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Cement and Concrete Research 35 (2005) 883–890

Cement and Concrete Research

Dispersing agents for cement based on modified polysaccharides

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Received 23 January 2003; accepted 21 September 2004

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 amylomaize starch (70% amylose) provides the most efficient dispersing agent. The results were comparable to those of superplasticizers (i.e., polycarboxylate ethers).

Keywords: Starch; Cellulose; Sulfoethylation; Carboxymethylation; Dispersing agent

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 for 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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doi:10.1016/j.cemconres.2004.09.022

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 amylomaize 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 1and 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.

Table 1
Mortar test results and characterization of starch derivatives and their comparison with commercial products

Starting starch material		Starch derivative[a]	DS[b]	Viscosity[c] (Pa s)		Air (%)	Spread (cm)
Amylose (%)	DP_w[d]			γ_1[e]	γ_{300}[e]		
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] γ_1 and γ_{300} are the shear rates at 1 and 300 s^{-1}, respectively.

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 mono-chloroacetic 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).

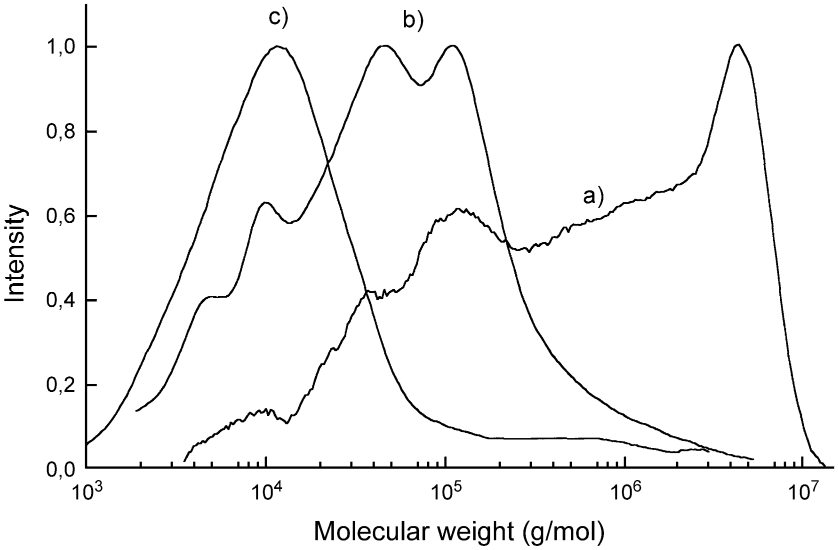

Fig. 1. Molecular weight distribution of different starches in dependence on the kind of acid hydrolysis: (a) waxy maizestarch in ethanol (——), (b) waxy maizestarch in butanol (· · · · · ·), and (c) amylomaize starch in butanol (-----).

2.7. Hydroxyethylation and subsequent carboxymethylation of cellulose

LODP-cellulose (146 g) was suspended in 1.3 l 87% (w/w) aq. *t*-butanol in a pressure vessel under argon atmosphere and alkalized with 45 ml (1.0 moleq.) 20 M aq. NaOH solution at 50 °C for 1 h. Gaseous ethylene oxide (200 g; 5.0 moleq.) was added to the reaction mixture during 30 min at RT. The slurry was heated at 70 °C for 3 h, cooled and neutralized with acetic acid. The cellulose product was precipitated in acetone, dissolved in distilled water, dialyzed against water, and finally freeze-dried. The molar substitution of hydroxyethylether (MS_{HE}) was determined by ^{1}H-NMR spectroscopy after peracetylation.

The HEC was carboxymethylated following the general method, using a 12% HEC (MS_{HE}=3.57)/2-propanol suspension, with 1 moleq. of 20 M aq. NaOH and 0.5 moleq. chloroacetic acid and finally reacted at 70 °C for 3 h. After isolation and neutralization, the product was dialyzed against water and freeze-dried. Using 2 or 3 moleq. of NaOH and 1.0 or 1.5 moleq. chloroacetic acid, CMHEC with a higher degree of substitution was obtained (Table 2).

2.8. Measurements

The sulfur content was determined by sulfur analysis on a CHNS 932 Analyzer (LECO).

The ^{1}H-NMR spectra were recorded on a Bruker DRX 400 spectrometer in $CDCl_3$ at 50 °C. An estimation of the MS_{HE} could be done from ^{1}H-NMR spectra [13].

