Study on the Synthesis Technology of High Molecular Weight Hydrophilic Polyether

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Abstract. KOH is used as a catalyst. The synthesis of a high molecular weight (relative molecular mass) hydrophilic polyether was carried out. One is to synthesize 1000 molecular weight (relative molecular mass) from the initiator, and then directly synthesize the product (original production process), and then carry out refining treatment by pipetting; the other is to synthesize 1000 molecular weight from the initiator. Molecular mass), further processing in the subsequent synthesis, when the molecular weight reaches 4000 (relative molecular mass), the curing degassing treatment is carried out, and after completion, the mixture of ethylene oxide and propylene oxide is continuously continued to synthesize the product (new production process), the synthesis is finished, and after aging, the liquid is pipetted to be refined. The results show that the quality of the new process product is improved, the yield of hydrophilic polyether is improved, and the waterproof effect is improved to 25%; the molecular weight of the old process is not up to the designed molecular weight, and the yield of hydrophilic polyether is lower and the waterproof application effect is less than 25%.

Keywords. Initiator; hydrophilic polyether; synthesis; refining.

1. Introduction

Polyurethane grouting material is abbreviated as cyanide. It is a prepolymer prepared by the reaction of polyisocyanate and polyhydroxy compound, and then a chemical slurry composed of some other additives such as catalysts, foam stabilizers, foaming agents, retarders, etc. [1]. Since the slurry contains unreacted terminal NCO groups, when the slurry is injected into porous buildings or loose formations, once the NCO groups come into contact with water, chemical reactions such as chain extension and cross-linking will occur, and the gaps of buildings or between the pores of the soil particles in the foundation, a water-insoluble gel-like consolidation is formed, and the consolidation contains a large number of polar groups, which has a strong affinity and strength with the crevices of the building and the surface of the particles, and can block the water gushing and flowing water in the foundation. The CO2 gas generated by the reaction presses the slurry further into the pores of the loose formation, so that the porous structure is completely packed and dense.

Polyurethane grouting materials can be divided into two categories: oil-soluble and water-soluble. The oil-soluble polyurethane grouting material has high strength and good permeability resistance, and is mostly used for reinforcement in engineering. Aqueous polyurethane grouting material is widely used in engineering waterproof plugging due to its good hydrophilicity, large water volume, and good elasticity of the consolidated body [2].

Water-soluble polyurethane slurry is usually pre-polymerized with high molecular weight hydrophilic polyether polyol and polyisocyanate. After the slurry meets with water, it is emulsified...
and dispersed in water to form a water-insoluble elastic gel consolidation body, which achieves the effect of stopping water with water [3]. Since polyisocyanate compounds do not contain hydrophilic groups, the hydrophilicity of polyether polyols determines the hydrophilicity of water-soluble polyurethane grouting materials. High molecular weight hydrophilic polyether is a high molecular weight (relative molecular weight) polyether polyol with high activity, which has excellent water solubility, compatibility, adhesion and thermal stability. It is widely used in water conservancy and hydropower, construction, transportation and mining in many aspects such as waterproof plugging and reinforcement [4-9].

Due to the relatively high molecular weight of high molecular weight (relative molecular weight) hydrophilic polyethers, it is difficult to achieve the use of theoretical proportions and conventional reaction processes. In this paper, by studying the reaction process conditions of high-molecular-weight hydrophilic polyethers, a process method for synthesizing high-molecular-weight hydrophilic polyethers is explored. A new route was explored for the synthesis of polyether with high molecular weight range from 12000 to 13000.

2. Experiment

2.1. Instrument
WBF type magnetic rotary stainless steel reactor 5L was purchased from Yantai Muping Shuguang Precision Instrument Factory. 5L standard measuring tank was purchased from Yantai Muping Shuguang Precision Instrument Factory. Electronic balance was purchased from METTLER TOLEDO Instruments Co., Ltd.

2.2. Raw Materials
Polyols with tri-functionality or higher for small molecules, industrial grade; Ethylene oxide, industrial products, Zhejiang Sanjiang New Chemical Materials Co., Ltd.; Propylene oxide, industrial products, Ningbo Zhenhai Refining & Chemical; KOH, industrial purity; Phosphoric acid, 65% concentration, industrial grade. Adsorbent, industrial grade, Hubei Zaoyang Chemical Industry.

