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(Carboxymethyl)cellulose with Xanthan Gum Like Rheology

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ABSTRACT: By manipulation of the alkalinity during (carboxymethyl)cellulose (CMC) preparation—aiming at the formation of poorly substituted segments, in fact at a cellulose-*co*-CMC segmented block copolymer—CMCs can be made with solution rheograms closely resembling those of xanthan gum. Such results were obtained by reacting both in an aqueous isopropyl alcohol slurry and in a "dry" phase with use of a kneader. Some salt resistance can be achieved, although not on the level that it can with xanthan gum. The new products show a temperature dependence of solution viscosity comparable with that of xanthan gum but do not show the discontinuity at 60 °C that is characteristic of xanthan gum.[6]

Introduction

The extreme pseudoplasticity of xanthan gum solutions has long served as both a yardstick of performance for other water-soluble polymers and as an unattainable ideal for semisynthetic cellulose derivatives.[1] Earlier work investigating the effect of oligosaccharide substituents flexibly coupled to a CMC backbone in a random substitution pattern—presenting a "random analogue" of xanthan gum's highly regular cellulose-*graft*-oligosaccharide structure—failed to produce unusual rheologies, although a very high level of viscosity was attained, normalized to 1% cellulosic solutions.[2]

Literature reports[3] that xanthan gum is organized into multistranded helical aggregates, forming fairly rigid, extremely long arrays, not unlike staple fiber yarn being built up from short fibers, inspired the approach described in this work. We aimed at the synthesis of CMC types that contain "cellulose blocks" consisting of segments of poorly substituted CMC, which would act as physical cross-links in the solution, to produce multistranded CMC colloidal fibers. Such a conjugation of CMC molecules via cellulose-like segments would tend to align the relatively rigid[4] cellulose derivative into bundles with an effective length far exceeding the individual molecular dimensions. This would lead to a strong increase of shear-thinning behavior due to increased orientability of such colloidal fibers, compared with the isolated molecules.

Table I
CMC-Cellulose Segmented Block Copolymers from Reaction of Linters Cellulose[a]

entry	MCA, equiv	MCA-Na, equiv	$\eta_{1s^{-1}}$, mPa·s	$\eta_{20s^{-1}}$, mPa·s	100B
1	0	1.0	1250	700	23
2	0.3	0.7	1750	880	35
3	0.5	0.5	1920	880	35
4	0.7	0.3	5920	1600	47
5	0.7	0.3	6750	1980	47[b]
6*	0.7	0.3	30200	4700	68
7*	0.7	0.3	23600	4200	63[c]
7*	0.75 wt % soln		13300	2460	61
7*	0.50 wt % soln		3800	1100	52
8	0	1.4	1810	650	40
9	0.1	1.3	1410	690	35[d]
10	0.2	1.2	2800	1060	22
11	0.4	1.0	insol		
various	>0.4	<1.0	insol		
1.0% xanthan gum			2800		70
AZC HS600[e]			149	77	22

[a] ER 4500; runs marked with * ER 8500, milled in the Pulverisette, with 1.5 equiv of NaOH (equivalents always relative to anhydroglucose) in 87% aqueous isopropyl alcohol and with various amounts of chloroacetic acid and sodium chloroacetate. Viscosity data for 1% solids unless indicated otherwise in all tables. Pseudoplasticity characterized by the factor B ($\log \tau = A - B \log \dot{\gamma}$); the mean value of B in the slightly curved plots between 10 and 100 s^{-1} shear rate is reported, cf. ref 6. [b] Run 5 checks the reproducibility of run 4. [c] Run 7 reproduces run 6. [d] Observe salt effect. [e] Cf. Table V.

Results

Our synthesis follows the same general outline as the preparation of regular CMC: Alkalization to open up the cellulose structure as well as to generate high nucleophilic reactivity, followed by reaction with chloroacetic acid or its derivatives.

We open the cellulose structure by using an amount of alkali in the usual range, normally regarded sufficient to destroy all crystallinity: then, just prior to the start of the carboxymethylation reaction, we adust the alkalinity to a much lower range, inviting incipient recrystallization. The microcrystals locally protect the cellulose from substitution reactions; the unsubstituted regions furnish the poorly substituted "cellulose blocks" in the block-copolymer-like product. Chloroacetic acid can be used for the partial neutralization if the temperature of the mixture is sufficiently low to preclude intervention of the etherification reaction in the neutralization step—i.e., below room temperature.

