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Carbohydrate Polymers 71 (2008) 80–84

Carbohydrate Polymers

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The study on the synthesis and action mechanism of starch succinate half ester as water-reducing agent with super retarding performance

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Received 13 February 2007; received in revised form 27 April 2007; accepted 14 May 2007
Available online 21 May 2007

Abstract

In this paper, starch succinate half ester (SSHE) was synthesized by a simple method and used as water-reducing agent. The effects of both dosage of SSHE and storing time on the fluidity of cement paste and ζ-potential of cement particles were studied in comparison with that of carboxymethyl starch (CMS) whose dispersion ability mainly depends on steric hindrance effect. The results indicate that SSHE is a novel kind of water-reducing agent with super retarding performance. The main dispersion capacity of SSHE comes from steric hindrance repulsion rather than electrostatic repulsive force and the super retarding performance results from the introduction of reactive succinate half ester groups in acid form.

Keywords: Starch succinate half ester; Water-reducing agent; Dispersing mechanism; Super retarding performance

1. Introduction

In building industry, the mixture of water-reducing agent and retarder always being used together for massive concrete, rolled concrete and pump concrete to improve the working efficiency of concrete by keeping the fluidity of cement for a long time. They were also used under special construction conditions to prolong setting time of concrete, such as hot climate, line-haul or extended storing (Akin & Yesim, 2004; Alshamsi, 1994; Tzouvalas, Dermatas, & Tsimas, 2004). However, many conventional water-reducing agents are condensation products of formaldehyde (such as naphthalene sulfonated formaldehyde condensates, sulfonated melamine formaldehyde polymers and aminosulfonic acid series), they may accidentally or intentionally release formaldehyde into environment and result in undesirable environmental effects. Furthermore, as new-generation water-reducing agent, the polycarboxylate-type water-reducing agent would face the problem of short resources in near future for non-regenerate ability of crylic acid derived from petroleum.

With the development of new products and materials, especially those which are non-petrochemicals and based on renewable organic resources, using innovative sustainable process is nowadays of increasing interest and deserves the attention of both academic and industrial research. Many studies on water-reducing agents based on the starch or cellulose were carried out in the last decades, such as carboxymethyl starch(CMS), sulfonic starch and so on (Cheng & Hou, 2006; Khan, Riaz, Ahmed, Mariotti, & Paolo, 1997; Reddy & Eoff, 2004; Vieira, Klemm, & Einfeldt, 2005). Based on the previously studies on CMS whose main dispersing mechanism came from steric hindrance repulsion, a novel kind of water-reducing agent with super retarding performance-starch succinate half ester (SSHE) was designed and synthesized by a simple method, using starch and succinic anhydride as reagents. The application performances of SSHE as water-reducing

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doi:10.1016/j.carbpol.2007.05.020

agent were studied in comparison with that of CMS, and the action mechanism of SSHE was obtained based on the experimental results.

2. Experimental

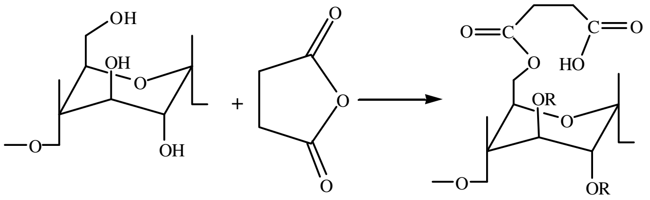
2.1. Materials

A commercially manufactured ordinary Porland cement 32.5R came from Dalian No. 3 Cement Plant in PR China. National cornstarch with 83% amylopectin (Shenyang Wanshun Starch Co., LTD, Shenyang, PR China) was used to prepare SSHE. Succinic anhydride was of analytical reagent quality and purchased from Shenyang reagent No. 1 factory (Shenyang, PR China). CMS (DS = 0.51) used in this study was synthesized according to the method of Vieira (Vieira et al., 2005).

2.2. Preparation of SSHE

SSHE was prepared according to the method of Minkema with some modifications (Minkema, 1959). The starch with 12% moisture content was mixed with succinic anhydride in grinder mixer for a certain time and put in a crucible with lid. Heated in a vacuum oven for 4 h at 100 °C, the products were extracted by Soxhlet extractor for 24 h with acetone as solvent and dried in vacuum oven at 50 °C.

The above reaction process may be described by the followings scheme:



The degree of substitution (DS) of succinic anhydride was determined according to the method of Wurzburg (Chong, Xing, Phillips, & Corke, 2001).

