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Synthesis and properties of anionic cellulose ethers: influence of functional groups and molecular weight on flowability of concrete

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Abstract

The suitability of anionic cellulose ethers as superplasticizers and the effect of chemical structure on the fluidity of cement mixtures was investigated. To elucidate the influence of molecular weight and degree of cellulose backbone substitution, cellulose and hydroxyethyl cellulose with molecular weights <50,000 g/mol were synthesized by acid-catalyzed and oxidative degradation. Commercial as well as degraded samples were functionalized by carboxymethylation and sulfobutylation, controlling the degree of substitution (DS) by the molar ratio of reactants and by taking advantage of the high reactivity of sultones towards salts of carboxylic acids, even in aqueous solutions. The fluidizing effect of the cellulose ethers with anionic 'cement-anchoring' groups was prescreened, measuring the static flow of cement pastes. The results indicated a high potential of sulfobutylated cellulose mixed ethers as dispersing agents for concrete. The fluidizing action increased with increasing DS and an optimum range of molecular weight between 100,000 and 150,000 g/mol was found.

Keywords: Degradation of cellulosic materials; Anionic cellulose ethers; Hydroxyethyl carboxymethyl cellulose; Sulfobutylated cellulose; Sulfobutylated hydroxyethyl carboxymethyl cellulose; Superplasticizers; Flowability of concrete

1. Introduction

In building industry the mixing, transporting and placing of fresh concrete presents a number of challenges as the paste must remain highly fluid and should ideally provide homogeneous transport of all particles. Excessive water is frequently added to the mixture in an effort to enhance flow. Unfortunately, excessive water can lead to a number of problems, such as bleeding (free water collection on the surface), segregation of particles, reduced strength and durability, and poor bonding to structural reinforcement members (Mehta, 1999; Sari, Prat, & Labastire, 1999; Skaggs, Rakitsky, Swazey, & Dial, 1997; Ramachandran, 1979). Several additives that influence the consistency and workability of concrete without the need of additional water exists(Veen, Lamberti, & Bleeker, 1999; Ramachandran, 1995). So-called superplasticizers are used, which interact with the surface of cement particles, provoking their dispersion and decreasing their natural tendency to coagulate in aqueous systems. As a result highly flowable mortars and concretes are obtained, showing increased workability at constant water/cement ratio (Biagini 1995; Popova, Geoffroy, Renou-Gonnord, Faucon, & Gartner, 2000; Faroug, Szwabowski, & Wild, 1999; Chen, Hwang, & Hsu, 1999). Water demand of concrete can be reduced up to 30% while still maintaining the flow characteristics of concrete and cohesion is largely improved as a consequence of the reduction of water. The superplasticizers presently used in the market are water-soluble anionic polymers, which can be broadly classified into four groups, sulfonated melamine-formaldehyde condensates, sulfonated naphthtalene-formaldehyde condensates, modified lignosulphonates and others including sulfonic acid esters and acrylic esters (Biagini, 1995; Ramachandran, 1979). Their mechanism is mainly based on their ability to be adsorbed on the surface of cement particles, causing deflocculation by electrostatic and/or steric repulsion. The duration of their effect is generally temporary and variable, and most of them generate significant set delays, which are detrimental to early strength. Moreover, even a slight variation in the water/cement ratio will produce bleeding (Sari et al., 1999). Therefore, water-retention agents, so-called rheological

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modifiers or viscosity modifying agents, are used. This class of additives comprises generally water-soluble polymers, which function by increasing the apparent viscosity of the mix water. Besides polysaccharides such as welan gum (Skaggs et al., 1997) or starch ethers (Veen, Lamberti, & Bleeker, 1999), non-ionic water-soluble cellulose ethers are the main representatives of this class of additives (Schweizer, & Sorg, 1995). Usually hydroxyethyl cellulose (HEC), methyl hydroxyethyl cellulose or hydrophobically modified HEC are added, counteracting segregation and bleeding because of their binding, suspension-stabilizing and water-retaining properties (Brandt, 1986; Anttila, Chu, Podlas, Young, 2000; Desmarais & Wint, 1993; Yamamuro, 1999). They improve the dispersion of cement and increase the cohesiveness of the concrete mainly by increasing the viscosity of water. Due to the water retention capacity of the cellulose ethers sufficient water is kept available to allow the cement to fully harden and to develop full strength properties (Silaghi, Rozenberg, & Lascu, 1999).

Within the last decades, several attempts have been made to use polysaccharides not only as viscosity agents, but also as superplasticizers introducing functional groups able to interact with the surface of cement particles. Several patents claim the suitability of polysaccharide derivatives containing ionic groups. The range of polysaccharides varies from 1,3-β-D-glucan to hemicellulose, starch, cellulose and cellulose ethers, functionalized by alkylsulfonation, sulfatization and carboxymethylation, respectively. For example, Tegiacchi & Casu (1984) claimed the use of alkylsulfonated hemicellulose and starch as superplasticizers for concrete, reporting that water-soluble sulfoalkyl derivatives with degrees of polymerization (DP) up to 100 and degrees of substitution (DS) of sulfoalkyl residues of 0.2–1.5 increase the flow of mortar. Improvement of the flowability of concrete using sulfated 1,3-β-D-glucan and methyl cellulose (MC) with molecular weights from 10 to 15 × 10^4 g/mol and sulfur contents of 5–20% (w/w) was reported by Tanaka, Uruy & Yaguchi (1994). Very recently the suitability of carboxymethyl cellulose (CMC), carboxymethyl hydroxyethyl cellulose (CMHEC), sulfate esters of cellulose, and sulfoalkylated starch as dispersing agents has been claimed (Einfeldt, Albrecht, Kern, Calado, & Klemm, 2002). According to the authors CMHEC obtained from partially hydrolyzed cellulose (DP 20–150) with DS of carboxymethyl groups (DS_{CM}) of 0.5–1.5 and degrees of molar substitution (MS) with respect to hydroxyethyl groups of 0.5–3.5 and cellulose sulfates with DS 0.1–2 show excellent liquefaction effects in mineral binder mixes. Quite typical for patent literature no conclusive data elucidating the dependence of the flow-increasing effect on structural parameters such as molecular weight, DS and the nature of the polymer backbone and the ionic residues are given.