2.3. Experimental Steps

2.3.1. Preparation of 1000 Molecular Weight Hydrophilic Polyether Intermediate. The raw material polyol and catalyst were put into the 5L stainless steel reactor. They were replaced with nitrogen twice, and pump the negative pressure to -0.098MPa (subject to the negative pressure, the time is about 20 minutes, depending on the efficiency of the vacuum pump). The temperature was increased to 120°C, and the mixture of ethylene oxide and propylene oxide was introduced. The mixing ratio is calculated according to the mass ratio of 2:1 or 5:2. The pressure in the reactor was not higher than 0.35MPa and kept. After the mixture was fed, the temperature of the reaction was maintained to perform a pressure reduction reaction, and the degassing treatment was performed to obtain a hydrophilic polyether intermediate. At this time, the molecular weight of the polyether is 1000.

2.3.2. Preparation of 4000 Molecular Weight Hydrophilic Polyether. The experimental procedure was the same as the preparation of the intermediate, but the temperature of the reaction was controlled at 120-140°C and the pressure was not higher than 0.35MPa. After the epoxide was fed, the temperature of the reaction was maintained for 2-5 hours until the pressure remains unchanged or the pressure was negative. Then the temperature was lowered to 120-130°C, and the vacuum was turned on to remove the low-molecular substances for 2-5 hours. It was continued to enter the mixture of ethylene oxide and propylene oxide until the end of the reaction. A crude hydrophilic polyether was prepared.

2.3.3. Preparation of Refined High Molecular Weight (Relative Molecular Weight) Hydrophilic Polyether. The crude hydrophilic polyether was pipetted into the neutralization reactor, degassed and
refined, phosphoric acid (65%, industrial grade) was added, then adsorbent was added, and the final product was obtained after the steps of neutralization, dehydration, crystallization, and filtration: high molecular weight affinity Water-based polyether. The general physical and chemical indicators of the product were as follows: the appearance is colorless and transparent viscous liquid without mechanical impurities, hydroxyl value is 14-19mgKOH/g, PH (5% aqueous solution) is 5.00-8.00, water content is below 0.05%, potassium sodium ion is less than or equal to 5ppm.

3. Results and Discussion

3.1. Selection of Synthesis Process
KOH was used as the catalyst. The synthesis of high molecular weight (relative molecular weight) hydrophilic polyether was performed. One was synthesized form a 1000-molecular weight feedstock by the initiator, and then the product was synthesized directly (the original production process). The temperature of the reaction was 120-140℃, the pressure was below 0.35 MPa. When the synthesis was completed, and the liquid was transferred after maturation for refining treatment; The other was synthesized a 1000 molecular weight (relative molecular weight) polyether from the initiator, and then a step was carried out in the subsequent synthesis. When the molecular weight is 4000, the degassing treatment was carried out. After the completion, the mixture of ethylene oxide and propane oxide were continued. The products were continued to synthesize (new production process), the temperature of the reaction was 120-140℃, and the pressure was below 0.35 MPa. When the reaction temperature is too low, the reaction will stop, low synthesis yield and long production cycle will be a result. The industrial production value was lost; and when the reaction temperature is too high, it was difficult to control for the reaction, it will result in excessive temperature during the reaction process, high side reactions will increase, the quality of the product was reduced, unsafe factors were added in the production process, and it does not have practical production value. When the synthesis was over, it was pipette into the neutralization reactor for refining treatment. Two processes were used to synthesize high molecular weight (relative molecular mass) hydrophilic polyether and the related data was compared, as shown in figure 1:

![Figure 1](image-url)

**Figure 1.** Comparison of synthetic routes for high molecular weight hydrophilic polyether GPC spectra.
Note: The abscissa is the time of separation, in minutes; the ordinate is the number average molecular weight. Curve A in the figure is the original process; curve B is the new process.

