

Viscosity Changes of Aqueous Carboxymethyl Starch by Partial Crosslinking and Montmorillonite Addition

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ABSTRACT: Slightly crosslinked carboxymethyl starch (cCMS) with degree of substitution (DS) 0.8–0.9 was prepared using mono- and di-chloroacetic acids (MCA and DCA, respectively). Constant molar ratio of halogenated acetic acid derivatives to anhydroglucosidic unit (AGU) was adjusted (MCA+DCA):AGU=1.75:1; whereas, DCA:AGU ratio was changed in a range 0–0.10:1. The viscosity of 2 wt % cCMS aqueous solutions increased substantially for very slightly crosslinked product (DCA:AGU molar ratio 0.0075), in comparison to unmodified CMS, up to 170,000 mPa·s at 1 rpm, and 16,000 mPa·s, respectively. Some viscosity decrease of cCMS solutions during storing was observed. The explanation of this phenomenon was discussed and supported by ¹H NMR results. The rheological properties of cCMS solutions as well as aqueous cCMS/clay dispersions with various type of montmorillonite (MMT): sodium, calcium and organophilized as shear-thinning systems were evaluated on a basis of power law model. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40793.

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INTRODUCTION

Starch has become one of the most attractive renewable and low cost polymer. Chemical modification of starch is performed to overcome the shortcomings of native starch such as insolubility in cold water, uncontrolled or hardly controlled viscosity of aqueous solution, tendency to retrogradation and so forth.^{1–3} The solubility in cold water can be ensured in various ways, for example, by introduction of anionic groups into starch macromolecules via carboxymethylation^{1–3} or succination.⁴ The properties of carboxymethyl starch (CMS) solutions are determined mainly by the degree of substitution (DS) and botanical origin of starch.¹

Additional chemical treatment of the polysaccharide during CMS synthesis, for example, partial crosslinking^{5,6} or posteriori introduction of hydrophilic nanofiller, such as montmorillonite⁷ can also result in higher viscosity level of CMS aqueous solutions (or clay slurries).

Despite unmodified CMS exhibits lower thickening effectiveness than cellulose ethers (e.g. carboxymethyl cellulose CMC) its lower price as well as more ecological technology of synthesis allowed CMS to replace cellulose ethers in many applications, that is: as thickening and sizing agent in textile industry,^{8,9}

pharmacy,¹⁰ personal care products and surfactant systems,¹¹ as flocculants,¹² drilling fluids¹³ or coating materials.⁵

Chemical modification of starch toward CMS derivatives with thickening properties can be performed by simultaneous carboxymethylation and partial crosslinking method.^{6,14}

Seidel et al.⁶ prepared hydrogels using dichloroacetic acid (DCA) in the presence of monochloroacetic acid (MCA)-typical carboxymethylation agent. CMS gels with DS in a range 0.4–0.5 were synthesized and designated for ultrasonic medical purposes. However, no data on reagents ratios (i.e. starch, MCA, DCA) were given. Hess et al.¹⁵ synthesized CMS with DS 0.45–1.20 containing both soluble as well as swellable fractions using molar ratios DCA:AGU 0.06–0.10 and MCA:AGU 1:1 and 1:2.5. The authors reported that fraction of water soluble polymer was ca. 11 wt %.

Cold-water swellable crosslinked CMS derivatives giving highly viscous aqueous solutions were claimed by Portnoy & Eastman.¹⁴ The manufacture method based on starch etherification with MCA (or its sodium salt, SMCA), subsequent neutralization (e.g. with acetic acid), and drying to cure.

Montmorillonite (MMT) has been used as thickening and thixotropic agent in paint and mineral oil industry, antifriction agent in building industry or emulsion stabilizer in pharmaceutical industry.¹⁶

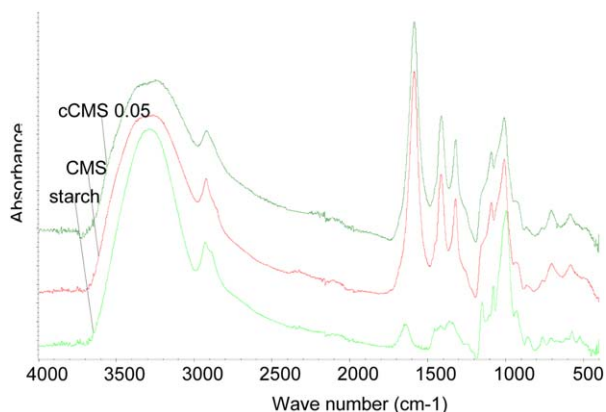


Figure 1. FTIR spectra of native potato starch, CMS (DS = 0.93) and cCMS 0.05 (DS = 0.86). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Reports on CMS/MMT aqueous dispersions viscosity characteristics are very limited,⁷ however some works on CMC/MMT aqueous systems are reported.^{17,18}

The aim of this article was to: (i) synthesize carboxymethyl starch derivatives by simultaneous etherification and slight crosslinking of potato starch using DCA, (ii) evaluate rheo-viscometric characteristics of 2 wt % aqueous solutions of prepared cCMS as well as dispersions with montmorillonites. Three types of montmorillonites have been applied for aqueous cCMS/clay dispersion preparation: sodium MMT (MMT-Na), calcium MMT (MMT-Ca), and organophilized MMT (MMT-ZS1).

