

Carboxymethyl-Cellulose-Grafted with Dextrin Synthesis and Solution Rheology

D. J. SIKKEMA, *Enka bv, Research Institute Arnhem, Velperweg 76,
Arnhem, The Netherlands*

Synopsis

Carboxymethyl cellulose grafted with dextrin (CMC-*g*-dextrin) products are easily accessible by reacting freshly prepared CMC with the acid alcoholysis product from starch and glycerol monochlorohydrin. The success of the grafting reaction depends on adjusting the alkalinity of the grafting reaction mass prior to addition of the dextrin chlorohydrin reagent. In all, less NaOH should be applied than theoretically necessary for all chlorine substitution. In some cases the products show interesting rheology at very low shear, but rather CMC-like rheology or more Newtonian behavior than CMC at shearing rates over a few reciprocal seconds. These results reinforce the credibility of the view that natural polysaccharide gums with unusual rheologies derive their special properties from their well-defined substitution pattern rather than from their overall degree of substitution with (oligo)saccharide units.

INTRODUCTION

Inspection of the structure of natural gums with unusual solution rheologies, such as locust bean gum and especially xanthan gum,¹ brings to mind the speculation that oligosaccharide side chains, flexibly coupled with a semirigid cellulose-analogous main chain, might give rise to more effective H-bonding between polymer molecules than is possible in solutions of simpler cellulose derivatives like CMC or hydroxyethyl cellulose, lacking such oligosaccharide side chains. This line of reasoning suggested a study of the synthesis and solution rheology of CMCs grafted with dextrin—including variation of the CMC degree of carboxymethylation, the degree of dextrin grafting, and the molecular weight of the reactive dextrin used.

EXPERIMENTAL

Materials. Cotton linters cellulose (DP \sim 4500) from one batch was used in all experiments. Dextrin chlorohydrin was prepared by heating dried (16 h, 80°C, 20 mbar) starch with the appropriate amount of glycerol monochlorohydrin and a catalytic amount of concentrated sulfuric acid, with kneading, to 140°C. The hot residence time was minimized in order to limit discoloration; 15–30 min proved amply sufficient to arrive at substantially homogeneous melts which were fairly viscous in the case of the higher MW dextrans. Upon cooling, the products with DP > 1 could be broken up and ground; the DP = 1 product remained a syrup. The ground products of DP < 5 had to be stored with refrigeration to avoid slow fusing. The further

necessary chemicals were of customary laboratory grade and used as received.

CMC-g-Dextrins. 6.5 g of cellulose was slurried in 108 mL of *i*-propanol and cooled with an ice-water bath. 0.9 . . . 1.5 eq of NaOH relative to anhydroglucose, as desired, in 16.1 g of water was added and the mixture was stirred for 1 h at 0°C.

The desired amount of sodium chloroacetate was then added at 0°C; after further mixing at 0°C for 1 h the reaction mixture was heated on a waterbath kept at 90°C for 2 h. The water bath then was removed until reflux stopped; if desired the alkalinity was adjusted using further NaOH (40% aqueous solution) or acetic acid and then the dextrin chlorohydrin reagent was added—powdered if its DP was 3 or higher, dissolved (40%) in hot aqueous *i*-propanol (13% of water) for DP = 1. Handling of dextrin chlorohydrin with DP = 3 was very difficult due to its semisolid, sticky character.

Further heating with a water bath at 90°C for 2 h usually completed the reaction, although in a few cases the mixture then was cooled to 0°C, some more chloroacetate was mixed in over 1 h at 0°C, and further heating took place at reflux for 1 h.

The products were isolated by cooling, addition of a little acetic acid to neutralize any remaining alkali, filtering with suction, and washing with 85% ethanol.

Analysis. NMR analysis (Bruker WH 270 machine) of the dextrin chlorohydrin of highest interest, viz., DP = 7, was difficult to be confidently interpreted in all details; proton and ¹³C spectra confirmed the chlorohydrin presence, the scrambling of glucosidic bond types. GPC analysis of the dextrin chlorohydrins (aqueous phase, PSK gels from Toyo Soda) confirmed the molecular weight range expected and showed only traces of high molecular weight materials (unchanged starch) for each of the dextrin chlorohydrin products.

