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# Carboxymethyl starch with high degree of substitution: synthesis, properties and application**)

**Summary** — Highly substituted (degree of substitution, *DS* about 0.9) carboxymethyl starch (CMS) was prepared in isopropanol/water suspension. The influence of etherification reaction parameters on *DS*, reaction efficiency, number average molar mass as well as the viscosity of 2 wt. % aqueous solution was determined. Using laser scanning microscopy, X-ray diffraction and infrared spectroscopy techniques allowed to evaluate the morphological changes of modified starch granules when compared to native starch ones. An attempt to apply CMS (of high and medium *DS*: 0.94 and 0.39, respectively) for flocculation or dispergation tests of selected aqueous suspensions [iron(II) sulphate, iron(III) oxide, iron(III) laurate and aluminosilicates: kaolinite and calcium montmorillonite] has been performed. In case of iron(II) sulphate and iron(III) oxide high substituted CMS exhibited effective flocculating properties. Moreover, it worked as a good dispersing agent for mineral aluminosilicate suspensions.

**Keywords**: carboxymethyl starch, degree of substitution, starch modification, flocculation, dispergation.

KARBOKSYMETYLOSKROBIA O WYSOKIM STOPNIU PODSTAWIENIA: SYNTEZA, WŁAŚCIWOŚCI, ZASTOSOWANIE

**Streszczenie** — Przedstawiono wyniki badań nad otrzymywaniem karboksymetyloskrobi (CMS) o wysokim stopniu podstawienia *DS* = 0,9, ze skrobi ziemniaczanej w zawiesinie izopropanol/woda. Dokonano oceny wpływu zmiennych parametrów reakcji eteryfikacji skrobi na wartości *DS*, efektywność reakcji (*RE*), liczbowo średnią masę molową ($M_n$) oraz lepkość 2-proc. roztworu wodnego. Pomiary metodami laserowej mikroskopii skaningowej (LSM), dyfrakcji rentgenowskiej (XRD) oraz spektroskopii w podczerwieni (FT-IR) pozwoliły na ocenę zmian struktury morfologicznej ziarna CMS oraz absorbancji widma skrobi natywnej po modyfikacji. Przeprowadzono również badania nad możliwością wykorzystania CMS (o wysokim stopniu podstawienia *DS* = 0,94, jak również w celach porównawczych o średnim stopniu podstawienia *DS* = 0,39) do flokulacji, ewentualnie dyspergowania, wybranych zawiesin wodnych: siarczanu żelaza(II), tlenku żelaza(III), laurynianu żelaza(III) oraz glinokrzemianów: kaolinu i montmorylonitu wapniowego.

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Stwierdzono, że CMS, zwłaszcza o wysokim *DS*, wykazuje cechy flokulanta względem siarczanu żelaza(II) oraz tlenku żelaza(III); natomiast jest dobrym środkiem dyspergującym w stosunku do zawiesin minerałów glinokrzemianowych.

**Słowa kluczowe**: karboksymetyloskrobia, stopień podstawienia, modyfikacja skrobi, flokulacja, dyspergowanie.

## INTRODUCTION

Chemical modification of starch is performed to overcome the shortcomings of native starch, such as: insolubility in cold water, hardly controlled viscosity after gelatinization, turbidity of aqueous solutions/gels or tendency to retrogradation.

Carboxymethyl starch (CMS) has been produced on industrial scale for many years. This anionic starch derivative can be considered as a green polymer with great importance in pharmacy, medicine, cosmetics, food industry, environmental protection and many other industrial applications [1].

The properties of CMS (viscosity of aqueous solutions, dissolution rate, clarity, film forming ability, gelatinization temperature, pH and storage stability) are determined in high extent by degree of glucosidic unit substitution (*DS*) [2—5]. Commercially available CMSs often exhibit low *DS* values up to *ca.* 0.3. Some of the mentioned CMS features can be substantially enhanced by increasing the *DS* value [1, 5]. The review of synthesis methods of medium and high substituted CMSs has been recently accessible [1].

According to the literature high substituted CMS (*DS* in a range 0.7—1.4) could be obtained from potato starch in alcohol/water mixtures (water content 10—15 wt. %) [6—10]. Monochloroacetic acid (MCA) or its sodium salt (SMCA) were used as etherifying agents; reaction efficiencies (*RE*) were *ca.* 60 % or higher. In most cases isopropanol as alcohol has been used [6—9]. Sodium hydroxide played a role of activating and catalyzing agent during alkalization and etherification steps. Typically, molar ratio of NaOH versus etherifying agent was in a range 1.0—2.0. Carboxymethylation temperature of potato starch was 35—50 °C to preserve granular shape of the final product, and reaction time was between 2.5 and 5 h.

In this contribution the results of high substituted CMS (with *DS* 0.8—1.0) synthesis in isopropanol/water mixtures were presented together with the basic physicochemical properties of obtained products. An influence of experimental parameters on *DS*, *RE* and $\overline{M}_n$ was investigated as well as the morphology changes of polysaccharide granules during carboxymethylation.

Among the fields of CMS application the environmental usage seems to be worth of special attention. There are limited examples of direct CMS use for iron [11, 12] or calcium [13] cation removal from aqueous systems or as dispersing phase for nanofillers such as kaolinite [14] or feldspar [15] in electrorheological fluids.

For that reason CMS flocculation or dispergation properties for model aqueous dispersions (ferric and ferrous compounds as well as aluminosilicates) have been evaluated using two starch derivatives differing in *DS* values (*ca.* 0.9 and 0.4, respectively).