EXPERIMENTAL

Materials

Potato starch (Nowamyl S.A, Nowogard, Poland) with amylopectine 69% and amylose 31 wt % content was applied after controlling the moisture content. Monochloroacetic acid (a.g. Chempur, Poland) was used as etherifying reagent. Dichloroacetic acid (99%, Acros Organics) acted as crosslinking agent, and isopropanol (IPA) (pure, Chempur) as a reaction medium. Sodium hydroxide (microgranules), acetic acid, and copper sulphate pentahydrate were the products of Chempur, Poland, murexide, and ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA) of Sigma-Aldrich.

Sodium montmorillonite and calcium montmorillonite (technical grade, ZGM Zebiec S.A., Poland) were purified via centrifugation (MLV K23D, 3000 rpm, 10 min) before use. Organophilized montmorillonite ZS1 modified with semihydrophilic ammonium salt bearing long chain aliphatic and aromatic substituents with several hydroxyl groups was the pilot plant product of ZGM Zebiec S.A.

Preparation of CMS and Slightly Crosslinked CMS

The reactions were performed in a glass bath reactor (1.0 L) equipped with mechanical anchor stirrer, thermocouple and capillary tube supplying nitrogen. MCA and DCA were dissolved in IPA in the glass reactor, and then aqueous solution of NaOH was

Table 1. Description of CMS Synthesized Using MCA and DCA as well as DS and Viscosity of 2 wt % Aqueous Solutions

Sample acronym	DCA : AGU [mol : mol]	(DCA+MCA) : AGU [mol : mol]	DS ^a	RE [%]	Viscosity 1→100 rpm [mPa·s]	n From eq. 3	R ²
CMS	0.00	(0 + 1.7500)	0.93 (0.94)	54	16,000 → 1260	0.445	0.998
cCMS 0.0075	0.0075	(0.0075 + 1.7425)	0.91 (0.93)	53	170,000 → 7100	0.315	0.999
cCMS 0.015	0.015	(0.0150 + 1.7350)	0.88 (0.89)	51	140,000 → 5000	0.266	0.996
cCMS 0.025	0.025	(0.0250 + 1.7250)	0.86 (0.86)	49	110,000 → 5800	0.357	0.999
cCMS 0.033	0.033	(0.0330 + 1.7170)	0.85 (0.86)	49	60,000 → 2700	0.316	0.996
cCMS 0.050	0.050	(0.0500 + 1.7000)	0.86 (0.86)	49	45,000 → 3000	0.406	0.995
cCMS 0.075	0.075	(0.0750 + 1.6750)	0.89 (0.88)	51	50,000 → 3000	0.396	0.995
cCMS 0.10	0.10	(0.1000 + 1.6500)	0.79 (0.79)	45	16,000 → 1000	0.384	0.994

Total of 9.5% starch; 10.5% water; NaOH : MCA = 2.25; T = 50°C; t = 2.5 h.

^a DS values in brackets determined after 9 months of storage; precision of determination ± 0.02 unit.