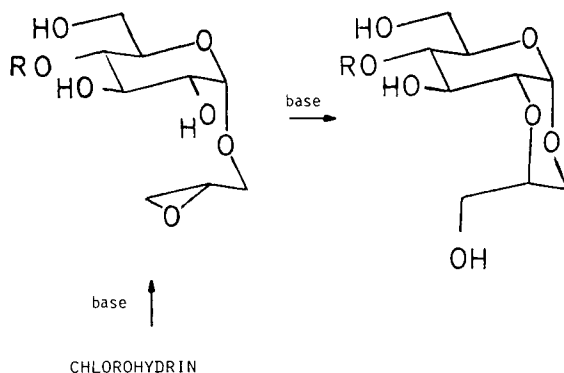
Reaction yields of the grafting reactions were estimated by ultrafiltration (Amicon): a filter with a cutoff of MW ~ 1000 was used for the dextrins with DP = 1–5, and a cutoff of MW ~ 5000 was used for the dextrin with DP = 7. In the case of products made with dextrin chlorohydrin with DP = 1, the results may be somewhat optimistic because of some removal of nongrafted dextrin during the washing step; the higher dextrins proved to be very poorly soluble in aqueous ethanol.

Rheology characterization was performed with 1 wt % aqueous solutions using a Haake Rotovisko RV 2 viscosimeter at shear rates of 20–900 s⁻¹ and with a HP 86 computer-controlled Weissenberg rheogoniometer (cone-plate, 1°) modified with a moving coil motor for shear rates of 0–2 s⁻¹.

RESULTS AND DISCUSSION

A number of experiments is summarized in Table I.

In view of the side reactions that may be anticipated for the grafting reaction envisioned (with intramolecular deactivation of the chlorohydrin functionality by ring closure in the dextrin reagent as the foremost candidate) the grafting efficiency recorded is gratifying (~70%):



Scheme I

Mild alkalinity during the grafting cycle appears very beneficial; poor results were obtained when unconsumed NaOH would remain after the chlorohydrin ring closure; alkalinity less than theoretically necessary for all chlorine substitution at the time of dextrin reagent addition proved preferable. It should be noted that the stoichiometry suggests that significant quantities of the dextrin were bound by ester formation between —COONa groups in the CMC base product and the chlorohydrin groups. Combining high alkalinity during the carboxymethylation step with (relatively) low alkalinity during the grafting reaction presents the optimum procedure; excellent solubility and thus higher viscosity at a given overall polymer concentration is achieved, with excellent reproducibility. For instance, 1.5 eq of NaOH for alkalization, 0.9 eq of sodium chloroacetate, then 0.3 eq of acetic acid just prior to addition of 0.5 eq of dextrin chlorohydrin (DP = 7) gave a product with grafting efficiency 65%, Brookfield viscosity of a solution containing 1% of cellulosic backbone material as high as 16.5 Pa s, but a rather more Newtonian rheology than regular CMC.

With but a few exceptions, rather poor results, both in terms of product appearance and of viscosity, were obtained when using dextrin chlorohydrins with DP 3, 4, and 5. These chlorohydrins are hygroscopic solids, insoluble in the reaction slurry medium, and become very sticky when wet. The poor results may be due mostly to these physical properties. By contrast, the dextrin with DP = 1 is soluble in hot aqueous *i*-propanol, and the material with DP = 7 is much less hygroscopic and less prone to form tacky lumps than the lower MW dextrans.

A curious effect of the addition of free dextrin chlorohydrins to 1% CMC solutions was observed. The oligomeric dextrin chlorohydrins (but not material with DP = 1) appreciably depressed the viscosity of CMC solutions (Table II). One may speculate on the mechanism of this peculiar interaction—at any rate the phenomenon may partly explain the especially low viscosities encountered in solutions of products that were expected to contain appreciable quantities of free dextrans (from inhomogeneous appearance, etc.).