A JASCO GPC with refractive index and two columns (type PHENOGEL 10 10^5Å and PHENOGEL 10 10^3Å) was

Table 2
Spread and characterization of LODP-cellulose derivatives and conventional cement dispersants

Starting cellulose material	DP_w[f]	Cellulose derivative[a]	MS_{HE}[b]	DS_{CM}[c]	Viscosity[d] (Pa s)		Air[e] (%)	Spread (cm)
					γ_1[g]	γ_{100}[g]		
Spruce sulfite pulp	139	CMC	–	1.44	0.83	0.78	3.9	14.5
Viscose	38	CMC	–	1.79	0.02	0.01	3.4	19.3
Spruce sulfite pulp	77	CMHEC	3.57	1.47	3.20	2.05	3.9	17.8
Spruce sulfite pulp	77	CMHEC	3.57	0.45	3.03	2.30	3.7	19.3
Spruce sulfite pulp	139	CMHEC	3.06	0.79	2.02	1.85	3.0	21.0
Viscose	38	CMHEC	2.15	0.96	0.02	0.01	4.1	21.3
MS02							3.3	31.0
Liquiment N							5.1	21.4

[a] CMC: carboxymethyl cellulose; CMHEC: carboxymethyl hydroxyethyl cellulose.
[b] Molar substitution of hydroxyethyl cellulose.
[c] Degree of substitution of carboxymethyl cellulose.
[d] Twenty percent (w/w) aqueous solution.
[e] Defoamed with 75 μl degreasol SD20.
[f] Degree of polymerization, calculated from the molecular weight M_w of the peracetylated LODP-cellulose obtained after aqueous HCl treatment.
[g] γ_1 and γ_{100} are the shear rates at 1 and 100 s^{-1}, respectively.

used for determination of the molecular weight of all peracetylated *limit*-dextrins and LODP-celluloses. As eluant chloroform was used, and the flow rate was 1.0 ml/min. Calibration was carried out with polystyrene standards giving an optimum linear function between the lowest (374 Da) and highest standard (2570 kDa).

Viscosity of diluted solutions was measured at 25.0±0.1 °C with a cylinder geometry and rotational rheometer (RheoStress RS 150, Haake) using 7 ml of a 20% (w/w) sample solution.

2.9. Mortar test

The dispersing properties of the starch and cellulose derivatives in mortar were determined according to DIN 1164/ EN-196. A Mixture of 450 g Portland cement (Mannersdorf 375 H), 450 g fine norm sand, 900 g coarse norm sand, and 225 g of a 0.9% (w/w) polysaccharide solution was prepared. The spread and the air content of the used standards Liquiment N (naphthalenesulfonate formaldehyde polycondensates) and MS02 (polycarboxylate ethers) were measured (Table 2).

2.10. Concrete test

The dispersing properties of the polysaccharide derivatives in concrete (10 and 40 min after mixed start) as well as the compressive strength of the concrete after 24 h were measured according to DIN 1164/EN-196. The concrete screening mixture was composed of 320 kg cement (Kiefersfelden 42,5 R) and 1972 kg addition (sieve line A/B 32) using a mixture composition of kg/m^3. As standard Melment L10 (melaminesulfonate formaldehyde polycondensates) and Glenium 51 (polycarboxylate ethers) were used.

3. Results and discussion

The dispersing properties of a polymer depends on many factors, in particular, the molecular weight and the polymer ionic groups. Recent works show that copolymers based on unsaturated dicarboxylacid derivatives and poloxyalkylene glycol alkenyl ethers, with a DP lower than 200 and a molecular weight between 1000 and 100 000, show a suitable flow behavior [14]. Naphthalenesulfonate formaldehyde and melaminesulfonate formaldehyde polycondensates are also well known as good dispersing agents [15,16]. Therefore, to design dispersing materials based on polysaccharides, it is essential that the biopolymers possess molecular weights in the range of 10.000 g/mol and are substituted with ionic groups like carboxyl and sulfate derivatives. These relatively low molecular weights could be obtained by well-known acid hydrolytic procedures of commercial starch [6,7] and cellulose [8–10]. The partial depolymerization of starches depends on the source of the native starch, i.e., the amylose/amylopectin content, since it is composed mainly of a mixture of an essentially linear amylose and up to 30–99% branched amylopectin, as well as on the reaction conditions of acid hydrolysis. The partial hydrolysis of cellulose gives so-called LODP-celluloses with relatively uniform DP$_w$, whose value depends on the type of cellulosic material. The LOPD-cellulose represents in its molecular dimensions microcrystals, microfibrils of cellulose [17].