2.3. Structure analysis of SSHE

Fourier transform-infrared (FT-IR) spectra were obtained from KBr pellets of native starch and SSHE with a Thermo Nicolet FT-IR Spectrometer (Model-Nexus 470FTIR).

GPC (Waters 1525/2414, US) with column (Waters 150c) was used for determination of the molecular weight of SSHE (pretreated to be water-soluble). The solution of sodium nitrate was used as eluant, and the flow rate was 0.8 ml/min. Calibration was carried out with polyethylene glycol (provided by Waters) standards giving an optimum linear function.

The thickness of the adsorbed layer of water-reducing agent on the surface of cement particles was determined by X-ray photo spectroscopy technology (MK II, UK). Cement was dipped for 15 min in solutions of water-reducing agent with concentration of 10 g/ml, with the ratio of water/cement was 0.5:1, and then dipped in methyl alcohol to stop hydration. Carbon is characteristic element that can distinct cement surface from admixture. Hence, adsorption peak strength of C_{1s} on cement surface at different etched depths, before and after adsorption, were measured by using XPS aid of Ar-ion etching analyzer. When peak strength was equal to that of plain cement (before adsorption), the etched depth was considered to be the thickness of the adsorption layer.

2.4. Fluidity of cement paste

A certain amount of water-reducing agent was added to water in advance. And then cement was added to solution of water-reducing agent with a water/cement ratio of 0.35. The fluidity of cement paste was evaluated by pullout spread of a sample from a flow cone specified according to GB8077-87. The maximum diameter of the spread sample and the maximum width perpendicular to that diameter were measured and the average of these two values was defined as the flow value.

2.5. ζ-potential measurement

A certain amount of cement was added to the solution with certain concentration of water-reducing agent according to a solid/liquid ratio of 0.0025. After mixing for 5 min by blender, the mixture was separated by centrifuge. Then the supernatant was added into electrophoresis pool and analyzed by ζ-potential analyzer (Brookhaven, US). The average of ten experimental potential data was regarded as ζ-potential of cement particles.

3. Results and discussion

3.1. Structure analysis of SSHE

The molecular structure of SSHE confirmed by IR spectrum is shown in Fig. 1. In comparison with IR spectrum of starch in Fig. 2, IR spectrum of SSHE had a new and strong absorption peak located at 1727 cm^{-1}. It was the characteristic adsorption of C=O which indicated that succinic anhydride was introduced to the cornstarch molecule in acid form.

The weight-average molecular weight and the degree of substitution of succinic anhydride of SSHE was determined to be 9.83×10^5 and 0.50 by GPC and method of Wurzburg, respectively.

3.2. Effect of water-reducing agents on the fluidity of cement paste

The fluidity and fluidity loss of cement paste are important application performance parameters of water-reducing

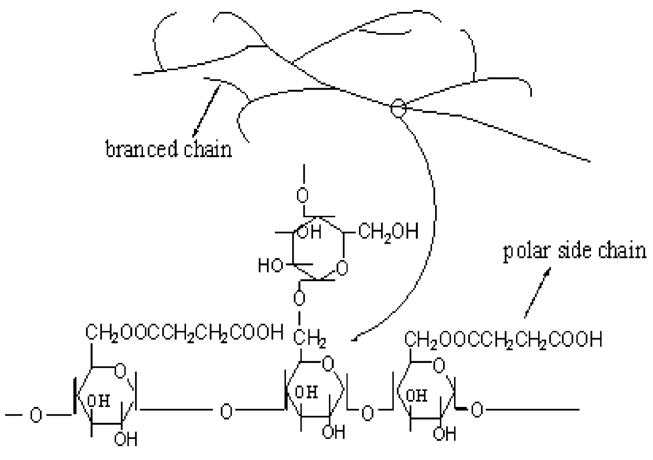


Fig. 1. The molecular structure of SSHE.

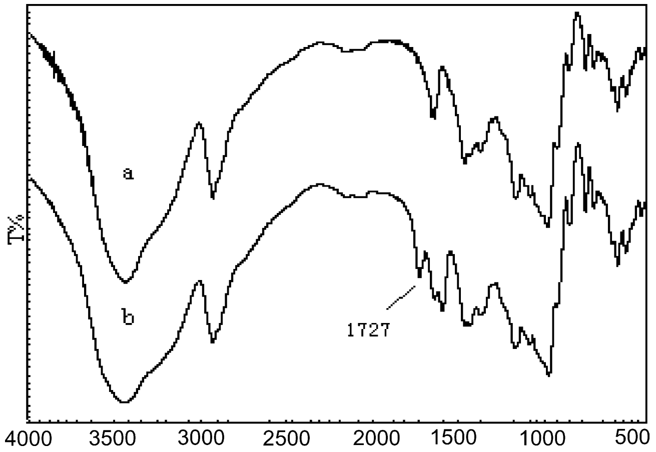


Fig. 2. IR spectra of starch (a) and SSHE (b).

agent. For evaluation of the applied capability of SSHE, the relationship between the fluidity of cement paste and dosage/storing time of SSHE were studied and compared with that of CMS.