In searching for a good procedure to achieve soluble products containing segments of poorly substituted cellulose (Table I) we observed a pronounced salt effect on the collapse of the alkali cellulose structure (bottom part of Table I). Note that salt is expected to exert its effect in a less homogeneous and reproducible manner than pH control should, because of slow salt diffusion compared to the rate of proton exchange. Thus, in striving for a higher overall degree of substitution (DS), the use of increased

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Table II
"Dry-Phase" Reactions To Prepare Xanthan Gum Like CMC[a]

entry	NaOH, equiv	MCA, equiv	MCA-Na, equiv	$\eta_{1s^{-1}}$, mPa·s	$\eta_{20s^{-1}}$, mPa·s	100B
1	1.5	0.7	0.3	insol		
2	2.0	0.7	0.3	15100	2560	62
2	0.6 wt % soln			3120	950	48
3	2.5	0.7	0.3	5380	1700	47
4	2.0	0.7	0.3	1790	800	36
5	2.0	0.7	0.3	3270	1000	43

[a] Consult Experimental Section for details. Viscosity data: compare Table I and ref 6.

Table III
Products Made from Linters Cellulose (ER 8500) in 87% Aqueous Isopropyl Alcohol Slurry with 1.5 equiv of NaOH and Chloroacetic Acid/Acrylamide Mixtures for the Etherification Step[a]

entry	MCA, equiv	AA, equiv	hydrol step?	DS (GC)	$\eta_{1s^{-1}}$, mPa·s	$\eta_{20s^{-1}}$, mPa·s	100B
1	0.7[c]	1.0	no	0.52	96	40	25.5
2	0.7	1.0[d]	no		4000	1280	46
3	0.7	1.0[e]	no		3470	1110	44
4	0.7	1.0	no		2770	1030	42
5	0.7	1.0	yes	0.80	1030	555	30
6	0.7	2.0	yes	0.91	1010	540	32.5
7	0.7	1.5	yes	0.85	367	325	18
8	0.5[b]	1.0	yes		145	130	10

[a] Hydrolysis of the amide functionality by further heating with 1.0 equiv of NaOH per acrylamide used proved to result in loss of viscosity. Yields on acrylamide proved to be on the order of 25%, as opposed to 70% that is normal in the dry-reaction process, in our experience. [b] +0.3 equiv of acetic acid. [c] +0.3 equiv of sodium chloroacetate (link to Table I). [d] AA added 45 min after the MCA, 30 min before start of heating. [e] 1.6 equiv of NaOH used. AA added after complete CMC reaction and cooling to 0 °C.

amounts of sodium chloroacetate (MCA-Na) led to insoluble products at a modest level of neutralization prior to etherification (Table I). A very favorable and reproducible effect was achieved by working at a relatively low level of etherifying agent and appreciable neutralization. The amount of "salt" that is optimal in this approach remains a question for further work: part or most of the MCA-Na used in these runs may be replaceable by, e.g., NaCl.

Translation of the experience gained in this work with slurry-type reactions, to prepare analogous products in a process without a dispersing medium, i.e., in a "dry" process, called for an increased alkalinity; reproducibility proved to be rather poor under our conditions (Table II, entries 2, 4, 5). Moreover, it should be recognized that so far the solution clarity of the slurry-reaction products is better (in fact virtually perfect) than the clarity of the dry-reaction products.

A poor salt tolerance of solutions for the present class of cellulose derivatives is to be expected: we envision microcrystal formation even in the "completely dissolved" state; decreasing the solubilizing effect of the ionic substituent must show dramatic effects. Increasing the salt resistance by nonionic substitution, notably with acrylamide, proved possible, but only at the expense of some pseudoplasticity of the solutions. Hydrolysis of the amide adduct with base gave further loss of pseudoplasticity and viscosity (Table III).

Table IV
Attempts at Improved Salt Resistance by a Slight Increase of Carboxymethylation[a]

entry	MCA, equiv	MCA-Na, equiv	$\eta_{1s^{-1}}$, mPa·s	$\eta_{20s^{-1}}$, mPa·s	100B
1	0.7	0.5	221	113	24
2	0.7	0.5	5250	1460	50
2[b]			1290	390	42
3	0.7	0.5	237	138	24

[a] Cellulose ER 8500 (DP = 5800); 2.0 equiv of NaOH. [b] In 4% NaCl.