3.1. Starch

To obtain a well-defined starch material with a DP$_w$ around 100, starches with different amylose contents were used: Hylon VII with 70% amylose, Amioca powder with 1% amylose, so as two different hydrolyses methods were

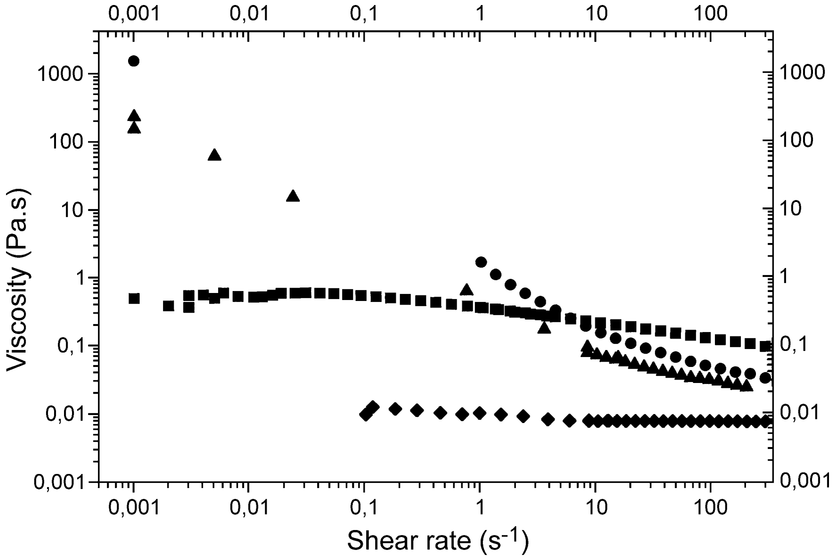

Fig. 2. Rheogram of 20% (w/w) aqueous solutions of sulfoethyl *limit*-dextrins with DS$_{SE}$=0.30 (■); 0.36 (●); 0.38 (▲); and 0.55 (◆).

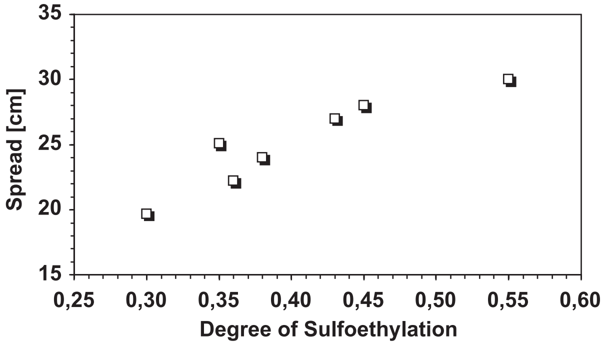

Fig. 3. Spread of different sulfoethyl *limit*-dextrin as function of the sulfoethyl content.

applied. The hydrolyzed samples were subsequently peracetylated, and their molecular weights were determined by means of GPC. The GPC-chromatogram (Fig. 1) shows that the hydrolyzed Amioca powder starch by method b (curve b, M_w=1.30×10^5) reached a higher depolymerization degree than by the method a (curve a, M_w=1.65×10^6). The many molecular weight maxima and shoulders in the low molecular weight area indicate that the product does not have a uniform distribution of the molecular weight. Under these conditions, the very high-molecular and branched amylose-poor starches could not be hydrolyzed to the required molecular weight range of dispersants, due to the fact that the DP_w is higher than 500. In contrast, the partially hydrolyzed Hylon VII starch by method b (curve c, M_w=2.03×10^4) shows the desired uniform molecular weight distribution and a DP_w about 70. The following treatment of amylose-rich starch with 3.6% HCl-containing 1-butanol resulted in depolymerization to molecular weights lower than 40.000 g/mol (DP_w<250; Table 1). The partially hydrolyzed starch samples—the so-called *limit*-dextrins—were insoluble in cold water. After introduction of anionic groups, like carboxymethyl, sulfoethyl, or sulfates, the *limit*-dextrins became water soluble. The 20% (w/w) aqueous partially hydrolyzed starch (DP_w≤500) derivatives solutions show lower viscosities (Table 1) when compared with the native starch (DP_w≥1600). In the case of the partial hydrolyzed sulfoethyl starch derivatives, their 20% aqueous solutions show nearly Newtonian behavior (Fig. 2).

