

Dispersing agents for cement based on modified polysaccharides

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Abstract

In this paper, starch and cellulose anionic derivatives are investigated with the objective to obtain new biodegradable dispersing agents for mortar and concrete mixtures. For that purpose, different starch and cellulose materials were partially depolymerized, giving *limit*-dextrins with DP_w 50–300 and *level-off*-DP (LODP) celluloses with DP_w 30–150. The subsequent hydroxyethylation, carboxymethylation, or sulfoethylation of these partially hydrolyzed polysaccharides occurred in 2-propanol, whereas the sulfation was carried out in dimethyl sulfoxide. The molecular weights of the samples were characterized by means of GPC, the chemical structure and functionalization pattern by means of NMR spectroscopy, and the rheological behavior of the sample solution was also determined. The dispersant products were tested as mortar and concrete admixtures. As a result, it could be shown that partially hydrolyzed and sulfoethylated amylo maize starch (70% amylose) provides the most efficient dispersing agent. The results were comparable to those of superplasticizers (i.e., polycarboxylate ethers). © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

It has become possible by a new generation of plasticizers, the so-called superplasticizers, to adjust the workability of the concrete in terms of both flowing behavior and plasticity, as well as cohesion and viscosity. The desired workability is obtained both by the action of the new plasticizer and by the complete encapsulation of the aggregate grains with a paste consisting of a mixture of fine grains and water.

The most used dispersing agents, especially for mortar and concrete, are water soluble products such as sulfonated naphthalene formaldehyde condensate, sulfonated melamine formaldehyde condensate [1], and polymer compounds like polycarboxylate [2]. These superplasticizers are not biodegradable. In contrast, biopolymers like cellulose or starch

are renewable raw materials and could be an ecological alternative to the petrochemical polymers.

Various polysaccharides have been used in concrete as viscosity modifying agents, i.e., pullulan, curdlan, dextran as microbial exopolysaccharides, alginates, agar as marine polysaccharides, and locust bean gum as vegetable exudates [3–5]. Polysaccharide derivatives like hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, or various starch esters and ethers have been applied as thickening and water-retention agents. These polysaccharides derivatives show hitherto the disadvantage that their high molecular weight has as consequence a high viscosity already at a low concentration in water and are not appropriate to act as dispersing agents.

Therefore, our study was focused on low molecular weight derivatives which should be cold-water-soluble and their solutions of low viscosity.

This paper reports about the preparation of low molecular weight carboxymethyl cellulose, carboxymethyl hydroxyethyl cellulose, sulfoethyl starch, carboxymethyl starch, and starch sulfate from partially hydrolyzed

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commercial cellulose or starch. The dispersing effect of the substances was determined by means of mortar and concrete tests and was compared with conventional cement dispersants.

2. Experimental

2.1. Materials

High amylo maize starch with 70% amylose content (Hylon VII) and waxymaize starch with 1% amylose content (Amioca Powder TF) were received from *National Starch*. As cellulose raw materials, viscose and spruce sulfite pulp were used. All other reagents are commercially available and were used without further purification.

2.2. Partial hydrolysis of starch and cellulose

Starch (25 g) was suspended in 100 ml ethanol with 1 ml of concentrated HCl, and the mixture was stirred at RT for 24 h (method A). Starch (25 g) was suspended in 100 ml *n*-butanol with 20 ml of concentrated HCl, and stirred at RT for 72 h (method B). The products were filtered, neutralized with dilute NaOH solution, washed with cold water, and dried under KOH at 50 °C in vacuum. The obtained molecular weights of the partially acid-hydrolyzed starches (so-called *limit-dextrins* [6,7]) are summarized in Table 1 and Fig. 1.

Cellulose (100 g) was suspended in 1 l 5% HCl solution and stirred at 100 °C for 1 h. After cooling, the cellulose

powder was filtered, washed until the pH 7 was reached, and dried. The DP_w of the so-called *level-off-DP* (LODP) celluloses [8–10] are summarized in Table 2.

The *limit-dextrins* and *level-off-DP* celluloses were peracetylated according to [11].

