrolyzed under alkaline conditions. The pH of the system is adjusted between $5\sim7$, and the temperature is $65\sim100^{\circ}$ C. Epoxidation reaction is then carried out using a peroxide catalyst and a vanadium catalyst as catalysts to generate epoxy succinic acid. Finally, a rare earth catalyst is used as a catalyst to polymerize to obtain polyepoxysuccinic acid.

This preparation process uses sodium hydroxide to create an alkaline environment and eliminates the effects of calcium ions in calcium hydroxide. In addition, the scale inhibition performance of the polyepoxysuccinic acid prepared by this method is affected by the synthetic conditions. These include reaction temperature, reaction time, and initiator usage.

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Fig. 1 Polyepoxysuccinic Acid Structure Formula

Li Meng et al. [5] broke the traditional idea of using calcium hydroxide and rare-earth catalysts and prepared them using sodium hydroxide as a catalyst. It investigated the calcium carbonate scale inhibition performance of polyepoxysuccinic acid, adjusted the factors affecting the scale inhibition performance of sodium polyepoxysuccinic acid, and determined the optimal synthesis conditions.

2.2 Multi-Step Synthesis

J. J. Benedict et al. [6] prepared polyepoxysuccinic acid by using maleic anhydride as raw material, acidic hydrolysis of maleic acid, sodium ditungstate as catalyst, and calcium hydroxide as initiator. This preparation method is simple, and raw materials are cheap and readily available, and are currently widely used. However, due to the use of calcium hydroxide in the preparation process, the content of calcium ions in the system is too high, which will affect the final scale inhibition effect.

Wang Yaquan et al. [7] used maleic anhydride as a raw material, dissolved maleic anhydride in water, and used sodium tungstate as a catalyst to perform epoxidation with hydrogen peroxide in the presence of sodium hydroxide to form sodium succinate. Then, calcium hydroxide is added, and at the same time, the system is adjusted with sodium hydroxide to pH=10 to 13 to perform polymerization to synthesize polyepoxysuccinic acid sodium salt. The sodium salt can be acidified to obtain polyepoxysuccinic acid. The advantage of this preparation process is that the calcium ion content in the obtained product is less than 0. 3%, which avoids the disadvantage of high calcium ion content in the system during the synthesis process of Benedict J J et al.

3. Research Progress on Modification of Polycyclosuccinic Acid

3.1 Modification Ideas of Polyepoxysuccinic Acid

For the performance of current polyepoxysuccinic acid corrosion and scale inhibitors, the purpose of modification is to solve the problems of production of by-products during production, pollution during production, and improvement of atomic utilization of raw materials. All in all, the idea of modifying polyepoxysuccinic acid should be based on the concept of "green" chemistry, and it should be based on reducing pollution, reducing costs and improving performance.

3.2 Research Progress in Modification of Polyepoxysuccinic Acid

In recent years, polyepoxysuccinic acid corrosion and scale inhibitors have shined in industrial water treatment. Many scholars have begun experimental research on the modification of polyepoxysuccinic acid.

An Hailiang et al.[8] carried out the homopolymerization of ESA and the copolymerization of 2-acrylamide-2-methylpropanesulfonic acid with homemade polyepoxysuccinate(ESA), respectively. Polyepoxysuccinic acid (PESA)and copolymers(MPESA)were obtained.

The experimental results show that MPESA is stronger than PESA in blocking calcium phosphate scale and stabilizing zinc salts, because the introduction of sulfonic acid groups prevents the cross-linking effect caused by the reaction of carboxyl groups with calcium ions, thereby inhibiting the generation of poorly soluble gels. However, the effect on the group of calcium carbonate scale is also relatively weakened, so it can be considered to use a combination of the two.

Li Jianbo et al. [9]used PESA, AMPS and β -CD-1 for ternary copolymerization into PESA/ β -CD/AMPS. β -CD-1 is prepared from β -cyclodextrin and allyl chloride under basic conditions using DMSO as a solvent. Using ammonium persulfate and sodium bisulfite as initiators, PESA/ β -CD/AMPS was prepared by polymerization reaction under the basic conditions.

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The test results show that the scale inhibition performance of PESA/ β -CD/AMPS is better than the commonly used scale inhibitors on the market and is environmentally friendly. It can be used in industrial water and oilfield water injection treatment.

Liu Xinhua et al. [10] prepared a 50% sodium hydroxide solution with deionized water, and then cooled to room temperature. Pour maleic anhydride into a three-necked flask, and then add a sodium hydroxide solution while stirring with a magnetic stirrer. The reaction temperature was 55°C, the catalyst was sodium tungstate, the epoxidation temperature was 65°C, and hydrogen peroxide was used as the initiator. The reaction was carried out under constant stirring for 2 h to obtain sodium succinate(ESA). Add deionized water to the three-necked flask, add ESA first, and add itaconic acid after it is completely dissolved. As an initiator, ammonium persulfate was stirred at a constant speed and the temperature was raised to 95°C. After reacting for 5 hours, an ester-flavored orange liquid was obtained as a copolymer of polyepoxysuccinic acid(IA-PESA).

ONa
$$H_2O_2$$
 Cyclizing ONa H_2O_3 ONa H_2O_4 ONa H_2O_5 ONa NaO H_2O_5 ONA

Fig. 2 The Combined Reaction Equation of Esa and Pesa

It has been proved through experiments that from the perspective of IA-PESA and PESA's scale inhibition of calcium carbonate and calcium sulfate, IA-PESA has better scale inhibition effect than PESA when the amount of scale inhibitor is the same. Reduce costs from the perspective of raw material use. The reason may be that IA-PESA has more carboxyl groups than PESA, which is more favorable for the dissolution of calcium ions.