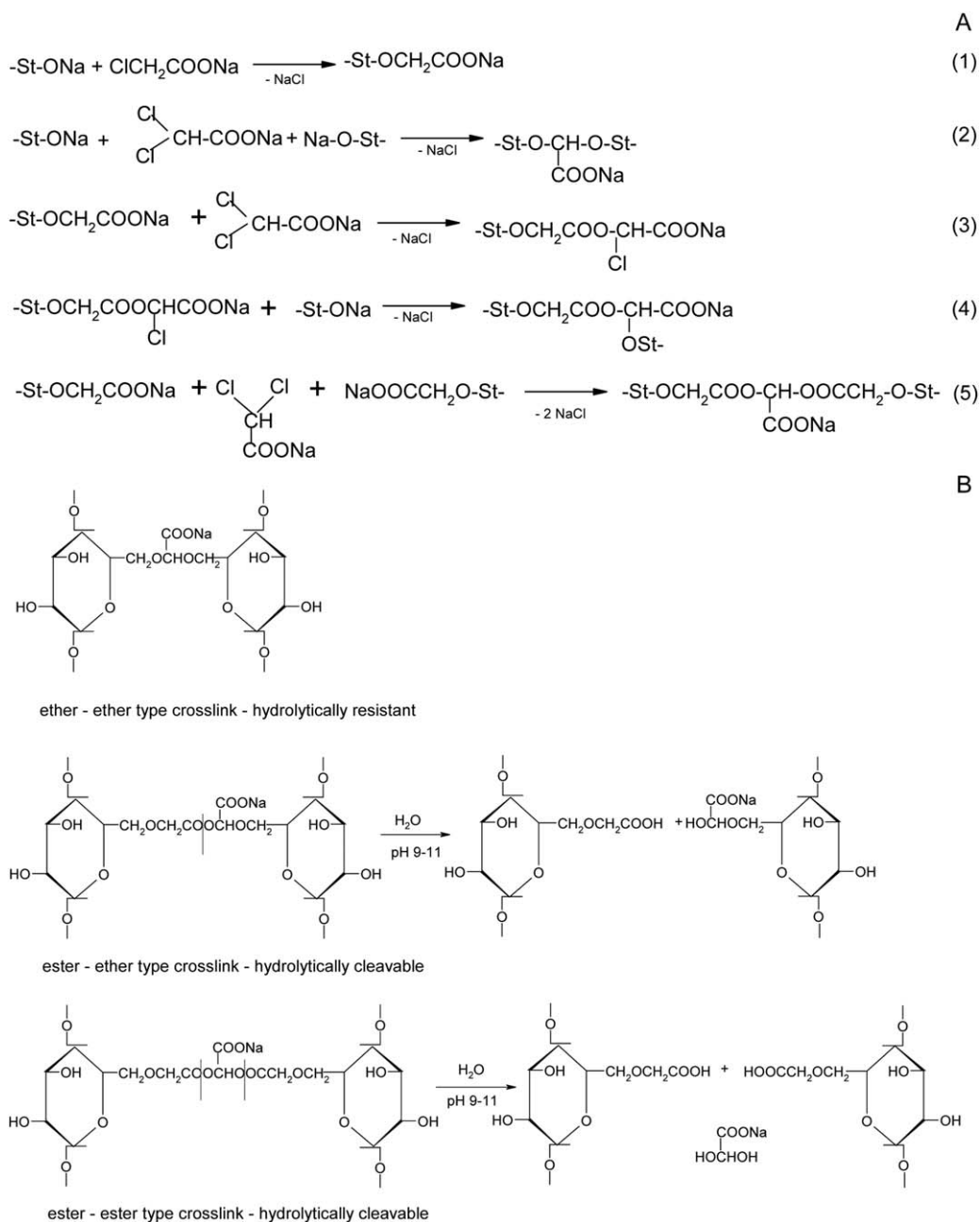


Figure 2. Chemical reactions between polysaccharide chains of starch and MCA and/or DCA —A; and scheme of bridging bonds between polysaccharide chains of starch—B.

added. After 15 min agitation, when the mixture became homogeneous, 30 g starch (ca. 14 wt % moisture) and remaining part of NaOH microgranules were slowly introduced. The final ratio of IPA/water was 89.5:10.5 wt/wt reaction was continued for 150 min at 50°C. After cooling to room temperature, the raw product was filtered, neutralized with glacial acetic acid, washed five times with 80 wt % methanol and eventually with pure methanol. The washed product was dried in the air (leaving on the warm surface at ca. 35°C).

Preparation of CMS/MMT Dispersions

Purified MMT-Na, MMT-Ca, or MMT ZS1 were dispersed in distilled water in 250 cm³ beaker and stirred for 30 min at 400 rpm.

Next, CMS or cCMS was introduced to the aqueous montmorillonite slurry continuously mixing for 60 min (500 rpm) at room temperature to obtain 2 wt % polymer concentration.

DS Determination

The degree of substitution was measured according to the method described in article.¹⁹ CMS or cCMS sample was moisturized by 1 cm³ of ethanol and dissolved in 50 cm³ distilled water. Subsequently 20 cm³ of buffer was added (0.187M NH₄Cl solution), adjusted to neutral pH, and then the whole mixture poured into measured flask with 50 cm³ of CuSO₄ (0.039M solution). After 15 minutes water was added and the

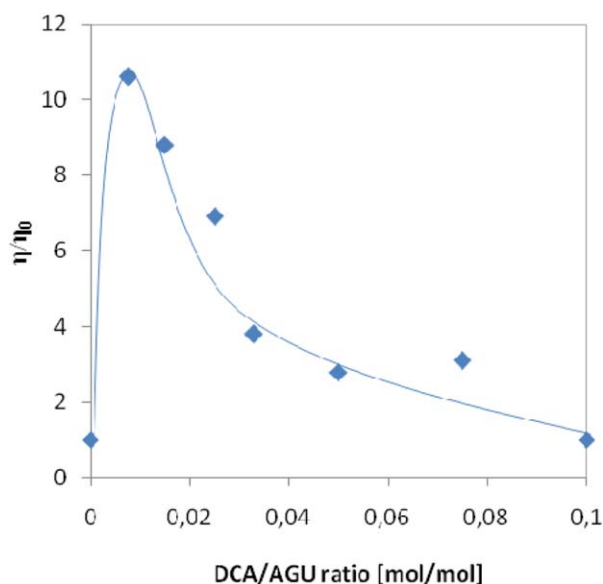


Figure 3. Change of relative viscosity of 2 wt % aqueous solutions as a function of DCA/AGU ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content was filtered. The filtrate was titrated with EDTA solution in presence of murexide as an indicator.

Viscosity Measurements and Shear-Thinning

The rheoviscometric characteristics of 2 wt % aqueous solutions of CMS and cCMS were evaluated at 25°C (usually 30 min after preparation or after predetermined storage time) adjusting spindle rotation from 1 up to 100 rpm (Bookfield RV).

Instrumental Methods

FTIR spectra of the starch samples before and after chemical modification were recorded by Nexus (Thermo-Nicolet) using ATR (Golden Gate) technique. For each sample 32 scans were taken from 4000–400 cm^{-1} .

Room temperature solution ^1H NMR spectra were recorded using Bruker Avancee DRX apparatus operating at 300 MHz. Samples for measurements were dissolved in D_2O .