3.2.1. The effect of storing time on the fluidity of cement paste

Fig. 3 shows the relationship between storing time and fluidity of cement paste. It can be seen that the maximal fluidity of CMS was its initial fluidity, and it reduced from 265 to 251 mm within the former 120 min, the loss rate of fluidity was 5.3%. Differently, with the process of hydration, the fluidity of cement paste with SSHE firstly increased from 226 mm to its maximal fluidity 276 mm, and then decreased to 269 mm, the loss rate of fluidity was just 2.5% within the latter 120 min. The loss rate of fluidity was lower than that of CMS during the same storing time, which indicates that the dispersion stability of SSHE was superior to that of CMS.

Because the fluidity can directly inflect the dispersing ability of water-reducing agent, it can be known from Fig. 3 that the dispersion capacity of SSHE was weaker than that of CMS at the beginning, but it would enhance with the prolongation of storing time and exceeded the dispersing ability of CMS.

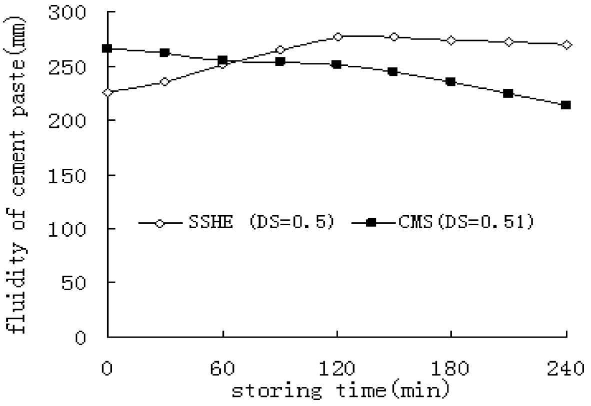


Fig. 3. The storing time dependency of the fluidity of cement paste.

3.2.2. Effect of dosage of water-reducing agent on the initial and maximal fluidity of cement paste

Since the maximal fluidity of cement paste with SSHE appeared after storing for 120 min. The effects of dosage of SSHE on initial and maximal fluidity of cement paste were investigated in Fig. 4.

As shown in Fig. 4, the water-reducing agent could significantly improve the fluidity of cement paste. The fluidity of cement paste with CMS increased from 65 to 255 mm when the dosage was increased from 0% to 3.0%. The initial and maximal fluidity cement paste with of SSHE increased from 65 to 233 and 275 mm, respectively, within the same variety of dosage. With the increase of dosage of CMS and SSHE, the fluidity of cement paste did not increase any more when the adsorption amount exceeded 8 and 6 mg/g, respectively. Thus, the optimal dosage of CMS and SSHE was 0.8% and 0.6%, respectively.

From the contrastive data of applied performance of CMS and SSHE above, a conclusion can be made that SSHE is a kind of water-reducing agent as CMS, but the

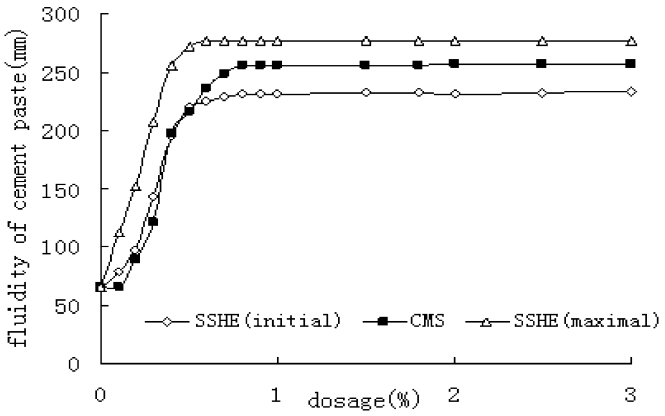


Fig. 4. Effect of water-reducing agent addition on the fluidity of cement paste.

fact that the dispersing ability of SSHE increased with prolongation of storing time means their action mechanism was different.