Xiao Jing et al. [11] used thiourea to modify polyepoxysuccinic acid. Weighed a certain amount of thiourea into epoxy succinic acid, adjusted the oil bath temperature to 100°C, and adjusted the stirring speed to 150 r/min, and continued the reaction for 2. 5 h to obtain thiourea-modified polyepoxysuccinic acid CSN-PESA)

Under the same conditions, the modified CSN-PESA has a comprehensive improvement in the performance of calcium phosphate scale, calcium carbonate scale and corrosion inhibition rate.

Yin et al. [12] used L-arginine to modify polyepoxysuccinic acid. Put a certain amount of PESA into a three-necked flask, and add a certain amount of water and L-arginine. Put it in a methyl silicone oil bath to heat it, adjust the pH after raising the temperature to a certain temperature, and stir for 2 h after sufficient stirring. The mass ratio of PESA and L-arginine is 9:1. When the reaction system turns into an orange-yellow viscous substance, heating is stopped to obtain an amino acid modified product (LAr-PESA).

Compared with PESA, the obtained product LAr-PESA has increased molecular structure of LAr-PESA with negatively charged amide and amino functional groups, enhanced chelation with calcium ions and lattice distortion ability. The experimental results also show that under the same calcium ion concentration and the amount of scale inhibitor used, the effect of LAr-PESA on calcium carbonate scale and calcium sulfate scale is better. It can be seen that compared with PESA, this product is more resistant to calcium ions and has a wider range of applications.

4. Conclusion

The shortcomings of polyepoxysuccinic acid as a scale inhibitor are the inhibition of calcium phosphate scale, the stability of zinc salts, and the poor effect of dispersing Fe2O3. In order to optimize these shortcomings and broaden the scope of application of polyepoxysuccinic scale inhibitors, different researchers have chosen different reagents to optimize the performance of polyepoxysuccinic acid. Most new comonomers adopt the idea of Certain groups of the body with scale inhibition properties impart polyepoxysuccinic acid, thereby optimizing the scale inhibition performance of polyepoxysuccinic acid. However, the introduction of monomers may lead to

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an increase in the degree of branching of the linear macromolecules in the polymer, and the increase in the degree of branching may be the cause of the decrease in the scale inhibition performance of the copolymer.

The author believes that the effect of the introduction of functional groups on polymers in the future research of polyepoxysuccinic acid and its derivatives is mixed, and this problem is likely to be faced in subsequent studies of derivatives. The biggest problem. How to solve the adverse effects brought about by the introduction of monomers needs to be considered in future research work.

Addition, some researchers chose to mix the new copolymer with polyepoxysuccinic acid at a certain ratio to achieve a better corrosion and scale inhibition effect. These are of significance to the subsequent research of polyepoxysuccinic acid corrosion inhibitors and scale inhibitors. The performance of polyepoxysuccinic acid is good, and its performance can be optimized by modifying, compounding and other methods.

From this point of view, polyepoxysuccinic acid and its derivatives have great development prospects. In order to improve the treatment effect of industrial water treatment agents, it is necessary to accelerate the research of its derivatives and industrialization of products.

References

- [1] Miao Beibei, Liu Xinhua, Wang Mengyi, et al (2018). Research progress of scale and corrosion inhibition properties of polyepoxysuccinic acid derivatives. Cleaning World, vol. 34, no. 7, pp. 37-48.
- [2] Song Shaofu, Lu Yutao (2019). Research progress of green water treatment agent polyepoxysuccinic acid. Chemical Technology and Development, vol. 48, no. 11, pp. 54-57.
- [3] Zhang Rui, Wang Jiaolong (2015). The latest research progress of green scale inhibitors. Industrial Water and Wastewater, vol. 46, no. 6, pp. 6-8+27.
- [4] Xiong Rongchun, Wei Gang (1999). Synthesis of green scale inhibitor polyepoxysuccinic acid. Industrial Water Treatment, vol. 19, no. 3, pp. 11-13.
- [5] Li Meng, Xie Fenglong (2012). Improvement of synthetic method of polyepoxysuccinic acid and its scale inhibition performance. Inner Mongolia Science and Technology and Economy, no. 16, pp. 106-108.
- [6] Wang Yaquan, Pan Ming (2004). Preparation methods of polyepoxysuccinic acid and its salts. Water Treatment Information Report, no. 3, pp. 34-36.
- [7] An Lianghai, Mu Zhanjun, Wu Chaojun, Li Jian (2014). Study on modification of polyepoxysuccinic acid and its scale inhibition mechanism. Guangdong Chemical Industry, vol. 41, no. 11, pp. 25-26.
- [8] Li Jianbo, Zeng Bo, Ye Zhengrong, Tang Mingjin, et al (2017). Synthesis and performance evaluation of modified polyepoxy sodium succinate. Fine Petrochemicals, vol. 36, no. 6, pp. 29-33.
- [9] Liu Xinhua, Wang Mengyi, Jia Jingxian, et al (2019). Synthesis of itaconic acid modified polyepoxysuccinic acid and its scale and corrosion inhibition properties. Surface Technology, no. 3, pp. 168-177.
- [10] Xiao Jing, Zeng Defang (2017). Synthesis of modified polyepoxysuccinic acid and its mechanism of scale and corrosion inhibition. Industrial Water Treatment, vol. 37, no. 12, pp. 68-71.
- [11] Yin Yiming, Zhang Yijiang, Cui Jifang, et al (2019). Study on the calcium scale inhibition and biodegradability of polyepoxysuccinic acid derivatives [J]. Industrial Water Treatment, vol. 39, no. 8, pp. 41-43+110.