The current work presents first results of a systematic investigation of the influence of molecular weight and DS of anionic cellulose ethers based on cellulose and HEC on the flowability of concrete. Since cellulosic materials are commercially available only in a range of molecular weight between 50,000 and >1,000,000 g/mol, samples with lower molecular weight were prepared by degradation. Carboxymethyl and sulfonic acid groups were chosen as anionic residues and we focused on functionalization over a broad range of DS using derivatization methods causing no or negligible degradation during reaction. For characterization FT-IR spectroscopy was applied as a qualitative tool. For quantitative determination of DS elemental microanalysis and volumetric analysis were applied. The molecular weights were determined by measuring the intrinsic viscosity in appropriate solvent systems and in some cases also evaluated by gel permeation chromatography (GPC). The fluidizing effect of the anionic cellulose ethers was prescreened by measuring the static flow of cement pastes.

2. Experimental

2.1. Materials

For degradation and derivatization, respectively, powdered beech sulfit cellulose (C1, DP 444, gift from Lenzing AG, Austria), cellulose acetate (DP 176, DS_{Ac} 2.35, purchased from Fluka), carboxymethylcellulose sodium salt (NaCMC, DP 444, DS_{CM} 0.7, purchased from Aldrich) and hydroxyethyl cellulose [HEC1 (DP 1200, MS 2) and HEC2 (DP 600, MS 2), respectively, gifts from Hoechst, Germany, and HEC3 (DP 355), purchased from Aldrich] were used. Acetic acid anhydride was distilled prior to use. All other reagents were used as supplied. For flowability tests normal portland cement, type Mannersdorf PZ 375 (H), was used. Commercial superplasticizers Liquiment N® and Liquiment MPK® were received as a gift from SKW Trostberg AG and used as reference substances. The average degree of substitution (DS_x) is defined as the number of substituents per anhydroglucose unit (AGU) of cellulose and HEC, respectively, with x = Ac for acetyl residues, x = CM for carboxymethyl groups and x = SB for sulfobutyl residues.

2.2. Degradation methods

2.2.1. Acid-catalyzed degradation

Prior to degradation, cellulose was activated by slurrying in water for several hours. Acid-catalyzed degradation was performed using 2N HCl (30 ml/g cellulose). The suspension was stirred at room temperature for the times given in Table 1. Degraded cellulose was filtered by suction, suspended in water and refiltered. The washing process was repeated until the washings gave a neutral reaction. The product was finally washed with acetone and dried in vacuum at 50 °C. HEC was added in small portions under vigorous stirring to 4N HCl (30 ml/g HEC). The reaction mixture was stirred at room temperature for the times given in Table 1. The product was precipitated by dropping into cold isopropanol (approx. 2.5 ml/ml reaction mixture),

Table 1
Cellulosic materials used for derivatization

Sample	DM[a]	t[b] (h)	Yield (%)	Molecular weight[c] (g/mol)		M_w/M_n	DP	MS
C1	–[d]	–	–	72,000	72,600	–	444	–
C2	A	5	100	40,000	40,300	–	247	–
C3	A	24	95	20,000	19,800	–	123	–
C4	B	4	95	6300	6500	–	39	–
C5	B	6	93	4500	4600	–	28	–
HEC1	–[d]	–	–	300,000	–	–	1200	2.0[e]/1.93[f]
HEC2	–[d]	–	–	150,000	125,000[g]	6.5	600	2.0[e]/1.97[f]
HEC3	–[d]	–	–	90,000	100,000[g]	5.4	355	2.08[f]
HEC4	A	28	98	40,000	42,400[g]	3.0	160	1.98[f]
HEC5	C	0.5	93	10,000	11,500[g]	1.6	40	~2.0[h]
HEC6	C	2 × 0.5	> 100[i]	3500	3600[g]	3.9	14	~2.0[h]

[a] Degradation method [A = acid-catalyzed degradation (cellulose: 2N HCl, HEC: 4N HCl); B = acid-catalyzed degradation of CA (AcOH/H_2SO_4) and subsequent deacetylation (MeOH/NaOMe); C = oxidative degradation (sodium perborate)].

[b] Degradation time.

[c] Determined from intrinsic viscosity measurements in appropriate solvent systems; left column: C1–C3 in cuoxam; C4 and C5: CTA in ethanol:CH_2Cl_2; HEC1–HEC6 in H_2O; right column: C1–C5: CTN in acetone.

[d] Commercially available.

[e] Specification of manufacturer.

[f] Determined by the Morgan modification of the Zeisel method.

[g] Determined by GPC.

[h] Estimated value (accurate determination of MS infeasible after oxidative degradation).

[i] Residual salt content (3–6% w/w).

filtered (Büchner funnel with cotton cloth), washed thoroughly with isopropanol and vacuum-dried at room temperature.

2.2.2. Degradation of cellulose acetate and deacetylation

Cellulose acetate (CA) (DS_{Ac} 2.35) was degraded in acetic acid solutions using a slightly modified procedure described by Steinmann (1970). Acetic acid anhydride (0.175 ml/g CA) was added to a homogeneous solution of CA in acetic acid (10 ml/g CA) at 60 °C. After 15 min a mixture of conc. H_2SO_4 and acetic acid (0.05 ml H_2SO_4 and 0.225 ml AcOH/g CA) was added. After another 15 min a mixture of acetic acid and water (0.225 ml acetic acid and 0.45 ml H_2O/g CA) was added and the reaction temperature increased to 70 °C. The mixture was stirred at this temperature for the times given in Table 1. After cooling to room temperature, the product was precipitated by dropping the mixture into aqueous sodium acetate (0.5% w/v, approx. 10 ml/ml reaction mixture). Degraded CA was filtered by suction, suspended carefully (foaming!) in a saturated sodium acetate solution, refiltered, washed with excess of water and vacuum-dried at 50 °C. Deacetylation was performed according to Thompson and Wolfrom (1963) using sodium methylate solutions (15 ml dry MeOH and 0.1 mg Na/g CA). The reaction mixture was stirred at room temperature for 24 h. The suspended solid was filtered by suction, washed with water, once with weak acetic acid (5% v/v) and several times with water until the washings gave a neutral reaction. The product was finally washed with acetone and dried in vacuum at 50 °C.

2.2.3. Oxidative degradation

Oxidative degradation of HEC was performed according to Dönges and Hilbig (1995). Caustic soda solution (50%, 7.5 mmol NaOH/g HEC) was added dropwise to a suspension of HEC in aqueous ispropanol (85%, 8 ml/g HEC). The temperature was increased up to 70 °C and half of sodium perborate tetrahydrate was added quickly under stirring. After 15 min the residual amount of perborate was added (total quantity 0.4 mmol/g HEC). The reaction mixture was stirred for another 15 min at 70 °C, cooled down to room temperature and neutralized by addition of a mixture of hydrochloric acid and acetic acid (6:1 v/v) using phenolphthalein as indicator. The degraded product was filtered by suction, washed thoroughly with aqueous isopropanol (85%) and dried in vacuum at 50 °C.

