Synthesis and Properties of an EPEG Slump Retaining Polycarboxylic Acid Superplasticizer

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Abstract. In order to meet the special requirements for long-term slump retention of concrete under extreme conditions such as long distance transportation and super high-rise pumping construction, an EPEG slump retaining polycarboxylic acid superplasticizer (LT-PCE) was prepared by free radical aqueous solution polymerization at room temperature, which used ethylene glycol monovinyl polyoxyethylene ether (EPEG-2400), acrylic acid (AA), hydroxypropyl acrylate (HPA) as comonomers, β-mercaptoethanol as chain transfer agent, hydrogen peroxide and binary complexes of ferrous sulfate/formaldehyde sodium bisulfate as oxidation-reduction system. The molecular structure and mechanical properties of LT-PCE and commercial high performance EPEG polycarboxylic acid slump retaining agent (CA-PCE) were compared and analyzed. The results showed that LT-PCE was a polymer containing a variety of functional groups, and its molecular chain was dominated by ether macromonomers and supplemented by ester macromonomers. Compared with CA-PCE, LT-PCE has significantly higher conversion rate and more uniform molecular chain distribution, which can significantly improve the dispersion retention performance and mechanical strength of concrete.

Keywords: EPEG; conversion rate; molecular chain distribution; dispersion retention

1 Introduction

At present, the problem of too fast slump loss of mixed concrete is common in commercial concrete industry. Slump retaining polycarboxylic acid superplasticizer, as a functional polycarboxylic acid superplasticizer, is widely used in engineering practice to improve the dispersion and retention performance of concrete and solve the problem of slump loss of concrete[1-3]. However, due to the influence of extreme construction conditions such as long-distance transportation and super high-rise pumping construction, as well as the increasingly normal quality fluctuation of raw materials such as cement, mixed materials and sand in the commercial concrete industry in recent years, the mainstream slump retention polycarboxylic acid water-reducing agent products in the existing market cannot fully meet the ideal expectations of concrete slump retention

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performance[4-5]. Therefore, the development of a new generation of high-performance slump retaining polycarboxylic acid superplasticizer products through technological innovation is of great significance to the development of concrete industry.

Ethylene glycol monovinyl polyoxyethylene ether (EPEG), as a high-reactivity six-carbon polyether macromonomer, can greatly shorten the reaction time and improve the production efficiency, so it has a good promotion prospect in the field of polycarboxylic acid water reducer[6-7]. However, the current preparation process of EPEG slump retaining polycarboxylic acid superplasticizer mostly requires low temperature conditions and generally adopts refrigeration equipment for production, which increases energy consumption and production cost[8]. The development of synthesis technology of EPEG slump retaining polycarboxylic acid superplasticizer at room temperature is conducive to the transformation of concrete industry towards low-carbon and energy-saving direction.

Therefore, an EPEG slump retaining polycarboxylic acid superplasticizer (LT-PCE) was prepared by free radical aqueous solution polymerization at the temperature range of 10°C-45°C, which used EPEG with an average molecular weight of 2400 (EPEG-2400), acrylic acid (AA), hydroxypropyl acrylate (HPA) as comonomers, β-mercaptoethanol as chain transfer agent, hydro-gen peroxide and binary complexes of ferrous sulfate/formaldehyde sodium bisulfate as oxidation-reduction system. The carboxyl group contained in AA and the carboxyl group released slowly by hydrolysis of ester group contained in HPA can synergistically enhance the water reducing and slump retaining properties of LT-PCE. β-mercaptopropionic acid can regulate the molecular weight and molecular weight distribution of the synthesized LT-PCE. In addition, ferrous sulfate in the composite oxidation-reduction system can also play a catalytic role in the reaction and improve the conversion rate, because the Fe^{2+} generated by its hydrolysis can coordinate with the carboxyl groups contained in AA to enhance the reactivity of C=C.

2 Results

2.1 Optimization of LT-PCE Synthesis Process

$L_9(3^4)$ orthogonal test was designed to study the dispersion retention performance of LT-PCE samples for concrete by four factors, including the proportion of reducing agent (the amount of reducing agent to the total mass of EPEG macromonomer), the proportion of chain transfer agent (the amount of chain transfer agent to the total mass of EPEG macromonomer), the ratio of acid to ether (molar mass ratio), and the ratio of ester to ether (molar mass ratio). The level table of orthogonal factors was shown in Table 1, the range analysis of slump flow loss rate at 150 minutes was shown in Table 2.

Table 1. Level table of orthogonal factors

Level	Factor			
	Proportion of reducing agent(A)/‰	Proportion of chain transfer agent(B)/‰	Acid-ether ratio(C)	Ester ether ratio(D)
1	5.5	2.0	1.6	2.0
2	6.0	2.5	2.0	2.2
3	6.5	3.0	2.4	2.4

Table 2. Range analysis table of slump flow loss rate at 150 minutes

Sample number	A	B	C	D	Slump flow loss rate at 150 minutes/%
LT-PCE-01	1	1	1	1	35.29
LT-PCE-02	1	2	2	2	38.74
LT-PCE-03	1	3	3	3	35.09
LT-PCE-04	2	1	2	3	19.66
LT-PCE-05	2	2	3	1	5.98
LT-PCE-06	2	3	1	2	17.09
LT-PCE-07	3	1	3	2	33.62
LT-PCE-08	3	2	1	3	26.05
LT-PCE-09	3	3	2	1	14.29
k1	36.37	29.52	26.14	18.52	-
k2	14.24	23.59	24.23	29.82	-
k3	24.65	22.16	24.90	26.93	-
R	22.13	7.36	1.91	11.3	-

It was found that the optimal combination of reaction parameters was A2B2C3D1 according to Table 2. The concrete sample LT-PCE-05 (the proportion of reducing agent is 6.0‰, the proportion of chain transfer agent is 2.5‰, the molar mass ratio of acid to ether is 2.4, the molar mass ratio of ester to ether is 2.0) had the best dispersion retention performance, and slump flow loss rate at 150 minutes was as low as 5.98%. The influence degree of each factor on the slump retention performance of the sample is from strong to weak: proportion of reducing agent > ratio of ester to ether >proportion of chain transfer agent > ratio of acid to ether.