RESULTS AND DISCUSSION

FTIR Spectroscopy

Starch carboxymethylation resulted in appearing new bands and influenced the intensity of those characteristic for native starch. FTIR spectra of native potato starch, CMS (DS = 0.93) and cCMS 0.015 (DS = 0.88) were given in Figure 1. A broad band at 2900–3600 cm^{-1} was assigned to hydrogen bonded hydrogels of the polysaccharide chains. The intensity of this band decreased with increased DS value. A band at 2950 cm^{-1} was attributed to CH_2 symmetrical stretching vibrations. The strong peaks at 1595, 1415, and 1315 cm^{-1} were assigned to carbonyl CO asymmetric and symmetric COO^- groups, CH_2 scissoring and OH bending vibrations, respectively. These bands confirmed the carboxymethylation modification.^{7,20}

Influence of DCA Content on DS Values of Carboxymethylated Starch

The synthesis of slightly crosslinked carboxymethyl starch was performed using variable content of both halogenated derivatives of acetic acid, that is, MCA and DCA; however, the molar ratio of MCA and DCA together to anhydroglucosidic unit of the polysaccharide chain (AGU) was constant, that is, (DCA+MCA) : AGU = 1.75 : 1 (Table I). DCA : AGU ratio was changed in a range 0–0.10 mol/AGU mol. Above this range too dense crosslinking net prevented CMS complete solubility in water, thus swellable hydrogels were formed.

It could be seen that an increase of DCA content in reaction system up to 0.10 mol/AGU resulted in slow decrease of DS from 0.93 to 0.79 (Table I). However, for DCA : AGU ratios in a range 0.015–0.075 the values of DS are very similar (0.86–0.89). Only when DCA introduced to reaction system was above 5 mol% in mixture of the both chloroacetic acid reagents (i.e. DCA : MCA 0.1 : 1.75) significant DS values decrease was observed. It was found that DS values were stable during samples storage of at least 9 months.

A reason of diminishing DS value observed with DCA content (whereas total molar ratio of anionic groups per AGU in substrates was constant) could be consumption of some carboxymethyl groups during synthesis (Figure 2). It may be seen [Figure 2(A), line 3 and 5] that self-catalyzed esterification reaction between strong acidic bifunctional DCA and carboxymethyl sodium salt functionality on polysaccharide chains caused a reduction of available anionic moieties. Such esterification reactions could be realized in alkali aqueous environment using gelatinized systems or suspended granular starch in alcohol solvent. Ester derivatives with various alkyl chain length (up to C_{10} – C_{18}) and DS up to 0.3 could be obtained.^{21,22} A consequence of ester bonds presence in bridging cross-links between polysaccharide chains [Figure 2(B)] will be discussed when cCMS aqueous solution viscosity changes during storage are

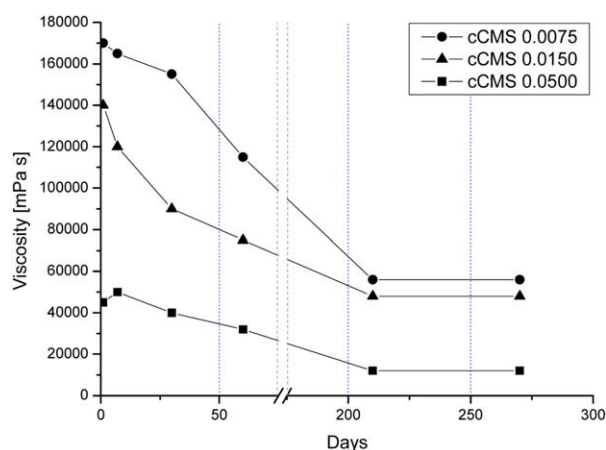


Figure 4. Viscosity changes during storage of 2 wt % aqueous solution of cCMS crosslinked with DCA (1 rpm, 25°C). Viscosity data are for cCMS solutions prepared from freshly synthesized samples—stored up to 60 days, as well as for newly prepared solutions from samples stored in solid form—after 210 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