2.3. Functionalization of HEC, cellulose and CMHEC

Synthesis of cellulose derivatives in alkaline media was always carried out under nitrogen atmosphere to avoid alkaline-oxidative degradation.

Carboxymethylation of HEC was carried out according to a slightly modified procedure for the preparation of CMC (Braun, Cherdron, & Ritter, 2001). DS_{CM} was controlled by varying the concentrations of chloroacetic acid and NaOH, using the molar ratios given in Table 2. A slurry of HEC in isopropanol (25 ml/g HEC) was stirred vigorously and within 30 min caustic soda solution (30%) was added dropwise. The reaction mixture was stirred for another 30 min and allowed to stand overnight. Subsequently a concentrated solution of chloroacetic acid in isopropanol was added dropwise within 30 min. The reaction mixture

Table 2
Experimental data, yields and characteristic values of CMHEC

Sample	Molar ratio AGU:NaOH:CAA [a]	Yield (%)	DS_{CM}	Mol. wt.[b] (g/mol)	d^c (%)	cfv [d] (cm)
					0.18	7.8
Educt: HEC1 (DP 1 200, MS 2.0)						
1a	1:4:2	93	0.78	375,200	0.22	7.5
1b	1:2:1	91	0.46	344,500	0.18	7.5
1c	1:1:0.5	95	0.24	323,400	0.21	7.7
1d	1:0.2:0.1	90	0.06	306,100	0.22	7.6
Educt: HEC2 (DP 600, MS 2.0)					0.23	8.2
2a	1:4:2	95	0.80	188,600	0.23	7.8
2b	1:2:1	92	0.53	175,600	0.21	7.7
2c	1:1:0.5	90	0.28	163,600	0.21	8.1
2d	1:0.4:0.2	93	0.11	155,400	0.21	8.1
2e	1:0.2:0.1	94	0.06	153,000	0.24	8.5
Educt: HEC3 (DP 355, MS 2.08)					0.21	8.6
3a	1:4:2	94	0.82	113,400	0.23	7.7
3b	1:2:1	94	0.47	103,400	0.21	7.7
3c	1:1:0.5	92	0.30	98,600	0.22	7.7
3d	1:0.4:0.2	91	0.14	94,100	0.23	7.7
3e	1:0.2:0.1	92	0.07	92,100	0.19	7.9
Educt: HEC4 (DP 160, MS 1.98)					0.19	9.2
4a	1:4:2	93	0.81	50,300	0.21	8.1
4b	1:2:1	95	0.42	45,300	0.23	8.5
4c	1:1:0.5	92	0.26	43,200	0.22	8.3
4d	1:0.4:0.2	94	0.08	40,900	0.18	8.5
Educt: HEC5 (DP 40, MS 2.0)					0.20	8.7
5a	1:4:2	93	0.77	12,500	0.19	7.9
5b	1:1:0.5	91	0.24	10,800	0.21	8.6
5c	1:0.4:0.2	91	0.09	10,300	0.23	8.8
5d	1:0.2:0.1	90	0.05	10,200	0.22	8.8
Educt: HEC6 (DP 14, MS 2.0)					0.25	13.5
6a	1:4:2	94	0.82	4400	0.19	9.1
6b	1:2:1	92	0.35	3900	0.20	9.3
6c	1:0.4:0.2	92	0.12	3600	0.23	9.4

[a] Anhydroglucose unit:NaOH:chloroacetic acid.
[b] Molecular weight calculated from DP and MS of educt and DS_{CM}.
[c] Dosage in the cement mixture with respect to the mass of cement.
[d] Cement flow value; blank 7.9; Liquiment N 15.5 (0.2%); Liquiment MPK 13.3 (0.2%).

was stirred at 60 °C for 4 h and carefully neutralized with acetic acid using phenolphthalein as indicator. The product was isolated by hot filtration and purified by washing three times with hot (60 °C) aqueous isopropanol (80%). CMHEC was dried to mass constancy in vacuum at 50 °C after a final washing with undiluted isopropanol.

Sulfobutylation of cellulose was carried out analoguously to a procedure applied for sulfopropylation (Engelskirchen, 1987). Caustic soda solution (30%, 2 mmol NaOH/mmol AGU) was added dropwise under vigorous stirring to a suspension of cellulose in isopropanol (8 ml/g cellulose) and water (0.9 ml/g cellulose). The reaction mixture was stirred at room temperature for 1 h, then 1,4-butanesultone (2 mmol/mmol AGU), dissolved in acetone (1 ml/g), was added. The suspension was stirred for 6 h at 45 °C, allowed to stand at room temperature for 12 h, poured into methanol (15 ml/g cellulose), and neutralized with acetic acid. The product was filtered by suction, washed with aqueous methanol (90%) and finally with undiluted methanol, and vacuum dried at room temperature.

Sulfobutylation of CMHEC was carried out using a modified procedure for the preparation of poly(meth)acrylates containing sulfopropyl residues (Röhm & Haas G, 1965). CMHEC was dissolved in water (5% w/v) at room temperature, stirred and 1,4-butanesultone (molar ratio COONa:sultone 1:1), dissolved in acetone (1 g/ml) was added. The reaction mixture was kept at 70 °C for 5 h, cooled to room temperature and poured into isopropanol. The sulfobutylated product was filtered by suction, washed with isopropanol and vacuum dried at 50 °C.

2.4. Methods of characterization

FT-IR spectra were recorded on a Biorad FTS 135 using KBr pellets. *Elemental analysis* was carried out by means of an EA 1108 CHNS-O analyzer from Carlo Erba.

2.4.1. Determination of DS and MS

The molar substitution with respect to hydroxyethyl groups (MS_{HE}) was determined by the Morgan modification of the Zeisel method (Morgan, 1946). The ethylene glycol residue was decomposed quantitatively by hot, constant-boiling hydroiodic acid into ethyl iodide and ethylene, which were collected and determined volumetrically in standard solutions of silver nitrate and bromine, respectively. Prior to analysis the water content of HEC was estimated by Karl Fischer technique (approx. 10%). DS_{CM} was determined by titration after converting a portion of the product into acid form by treating with nitric acid/methanol (Green, 1963). DS_{Ac} was determined by titration after saponification (Tanghe, Genung, & Mench, 1963a,b). DS_{SB} of sulfobutylated cellulosic materials was calculated from the results of elemental microanalysis.