## EXPERIMENTAL

### Materials

Potato starch was purchased from Nowamyl S.A., Nowogard, Poland. Monochloroacetic acid (MCA, a.g. Chempur, Poland) and sodium monochloroacetate (SMCA, Sigma-Aldrich) were used as etherifying agents, isopropanol (IPOH, pure, Chempur) as a reaction medium. Sodium hydroxide (microgranules), acetic acid, copper sulphate penthahydrate, and Fe(II) sulphate heptahydrate (pure) were the products of Chempur (Poland), murexide (indicator), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), lauric acid 98 %, Fe(III) chloride (97 %) of Sigma-Aldrich (Germany) and Fe(III) oxide of Worlée-Chemie.

### CMS preparation

Modification of potato starch was carried out in a glass batch reactor equipped with mechanical stirrer, thermocouple and capillary tube supplying nitrogen to the reaction system. Starch was etherified in isopropanol/water as a one-step process.

MCA or SMCA was dissolved with IPOH in reactor, and then NaOH water solution was added. When the mixture became white and homogenous, 30 g starch (13.6—14.0 wt. % moisture) and remaining part of NaOH microgranules were introduced. Reaction was performed for 2.5 h at 50 °C. The obtained product was filtered, neutralized with glacial acetic acid, washed five times with 80 wt. % methanol, once with methanol and dried in the air, leaving on the warm surface.

### Methods of testing

#### *DS* determination

The degree of substitution was measured according to the method described in work [16]. CMS sample was moisturized by 1 $cm^3$ of ethanol and dissolved in 50 $cm^3$ of distilled water. Subsequently 20 $cm^3$ of buffer was added ($NH_4Cl$ 0.187 M aqueous solution), adjusted to neutral pH, and then the whole mixture poured into flask with 50 cm$^3$ of $CuSO_4$ (0.039 M solution). After 15 minutes water was added to the slurry and content was filtered. Filtrate was titrated with EDTA solution.

### Viscosity measurements

Rheological characteristics of 2 wt. % aqueous CMS solutions were evaluated at 25 °C using Brookfield RV rheoviscometer, changing spindle rotation from 1 up to 100 rpm. Carboxymethyl starch aqueous solution was prepared by adding CMS to distilled water during stirring using magnetic stirrer, and mixed until homogeneity, after 30 minutes the viscosity was measured.

### Instrumental methods

For Gel Permeation Chromatography (GPC) analysis — Shodex OHpak SB-806M MQ column with Shodex OHpak SB-G pre-column in Merck Hitachi Liquid Chromatography (pump L-7100, interface D-7000) with RI detector (Merck Lachrom RI L-7490) have been used. Dextran standards for the column calibration and chromatography eluent: sodium nitrate solution 0.1 M, were applied (flow rate 0.5 cm$^3$/min).

Morphology and granules structure were observed using Laser Scanning Microscope (LSM) Keyence VK-9710.

Crystallinity of modified polysaccharide material was investigated with X-ray diffraction analysis (diffractometer X'pertPro, PANalytical operated at the CoKα wavelength 1.514 Å).

FT-IR spectra were recorded by Nexus (Thermo-Nicolet, USA) using ATR (Golden Gate) technique. For each sample 32 scans were taken from 4000 to 400 cm$^{-1}$.

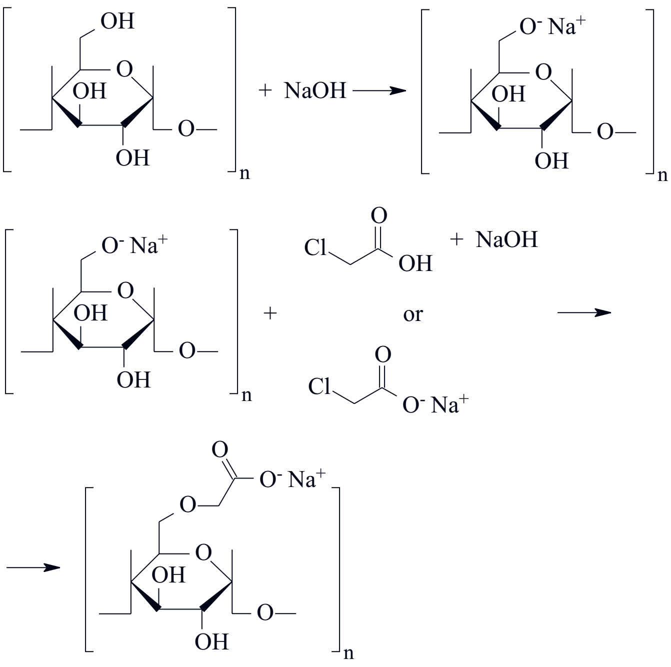
### Flocculation and dispergation tests

To prepare a model suspension 5 g of the given material was mixed with 1 dm$^3$ of distilled water and stirred for 15 min at 600 rpm in a beaker. Then required amount of the CMS solution was added into the beaker. Stirring rate was reduced to 400 rpm and mixing was continued for 10 s. The stirring rate was then reduced to 50 rpm and continued for 10 min. The entire suspension was then transferred to a calibrated Imhoff funnel and allowed to settle down. The extinction of the aqueous phase was measured using Spekol 11 (Carl Zeis Jena; wavelength 608 nm for $FeSO_4$ suspension and 470 nm for other ones) every 10 minutes for 2 h. Supernatant liquid was drawn from an upper depth of 1.0—2.0 cm from Imhoff funnel for measurements. The same measurements without the CMS addition (blank test) were carried out for comparison. The volume of sludge on a bottom of the testing funnel has been measured simultaneously with the extinction measurements.

## RESULTS AND DISCUSSION

### General characteristics of starch carboxymethylation reaction

Carboxymethylation reaction occurs in two stages: (i) alkalization, and (ii) etherification, which could be performed together or in separated steps. The scheme of starch carboxymethylation reaction is presented in Scheme A. Simultaneously NaCl and glycolates as byproducts are formed. Many industrial applications require removing byproducts from the final material.