TABLE I
Data Illustrating the Effect of Alkalinity During the Grafting Reaction^a

Run no.	eq of MCA-Na added	g of dextrin added	DP of dextrin	Graft efficiency (%)	Viscosity Brookf, 1% cel (mPa)	Rheol. type	Appearance
(A)							
1	0.9	0	—	—	1250	C	Good ^b
2	0.5	4.4	1	73	400	N	Good
3	0.5	8.7	1	65	1200	N	Good
4	0.9	8.7+NaOH	1	78	700	N	Good
5	0.5	9.3	3	62	3000	X	Good
6	0.5	14.7	5	65	400	—	Fused lumps
7	0.5	19.9	7	56	200	—	Fused lumps
8	0.9	19.0	3	—	1600	N	Inhomog
9	0.9	24.2+NaOH	4	—	1300	—	Inhomog
10	0.7	6.6	1	—	15000	CC	Good
11	0.7	24.2	4	—	4000	X	Pellets
12	0.7	9.9	7	80	2800	X	Good
13	0.9	19.9+NaOH	7	80	5300	N;CC	Good
14	0.5	10.0	7	82	1200	N	Good
15	0.7 ^c	10.0	7	80	1200	X	Good
16	0.9	10.0	7	79	2100	CC	Good
17	0.7	8.7	1	69	8000	C	Good
(B)							
1	0.5	8.7	1	—	70	—	Inhomog
2	0.5	9.3	3	—	7	—	Inhomog
3	0.9	10.0	7	—	45	—	Inhomog
(C) optimized alkalinity profile							
1	0.9	10.0	7	65	16500	N	Good

1.5 eq NaOH for alkalization; 0.3 eq of acetic acid prior to dextrin

^a 0.9 eq of NaOH during alkalization (A runs) gave good grafting efficiency but poor access of the cellulose during carboxymethylation, resulting in mediocre solubility. 1.5 eq of NaOH for alkalization (B runs) gave very poor dextrin incorporation; optimized alkalinity is shown in the last example. Poor reproducibility was recorded with the dextrin chlorohydrins of DP 3–5. Generally, poor results were obtained if more than about 2.5–3 times as much dextrin was used as cellulose substrate (g). Rheology type: N = less pseudoplastic than regular CMC; C = resembles regular CMC—20 . . . 1000 s⁻¹; X = somewhat xanthan like at 0–2 s⁻¹; CC = CMC like at 0–2 s⁻¹. Note that ALL products showed either CMC type or more Newtonian behavior at higher shear rates. Brookfield viscosities are given for solutions containing 1% of cellulose backbone material (i.e., substantially more in the case of products made with large amounts of dextrin).

^b Good appearance: homogeneous, somewhat fibrous.

^c 0.2 eq of MCA-Na added after the grafting cycle.

Rheological studies at shearing rates of 20–900 s⁻¹, and especially at 0.02–2 s⁻¹ (Figs. 1–3) point to the existence of a weak gel-like structure in a xanthan gum solution-at-rest, and, perhaps more importantly, to pronounced orientation effects in the xanthan solution which relax slowly—possibly further retarded by the formation of a new gel-like structure in the oriented solution upon termination of the shearing action. Liquid crystalline behavior of concentrated xanthan gum solutions was reported recently.²

TABLE II
 Brookfield Viscosities Found for Physical Mixtures of CMC Staflo HZ 900 (Enka) upon
 Addition of Various Sugar Derivatives (mPa s); pH = 7

Blank (1% CMC)	1305
+1% dextr. chloroh. DP = 7	920
+3% dextr. chloroh.	595
+1% dextr. chloroh., DP = 3	600
+3% dextr. chloroh.	340
+3% dextr. chloroh., DP = 1	2040
+1% starch Cellocol LZ	1185
+3% starch Cellucol LZ (Avebe)	1980
+1% fructose	1335
+3% fructose	1320
+2% sucrose	1265
+1% methyl glucoside	1215
+3% methyl glucoside	1200
+2% butyl glucoside	1140
+1% benzyl glucoside	1450