2.4.2. Determination of molecular weight

The average molar mass (M) of cellulose, CA and HEC was determined by measuring the intrinsic viscosity $[\eta]$ in appropriate solvent systems in a capillary viscometer. For cellulose two methods were applied: preparation of cuoxam-solutions (Jamey & Lang, 1963) and conversion into cellulose trinitrates (CTN) (Marx--Figini, 1961) with subsequent dissolution in acetone. CA was converted into cellulose triacetate (CTA) as described by Tanghe, Genung, & Mench (1963a, b) and dissolved in ethanol/CH_2Cl_2 (2:8 v/v). Viscosity measurements of HEC were performed in aqueous solutions. The molecular weight of cellulose, CTN and CTA was calculated according to the following equations,

$$[\eta] = \lim \eta_{red} = K_M M^{\alpha}$$

$$\eta_{red} = \text{ reduced specific viscosity} = \eta_{sp}/c$$

$$\eta_{sp} = \text{specific viscosity} = (t_{ps} - t_s)/t_s$$

where t_{ps} is the flow time of the dilute polymer solution, t_s is the flow time of the solvent and c is the concentration. The following constants were used for calculation:

cellulose (25 °C): $K_M = 8.5 \times 10^{-3}$, $\alpha = 0.81$ (Kurata and Tsunashima, 1975)

CTN (20 °C): $K_M = 2.83 \times 10^{-3}$, $\alpha = 1$ (Krässig, 1993)

CTA (25 °C): $K_M = 13.9 \times 10^{-3}$, $\alpha = 0.834$ (Kurata & Tsunashima, 1975)

The degree of polymerization (DP) of HEC was calculated according to Schultz–Blaschke,

$$DP = ([\eta]/K')^{1/\alpha}$$

$$[\eta] = (\eta_{sp}/c)/(1 + K\eta\eta_{sp})$$

using the following constants (Vink, 1966): $K\eta = 0.4$, $K' = 0.012$, $\alpha = 0.87$ (25 °C). M was then calculated from DP and the molar mass of the monomer unit.

The molecular weight of HEC was also estimated by GPC analysis, which was performed on a Hewlett–Packard 1100 system using Hydrogel Guard Linear columns in 0.1 N $NaNO_3$ at 40 °C. Pullulan standards were used for conventional external calibration using a Waters RI 410 refractive index detector.

The molecular weight of CMHEC and sulfobutylated cellulosic materials was calculated from the DP of the parent material and the molar mass of the monomer unit.

2.5. Cement paste flow tests

The cellulose samples were dissolved in water (0.18–0.25% with respect to the mass of cement) and the solution was added to 400 g of cement (water-to-cement ratio 0.385). The mixture was allowed to stand for 30 s, then vigorously stirred for 90 s. The fluidity of the cement paste was assessed by measuring the static spread of a truncated cone having upper and lower diameter of 65 and 75 mm, respectively, and 40 mm height (DIN 1164). The cone filled with the mixed cement was pulled away vertically and the spread was measured at the end of the flow process [= cement flow value (cm)].

For reference two commercial superplasticizers, Liquiment N® and Liquiment MPK®, were used in the form of aqueous solutions with a solid concentration of 40%.

3. Results and discussion

3.1. Degradation of cellulosic materials

Degradation of cellulose and cellulose derivatives can be performed by various processes, such as acid- or alkaline-catalyzed hydrolysis, enzymatic hydrolysis of the β-glucosidic linkages, oxidative, thermal or mechanical degradation (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). The main problems are the control of the DP and relatively broad chain length distributions. In addition most of the abovementioned processes lead to the formation of new functional groups within the polymer moiety, and are sometimes accompanied by some cross-linking, resulting in an incomplete solubility of the degraded sample in conventional cellulose solvents. The most important route of controlled cellulose degradation is the acid-catalyzed hydrolytic cleavage of glycosidic bonds between two anhydroglucose units, yielding rather narrow molecular weight distributions and negligible formation of new functional groups within the polymer moiety. Therefore, we chose acid-catalyzed degradation to obtain cellulosic materials with molecular weights <50,000 g/mol for subsequent derivatization. Acid-catalyzed degradation of cellulose was performed heterogeneously with 2N

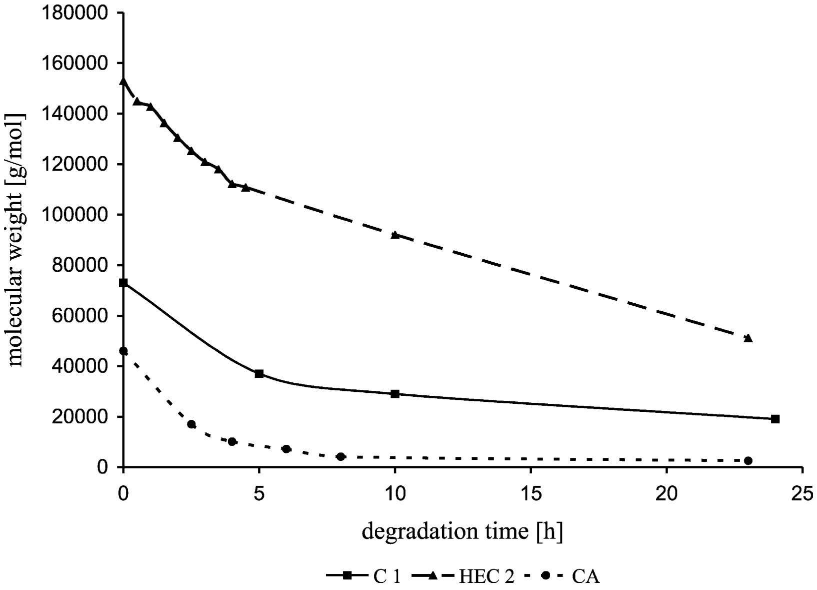


Fig. 1. Degradation curves for cellulose (2N HCl), HEC (4N HCl) and CA (AcOH/H_2SO_4).

HCl. HEC was degraded homogeneously in 4N HCl. Molecular weights of the degraded cellulose samples were determined by measuring the intrinsic viscosity, using two methods: dissolving the samples in cuoxam and converting cellulose into acetone-soluble CTN. Molecular weights obtained by both methods were in good agreement. The molecular weight of degraded HEC was determined viscosimetrically in aqueous solutions. The degradation curves of cellulose and HEC within the first 24 h of acid-catalyzed degradation at room temperature are depicted in Fig. 1.