The amylose-poor starch derivatives with or without acid treatment show no good dispersing properties. In most of the cases, it was not possible to obtain a 10% (w/w) solution due to their thickening behavior. Nevertheless, two samples could be intensively tested, but showed a small spread size (8.5 and 12.0 cm; Table 1). Therefore, our work was focus on amylose-rich starch. The dispersing behavior, i.e., the spread size in the mortar test, of the amylose-rich starch derivatives depends strongly on the DP_w value. This can be seen, in particular, on the sulfoethyl starch (SES) derivatives and starch sulfate (SS) derivatives. The products with DP_w values between 230 and 50 shows spread size higher than 22.4 cm. On the other side, the derivatives with a higher molecular weight (DP_w≥500) show a spread size lower than 14.3 cm. The dispersing behavior depends also on the kind of the introduced anionic group and the respective DS value. The salt tolerance against electrolytes in aqueous solution is another important factor. The SES and starch sulfates are well salt-tolerating starch derivatives, whereas carboxymethyl starches (CMS) show structural instability against electrolytes (results are not shown), thus the CMS shows spread size values below 18.0 cm. The conventional cement dispersants reach under the same condition spread size values of 21.4 cm (Liquiment N) and 31.0 cm (MS02). In our study, the SS with low molecular weight and DS value of 0.8 shows spread size higher than 22.0 cm,

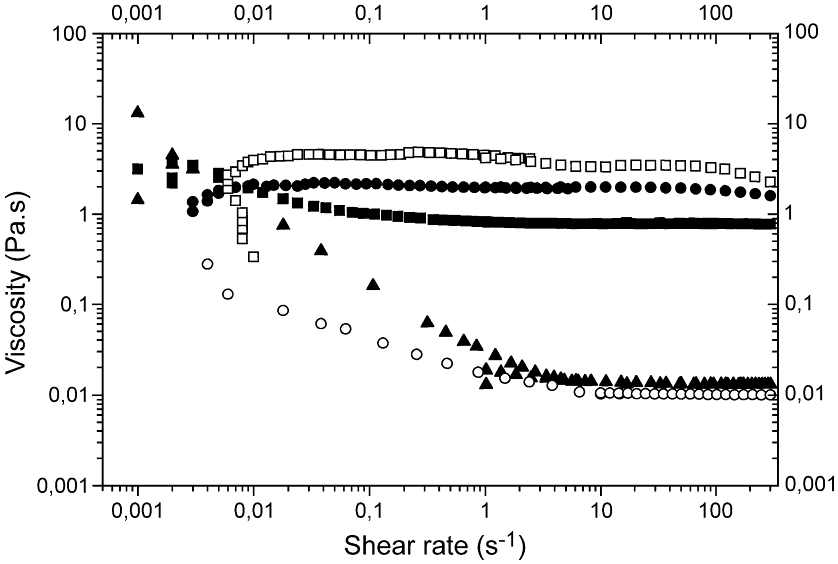

Fig. 4. Rheogram of 20% (w/w) aqueous solution of partially hydrolyzed carboxymethyl cellulose with DS_{CM}=1.44 (■) and 1.79 (○), and partially hydrolyzed carboxymethyl hydroxyethyl celluloses with MS_{HE}=3.57, DS_{CM}=1.47 (□); MS_{HE}=3.06, DS_{CM}=0.79 (●); and MS_{HE}=2.15, DS_{CM}=0.96 (▲).