2.2 Comparative Analysis of Molecular Structure

2.2.1 FT-IR Comparative Analysis.

FT-IR was used to characterize the chemical bonds or functional groups of LT-PCE and CA-PCE. It could be seen from the Figure 1 that the positions of absorption peaks in the infrared spectra of LT-PCE and CA-PCE were basically similar, indicating that their functional group compositions were similar. Further analysis showed that the C-H stretching vibration peak of CH_3- and -CH_2- appeared at wavelength 2870cm^{-1}, the C=O stretching vibration peak of unsaturated ester or acid appeared at wavelength 1728cm^{-1}, and the stretching vibration peak of carboxylic acid group appeared at wavelength 1580-1650cm^{-1}. C-H plane bending vibration peaks of CH_3- and -CH_2- appeared at wavelengths around 1656cm^{-1}. In addition, 1247cm^{-1} was C-C stretching vibration peak, and 1104cm^{-1} was the stretching vibration peak of fat ether, indicating that LT-PCE and CA-PCE were polymers containing various functional groups. Therefore, the polymer chains of both are dominated by ether macromonomers and supplemented by ester macromonomers.

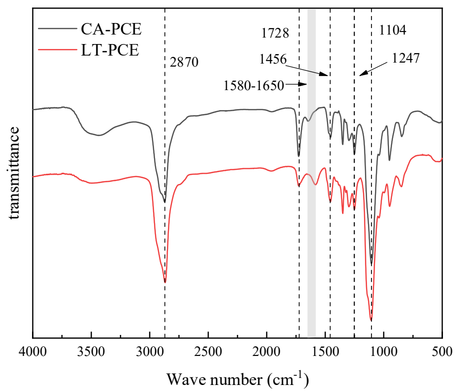

Fig. 1. Comparison of infrared spectra of LT-PCE and CA-PCE

2.2.2 GPC Comparative Analysis.

GPC was used to determine the relative molecular weight and distribution of LT-PCE and CA-PCE, the relative molecular mass and conversion rate were respectively obtained. The test results are shown in Table 3.

Table 3. Comparison of gel permeation chromatographic data between HS-PCE and CB-PCE

Sample code	M_n×10^4	M_w/M_n	M_z×10^5	Conversion rate/%
CA-PCE	3.2	2.80	2.37	85.83
LT-PCE	3.9	2.53	3.05	92.32

It was found that the conversion rate of LT-PCE was 92.32%, which was significantly higher than that of CA-PCE (85.83%), indicating that comonomers had higher reactivity in the complex reoxidation and reduction system composed of hydrogen peroxide and ferrous sulfate/sodium formaldehyde bisulfate. In addition, the molecular weight of LT-PCE was significantly higher than that of CA-PCE, while the molecular weight distribution index PDI (M_w/M_n) of LT-PCE was lower than that of CB-PCE. The above experimental results indicate that the EPEG polyether monomer has entered the polymer chain, and its molecular chain distribution is more uniform.

2.3 Comparative Analysis of Mechanical Properties of Test Concrete

The mechanical properties of concrete prepared by LT-PCE and CA-PCE were further compared and analyzed. The flexural strength strength and compressive strength of concrete at different ages prepared by block group (i.e. without adding polycarboxylate water reducing agent), LT-PCE and CA-PCE were respectively tested. The test results are shown in Table 4.

Table 4. Comparison of mechanical properties data of concrete

Sample code	Flexural strength/MPa			Compressive strength/MPa		
	3d	7d	28d	3d	7d	28d
Blank group	4.8	5.6	6.5	19.4	27.1	33.0
CA-PCE	5.3	6.0	7.1	22.1	27.8	35.0
LT-PCE	5.7	6.2	7.6	24.1	29.6	38.2

It was found that the flexural strength, compressive strength of concrete prepared with LT-PCE and CA-PCE were significantly higher than that of the blank group at different ages of concrete, because polycarboxylate water reducing agent could release more free water through adsorption-dispersion to improve the dispersion of cement slurry, and thus improve the mechanical strength of test concrete. Compared with CA-PCE, the 28d flexural strength and compressive strength of concrete added with LT-PCE are increased by 7.0% and 9.1%, respectively.

3 Conclusions

An EPEG slump retaining polycarboxylic acid superplasticizer (LT-PCE) was synthesized through a low-carbon and energy-saving room temperature process, which could significantly improve the dispersion retention performance and mechanical strength of concrete, thereby meeting the demand for concrete slump retention performance in construction engineering. Compared with commercially available high-performance EPEG polycarboxylate slump maintainer (CA-PCE), LT-PCE has higher conversion rate and more uniform molecular chain distribution, which can significantly improve the flexural strength and compressive strength of test concrete.

However, the adaptability of LT-PCE to extreme concrete raw materials such as machine sand with high mud and powder content needs to be studied.

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