As expected, the heterogeneous degradation reaction of cellulose (72,000 g/mol) proceeded rather fast within the first few hours (37,000 g/mol after 5 h), then the rate decreased continuously. After 24 h a molecular weight of about 20,000 g/mol was achieved. Prolongation of the degradation time up to 48 h yielded a molecular weight of approx. 12,000, prolongation of the degradation time up to 7 days resulted in no further decrease of DP. These results are in accordance with literature, since it is well-known that in heterogeneous hydrolysis degradation stops almost completely when the number average DP reaches 25–100 (Krässig, Steadman, Schliefer, & Albrecht, 1986; Klemm et al., 1998). In order to obtain celluloses with average molecular weights $<10{,}000$ g/mol, we used commercial cellulose acetate (CA) for acid-catalyzed degradation. By this degradation method no side reactions occur and no additional functional groups are generated. Reaction was performed in acetic acid solutions according to a slightly modified procedure described by Steinmann (1970), followed by sodium methylate catalyzed deacetylation in methanol (Thompson & Wolfrom, 1963). Determination of the intrinsic viscosity was performed in ethanol/dichloromethane after converting degraded CA into triacetates. The degradation curve of CA is also depicted in Fig. 1. Starting from CA with a molecular weight of 46,000 g/mol (DS_{Ac} 2.35), hydrolysis proceeded rather fast within the first few hours and after 4 h a molecular weight of approx. 10,000 was achieved, corresponding to a molecular weight of cellulose of 6,300 g/mol after deacetylation. Complete deacetylation was confirmed by titration and IR spectroscopy.

Acid-catalyzed degradation of HEC was performed in solution. As known from cellulose chemistry, degradation in homogeneous systems proceeds rather slowly, but at a constant rate until all of the cellulose is degraded to cellobiose or glucose (Krässig, Steadman, Schliefer, & Albrecht, 1986). As can be seen in Fig. 1, starting with HEC with a molecular weight of 150 000 g/mol, the molecular weight decreased to 130,500 g/mol after 2 h, to 112 000 g/mol after 4 h and after 23 h to approx. 51 000 g/mol. The molar substitution with respect to hydroxyethyl groups (MS_{HE}) was determined by the Morgan modification of the Zeisel method (Morgan, 1946) and no change of MS_{HE} due to acid-catalyzed degradation was observed. A considerable drawback of this degradation method is the reaction times needed (approximately 80 h for HEC with 10,000 g/mol). Therefore, we were interested in a more efficient degradation method. According to Dönges & Hilbig (1995), low-molecular-weight cellulose ethers can be obtained by oxidative degradation with sodium perborate within 30 min. We used this method to synthesize low-molecular weight HECs, accepting the risk of functional groups formed by oxidation. Using HEC with 150,000 g/mol as starting material, heterogeneous degradation yielded products with approximately 10,000 g/mol within 30 min. The molecular weight was determined by viscosimetry and calculated according to Schultz–Blaschke, neglecting the formation of any new functionalities. To verify the molecular weight obtained by viscosimetry, GPC analysis was performed, and the results were in good agreement. According to GPC data, oxidative degradation resulted in an even narrower molecular-weight distribution than acid-catalyzed degradation of HEC. IR spectroscopy showed the formation of only a very small amount of C=O functionalities. Determination of MS of the oxidatively degraded product did not yield reproducible results, but this method is highly sensitive and even otherwise negligible amounts of carbonyl functionalities could interfere with analysis.

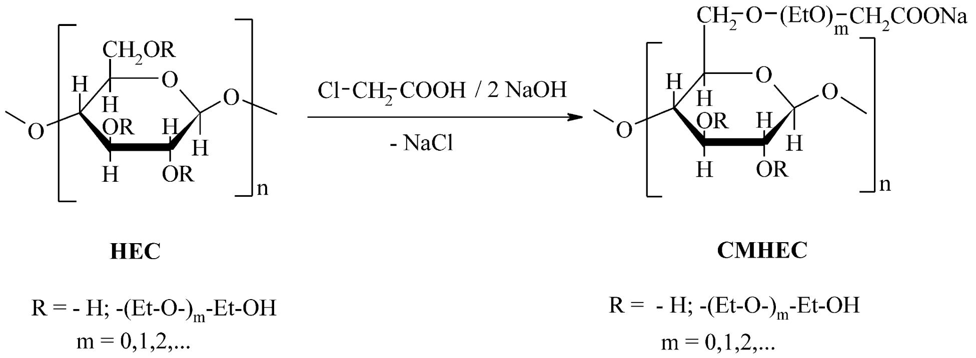
Experiments to prepare HEC with molecular weights $<10{,}000$ g/mol by using higher perborate concentrations and longer reaction times failed due to problems accompanied with purification of the product, particularly the removal of salts. Performing a second degradation step using the already oxidatively degraded HEC yielded a product with approx. 3500 g/mol, containing only small amounts of salts (3–6%). IR-spectra showed an intensification of characteristic resonances of functional groups formed by oxidation.

Based on the results of the small-scale degradation experiments, several celluloses and hydroxyethyl celluloses were synthesized for subsequent derivatization, covering together with commercial cellulosic materials a range of molecular weight between <5000 and 3×10^5 g/mol. Experimental data (degradation method, degradation time) yields and characteristic values (MS, DP, molecular weight) of all samples used for carboxymethylation and sulfobutylation are summarized in Table 1.

3.2. Functionalization of cellulosic materials

The carboxymethylation of cellulose represents the most versatile method for the synthesis of anionic cellulose ethers. CMC represents the commercially most important cellulose ether, and has found ample scientific attention, especially due to its character as a polyelectrolyte (Klemm et al., 1998). DS levels of commercial CMC range from 0.3 to 1.2, but clear and fiber-free CMC solutions require a minimum DS value of about 0.5 (Brandt, 1986). One of the drawbacks of CMC is the incompatibility with polyvalent counterions, which in general tend to precipitate polyelectrolytes from solution. Since the conditions in concrete mixing water are strongly alkaline and a large amount of Ca^{2+} ions are present, CMC would not show sufficient stability. Less sensitive to the presence of multivalent counterions are mixed ethers such as CMHEC. The increased stability is caused by the hydroxyethyl groups, that act as spacers and maintain a soluble hydrated structure (Brandt, 1986). Therefore, we used HEC as starting material for carboxymethylation. The use of an already water-soluble starting material for carboxymethylation offers an additional advantage: a much lower amount of groups is necessary to achieve water-solubility, hence allowing investigations of the influence of DS_{CM} on flowability of concrete over a broader range of DS. Several approaches are known to control the DS of the products with respect to carboxymethyl groups, such as varying the proportions of the reactants, the time of reaction, or the temperature. Pratically no degradation of the samples occurs, if the carboxymethylation is carried out under nitrogen atmosphere (Vink, 1969). In the present experiments only the concentration of chloroacetic acid and NaOH was varied. CMHEC were synthesized according to a slightly modified procedure for the preparation of CMC (Braun et al., 2001). Scheme 1 depicts the reaction scheme and the structure of an isolated segment of a CMHEC with a DS_{CM} of 1, carboxymethylated at the C-6 position. The DS were determined by titration. The molecular weight was calculated from the DP of the parent material and the molar mass of the monomer unit, assuming that no degradation had taken place during derivatization. The conditions of the carboxymethylation reactions, yields and data of the resultant samples **1a**–**6c** are given in Table 2. As can be clearly seen variation of the molar ratios of the reactants, keeping reaction time and temperature constant, yielded very similar DS independent of the molecular weight of the starting material. Also HEC5 and HEC6, obtained by oxidative degradation and containing small amounts of C=O functionalities, yielded comparable DS values, indicating no interference of these groups with the carboxymethylation reaction.