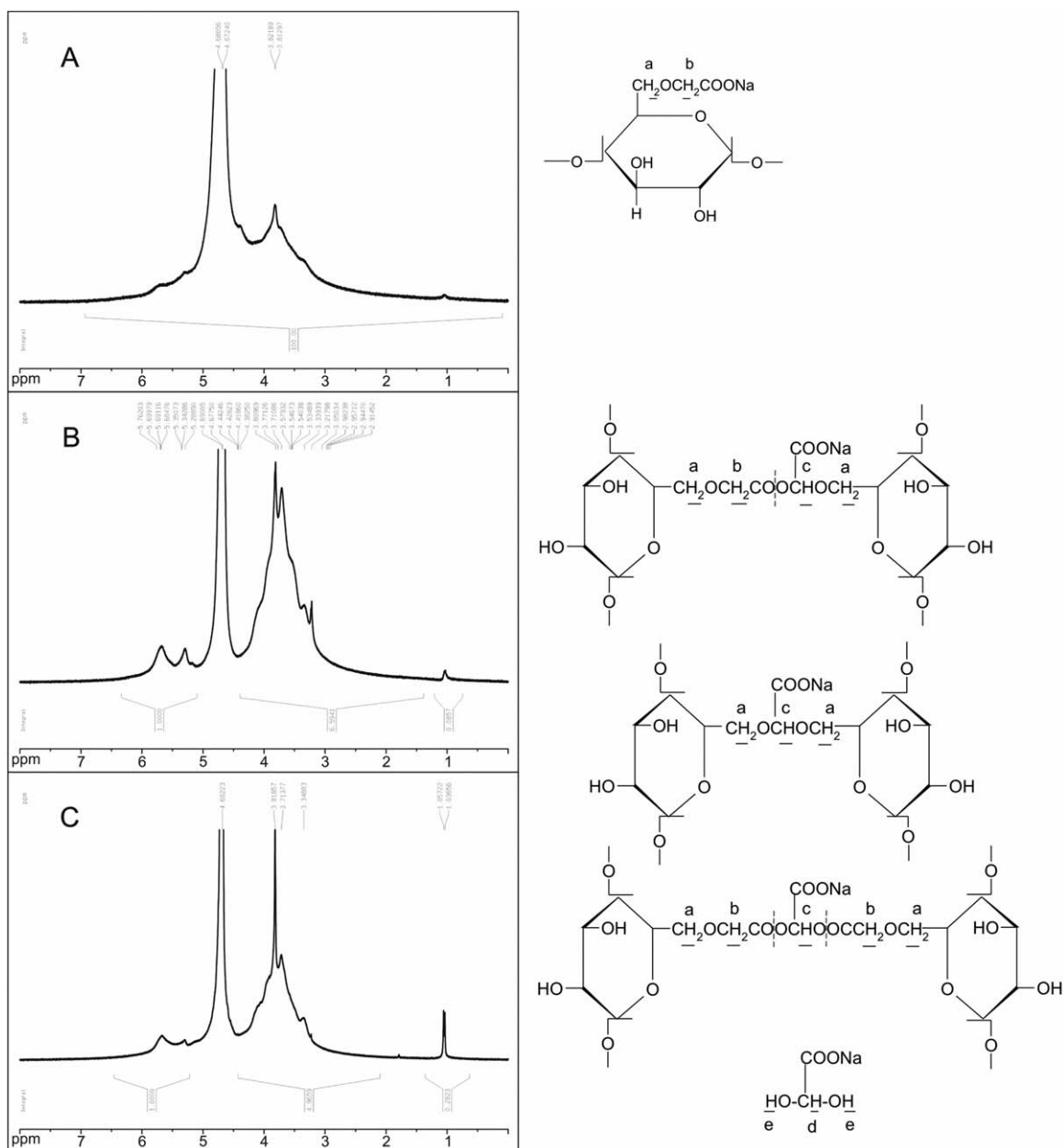


Figure 5. ^1H NMR spectra of CMS (DS = 0.93)—A; and cCMS 0.015 (DS 0.88) after few days since synthesis—B; as well as after 9 months of storage—C.

considered. The determined DS values of carboxymethylated starch were in a rather narrow range $0.85 \pm 10\%$ and in the first approximation can be used to evaluate the effect of DCA crosslinker content on viscosity of cCMS aqueous solutions or cCMS/MMT aqueous dispersions.

The efficiency of carboxymethylation was in a range 54–45% and decreased with DCA content (Table I).

Viscosity of Slightly Crosslinked Carboxymethyl Starch Aqueous Solutions

Generally, 2 wt % aqueous solutions of slightly crosslinked carboxymethyl starches exhibited higher viscosities in comparison to those based on CMS synthesized without DCA (Table I). The

maximum relative viscosity increase, that is, η/η_0 versus DCA/AGU ratio (where η and η_0 were viscosity of 2 wt % solutions of cCMS and CMS, respectively) was found for very slightly crosslinked cCMS products, that is, 170,000 mPa·s and 140,000 mPa·s for 0.0075 and 0.0150 mol DCA : AGU ratios, respectively (measured at 1 rpm spindle rotation) (Figure 3). An increase of DCA content up to 0.10 mol DCA/AGU resulted in gradual viscosity decrease to the same level as for uncrosslinked CMS (i.e. 16 000 mPa·s).

The observed viscosity increase was probably caused by an increase of chain entanglements level as result of interchain crosslinking causing enhanced ability to trap water molecules inside.²³ Viscosity enhancement for aqueous solutions of slightly

Table II. Viscosity of Aqueous Dispersions for System 2 wt % CMS and cCMS Crosslinked with Two DCA Ratios for Various Clay Types and Their Contents