*Scheme A. Scheme of starch carboxymethylation with monochloroacetic acid or its sodium salt*

### The influence of reaction parameters on physicochemical properties of CMS

The effect of: (i) the kind (MCA or SMCA) and concentration of etherifying agent, (ii) water content in IPOH/water reaction medium, (iii) starch content in IPOH/water suspension, (iv) NaOH/etherifying agent molar ratio, and (v) time of carboxymethylation reaction on key physicochemical parameters: *DS*, *RE*, $\overline{M}_n$, and viscosity of 2 wt. % of CMS aqueous solution was determined.

The authors are not familiar with the reports on the influence of etherifying agent as well as highly alkali conditions on CMS molecular weight. Moreover, determining the viscosity of CMS aqueous solutions seemed important from application viewpoint. The effect of etherifying agents: MCA and SMCA on *DS* and $\overline{M}_n$ values as well as molar ratio: (S)MCA/polysaccharide recurrent

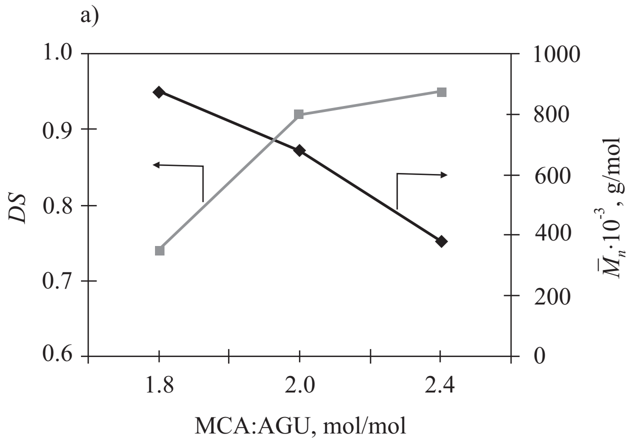


Fig. 1. *Changes of DS and $\overline{M}_n$ values in dependence on MCA/AGU molar ratios (10 wt. % starch, 10 wt. % water, NaOH/MCA 1.85 mol/mol)*

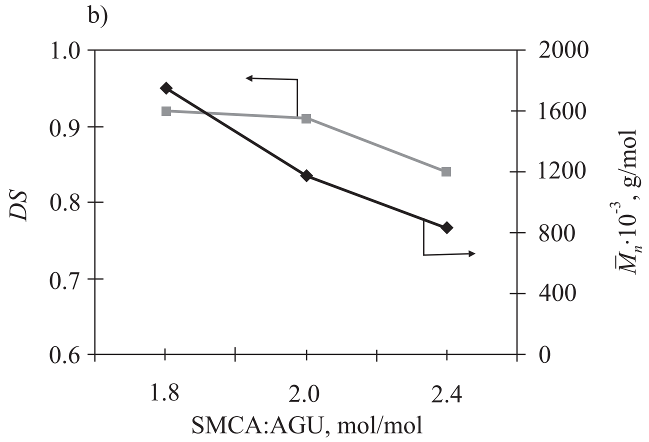


Fig. 2. *Changes of DS and $\overline{M}_n$ values in dependence on SMCA/AGU molar ratio (9.5 wt. % starch, 9.5 wt. % water; NaOH/SMCA 1.2 mol/mol)*

unit (AGU) was presented in Fig. 1 and 2. The degree of substitution increased up to *ca.* 0.9 for (S)MCA/AGU ratio 1.8—2.0, and subsequently was stabilized (for lower NaOH/MCA ratio: 1.85) or decreased (for higher NaOH/MCA ratio: 2.2).

Carboxymethyl starch number average molar mass was almost twice as high (for the same reaction parameters) for SMCA (Fig. 2) than when MCA was used (Fig. 1). The $\overline{M}_n$ value of CMS decreased with etherifying agent content increase.

Subsequently, the effect of NaOH content on *DS* and *RE* values was determined. The results were similar to previous reports [17—20]. On one hand NaOH present in the system allowed forming the active centers, *i.e.* alcoholate groups where nucleophilic substitution of (S)MCA occurred, resulting in higher *DS* value. However, higher NaOH content caused shifting of reaction balance towards hydrolysis of etherifying agent and forming glycolate byproducts.

More detailed report on CMS physicochemical properties was collected in Tables 1—4. In Table 1 data for starch etherification reaction (with MCA or SMCA) for two (S)MCA/AGU molar ratios: 1.75:1 and 2:1 were collected.

Slightly higher *DS* (and *RE* 45—47 %) were obtained for higher (S)MCA/AGU ratio. However, the differences of *DS* and *RE* values for starch products carboxymethylated in the same reaction conditions but using various etherifying agents were marginal — did not exceed 3 % (*DS* 0.94 and 0.91) and 5 % (*RE* 47.0 and 45.5) for MCA and SMCA, respectively.

It should be noticed that the viscosity values of 2 wt. % CMS solutions obtained by etherification with MCA were significantly higher (2—6 times, depending on measurement conditions) when compared to these CMS solutions modified by SMCA (Table 1).

In Table 2 the characteristics of CMS prepared for SMCA/AGU in a range 1.8:1—2.4:1 (the same reaction conditions) were collected. An increase of etherifying agent content resulted in decrease of: (i) $\overline{M}_n$ (1 750 000 → 830 000 g/mol), (ii) *DS* (0.92 → 0.84), (iii) *RE* (51 → 36 %). Many research works related to CMS preparation reported the effect of etherifying agent content on the *DS* of obtained CMS products [17—19]; however, no data on the influence on CMS molar mass were given.