Table 3
Concrete test parameter of starch and cellulose derivatives and conventional cement dispersants

	Dispersing agent			Slump (cm)		Density (kg/dm^3)	Compressive strength (N/mm^2)
	DP$_w$[a]	MS[b]	DS[c]	10 min	40 min		24 h
SES[d]	56		0.38	53.0	50.0	2.46	0.15
SES[d]	56		0.55	64.0[e]	62.0	2.45	0.13
CMHEC[d]	77	3.57	0.45	40.0	–	n.d.[f]	n.d.[f]
CMHEC[d]	77	3.57	1.47	45.0	–	n.d.[f]	n.d.[f]
Glenium51				61.0	56.0	2.45	26.6
Melment SL				48.0	43.0	2.44	27.7

[a] Degree of polymerization, calculated from the molecular weight M_w of the peracetylated *limit*-dextrins and LODP-cellulose.
[b] Molar substitution.
[c] Degree of substitution.
[d] SES: sulfoethyl starch; CMHEC: carboxymethyl hydroxyethyl cellulose.
[e] The mixture starts bleeding.
[f] Not determinate.

indicating that they are comparable to the commercial products. Better results are observed for the SES samples with DS_{SE} 0.30–0.60, they show spread size in the mortar test between 24.0 and 30.0 cm, which increases with increasing degree of sulfoethylation (Fig. 3). Tegiacchi and Casu [18] report about a SES with suitable dispersing properties, but their product has a DS value of 1.3, i.e., much higher compared with our sample described in this paper. We also found that a partial depolymerization of starch is essential for a dispersing effect of the corresponding SES. For DP$_w$ lower than 250, the molecular weight has no significant influence on the viscosity or on the dispersing properties. From this result, we conclude that sulfoethylation of partial depolymerized amylose-rich starch has excellent dispersing effect in mortar.

3.2. Cellulose

Cellulose is a strong linear biopolymer having high chain stiffness due to the β-glycosidic linkages of the anhydroglucose units (AGU). Therefore, conventional water-soluble derivatives like cellulose methylether, mixed cellulose ether, or carboxymethyl cellulose, are applied as thickening agents. Viscose and spruce sulfite pulp, as starting cellulose materials, were treated with diluted hydrochloric acid, and LODP-celluloses with DP$_w$ lower than 150 were obtained. These LODP-celluloses were subsequently etherified in a 2-propanol slurry with ethylene oxide and/or chloroacetic acid, under alkaline conditions, to form carboxymethyl hydroxyethyl celluloses (CMHEC) and carboxymethyl cellulose (CMC), respectively. In contrast to the cellulose ethers thickening, the 20% (w/w) aqueous CMHEC and the CMC solution show low viscosities (Table 2; Fig. 4). The samples with a molar degree of hydroxyethylation $MS_{HE}>2.0$ and additional carboxylate groups have reached a spread size between 17.8 and 21.5 cm, which is nearly as the Liquiment N (spread size of 21.4 cm). The LODP-cellulose sulfates and sulfoethyl LODP-cellulose showed a much lower spread size in the mortar test compared to the standard Liquiment N (data not shown).

3.3. Dispersing behavior in concrete

We found with success dispersants agent or basis of polysaccharides, in particular, the acid-treated starch and cellulose derivatives SES and CMHEC; therefore, these samples were subsequently submitted under concrete test.

The concrete tests (Table 3) show that the slump sizes after 10 min for SES and CMHEC have similar values (40.0–64.0 cm) as the superplasticizers Glenium 51 and Melment L10 (48.0–61.0). After 40 min, the slump with CMHEC disperse, and the slump with SES decreases 2.0–3.0 cm, like the superplasticizers Glenium 51 and Melment L10 (5.0 cm). But after 24 h, no significant compressive

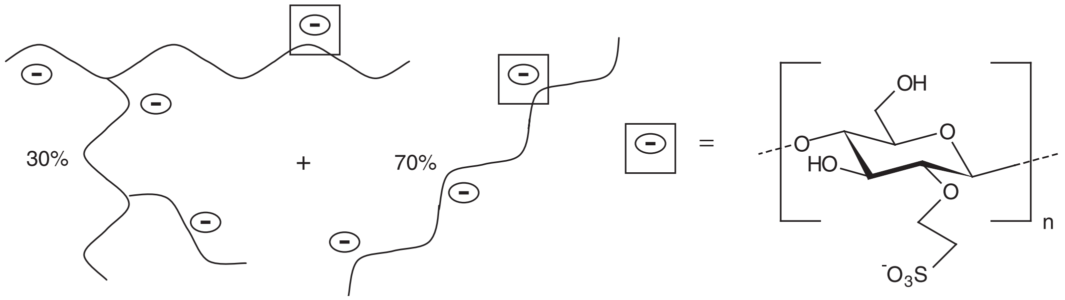

Fig. 5. Structure of sulfoethyl starch (30% amylopectine and 70% amylose).