3.3. The discussion of action mechanism of SSHE

3.3.1. The study of retardation mechanism of SSHE

The molecular structure of CMS was shown in Fig. 5. It can be known that the carboxymethyl groups exist in the form of sodium salt which makes CMS water-soluble. It would dissolve and ionize carboxyl groups very soon when it was added to water. However, the succinate groups were introduced into starch in acid form and result in insolubility of SSHE. But under alkaline conditions, —COOH of SSHE would converted to —COO$^-$ and dissolve slowly.

To study the behavior of succinic group in cement paste, the relationship between storing time and ζ-potential of cement particles was investigated. It can be seen from Fig. 6 that ζ-potential of cement particles with CMS kept about −24.00 mV for 240 min. Whereas, the ζ-potential of cement particles with SSHE firstly increased from −20.01 to −23.90 mV, and after 120 min, it kept invariable in our experiments.

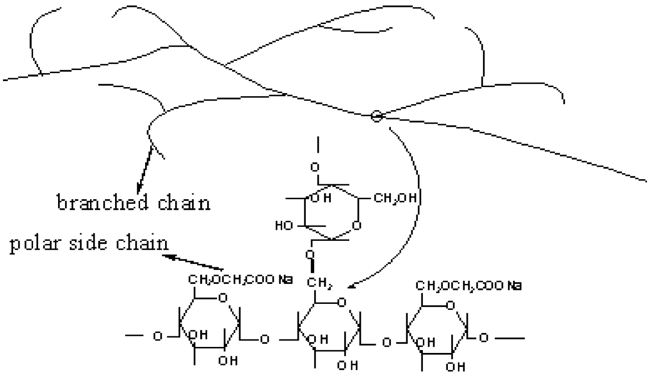


Fig. 5. The molecular structure of CMS.

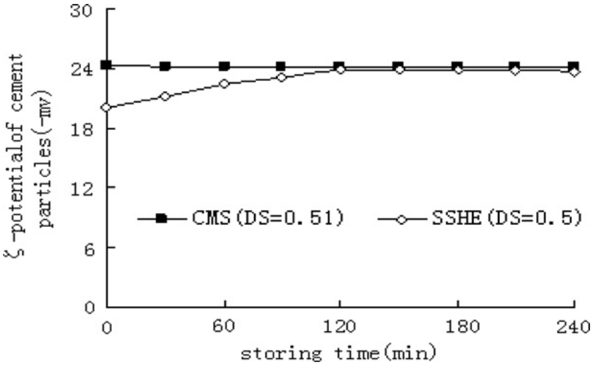


Fig. 6. Effect of storing time on ζ-potential of cement particles.

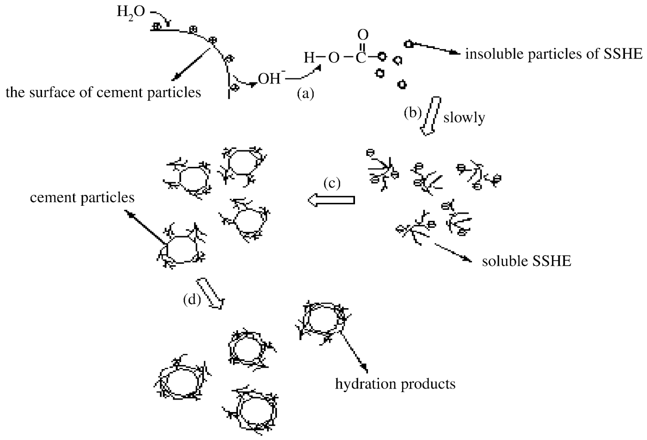


Fig. 7. Retarding mechanism of SSHE.

Carboxyl play a very important role in water-reducing agent (Peng & Qu, 2005; Reddy & Eoff, 2004; Takeshi & Yoshiya, 1990). CMS would expose —COO$^-$ in water at once due to its solubility, whereas SSHE could release —COO$^-$ only under alkaline conditions. When the cement was added to the mixture of water and SSHE, the cement particles would produce OH$^-$ under effect of H_2O and present positive potential, then OH$^-$ would attack the bond of H—O of SSHE and produce free —COO$^-$ as shown in Fig. 7(a) and (b). Owing to the excellent permeability of starch particles, succinic groups distributed on their surface and inside. The succinic groups on the surface of starch particles were tend to be attacked by OH$^-$ which made the outer layer of particles dissolve firstly, and then exposed succinic groups could react with OH$^-$, the whole process was slowly, being like "erosion". Thus, with the progress of hydration, there were more and more soluble anions of SSHE "anchored" on the cement surface by complex action between the carboxyl groups and Ca^{2+} and steric hindrance was produced due to the branched and polar side chains protruded in the liquid phase (Fig. 7(c)). As a result, the fluidity of cement paste and ζ-potential of cement particles with SSHE increased at the beginning of cement hydration and kept stable for a long time.