The viscosity of 2 wt. % CMS aqueous solutions was in a range of 2000—6500 mPa · s and 365—775 at 1 rpm and 100 rpm, respectively. No evident effect of SMCA content

**Table 1. CMS characterization in dependence on type of etherifying agent**

| Sample akronym | Etheryfing agent | $\overline{M}_n$, g/mol | *DS* | *RE*, % | Viscosity, 2 wt. % solution 1 → 100 rpm mPa·s |
|---|---|---|---|---|---|
| 9.5 % starch; 9.5 % water; (S)MCA:AGU = 1.75/1; NaOH/(S)MCA = 2.25:1*); *T* = 50 °C; *t* = 150 min | | | | | |
| CMS 19 | MCA | n.d. | 0.87 | 49.7 | 11 500 → 690 |
| CMS 48 | SMCA | n.d. | 0.86 | 49.2 | 1 900 → 345 |
| 9.5 % starch; 9.5 % water; (S)MCA/AGU = 2:1; NaOH/(S)MCA = 2.2:1**); *T* = 50 °C; *t* = 150 min | | | | | |
| CMS 16 | MCA | 400 000 | 0.94 | 47.0 | 13 050 → 890 |
| CMS 41 | SMCA | 1 180 000 | 0.91 | 45.5 | 2 000 → 365 |

n.d. — not determined; *) for NaOH/SMCA = 1.25:1; **) for NaOH/SMCA = 1.2:1.

*DS* — degree of substitution, *RE* — reaction efficiency, AGU — anhydroglucosidic unit.

**T a b l e 2. CMS characterization in dependence on molar ratio of SMCA/AGU**

| Sample akronym | SMCA/AGU | $\overline{M}_n$, g/mol | *DS* | *RE*, % | Viscosity, 2 wt. % solution 1 → 100 rpm mPa·s |
|---|---|---|---|---|---|
| 9.5 % starch; 9.5 % water; NaOH/SMCA = 12:1. *T* = 50 °C; *t* = 150 min | | | | | |
| CMS 45 | 18:1 | 1 750 000 | 0.92 | 51.3 | 6 500 → 775 |
| CMS 41 | 2.0:1 | 1 180 000 | 0.91 | 45.5 | 2 000 → 365 |
| CMS 46 | 2.4:1 | 830 000 | 0.84 | 35.5 | 4 300 → 540 |

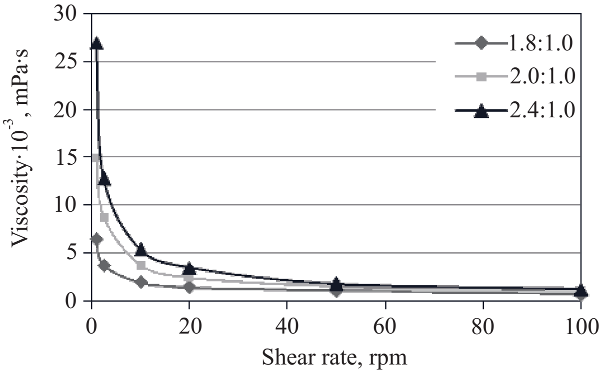


*Fig. 3. Changes of viscosity for 2 wt. % aqueous solutions as a function of shear rate (CMS etherified with MCA)*

was noted (see Table 2). For comparison, in Fig. 3 the influence of MCA content on viscosity of CMS 2 wt. % aqueous solution was presented. Significantly higher viscosity values were observed in low range of shear force (<10 rpm).

An attempt of polysaccharide modification applying starch content in a range 8—10 wt. % (in IPOH/water 90.5/9.5 wt. % suspension) resulted in conclusion that 9.5 wt. % starch content was the most appropriate for *DS* (0.94), *RE* (47 %), and viscosity of 2 wt. % aqueous solutions (13 050 → 890 mPa·s, at 1 → 100 rpm) — Table 3.

Moreover, slight decrease of $\overline{M}_n$ value with starch concentration increase was noted. An increase of water content resulted in more intensive byproducts formation and starch hydrolysis (CMS molar mass decrease). Water extent (>10.5 wt. %) caused granules agglomeration that hindered homogenous mixing during reaction and as a consequence *DS* of the final product decreased. The effect of water content was reported in a few works [19, 20], where similar trend was observed.

Prolonged etherification time resulted in slight increase of both *DS* (from 0.87 to 0.96 after 90 and 210 min, respectively) and *RE* (from 43.5 to 48 %, respectively) — Table 4. Although during carboxymethylation reaction granule structure of starch was preserved, some changes of its morphology, *i.e.* decreasing crystallinity degree were observed. In Figs. 4 and 5 the laser scanning microscopy micrographs of native potato starch granules and CMS (*DS* 0.94), as well as XRD diffractograms, respectively were presented. Similar conclusions, *i.e.* confirmation of starch semi-crystalline structure loss after etherification, were noted by other research groups [17, 18].

Introducing of carboxymethyl groups into recurrent polysaccharide units could be noted by IR spectroscopy. Some new bands of absorption could be observed in a range 1580—1600 $cm^{-1}$, 1410 $cm^{-1}$, and 1318 $cm^{-1}$ assigned to carboxymethyl groups [18] (Fig. 6).

**T a b l e 3. CMS properties as a function of starch content in the isopropanol/water mixture**

| Sample akronym | Starch content in water/IPOH mixture, wt. % | $\overline{M}_n$, g/mol | *DS* | *RE*, % | Viscosity, 2 wt. % solution 1 → 100 rpm mPa·s |
|---|---|---|---|---|---|
| 9.5 % water; NaOH/MCA = 2.2:1; MCA/AGU = 2:1; *T* = 50 °C; *t* = 150 min | | | | | |
| CMS 33 | 8.0 | 590 000 | 0.88 | 44.0 | 11 500 → 840 |
| CMS 16 | 9.5 | 400 000 | 0.94 | 47.0 | 13 050 → 890 |
| CMS 32 | 10.5 | 380 000 | 0.65 | 32.5 | 6 000 → 380 |