2.3. Sulfoethylation of starch

Limit-dextrins (10.0 g) was suspended in 270 ml 2-propanol, and 20.0 g (1.2 moleq.) of a 50% (w/w) sodium vinylsulfonate solution [freshly obtained from a 30% (w/w) solution by evaporation] was added dropwise under argon atmosphere. The reaction mixture was stirred at RT for 15 min, and 17.1 g (2.3 moleq.) of powdered NaOH was dispersed in the mixture. After stirring at 75 °C for 3.5 h, the mixture was cooled and filtered. The product was dissolved in 100 ml distilled water, neutralized with diluted HCl, dialyzed against water, and freeze-dried. The degree of substitution (DS_{SE}) of sulfoethyl starch (SES) was determined by elemental analysis. DS_{SE} values higher than 0.5 were reached by a second sulfoethylation (Table 1).

2.4. Sulfation of starch

Starch (5.0 g) or *limit-dextrins* was suspended in 25 ml dimethylsulfoxide and stirred for 15 min at 80 °C giving a clear solution. The solution was allowed to cool down, and 9.5 g (2 moleq.) of an *N,N*-dimethylformamide/sulfate complex was added at RT. After stirring for 3 h, the solution was diluted with 50 ml water and neutralized with aq. NaOH solution. The product was dialyzed against water and freeze-dried. The degree of sulfation (DS_S) was estimated by elemental analysis (Table 1).

2.5. Carboxymethylation of limit-dextrin (general method)

Limit-dextrins (15.0 g) was suspended in 350 ml 2-propanol, and under stirring 55 g of 33% aq. NaOH solution was added dropwise during 30 min at RT. The stirring was continued for 1 h, and 17.5 g of monochloroacetic acid was then added during 30 min. After stirring for 5 h at 55 °C, the reaction mixture was filtrated, neutralized with aq. acetic acid, washed three times in 90% methanol, and finally dried. The degree of carboxymethylation (DS_{CM}) was determined according to Ref. [12].

2.6. Carboxymethylation of LODP-cellulose

Following the general method and using an 8% LODP-cellulose/2-propanol suspension, under argon atmosphere, with 3 moleq. of 20 M aq. NaOH and 1.5 moleq. chloroacetic acid, reacting at 70 °C for 2 h, CMC with DS_{CM} of 1.44 was obtained. In a second carboxymethylation, a DS_{CM} of 1.79 was reached (Table 2).

Table 1

Mortar test results and characterization of starch derivatives and their comparison with commercial products

Starting starch material	Starch	DS ^b	Viscosity ^c (Pa s)		Air	Spread
Amylose (%)	DP _w ^d	derivative ^a	γ ₁ ^c	γ ₃₀₀ ^c	(%)	(cm)
1	500	SES	0.45	0.070	0.050	5.7 12.0
70	1600	SES	0.56	0.230	0.120	2.7 11.3
70	70	SES	0.35	0.020	0.015	2.6 25.1
70	70	SES	0.43	0.020	0.015	2.3 27.0
70	234	SES	0.45	0.030	0.027	4.0 28.0
70	56	SES	0.55	0.010	0.008	2.1 30.0
70	1600	SS	1.17	0.210	0.150	6.4 14.3
70	56	SS	0.85	0.060	0.009	4.1 22.4
70	70	SS	0.82	0.015	0.009	3.8 23.9
1	2600	CMS	1.53	0.500	0.114	7.7 8.5
70	122	CMS	0.80	0.090	0.080	6.0 16.0
70	245	CMS	1.32	0.023	0.020	4.6 17.3

^a SES: sulfoethyl starch; SS: starch sulfate; CMS: carboxymethyl starch.

^b Degree of substitution.

^c Twenty percent (w/w) aqueous solution.

^d Degree of polymerization, calculated from the molecular weight M_w of the peracetylated *limit-dextrins*. The samples with DP_w<1600 were partial depolymerized with acid hydrolysis in 1-butanol.

^e γ₁ and γ₃₀₀ are the shear rates at 1 and 300 s⁻¹, respectively.

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