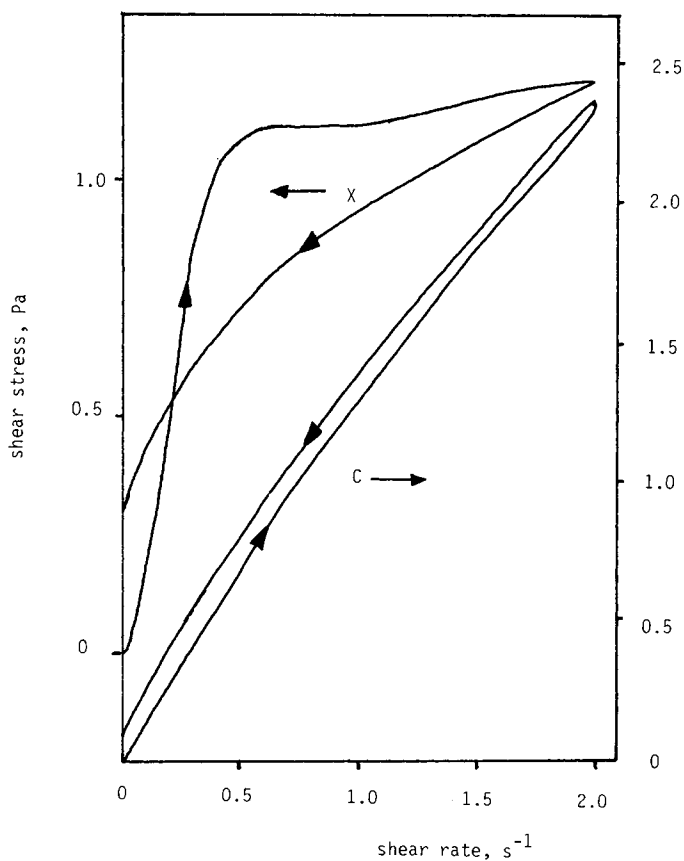


Fig. 1. Low shear rate rheograms of 0.5% xanthan gum (Kelco; curve X) and of 1% CMC (sample A1, Table 1; curve C) solutions. Sample A 15 showed a curve almost identical to the CMC curve shown, but the hysteresis was limited to shear rates < 1/s.

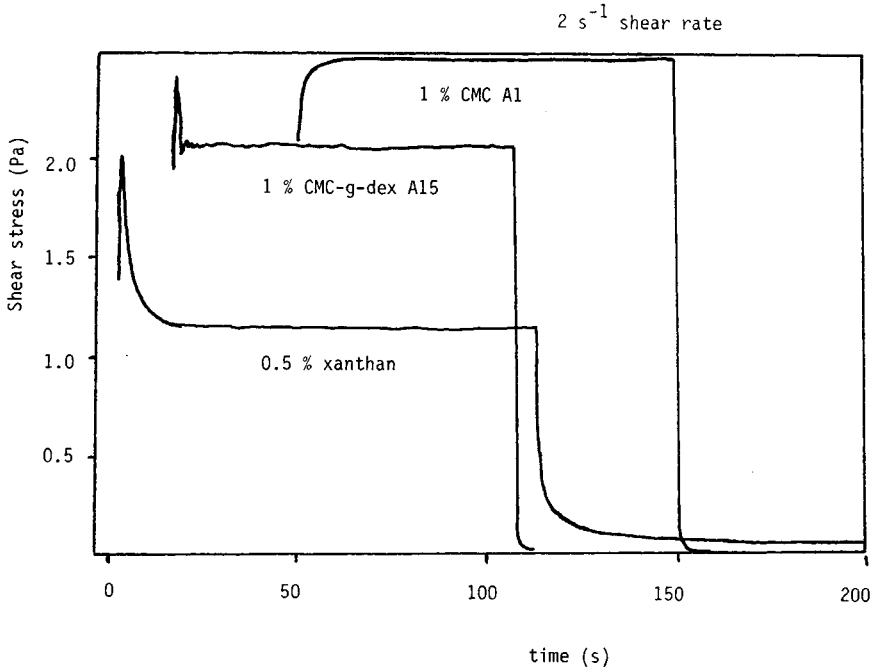


Fig. 2. Studies at low shear rate (2 s^{-1}) with abrupt start and stop of shearing. Note the overshoot in the xanthan gum solution, emulated by CMC-*g*-dextrin A 15; note the fact that, after 100 s of rest, the xanthan gum solution is not yet fully relaxed.