Besides CMC, cellulose ethers with sulfonic acid groups are also well-known anionic cellulose derivatives, although not of commercial importance. Sulfoalkyl celluloses are

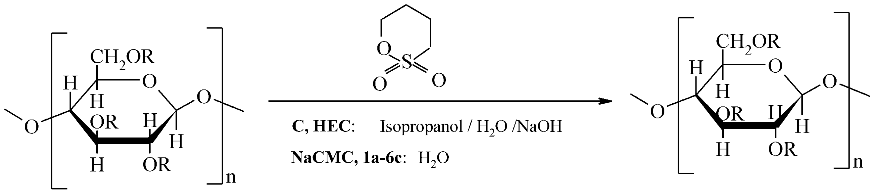


Scheme 1. Synthesis of CMHEC.

accessible via reaction with chloromethane sulfonate, 2-chloroethane sulfonate, ethylene sulfonate or sultones (Klemm et al., 1998). Contrary to CMC, they are highly compatible with large amounts of alkali-metal salts. Sultones are rather harmful reagents, but they are very reactive and mild reaction conditions are sufficient, thus avoiding a decrease of the molecular weight during functionalization. We synthesized sulfonic acid groups containing cellulosic materials by reacting cellulose and hydroxyethylcellulose with 1,4-butanesultone analoguously to a procedure applied for sulfopropylcellulose (Engelskirchen, 1987). Reaction was carried out under nitrogen atmosphere at 45 °C in a slurry (isopropanol/water), adding a solution of 1,4-butanesultone in acetone after alkalization with NaOH. The molar ratios of the reactants were kept constant for all samples (AGU:NaOH:butanesultone = 1:2:2). The reaction scheme is depicted in Scheme 2. The DS were calculated from the results of elemental analysis and used for the calculation of the molecular weights, assuming that no degradation had been caused by derivatization. The obtained data are summarized in Table 3. As can be seen, the degrees of substitution of the sulfobutylated cellulose samples **7a–7e** varied from 0.46 to 0.78, indicating an influence of the molecular weight on substitution, although the opposite effect would be expected due to the higher swelling potential of degraded cellulose. No tendency was observed in the case of HEC derivatives **8a–8e**, showing even stronger variation of DS_{SB} values (0.5–0.9). Although the calculation of DS values strongly depends on slight deviations in elemental analysis, the divergences of DS_{SB} were too significant to be explained only by this reason. We did not try to find a preparation method leading to a better control of the DS, but took advantage of the known reactivity of sultones towards salts of carboxylic acids (Quaedvlieg, 1955). Using sodium salts of CMHEC as starting materials, an indirect control of the DS should be possible, if butanesultone reacts selectively and completely. In order to verify this assumption, commercial NaCMC (DP 444, DS 0.7) was reacted with butanesulfone (molar ratio COONa-groups:sultone = 1:1) in water according to a modified procedure for the preparation of poly(meth)acrylates containing sulfopropyl residues (Röhm & Haas GmbH, 1965). Water-soluble product **9** was obtained in a yield of 98%. In IR spectra a shift of the broad band at 1625 (carboxylate group) to 1738 cm^{-1} (ester group) could be clearly observed (Fig. 2). A DS of 0.71 was calculated from the results of elemental analysis, indicating complete substitution of the carboxyl groups. Therefore, all CMHEC samples were reacted with butanesulfone analoguously (Scheme 2). Since the reaction conditions should not favour any degradation of the products (no excess of alkali, temperatures of only 70 °C), the molecular weights were calculated using the DP as well as the DS_{CM} of the starting materials, which were determined by titration, a much more accurate method than calculation of DS from elemental analysis data. Spot checks showed good agreement of values obtained by both methods. Yields and characteristic values of all products (**10a–15c**) are summarized in Table 4.

3.3. Influence on flowability of concrete

A quick evaluation of the suitability of the products as superplasticizers was possible by measuring the spread of a cement/water mixture. The anionic cellulose ethers were dissolved in water (0.18–0.25% with respect to the mass of cement) and then mixed with normal portland cement using standard conditions. A water/cement ratio of 0.385 was employed. The mixture was filled in a rubber conus and after removing the conus the spread was measured at the end of the flow process (= cement flow value). For reference Liquiment N®, a superplasticizer based on sulfonated



C 1-5: R = - H

HEC 1-6: R = - H; -$(Et\text{-}O\text{-})_m$-Et-OH
m = 0,1,2,...

NaCMC: R = - H; -O-CH_2-COONa

1a - 6c: R = - H; -$(Et\text{-}O\text{-})_m$-Et-OH;
-$(Et\text{-}O\text{-})_m$-Et-O-CH_2-COONa
m = 0,1,2,...

7a - 7e: R = - H; -$(CH_2)_4$-SO_3Na

8a - 8e: R = -$(CH_2)_4$-SO_3Na
- H; -$(Et\text{-}O\text{-})_m$-Et-OH;
-$(Et\text{-}O\text{-})_m$-Et-O-$(CH_2)_4$-SO_3Na
m = 0,1,2,...

9: R = - H; -O-CH_2-COO-$(CH_2)_4$-SO_3Na

10a - 15c: R = - H; -$(Et\text{-}O\text{-})_m$-Et-OH;
-$(Et\text{-}O\text{-})_m$-Et-O-CH_2-COO-$(CH_2)_4$-SO_3Na
m = 0,1,2,...