Sample acronym	DCA : AGU [mol : mol]	(DCA+MCA) : AGU [mol : mol]	DS	Viscosity 1→100 rpm [mPa·s]
CMS without clay	0.000	(0 + 1.7500)	0.87	13,000 → 780
CMS MMT-Na 2	0.000	(0 + 1.7500)	0.87	28,600 → 1610
CMS MMT-Na 5 phr	0.000	(0 + 1.7500)	0.87	28,000 → 1590
CMS MMT-Ca 2 phr	0.000	(0 + 1.7500)	0.87	31,000 → 1820
CMS MMT-Ca 5 phr	0.000	(0 + 1.7500)	0.87	28,000 → 1610
CMS MMT-ZS1 2 phr	0.000	(0 + 1.7500)	0.87	25,000 → 1530
CMS MMT-ZS1 5 phr	0.000	(0 + 1.7500)	0.87	22,000 → 1470
cCMS 0.015 without Clay	0.015	(0.015 + 1.7350)	0.81	46,000 → 2600
cCMS 0.015 MMT-Na 2 phr	0.015	(0.015 + 1.7350)	0.81	75,000 → 2750
cCMS 0.015 MMT-Na 5 phr	0.015	(0.015 + 1.7350)	0.81	70,000 → 3000
cCMS 0.015 MMT-Ca 2 phr	0.015	(0.015 + 1.7350)	0.81	75,000 → 3350
cCMS 0.015 MMT-Ca 5 phr	0.015	(0.015 + 1.7350)	0.81	70,000 → 3200
cCMS 0.015 ZS1 2 phr	0.015	(0.015 + 1.7350)	0.81	55,000 → 2700
cCMS 0.015 ZS2 5 phr	0.015	(0.015 + 1.7350)	0.81	60,000 → 2850
cCMS 0.05 without clay	0.050	(0.050 + 1.7000)	0.86	11,200 → 670
cCMS 0.05 MMT-Na 2 phr	0.050	(0.050 + 1.7000)	0.86	13,000 → 720
cCMS 0.05 MMT-Na 5 phr	0.050	(0.050 + 1.7000)	0.86	14,000 → 890
cCMS 0.05 MMT-Ca 2 phr	0.050	(0.050 + 1.7000)	0.86	16,000 → 960
cCMS 0.05 MMT-Ca 5 phr	0.050	(0.050 + 1.7000)	0.86	16,000 → 880
cCMS 0.05 MMT-ZS1 2 phr	0.050	(0.050 + 1.7000)	0.86	13,000 → 1000
cCMS 0.05 MMT-ZS1 5 phr	0.050	(0.050 + 1.7000)	0.86	65,000 → 2200

crosslinked CMS obtained using other crosslinking agents than DCA has also been reported.^{5,23}

All investigated CMS or cCMS solutions were shear-thinned liquids and their apparent viscosities dramatically decreased at high shear rates (Table I). Relevant high shear apparent viscosities lay in a rather narrow range of values 1000–7100 mPa·s (100 rpm). In that case similar tendency of viscosity changes with DCA content increase as for low shear rate was observed.

The power law model is widely used for describing non-Newtonian fluids.²⁴ The apparent viscosity is given in that model by equation:

$$\eta = K \cdot \dot{\gamma}^{n-1} \quad (1)$$

where K is consistency index, $\dot{\gamma}$ is shear rate, and n is flow behavior index.

The power law model holds many solutions and can describe Newtonian, shear-thinning, and shear-thickening behavior depending on the power factor n . For a Newtonian fluid $n = 1$ and the equation reduces to Newtonian model. If it is < 1 , the fluid is shear-thinning, if it is > 1 , the fluid is shear thickening. Shear viscosity dependences for cCMS solutions in log scale (plot is not shown) fitted the power law equation [$\lg \eta = \lg K + (n-1) \lg \dot{\gamma}$] with n values in a range 0.266–0.445 (Table I). The aqueous solutions of slightly crosslinked CMS were pseudo-plastic liquids and their shear-thinning characteristics changed in

some extent with crosslinking density. The dependence between n value and the amount of used crosslinking agent (Table I) exhibited minimum for DCA/AGU molar ratio equal 0.015; so the most viscous aqueous solutions of cCMS showed more pronounced shear-thinning properties in comparison to unmodified CMS as well as cCMS prepared with higher DCA dose.

Additionally, the viscosity values of some freshly prepared cCMS 2 wt % solutions were controlled during storage in closed jars up to 60 days. The second series of viscosity measurements was performed using cCMS granules stored for several months in closed jars. Cumulative results were presented in Figure 4. Some decrease of that parameter with storage time could be observed. It had been also found that cCMS samples stored in granular form in normal laboratory conditions (room temperature and ca. 40% moisture, powder containing ca. 12% water) gradually lost their ability of giving aqueous solution with enhanced viscosity. That observation could mean that some chemical crosslinks between polysaccharide chains are weaker than other, that is, susceptible to hydrolysis. For instance aqueous solution viscosity drop for cCMS 0.05 from ca. 45 000 to 16 000 mPa·s (i.e. to the level of unmodified CMS, Figure 4, Table I) was found after 7 months storage. An explanation of this phenomenon could be related to both etherification and esterification in the investigated