Relevant data obtained from the GPC spectrum are shown in table 1.
Table 1. GPC Data analysis.

| Sample type      | Main peak molecular weight/content (%) | Main peak distribution coefficient Mw/Mn | Impurity 1 molecular weight (%) | Impurity 2 molecular weight (%) |
|------------------|----------------------------------------|----------------------------------------|---------------------------------|---------------------------------|
| Original process | 9566/99.13                             | 1.09712                                | 1455/0.87                       | ----                            |
| New process      | 10414/98.35                            | 1.08400                                | 1636/1.65                       | ----                            |

It can be seen from figure 1 and table 1 that the distribution coefficient of the new process is lower than that of the original process, so the effect of the distribution is better, which is conducive to the improvement of application performance. In the synthesis of hydrophilic polyether, the impurity content increases after reaching a certain number average molecular weight (more than 4000), which makes the molecular distribution worse and the curve wider. The new synthetic route product meets the design molecular weight requirements, the molecular distribution is narrowed, and the molecular weight is increased, which will increase the reaction rate of polyether, reduce the amount of catalyst used in the application, and reduce the cost.

3.2. The Ratio of Raw Materials

High molecular weight (relative molecular weight) hydrophilic polyether has a relatively high molecular weight, which is difficult to achieve by using theoretical proportions and ordinary processes. In this paper, two sets of process schemes are designed, as shown in table 2.

Table 2. The ratio of route.

| Process route  | Initiator (w%) | Epoxide content (w%) | Yield (%) |
|----------------|----------------|----------------------|-----------|
| Original process 1 | 0.736          | 99.264               | 98.35     |
| Original process 2 | 0.750          | 99.250               | 98.45     |
| New process 1    | 0.707          | 99.293               | 99.25     |
| New process 2    | 0.700          | 99.300               | 99.35     |

It can be seen from table 2 that the new process has a significant increase in yield compared with the original production process, from 98.35% to 99.35%, indicating that it has contributed to energy conservation and emission reduction.

After synthesis, it passes the index test, and the results are shown in table 3.

Table 3. Comparison of detection data for each route.

| Process route  | Theoretical hydroxyl value (mgKOH/g) | Measured hydroxyl value (mgKOH/g) | Number average molecular weight |
|----------------|--------------------------------------|-----------------------------------|--------------------------------|
| Original process 1 | 17.95                                | 20                                | 11220                          |
| Original process 2 | 17.95                                | 20.12                             | 11153                          |
| New process 1    | 17.26                                | 16.98                             | 13215                          |
| New process 2    | 17.26                                | 16.88                             | 13293                          |

The number average molecular weight M is calculated based on the hydroxyl value, and the formula is as follows: \( M = \frac{56100 \times n}{\text{measured hydroxyl value}} \). Where \( n > 3 \) is polyol functionality. It can be seen from Table 3 that the theoretical hydroxyl value is inconsistent with the measured hydroxyl value. This is mainly due to the by-products produced during the synthesis process, which makes the measured hydroxyl value higher than the theoretical hydroxyl value. Therefore, a proper process route can be used to synthesize hydrophilic high molecular weight polyethers.
3.3. Comparison of Application Effects

The waterproof grouting material was made by the use of the two products polyether, and the performance list analysis is as follows: see Table 4.

| Process route       | Foaming time (s) | Water retention rate (%) | Remarks               |
|---------------------|------------------|--------------------------|-----------------------|
| Original process product 1 | 25               | 20                       | Good water retention  |
| New process product 1     | 22               | 20                       | Good water retention  |
| Original process product 2 | 30               | 25                       | water leakage         |
| New process product 2     | 28               | 25                       | Good water retention  |

It can be seen from Table 4 that different products have a significant impact on the water retention rate of the grouting material. It can be said that the polyether produced by the new process increases the water retention rate of the waterproof material by 25% and enhances the waterproof performance of the waterproof grouting material.

4. Conclusion

(1) In the process of synthesizing high molecular weight (relative molecular weight) hydrophilic polyether with KOH as a catalyst, the removal of impurities from the intermediate (4000 molecular weight) is critical, which will affect the quality of the later product. The molecular weight is less than 12,000, which is about 11150; while the molecular weight of the hydrophilic polyether produced by the new process is about 13,000, and the yield has also increased from 98.36% to 99.35%, which shows that the new process reduces the residual epoxide content.

(2) The hydrophilic polyether synthesized under the new process route has improved the water retention rate of the waterproof grout to 25% in application and improved its waterproof performance.

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