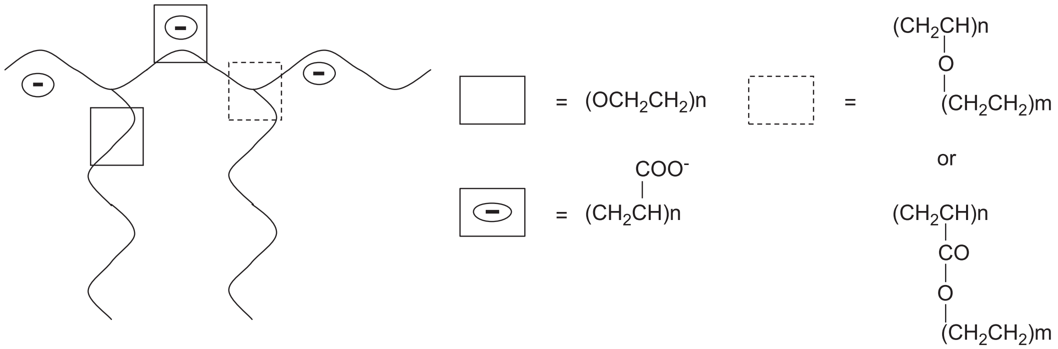

Fig. 6. Structure of polycarboxylate ether: a commercially used cement dispersants.

strength could be observed for the SES, as it was observed for the superplasticizers. What could explain these phenomena: the excellent dispersing performance in mineral mixes and the missing compressive strength of the hardened concrete?

The polycarboxylate ethers (MS02 and Glenium 51) have a polymer backbone with anionic substituents, but with substantially lower charge density, due to the fact that the anionic groups are found exclusively on the main polymer chain (Fig. 5). The free hydroxyl groups of the glucan chains of SES (Fig. 6) and CMHEC produce, compared with the polycarboxylate ethers, an essential amount of electrostatic interactions OH, due to a higher amount but also because the ionic groups are statistically distributed along the biopolymer.

Furthermore, the best dispersing properties for *limit*-dextrins were obtained with ionic function sulfoethyl, but the corresponding cellulose derivative was not so efficient. As for cellulose, it was found that the samples with higher spread size were obtained with the ionic group carboxymethyl. The carboxylates can act as anionic group on the stiff cellulose, on the other hand, only the sulfur containing anionic substituents (sulfonate, sulfate) have a positive effect on the dispersing performance of the helical starch. It can be assumed that the polysaccharide structure, in solution, plays a substantial role. Furthermore, a low crystal formation of Ettringite is necessary for the hardness of concrete, which depends on the concentration of calcium ions, but none of the investigated sample possessed calcium ions [19–21]. The retardation of the concrete compression strength could thus be explained. Further investigations on this area are necessary.

4. Conclusion

For the first time, dispersing agents for cementitious mixtures on the basis of starch and cellulose could be obtained, which have a dispersing performance that is in the range of conventional dispersants or even higher. With starch, the best results were reached when high amylose content starch was partially degraded to a molecular weight beyond 40.000 g/mol, and subsequent sulfoethylations (DS_{SE} 0.55) or sulfations (DS_S 0.82) were carried out. With celluloses, the best dispersing performance was obtained when by acid hydrolysis, a degree of polymerization lower than DP_w 100 was achieved, and chemical derivations in the form of hydroxyethylation (MS_{HE}>2.00) and carboxymethylation (DS_{CM}>0.30) were carried out. Structurally, these macromolecules have a relatively low molecular weight distribution and a statistical substitution pattern along the glucan chains. The viscosities of these polysaccharide derivatives are very low even at high aqueous concentrations. It could be shown in mortar and concrete that the dispersing properties of these carboxymethyl hydroxyethyl celluloses (CMHEC) were similar to naphthenesulfonate formaldehyde polycondensates (Liquiment N). By using sulfoethyl starches (SES), slumps and mortar spreads were obtained that were equal or better than polycarboxylate ethers (MS02 and Glenium 51) conventional cement dispersants. The fact why these substances have a retardation of the concrete hardness The fact is unsolved why these substances have a retardation of the concrete hardness. Therefore, more investigations are needed into these biopolymeric dispersants.

Acknowledgements

The financial support from Degussa Construction Chemicals is gratefully acknowledged by M.C.V.

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