**T a b le 4. CMS properties as a function of reaction time**

| Sample akronym | Time, min | $\overline{M}_n$, g/mol | *DS* | *RE*, % | Viscosity, 2 wt. % solution 1 → 100 rpm mPa·s |
|---|---|---|---|---|---|
| 9.5 % starch; 9.5 %water; MCA/AGU = 2:1; NaOH/MCA = 2.2:1; *T* = 50 °C | | | | | |
| CMS 35 | 90 | 680 000 | 0.87 | 43.5 | 18 000 → 1 040 |
| CMS 16 | 150 | 400 000 | 0.94 | 47.0 | 13 050 → 890 |
| CMS 26 | 210 | 760 000 | 0.96 | 48.0 | 20 000 → 1 200 |

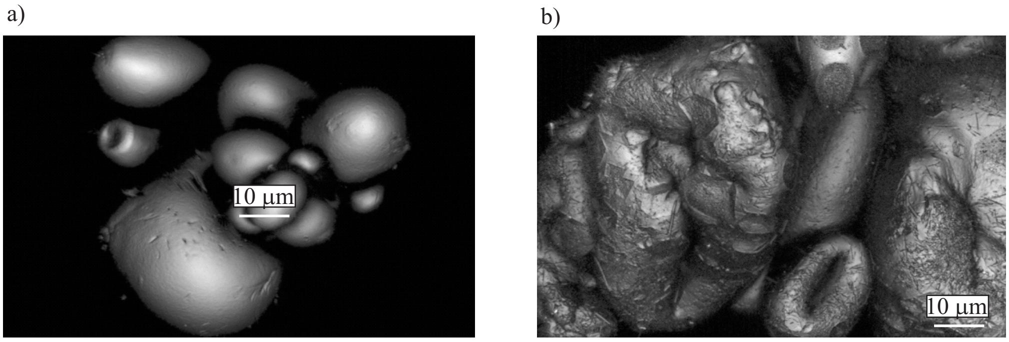


*Fig. 4. Laser scanning micrographs of native potato starch granules (a) and CMS 16 grain particles with DS = 0.94 (b)*

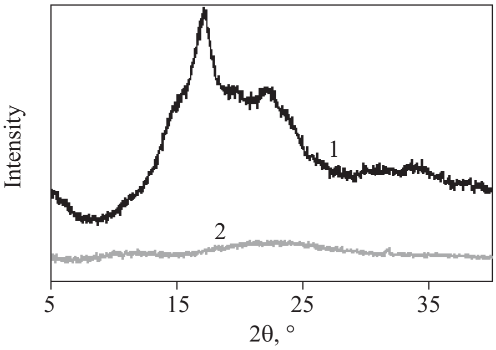


*Fig. 5. XRD diffractograms for native potato starch (1) and CMS 16 with DS = 0.94 (2)*

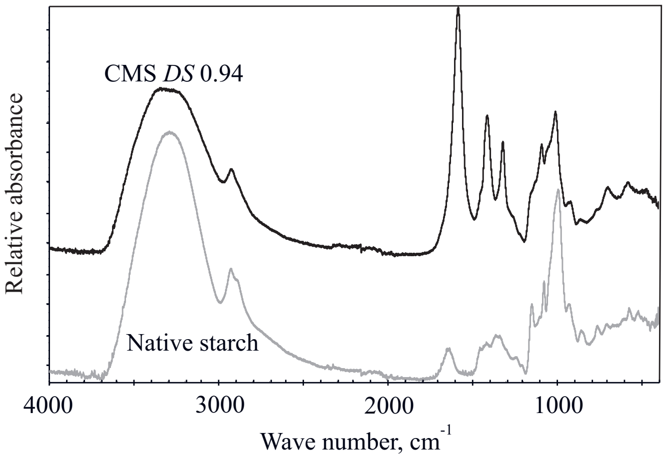


*Fig. 6. FT-IR spectra of native potato starch (1) and CMS 16 with DS = 0.94 (2)*

## CMS flocculation or dispergation properties

CMS application depends significantly on its *DS* as well as the viscosity of its aqueous solutions. In this paper some possibilities of using CMS (high and medium substituted) solutions as flocculant, or dispersing agent for some model suspensions were presented.

CMS 19c sample (*DS* 0.93) was prepared in IPOH/water suspensions, whereas CMS H6 (*DS* 0.39) using semidry method [21]. The CMS concentrations in the testing suspensions were: 25 and 500 ppm. Model suspensions were: iron(II) sulfate, iron(III) oxide, and iron(III) laurate as well as mineral aluminosilicates: kaolinite and calcium montmorillonite. The flocculation/dispergation tests were performed for 2 h — simultaneously extinction and sludge measurements — in Imhoff funnel were reported. In case of inorganic iron compounds it could be concluded that (Fig. 7 and Table 5): (i) both CMS concen-

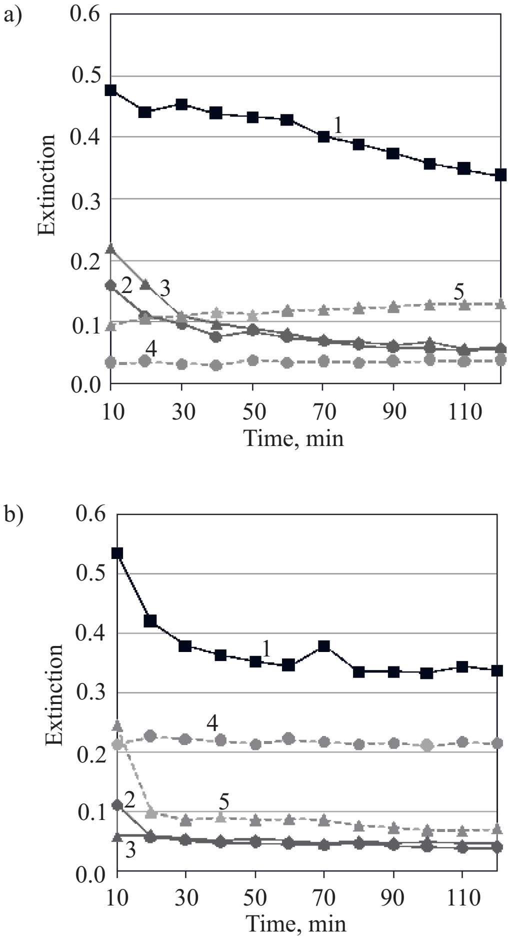


*Fig. 7. Extinction as a function flocculation of time for: $FeSO_4$ (a) and $Fe_2O_3$ (b): 1 — blank, 2 — 25 ppm CMS H6, 3 — 25 ppm CMS 19c, 4 — 500 ppm CMS H6, 5 — 500 ppm CMS 19c suspensions*