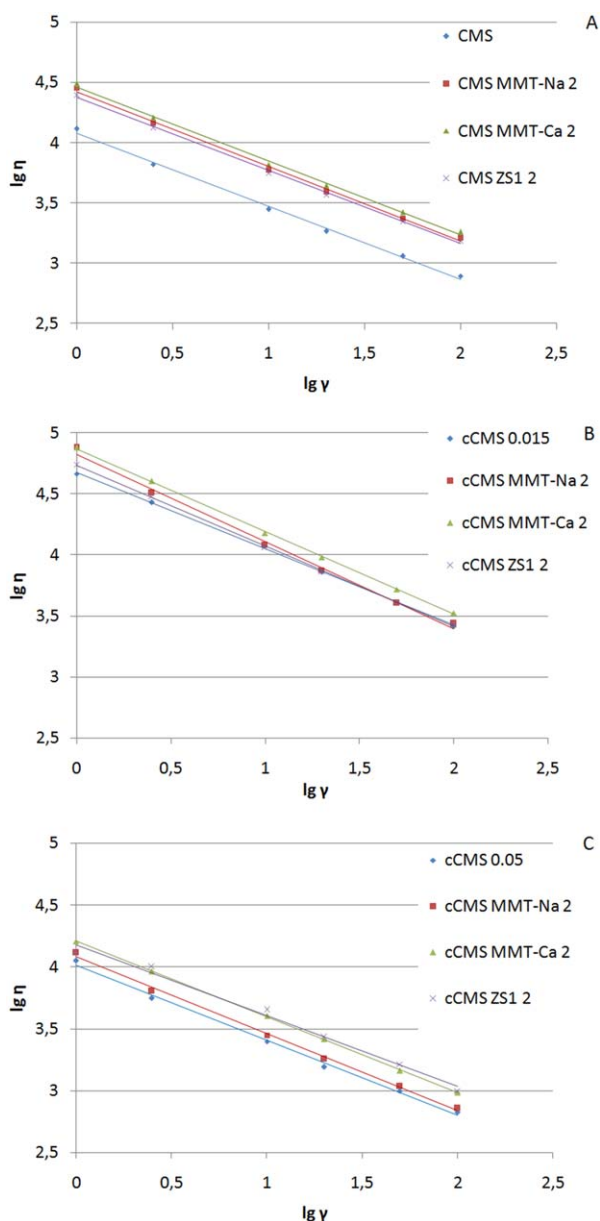


Figure 6. The shear-thinning characteristics of: 2 wt % CMS (DS = 0.87) solution and its dispersions with various montmorillonites—A; 2 wt % cCMS 0.015 (DS = 0.88) solutions and its dispersions with various montmorillonites—B; 2 wt % cCMS 0.050 (DS = 0.86) solutions and its dispersions with various montmorillonites—C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction system: starch/MCA/DCA in isopropanol/water slurry. Figure 2(B) presented the schemes of possible reactions including bridging polysaccharide chains via ether and ester cross-linking bonds. Ester bonds could gradually hydrolyze in aqueous environment influencing the viscosity solutions exhibited high pH values (9–11). High range of pH what even intensified the tendency to ester bond hydrolysis in presence of water (or residual humidity in cCMS granules).

Seidel et al.²⁵ synthesized hydrogels based on CMS crosslinked with polyfunctional carboxylic acid. These gels were susceptible

to hydrolysis, and showed only limited stability after preparation.⁶ Liebert and Klemm²⁶ prepared hydrolytically cleavable cellulose dichloroacetates with high DS values up to 1.9; the syntheses were performed in DCA/dichloroacetic anhydride mixtures. The ester cellulose derivatives were quickly saponified (total hydrolysis within 7 min time).

In order to confirm the hypothesis on ether and ester bonds in polysaccharide linking bridges proton NMR spectra for CMS and cCMS were registered.

¹H NMR Spectroscopy

Proton spectra of CMS (DS = 0.93) and cCMS 0.015 (DS = 0.88) were presented in Figure 5. The latter sample has been tested few days after preparation and after 9 months storage of granular product (residual humidity ca. 12 wt %). The signals of hydroxyl protons of AGU (i.e. at positions 2, 3, and 6) were placed in shifting values 3.3–4.2 ppm.^{20,27} Comparing the spectra of CMS as well as cCMS 0.015 some differences could be noticed: the signals with peaks at 3.81 ppm were attributed to protons (b) of the O—CH₂—CO groups and the signal at 4.20 ppm to the protons (a) of the C—CH₂—O group. At 3.71 ppm protons of OCHCO or OCHO present in cCMS sample structures were registered [see also Figure 2(B)]; its intensity decreased with storage time of cCMS sample [compare Figure 5(B and C)]. Simultaneously, originally very slight signal of the proton doublet at 1.04–1.06 ppm increased with storage time. It could be assigned to low molecular weight dihydroxyl derivative of acetic acid (salt)—a final product of diester cross-links hydrolysis [Figures 2(B) and 5]. Eventually, ¹H NMR spectra of cCMS supported our assumption on cleavable ester linkages between polysaccharide chains that were responsible for cCMS aqueous solution viscosity decrease observed during storage.

Viscosity of Aqueous Dispersions of Slightly Crosslinked Carboxymethyl Starches with Montmorillonites

On a basis of CMS and two cCMS samples having similar DS values (but obtained using various DCA ratios) aqueous dispersions containing one of three clay types were prepared.

The viscosity measurements of CMS and cCMS aqueous dispersions with clays were performed after ca. 7 months from carboxymethyl starches syntheses. This is the reason of lower viscosity values for neat solutions of CMS and cCMS (1 rpm) in Table II than in Table I (see also Figure 4). The results of viscosity measurements for dispersions of carboxymethyl starches with clays were presented in Table II and Figure 6.