Scheme 2. Synthesis of sulfobutylated cellulose, HEC, CMC and CMHEC.

Table 3
Yields and characteristic values of sulfobutylated cellulose and HEC samples

Sample	Educt	DP	Yield (%)	DS$_{SB}$ [a]	Mol. wt.[b] (g/mol)	d[c] (%)	cfv[d] (cm)
7a	C1	444	86	0.78	114,800	0.23	9.3
7b	C2	247	92	0.65	65,600	0.21	8.2
7c	C3	123	89	0.63	32,200	0.24	8.4
7d	C4	39	84	0.57	9800	0.25	8.4
7e	C5	28	91	0.46	6600	0.25	8.5
8a	HEC1	1200	98	0.8	452,100	0.22	8.2
8b	HEC2	600	93	0.5	197,600	0.24	8.5
8c	HEC3	355	90	0.7	129,400	0.25	8.4
8d	HEC4	160	90	0.9	62,700	0.20	8.6
8e	HEC5	40	92	0.7	14,400	0.24	8.7

[a] Calculated from the results of elemental microanalysis.
[b] Molecular weight calculated from DP and MS of educt and DS$_{SB}$.
[c] Dosage in the cement mixture with respect to the mass of cement.
[d] Cement flow value; blank 7.9; Liquiment N 15.5 (0.2%); Liquiment MPK 13.3 (0.2%).

naphthalene–formaldehyde condensates, and Liquiment MPK®, based on melamine–formaldehyde condensates, were used, which are representative products of the kinds available in the market. For comparison the water-soluble starting materials HEC1–HEC6 were also tested. As can be seen in Table 2, by addition of HEC1–HEC5 no or only a small increase of the cement flow value compared to the blank was detected (blank: 7.9 cm, samples: 7.8–9.2 cm). Surprisingly, HEC6 was very effective (13.5 cm), which could be attributed to functional groups, which were formed by twice repeated oxidative degradation. It would be expected that further functionalization of these samples with groups able to interact with cement particles should lead to an increase of the fluidizing action, but just the opposite effect was observed. Addition of the carboxymethylated samples **6a–6c** resulted in a much smaller increase of spread (9.1–9.4 cm). An even smaller or no fluidizing effect at all was achieved by additon of the carboxymethylated samples **1a–5c** (7.5–8.8 cm). These results are rather contradictory to the findings of Einfeldt et.al. (2002), claiming the suitability of CMHEC with DP 20–150 as dispersing agents with an excellent liquefaction effect. The poor performance of the CMHEC-samples could be attributed to a still too high sensitivity towards 'free' Ca^{2+}-ions in the cement water, which would lead to precipitation before adsorption can take place. To verify this assumption, aqueous solutions of these samples were added to water with a Ca^{2+}-content similar to cement mixing water (1.3 g Ca/l). In all cases precipiation or at least the formation of hazy solutions was observed.

Addition of the sulfobutylated samples **7a–7e** and **8a–8e** to the cement paste showed a small increase of spread (9.2–9.3 cm, Table 3), but a surprisingly strong fluidizing effect was caused by the sulfobutylated carboxymethyl derivatives **9–15c** (Table 4). Cement flow values varied from 10.2 to 16.4 cm. The fluidizing action of Liquiment N® (20.4 cm) could not be exceeded, but several samples gave similar (**11a**, **11b**, **12c**, **12d**, **13b**, **13c**, **14a**) or even significantly higher (**12a**, **12b**, **13a**) values than Liquiment MPK® (13.9 cm). Obviously, the fluidizing action depends on the molecular weight and the DS$_{SB}$ of the samples. Fig. 3 illustrates this correlation. As far as the molecular weight is concerned, neither a very high, nor a low molecular weight seem to be beneficial. The results indicate an optimum range between 100,000 and 150,000 g/mol. The maximum of the curves shifts to lower molecular weights, if the DS is very low (~0.1). As far as the DS is concerned, it can be clearly seen, that at similar molecular weights the fluidizing effect increases with increasing DS. All mechanisms used to explain the deflocculation of cement particles by conventional superplasticizers require the admixture to be adsorbed on the surface of the particles to be effective (Popova et al.,

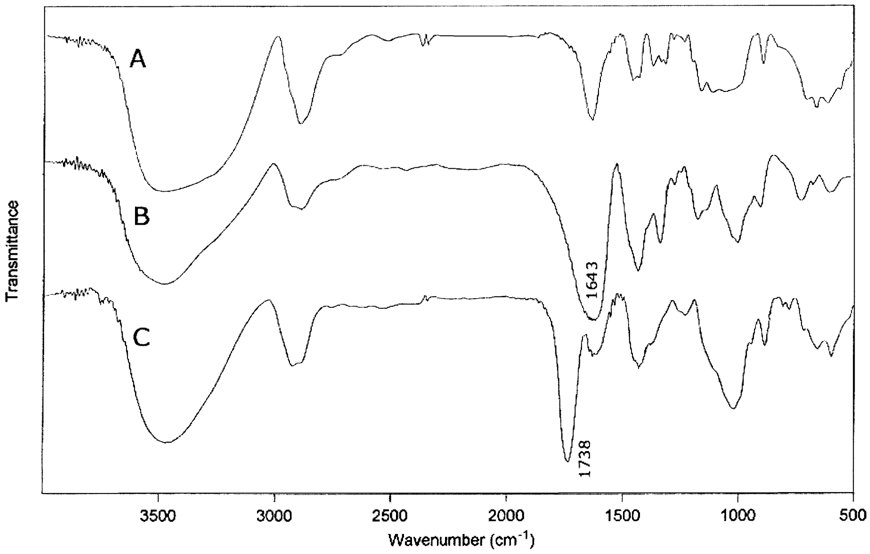


Fig. 2. FT-IR spectra of (A) cellulose, (B) NaCMC and (C) sulfobutylated CMC **9**.

2000). Adsorption is caused by the sulfonic or carboxylic acid groups of the superplasticizer, which function as 'cement-anchoring' groups. Consequently, an increasing amount of these groups should lead to stronger interaction and enhanced adsorption. The sulfobutylated samples meet these expectations.