trations in aqueous solution exhibited flocculating properties towards iron(II) sulfate (Fig. 7a), (ii) the highest flocculation efficiency (when initial and final extinction values compared) was noted for 500 ppm dosage of medium substituted CMS H6 (*DS* 0.39); 90 % turbidity reduction, (iii) when higher concentration of CMS H6 was applied 3—5 cm diameter floccules were formed, that eventually compressed, (iv) the final extinction values of suspensions treated with CMS H6 (for both concentration values) and CMS 19c (for 25 ppm) were similar, and ranged from *ca.* 0.040—0.060 standard unit (Fig. 7a), (v) using higher CMS concentration resulted in „more loose" (*i.e.* containing more water) sludge in Imhoff funnel than when compared to lower CMS dosage [maximal sludge volume ratio of CMS H6 (500 ppm)/CMS H6 (25 ppm) was *ca.* 5.5; lower value of such a ratio was noted for CMS 19c products — *ca.* 2] (Table 5).

**Table 5. Sludge volumes during flocculation experiments performed for $FeSO_4$ and $Fe_2O_3$ suspensions**

| Suspension type | Time min | Sludge volume, cm$^3$ | | | | |
|---|---|---|---|---|---|---|
| | | blank | CMS H6 25 ppm | CMS 19c 25 ppm | CMS H6 500 ppm | CMS 19c 500 ppm |
| $FeSO_4$ | 10 | 0.10 | 13.0 | 15.00 | 60 | 40.0 |
| | 20 | 0.20 | 14.0 | 17.00 | 60 | 34.0 |
| | 30 | 0.20 | 13.0 | 16.00 | 59 | 30.0 |
| | 40 | 0.20 | 12.0 | 15.00 | 59 | 28.0 |
| | 50 | 0.20 | 12.0 | 14.75 | 59 | 26.0 |
| | 60 | 0.25 | 11.5 | 14.25 | 58 | 25.0 |
| | 70 | 0.30 | 11.0 | 13.75 | 58 | 23.0 |
| | 80 | 0.30 | 10.0 | 13.25 | 57 | 22.0 |
| | 90 | 0.35 | 10.0 | 13.00 | 57 | 22.0 |
| | 100 | 0.40 | 9.5 | 12.50 | 57 | 21.5 |
| | 110 | 0.45 | 9.5 | 12.50 | 57 | 21.0 |
| | 120 | 0.50 | 9.5 | 12.00 | 57 | 21.0 |
| $Fe_2O_3$ | 10 | >100 | >100 | >100 | >100 | >100 |
| | 20 | >100 | >100 | >100 | >100 | >100 |
| | 30 | >100 | >100 | >100 | >100 | >100 |
| | 40 | >100 | 100 | >100 | >100 | >100 |
| | 50 | >100 | 98 | >100 | >100 | >100 |
| | 60 | >100 | 96 | >100 | >100 | >100 |
| | 70 | 96 | 94 | >100 | >100 | >100 |
| | 80 | 94 | 92 | >100 | >100 | >100 |
| | 90 | 92 | 92 | >100 | >100 | >100 |
| | 100 | 90 | 90 | >100 | >100 | >100 |
| | 110 | 88 | 90 | 100 | >100 | >100 |
| | 120 | 87 | 89 | 100 | >100 | >100 |

Carboxymethyl starch exhibited lower flocculation efficiency towards $Fe_2O_3$ suspensions (Fig. 7b, Table 5). The highest extinction drop (10 %) was noted for lower concentration value of both CMSs (to *ca.* 0.050 units). This result suggested that *DS* [*i.e.* concentration of carboxylate groups able to react with Fe(III) cations] did not influenced the efficiency of iron(III) oxide removed from the model suspension. The lowest flocculation efficiency exhibited CMS H6 (500 ppm) when compared to blank test, extinction *ca.* 0.220 and *ca.* 0.350 units, respectively.

Despite the kind of CMS used the sludge volumes for $Fe_2O_3$ suspensions were high. Only in case of CMS H6 (25 ppm) sludge volume value was similar to blank test, in other cases they were significantly higher, *i.e.* >100 cm$^3$ (see Table 5).

**Table 6. Sludge volumes during flocculation/antiflocculation experiments performed for Fe(III) laurate suspension**

| Suspension | Time min | Sludge volume, cm$^3$ | | | | |
|---|---|---|---|---|---|---|
| | | blank | CMS H6 25 ppm | CMS 19c 25 ppm | CMS H6 500 ppm | CMS 19c 500 ppm |
| Fe(III) laurate | 10 | 0.2 | 0.00 | 0 | 0 | 0 |
| | 20 | 0.8 | 0.10 | 0.0 | 0 | 0.3 |
| | 30 | 1.5 | 0.30 | 0.0 | 0 | 0.6 |
| | 40 | 2.5 | 0.35 | 0.0 | 0 | 1.2 |
| | 50 | 3.0 | 0.50 | 0.1 | 0 | 1.8 |
| | 60 | 3.5 | 0.90 | 0.1 | 0 | 2.0 |
| | 70 | 3.5 | 1.00 | 0.1 | 0 | 3.0 |
| | 80 | 3.8 | 1.30 | 0.1 | 0 | 3.0 |
| | 90 | 4.0 | 1.70 | 0.1 | 0 | 3.5 |
| | 100 | 4.0 | 2.00 | 0.1 | 0 | 4.0 |
| | 110 | 4.0 | 2.00 | 0.1 | 0 | 4.5 |
| | 120 | 4.2 | 2.00 | 0.1 | 0 | 5.0 |