Despite the MMT type the highest apparent viscosities were found for dispersions of cCMS synthesized with lower DCA content. These values changed from 46,000 mPa·s (1 rpm) for neat cCMS 0.015 up to 75,000 mPa·s for cCMS 0.015 MMT-Na 2 wt part/100 wt part CMS or cCMS (phr) and cCMS 0.015 MMT-Ca 2 phr systems. The relevant dispersion containing MMT-ZS1 exhibited lower viscosity than these with MMT-Na or MMT-Ca ones. In cases of the latter systems an increase of MMT content from 2 to 5 phr caused slight decrease of apparent viscosity values. An opposite situation was observed for dispersions with

Table III. Equation 1 Coefficients for CMS, cCMS Solutions and Relevant Dispersions with Montmorillonites

Sample acronym	Coefficient of eq. 1		R^2
	lg K	n	
CMS (DS = 0.87)	4.079	0.394	0.998
CMS MMT-Na 2	4.423	0.378	0.996
CMS MMT-Ca 2	4.461	0.387	0.997
CMS ZS1 2	4.373	0.395	0.998
cCMS 0.015	4.676	0.375	0.999
cCMS 0.015 MMT-Na 2	4.823	0.287	0.995
cCMS 0.015 MMT-Ca 2	4.867	0.323	0.999
cCMS 0.015 ZS1 2	4.733	0.341	0.999
cCMS 0.05	4.013	0.396	0.996
cCMS 0.05 MMT-Na 2	4.080	0.380	0.997
cCMS 0.05 MMT-Ca 2	4.207	0.387	0.999
cCMS 0.05 ZS1 2	4.176	0.430	0.989

MMT-ZS1 (slight viscosity increase from 55,000 up to 60,000 mPa·s for 2 to 5 phr clay, respectively). The dispersions prepared on a basis of cCMS with higher DCA/AGU ratio (cCMS 0.05) exhibited usually lower viscosities (13,000–16,000 mPa·s) only slightly higher than that for the reference cCMS 0.05 solution (11,200 mPa·s). However, one exception for the highest dose of MMT-ZS1 (5 phr), that is, viscosity jump up to 65,000 mPa·s was noticed. This finding might be explained by the effect of semi-hydrophobic alkyl chains of amphiphilic clay modifier association in aqueous solution from one side, and interaction of OH groups of the modifier with polysaccharide hydroxyls as well as electrostatic interaction between carboxylate groups with ammonium cations of MMT modifier on the other.

In Figure 6 the full shear viscosity dependences determined at shear rate range 1–100 rpm for CMS solutions and CMS/MMT 2 phr dispersions [Figure 6(A)] as well as cCMS solutions and cCMS/MMT 2 phr dispersions with lower [Figure 6(B)] and higher [Figure 6(C)] crosslinker ratios have been presented. The shear-thinning dependences fitted to the eq. 1 with high correlation coefficients. Coefficients of eq. 1 for these systems are collected in Table III. Basing on the results presented in Figure 6 and Table III the following could be concluded: (i) the lowest n coefficient, that is, the more pronounced shear-thinning properties were observed for dispersion based on cCMS 0.015: 0.287, 0.323, and 0.341 for, MMT-Na, MMT-Ca, and MMT-ZS1, respectively (for comparison 0.375 for pristine cCMS); (ii) n value changed within 0.287–0.430 range, and the highest value was observed for cCMS 0.05 ZS1, (iii) lg K values were in the range from 4.013 to 4.867, and the highest value was noted for dispersion based on cCMS 0.015 (4.823, 4.867, and 4.733 for MMT-Na, MMT-Ca, and for MMT-ZS1, respectively). Presented results showed that by slight crosslinking of CMS as well as introducing MMT the viscosity of polysaccharide aqueous solution (or dispersion) could

be significantly improved, and rheological characteristics (i.e. shear-thinning properties) could be modified.

All these systems exhibited some degree of stability, that is, no sedimentation of aluminosilicate nanofillers was noticed.

CONCLUSIONS

Simultaneous CMS synthesis and crosslinking reactions allowed to obtain products with DS values in a range 0.8–0.9. The viscosity of slightly crosslinked cCMS aqueous solutions was substantially higher than that of unmodified CMS. The highest apparent viscosity of 2 wt % solution 170,000 mPa·s (1 rpm, 25°C) was reported for DCA : AGU molar ratio as low as 0.0075 [(MCA+DCA) : AGU=1.75 : 1], With increasing DCA : AGU ratios in the reaction systems cCMS aqueous solutions viscosity values gradually decreased. Above 0.1 : 1 DCA : AGU molar ratio crosslinked CMS derivatives formed hydrogels.

During cCMS preparation process ether and ester bridges between polysaccharide chains could be formed. The ester bridging was susceptible to hydrolysis even during storage of cCMS granules with residual humidity as it was supported by ^1H NMR results. In a consequence during storage viscosity decrease of cCMS solutions was observed. The viscosities of prepared CMS dispersions with clays were doubled up to 22,000–31,000 mPa·s and strongly depended on clay type and its concentration. Introduction of 2–5 phr of clays into 2 wt % cCMS solutions caused an increase of initial viscosity for slightly crosslinked cCMS 0.0150 (46,000–75,000 mPa·s) when MMT-Na or MMT-Ca (2 phr) were used. Unexpectedly high viscosity jump (11,200–65,000 mPa·s) for dispersion with MMT-ZS1 5 phr was found whereas significantly lower values (below 20,000 mPa·s) were observed for relevant systems with MMT-Na and MMT-Ca. Interactions between hydroxyls of clay modifier, hydroxyls, and carboxylate groups of CMS as well as ammonium cationic centers of clay modifier could be responsible for this phenomenon. All the investigated cCMS aqueous systems exhibited shear-thinning properties with n flow behavior index of power law equation in a range 0.27–0.45. The minimum n value, that is, the distinct shear thinning feature, was found for very slightly crosslinked cCMS 0.015.

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