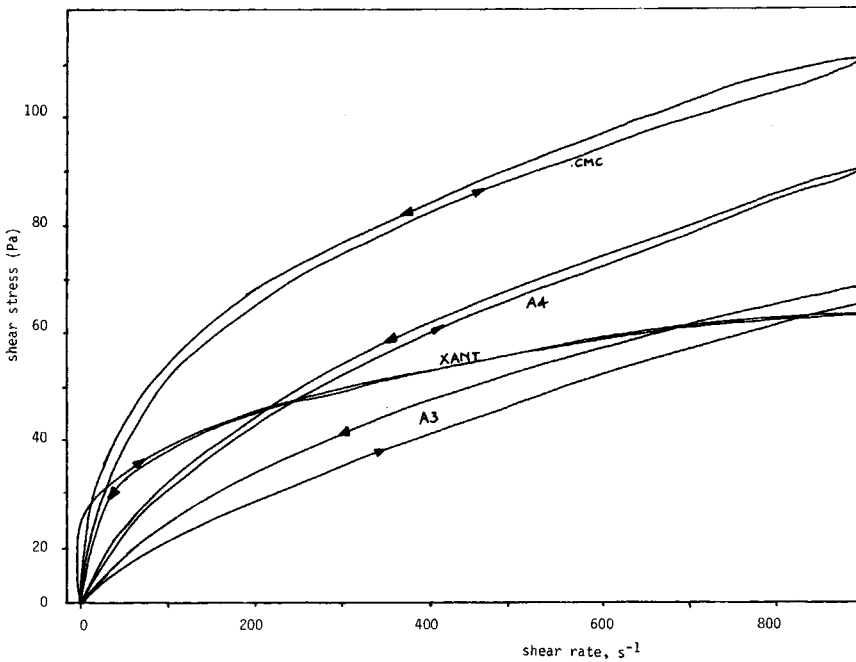


Fig. 3. High shear rate rheograms showing the behavior of CMC (sample similar to experiment B 3, leaving out the dextrin grafting step), the somewhat less pseudoplastic behavior typical of CMC-*g*-dextrin products, and xanthan gum. Concentrations: 1 wt %.

By contrast, the CMC solution appears to require some orientation in order to arrive at equilibrium shear stress; relaxation is very fast. The hysteresis in shear stress found for xanthan upon increasing vs. decreasing the shear rate is wide, but concentrated at low shear rate values; CMC solutions show a narrow hysteresis loop that continues over the whole range of shear rates applied.

The dextrin grafted CMCs, with carboxymethylation degree of substitution varying from 0.3 to 0.7, and with dextrin DS 0.35–0.7 at a dextrin DP of 1–7 (reaction results were best with DP = 1 and DP = 7; at intermediate DPs reproducibility was a problem) showed a rheology similar to regular CMC, or somewhat better Newtonian behavior than CMC, at 20–900 s⁻¹. At very low shear rates, a few of the new products differ markedly from CMC in the point that (in the time studies) they jump immediately to the equilibrium shear stress, with the suggestion of overshoot as it is so pronounced in xanthan gum (i.e., breakup of a weak gel-like structure). These products also show a xanthan-like limitation of hysteresis effects to the low shear rate region.

The present results suggest that nonspecific intermolecular H-bond structure formation present in the fairly concentrated solutions of the randomly dextrin substituted CMCs studied in this work may be responsible for gel-like structures that are important in the solution at rest, but the response to higher shear rates that is characteristic for xanthan gum clearly depends on other factors, the extremely large effective chain length of xanthan aggregates³ being a likely candidate. There can be little doubt that this aggregation of xanthan gum in solution—at room temperature^{3,4}—stems from the specificity and regularity of the cellulose backbone substitution with trisaccharide units, giving rise to optimal fit in the H-bonds stabilizing the aggregates.⁵

CONCLUSION

An efficient synthesis of CMC-*g*-dextrin was developed; very high viscosities are exhibited by their solutions (if concentrations are normalized to 1% of cellulosic material) compared with regular CMC. The rheology of the solutions proved to be unspectacular, however. Duplication of the special rheology shown by some natural gums may require duplication of the specificity of the substitution pattern in those natural gums.

The assistance of D. B. van Guldener, T. Kuipers, and H. Jansen in synthetic, analytical, and rheological work, NMR experiments by A. J. M. Weber and A. J. J. de Breet, rheology work at very small shear rates by J. G. Westra, and GPC experiments by F. A. Buytenhuys and Ms. M. Meerinx are gratefully acknowledged.

References

1. P. E. Jansson, L. Kenne, and B. Lindberg, *Carboh. Res.*, **45**, 275 (1975).
2. M. Milas and M. Rinaudo, *Polym. Bull.*, **10**, 271 (1983).
3. C. Holzwarth and E. B. Prestridge, *Science*, **197**, 757 (1977).
4. S. Paoletti, A. Cesaro, and F. Delben, *Carboh. Res.*, **123**, 173 (1983).
5. A. Jeanes, J. E. Pittsley, and F. R. Senti, *J. Appl. Polym. Sci.*, **5**, 519 (1961).

Received July 22, 1984

Accepted December 12, 1984