Flocculation efficiency was also tested on aqueous suspension prepared in reaction of lauric acid with Fe(III) chloride as well. Obtained Fe(III) laureate was organic-inorganic substance able to form emulsion-like particles in water. The results of flocculation tests were pre-

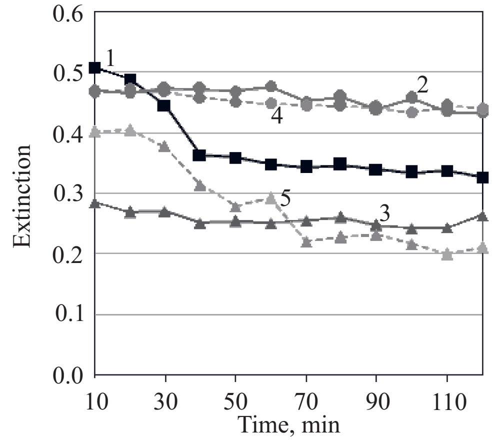


*Fig. 8. Extinction as a function of flocculation/antiflocculation time for Fe(III) laurate suspension; designation see Fig. 7*

sented in Fig. 8; the sludge volumes were collected in Table 6. The degree of substitution of carboxymethyl starch derivative notably affected flocculation efficiency. High substituted CMS 19c (0.93) was not an effective flocculant (extinction drop: 0.500 to 0.200—0.250 units, *i.e. ca.* 50 %). The sludge volume for higher polymer concentration was significantly higher than for blank test. However, when lower CMS 19c dosage applied only trace sludge was observed.

On the other hand, using medium substituted CMS H6 (0.39) for both concentrations resulted in stabilization of iron(III) laurate suspension, confirmed by extinction measurements: 0.460—0.440 units, *i.e.* higher than blank test 0.350—0.330 units after 60 min.

It is worth to notice, that when CMS H6 (500 ppm) was used, no sludge in Imhoff funnel was observed. However, for CMS H6 25 ppm the sludge volume was two times lower than for blank test (2.0 and 4.2 cm$^3$, respectively) (see Table 6). The flocculation of iron(II) laurate suspension using 90—145 ppm CMS (*DS* not given) has been already reported [12]. These authors concluded that CMS exhibited the lowest flocculation ability when compared to other anionic starch derivatives.

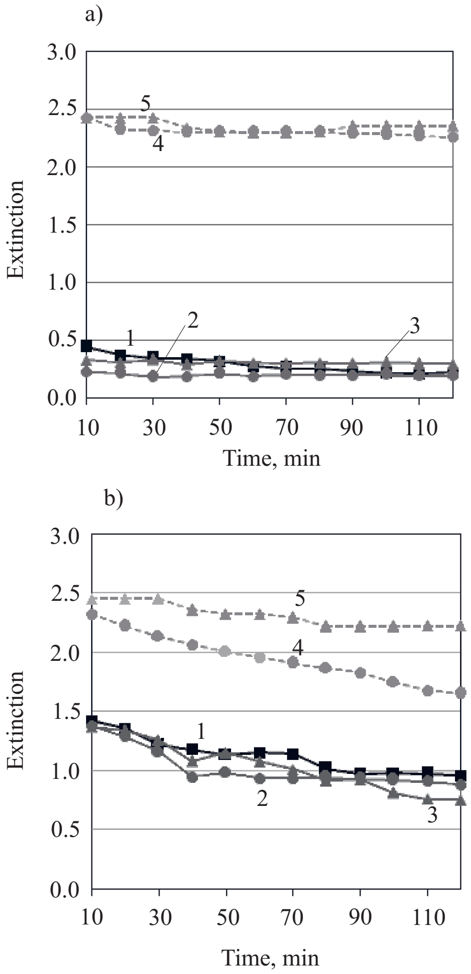


*Fig. 9. Extinction as a function of antiflocculation time for: kaolinite (a) and calcium montmorillonite (b) suspensions; designation see Fig. 7*

To evaluate the interactions between anionic derivatives of starch (amylopectin and amylose) and suspended aluminosilicates kaolinite and calcium montmorillonite were applied. Fig. 9 presents the extinction changes as a function of time; in Table 7 sludge volume values were collected.

**Table 7. Sludge volumes during antiflocculation experiments performed for kaolinite and calcium montmorillonite suspensions**