3.3.2. The study of dispersing mechanism of SSHE

For water-reducing agents, both electrostatic repulsive force and steric hindrance effect contributed to their dispersing capacity (He, Zhan, & Song, 2002; Peng & Qu, 2005). To study the main dispersing mechanism of SSHE, the relationship between the concentration of water-reducing agent and ζ-potential of cement particles was investigated.

As shown in Fig. 8, ζ-potential of CMS changed from 15.00 to −27.34 mV with its concentration increasing from 0 to 20 g/L. The initial and maximal ζ-potentials of SSHE increased from 15.00 to −22.77 and 26.06 mV, respectively, within the same variety of concentration. The reason for this fact was the adsorption of CMS and SSHE changed the charge distribution of double-electrical layer of cement surface. Fig. 8 further shows that both initial and maximal ζ-potentials of CMS was higher than that of SSHE at the same concentration, which indicated that the electrostatic

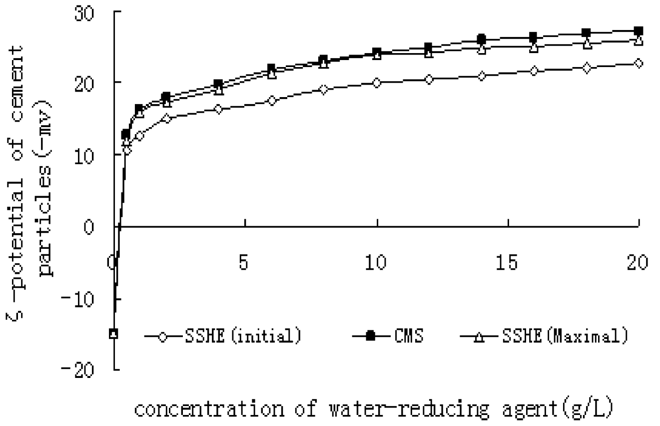


Fig. 8. ζ-potential of water-reducing agents with different concentration.

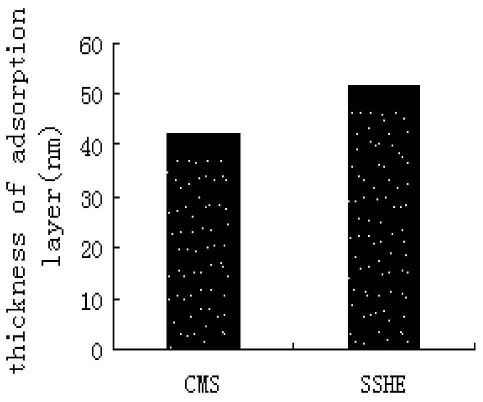


Fig. 9. The thickness of adsorption layer of water-reducing agent.

repulsion force among cement particles adsorbing CMS was higher.

Based on the experimental facts that the electrostatic repulsion force among cement particles adsorbing SSHE was less than that of CMS, whereas its maximal fluidity was higher, a conclusion can be made that the main dispersing ability of SSHE came from steric hindrance effect rather than electrostatic repulsive force.

As shown in Fig. 9, the thickness of the adsorption layer of CMS and SSHE was 42.2 and 51.6 nm, respectively. The thickness of the adsorption layer of SSHE was 9.4 nm thicker than that of CMS, which can be explained as follows: the length of polar side chain contributed to the steric hindrance of water-reducing agent molecules. That is to say, the steric hindrance repulsion among cement particles with SSHE is higher than that of CMS, so cement particles need more time to cover the SSHE adsorbing on it by hydration products. It is also the reason for superior dispersing ability and stability of SSHE to that of CMS (Figs. 3 and 4).

4. Conclusions

(1) SSHE was synthesized by a simple method and proved to be a novel kind of water-reducing agent with super retarding performance.
(2) The main dispersing mechanism of SSHE comes from steric hindrance repulsion rather than electrostatic repulsion force. The length of polar side chain contributed to the steric hindrance repulsion of water-reducing agent. Therefore, steric hindrance repulsion of SSHE was stronger due to longer polar side chain which resulted in better dispersing capacity and stability for SSHE when compared with CMS.
(3) The super retarding performance of SSHE is attributed to the introduction of succinate groups in acid form. Under alkaline conditions, anions of SSHE were released slowly and steric hindrance repulsion was produced by adsorbing on the surface of cement particles. The continuous growth of steric hindrance repulsion among cement particles was the cause of super retarding performance of SSHE.

Acknowledgement

We are grateful to the China National Nature Science Foundation (No. 20576015) for financial support of this research.

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