Quite unexpected was the significantly better performance of **12a** (16.4 cm) compared to **9** (11.3 cm), both samples in a similiar range of DS (0.81 and 0.7, respectively) and molecular weight (139,200 and 153,000 g/mol, respectively). Also samples **11a**, **13a**, and **14a** with similiar DS, but with molecular weights outside the optimum molecular weight range, showed much better action (14.2–16.2 cm) than sulfobutylated CMC **9**. Assuming that the amount of adsorbed cellulose derivative mainly depends on the number of anionic groups interacting with the surface of cement particles, the discrepancy in fluidizing action has to be attributed to the molecular structure. In **9** the sulfobutyl residues are bonded to the carboxyl groups at the cellulosic polymer backbone. In the sulfobutylated CMHEC samples these groups are bonded to carboxymethyl groups, which are either situated at the polymer backbone or at the hydroxyethyl groups. In the first case, the structure resembles a comb-type polymer with alternating sulfobutyl side chains and 'free' hydroxyethyl side chains. In the second case, the number of the side chains would be lower, but chain length would increase. In any case the adsorption behaviour should be affected. To draw any stronger conclusions, a determination of the substituent distribution in sulfobutylated CMHEC and also sulfobutylated HEC is required. The latter also contain hydroxyethyl side chains, but do not increase flowability of concrete.

Table 4
Yields and characteristic values of sulfobutylated CMC and CMHEC

Sample	Educt	DP	Yield (%)	DS_{SB}[a]	Mol.wt.[b] (g/mol)	cfv[c] (cm)
9	NaCMC	444	98	0.7/0.71[d]	139,200	11.3
10a	1a	1200	97	0.78	502,700	11.2
10b	1b	1200	98	0.46	419,600	10.8
10c	1c	1200	95	0.24/0.23[d]	362,600	10.2
10d	1d	1200	92	0.06	315,900	–[e]
11a	2a	600	98	0.8	253,900	14.2
11b	2b	600	98	0.53/0.59[d]	218,900	13.2
11c	2c	600	96	0.28	186,500	12.8
11d	2d	600	90	0.11	164,400	–[e]
11e	2e	600	92	0.06	158,000	10.5
12a	3a	355	95	0.81	153,000	16.4
12b	3b	355	96	0.47 / 0.56[d]	126,200	15.5
12c	3c	355	92	0.30 / 0.29[d]	113,100	14.0
12d	3d	355	92	0.14	100,800	12.9
12e	3e	355	95	0.07 / 0.10[d]	95,500	–[e]
13a	4a	160	97	0.81	67,900	16.2
13b	4b	160	97	0.42	54,400	14.5
13c	4c	160	96	0.26	48,900	13.5
13d	4d	160	93	0.08	42,700	12.5
14a	5a	40	94	0.77	16,700	14.7
14b	5b	40	95	0.24	12,100	12.5
14c	5c	40	95	0.09 / 0.05[d]	10,800	–[e]
14d	5d	40	91	0.05	10,400	11.2
15a	6a	14	93	0.82	6000	–[e]
15b	6b	14	93	0.35	4600	12.0
15c	6c	14	90	0.12	3900	11.0

[a] $DS_{SB} = DS_{CM}$ of educt (determined by titration).

[b] Molecular weight calculated from DP, MS and DS_{CM} of educt and DS_{SB}.

[c] Calculated from the results of elemental microanalysis.

[d] Cement flow value at a dosage of 0.25% with respect to mass of cement; blank 7.9; Liquiment N 20.4; Liquiment MPK 13.9.

[e] Not determined.

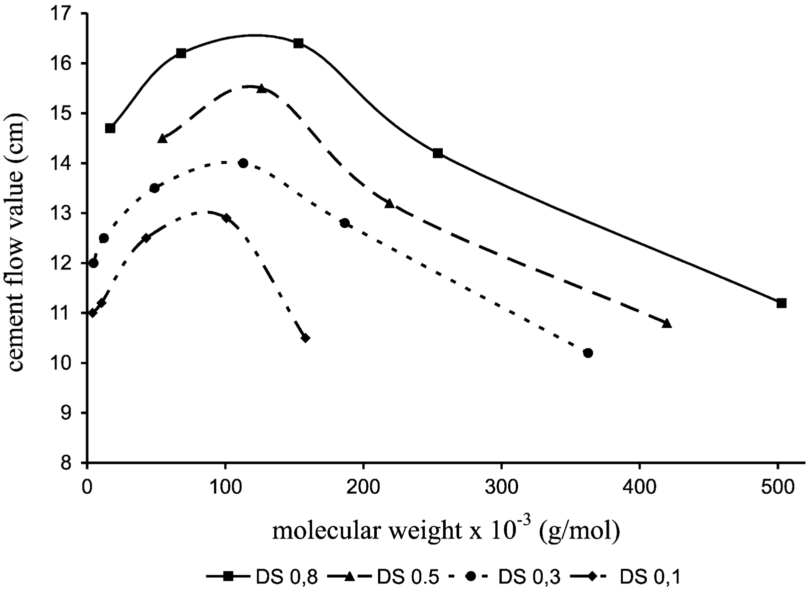


Fig. 3. Dependence of cement flow value on molecular weight and DS.

4. Conclusions

Focusing on the investigation of the suitability of cellulose derivatives as superplasticizers and the influence of molecular weight and DS of the flowability of concrete, a large number of water-soluble cellulose ethers having either carboxylic of sulfonic acid residues as anionic 'cement-anchoring' groups in their molecule were synthesized. The results of cement flow tests indicated that contrary to CMHEC, which seems to be unsuitable for this kind of application due to a still too high sensitivity towards Ca^{2+}, sulfobutylated CMC and CMHEC are suitable as cement admixtures with flow-enhancing properties. A strong dependence of fluidity of cement mixtures on DS and molecular weight of the samples was observed. It was shown that flowability of cement was increased with increasing DS and an optimum range of molecular weight between 100,000 and 150,000 g/mol was indicated. In addition, hydroxethyl groups seem to have a beneficial effect. At this early stage of the investigations no final conclusions can be drawn, but the results indicate a high potential of CMHEC with sulfonic acid groups as dispersing agents for concrete. Future work will deal with the synthesis of CMHEC with $DS > 1$ by repeated alkalization-etherification steps using commercial HEC fulfilling the requirement of molecular weights in the above mentioned optimum range, and the investigation of substituent distribution to elucidate the effect of hydroxyethyl groups. In addition, it is essential to determine the rate of adsorption and to investigate the influence of the not-adsorbed portion on the viscosity of the cement mixture. At a balanced ratio between adsorption and dissolution anionic cellulose derivatives with molecular weights $> 100{,}000$ g/mol could not only act as dispersing agents, but also increase the viscosity and act as water-keeping agent. Consequently, such additives could have the potential to combine the desirable properties of a superplasticizer (increased flow) with those of a normal viscosity agent (resistance to segregation and bleeding).

Acknowledgements

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