Table V
Analytical Data for a Few Representative Products[a]

	HS 600	entry 6, Table I	entry 2, Table II	entry 3, Table II
overall DS	0.68	0.69	0.40	0.49
K_2	3.91	2.63	2.15	2.19
K_6	3.03	2.37	1.93	2.00
top MWD				
before enzym hydrolysis	2.3×10^6	1.5×10^6	0.5×10^6	0.5×10^6
after enzym hydrolysis	38000	6600	1200	1200

[a] Degree of substitution values and relative substitution rates $K_2 = R_2/R_3$; $K_6 = R_6/R_3$ from methanolysis–GC analysis;[5] GPC analysis yielded no informative M_n and M_w values for the enzymatically hydrolyzed new products, cf. Figure 1. The commercial product AZC-HS 600, made at high alkalinity, is compared with a slurry product (entry 6, Table I) and with two dry-phase products (entries 2 and 3, Table II). Qualitatively, the GPC response of the experimental products after enzymic hydrolysis was very similar and profoundly different from the HS 600 results. Molecular weights against polymannotriose standards are given.

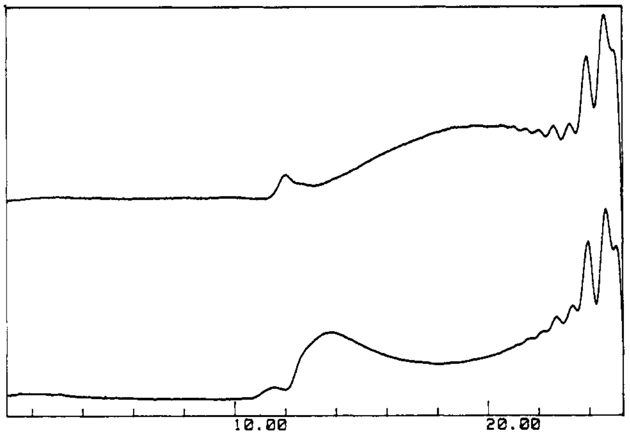

Figure 1. GPC traces of enzymatically hydrolyzed samples of AZC HS 600 (lower trace) and of sample 6, Table I (upper trace). The broad maximum in the latter at about 19.5-mL elution volume corresponds to an MW of 6600 in polymannotriose. The other products made at lowered alkalinity showed a response similar to the upper trace, albeit at lower DS the maximum proved to lie at still lower MW, as expected.

It proved possible to obtain a modicum of salt resistance by SLIGHTLY increasing the overall DS in the dry-reaction products (where sufficient alkalinity remains after partial neutralization to accommodate some further reaction with MCA-Na; recall that in the slurry process part of the MCA-Na was used as excess salt). We observed gratifying viscosity and pseudoplasticity in 4% NaCl solutions of some such products, albeit that the polymers had to be dissolved in demineralized (or drinking) water prior to the addition of salt (Table IV).

Support for the blocky character of the new CMCs was obtained by GPC analysis in conjunction with enzymatic digestion (Table V, Figure 1). Digestion of a commercial CMC with DS similar to entry 6, Table I, viz., AZC HS 600, made at high alkalinity, produces fragments with a conspicuous, main constituent at fairly high molecular weight—i.e., in long stretches of the polymer, unsubstituted oligoglucosidic sequences long enough to be recognized by the cellulase are absent. By contrast, the experimental CMCs, either from slurry- or dry-phase reactions, were hydrolyzed to fairly low molecular weight fragments—i.e., cellulase-sensitive unsubstituted "cellulose blocks" are much more frequent. We also studied bacterial digestion; it turned out that here the main factor determining the rate of oxygen uptake was the degree of substitution of the CMC rather than the method of preparation.

An alternative method of forcing aggregation of CMC molecules, viz., a minor level of chemical cross-linking, proved ineffective because of very poor reproducibility, although in a number of runs pseudoplasticity equivalent to that of xanthan was achieved. These experiments were carried out in an aqueous isopropyl alcohol slurry, with 1.5 equiv of sodium hydroxide, 1.0 equiv of sodium chloroacetate, and 0–1.6 mol % of (3-chloro-2-hydroxypropyl)trimethylammonium chloride relative to anhydroglucose. The ammonium compound was utilized as a cross-linking agent: the second functionality must evolve due to loss of trimethylamine in the warm, highly alkaline environment of the later stages of the CMC preparation.