| Suspension type | Time min | Sludge volume, cm$^3$ | | | | |
|---|---|---|---|---|---|---|
| | | blank | CMS H6 25 ppm | CMS 19c 25 ppm | CMS H6 500 ppm | CMS 19c 500 ppm |
| Kaolinite | 10 | 37 | 45 | 75 | 1.50 | 0 |
| | 20 | 27 | 39 | 62 | 3.00 | 0 |
| | 30 | 26 | 37 | 57 | 4.00 | 0 |
| | 40 | 24 | 36 | 53 | 4.50 | 0 |
| | 50 | 24 | 35 | 51 | 4.75 | 0 |
| | 60 | 23 | 35 | 50 | 4.75 | 0 |
| | 70 | 23 | 34 | 48 | 5.00 | 0 |
| | 80 | 22 | 34 | 48 | 5.00 | 0 |
| | 90 | 22 | 34 | 46 | 5.25 | 0 |
| | 100 | 22 | 33 | 46 | 5.50 | 0 |
| | 110 | 22 | 33 | 46 | 5.50 | 0 |
| | 120 | 21 | 33 | 44 | 5.50 | 0 |
| Calcium montmorillonite | 10 | 3.50 | 3.00 | 7.00 | 2.50 | 1.80 |
| | 20 | 5.00 | 5.50 | 9.00 | 3.50 | 3.75 |
| | 30 | 6.00 | 7.00 | 11.00 | 3.50 | 4.50 |
| | 40 | 7.75 | 8.00 | 12.00 | 3.75 | 5.00 |
| | 50 | 7.50 | 8.00 | 12.00 | 4.00 | 6.00 |
| | 60 | 8.00 | 8.50 | 12.50 | 4.00 | 6.75 |
| | 70 | 8.25 | 9.00 | 12.75 | 4.00 | 7.00 |
| | 80 | 8.75 | 9.50 | 13.00 | 4.00 | 7.50 |
| | 90 | 9.00 | 9.75 | 13.50 | 4.00 | 8.00 |
| | 100 | 9.25 | 10.00 | 13.75 | 4.00 | 8.50 |
| | 110 | 9.50 | 10.00 | 14.00 | 4.25 | 8.75 |
| | 120 | 10.00 | 10.50 | 14.25 | 4.25 | 9.00 |

For both CMS kinds using higher dosage resulted in stable kaolinite suspension in water (extinction increased from *ca.* 0.500 up to 2.300—2.400 units) — Fig. 9a. When lower dosage was applied (25 ppm) no turbidity change was observed (no *DS* effect). After 120 min no sludge for CMS 19c (500 ppm) and insignificant sludge volume for CMS H6 when compared to blank test was reported (5.5 and 21 cm$^3$, respectively — Table 7). However, when lower concentration was applied for both CMSs the sludge volume increase was noted: *ca.* 50 % and 100 % for CMS H6 and CMS 19c, respectively. Similar trend, *i.e.*

CMS „antiflocculation effect" was observed for montmorillonite suspension (Fig. 9b). The most effective dispersant for MMT-Ca suspension was CMS 19c (500 ppm); extinction increased from 1.500 up to 2.450 units and from 1.000 up to 2.200, after 10 min and 120 min, respectively. Similar MMT-Ca dispergation stability exhibited medium substituted CMS H6 (500 rpm).

Although high extinction values were noted the sludge volumes were similar: 9.0, 10.5 and 10 $cm^3$ for CMS 19c, CMS H6, and blank test, respectively. Significantly lower sludge volume was observed for CMS H6 (500 rpm) only.

## CONCLUSIONS

A series of highly substituted CMS (0.80—0.95) in isopropanol/water solution was obtained. The determination of experimental parameters effect, *i.e.* type of etherifying agent, starch and water content as well as reaction time on essential physicochemical properties (*DS*, *RE*, number average molar mass, viscosity of 2 wt. % aqueous solution) of CMS derivatives was performed.

Etherification reaction in applied conditions allowed preserving the granular form of starch. However, some changes in morphology occurred as increase of amorphous region content, observed by laser scanning microscopy, XRD as well as FT-IR techniques was reported.

Depending on CMS degree of substitution and its concentration in aqueous solution CMS could be an effective flocculant for aqueous solutions/dispersions of iron compounds. On the other hand it could work as dispersing agent for mineral aluminosilicates (kaolinite and calcium montmorillonite).

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## REFERENCES

1. Spychaj T., Wilpiszewska K., Zdanowicz M.: *Starch* 2013, **65**, 22.
2. Zhou X., Yang J., Qu G.: *J. Mater. Process. Technol.* 2007, **183**, 407.
3. Tatongjai J., Lumdubwong N.: *Carbohydr. Polym.* 2010, **81**, 377.
4. Bhattacharyya D., Singhal R. S., Kulkarni P. R.: *Carbohydr. Polym.* 1995, **27**, 167.
5. Lawal O. S., Lechner M. D., Hartmann B., Kulicke W. M.: *Starch* 2007, **59**, 224.
6. Tijsen C. J., Scherpenkate H. J., Stamhuis E. J., Beenackers A. A. C. M.: *Chem. Eng. Sci.* 1999, **54**, 2765.
7. Tijsen C. J., Voncken R. M., Beenackers A. A. C. M.: *Chem. Eng. Sci.* 2001, **56**, 411.
8. *Pat. EP* 1 299 423 (2005).
9. Bi Y., Liu M., Wu L., Cui D.: *Polym. Adv. Technol.* 2008, **19**, 1185.
10. Bi Y., Liu M., Wu, L., Cui D.: *J. Appl. Polym. Sci.* 2009, **113**, 24.
11. Pant B. R., Jeon H. J., Song H. H.: *Macromol. Res.* 2011, **19**, 307.
12. Khalil M. I., Aly A. A.: *Starch* 2002, **54**, 132.
13. Volkert B., Loth F., Lazik W., Engelhardt J.: *Starch* 2004, **56**, 307.
14. Wang B.-X., Zhao X.-P.: *J. Solid State Chem.* 2006, **179**, 949.
15. Saboktakin M. R., Tabatabaie R. M., Maharramov A., Ramazanov M. A.: *Carbohydr. Polym.* 2010, **79**, 1113.
16. Kessel H.: *Starch* 1985, **37**, 334.
17. Yaacob B., Amin M. C. I. M., Hashim K., Bakar B. A.: *Iranian Polym J.* 2011, **20**, 195.
18. Jiang Q., Gao W., Li X., Liu Z., Huang L., Xiao P.: *Starch* 2011, **63**, 699.
19. Stojanovič Z., Jeremič K., Jovanovič S.: *Starch* 2000, **52**, 413.
20. Kooijman L. M., Ganzeveld K. J., Manurung R. M.: *Starch* 2003, **55**, 495.
21. Zdanowicz M., Spychaj T., unpublished results.

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