Discussion

Our aim, viz., influencing the association behavior of CMC in solution to mimic xanthan gum's reported[3] association tendency (at room temperature), seems to have been reached. A simple modification of the usual process for CMC preparation suffices to arrive at a segmented block copolymer structure, supported by a response to enzymatic hydrolysis different from the one displayed by regular CMC, in the sense expected. The thermal behavior of xanthan gum—viz., dissociation of the complex structure at ~60 °C—is, however, NOT duplicated by the experimental CMC.[6] One is tempted to rationalize this by pointing out the high energy of cellulose crystallization, compared with the weak interactions between highly charged xanthan gum molecules.

The practical value of the experimental products may suffer from the imperfect salt tolerance; however, we may hope that in many potential applications a limited salt tolerance would not be a serious drawback.

Experimental Section

Starting Materials. Linters cellulose ER 8500 (Buckeye) was ground in a Fritsch Pulverisette mill with a 0.5-mm rasp. The molecular weight was not significantly reduced by this method of comminution. ER 4500 type linters cellulose could be used without further grinding, at least in slurry-type reactions. Its performance in a dry reaction regime was not ascertained. Technical grade MCA and MCA-Na (Akzo Zout Chemie) were used; the other chemicals used were normal laboratory grade materials.

Slurry Reactions. Ground linters cellulose, 6.5 g, is suspended in 85 g of isopropyl alcohol and cooled to 0 °C. NaOH, 6.5 g, 36.5% aqueous, and 9.4 g of water are added; the mixture is stirred vigorously for 1 h at 0 °C. Etherifying agents (MCA, MCA-Na, acrylamide, (3-chloro-2-hydroxypropyl)trimethylammonium chloride) as desired are then added and stirring is continued for 1 h at 0 °C. Then the cooling bath is substituted by a hot water bath (90 °C) and stirring is continued for 2 h under a reflux condenser. After the mixture is cooled, the product is neutralized to pH 7 with acetic acid, filtered, washed twice with 85% aqueous ethanol, and then dried at 60–70 °C, 20 mbar, 16 h.

Dry-Process Reactions. Short-duration kneading steps are used to limit mechanically induced chain scission—cf., Table V. Cellulose, 120 g, 162 g of 36.5% NaOH (2 equiv) and 1.5 g of thiourea in 72 g of 96% ethanol (2 equiv) are charged into an IKA HKD 2.5 Duplex kneader cooled to 0 °C (pumping thermostat). Three cycles of evacuation and nitrogen blanketing are used to displace air. The mixture is kneaded for 5 min at 0 °C. MCA and MCA-Na are added in the amounts desired; air is displaced again with nitrogen (3×). Five more minutes of kneading at 0 °C are used to mix the reactants. The heating/cooling system is heated to 90 °C in 5–10 min by injecting live steam into the thermostat tank; kneading is continued. After kneading is continued for 15 min the reactor is opened to check whether any of the reaction mixture has escaped kneading by sticking to an unscraped section of the reactor. If so it is cut loose. Air is displaced again and five more minutes of kneading complete the reaction. The product is discharged into a 3-L beaker and quenched with 1.5 L of 85% aqueous ethanol, neutralized with acetic acid to pH 7 in the supernatant, filtered off, and washed a second time with 1.5 L of 85% ethanol. After filtration it is dried at 60–70 °C, 0.5 mbar, 16 h.

Analyses. DP (Cu-ethylenediamine), DS and substitution pattern (acid wash/titration; hydrolysis/derivatization/GC), and bacterial digestion all were performed according to procedures published elsewhere.[5] Enzymatic hydrolysis/GPC was performed by incubating 60 mg of CMC dissolved in 47 mL of phosphate buffer (pH 6) with 3 mL of 0.5 g/L solution of cellulase (Trichoderma viride) in phosphate buffer for 24 at 37 °C and then analyzing over a Nucleosil 50 column with RI detector.

Rheological Measurements. Solutions of products (1 wt % solids, unless indicated otherwise) were prepared by slow agitation (tumbling and rolling) and studied by using a Weissenberg cone and plate rheometer and a Carri-Med machine: cf. ref 6.

Registry No. CMC, 9000-11-7; xanthan gum, 11138-66-2; acrylamide, 79-06-1; (3-chloro-2-hydroxypropyl)trimethylammonium chloride, 3327-22-8.

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