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SYNTHESIS AND CHARACTERIZATION OF CARBOXYMETHYLATED CORNSTARCH

Abstract. The aim of this study is preparation and characterization of carboxymethylated cornstarch (CMCS) for potential application as water based drilling fluids. The cornstarch was modified by sodium monochloroacetate. The structure of cornstarch and CMCS was established by H^1 NMR and FTIR spectroscopy. The degree of carboxymethylation of cornstarch determined by H^1 NMR spectroscopy was equal to 80%. The viscosity-average molecular weights (M_η) of pristine cornstarch and CMCS calculated from Mark-Kuhn-Houwink equation $[\eta]=K_\eta \cdot M^a$ are equal to $2.15 \cdot 10^3$ g·mol^{-1} and $2.75 \cdot 10^5$ g·mol^{-1} respectively. The temperature dependent viscosity of CMCS was measured in water by Ubbelohde viscometer, while the rheological properties of CMCS in dependence of polymer concentration and ionic strength of the solution were evaluated by rheoviscometer. The thermal characteristics of samples were determined by differential scanning calorimeter (DSC) and thermogravimetric (TGA) and differential thermal analyzer (DTA). The morphological properties of cornstarch and CMCS were studied by scanning electron microscopy (SEM). The structural-mechanical, filtration and filter cake forming properties of drilling fluids and fluid loss indicators of CMCS were found.

Keywords: cornstarch, modification, carboxymethylated cornstarch, degree of substitution, viscosity-average molecular weight, viscosity, rheology, drilling fluids.

Introduction

The interest in natural polysaccharides has increased considerably in recent years, as they are candidates for many commercial applications in different industrial sectors like food, textile, paper, petroleum, and pharmaceuticals [1]. Products made from starch have attracted the interest of researchers and companies due to the abundance of starch in nature, its low cost and biodegradability [2-5]. The carboxymethylation of starch in alkaline solution with sodium monochloroacetate was first carried out in 1924 [6]. Currently many papers concerning the carboxymethylation of starch were published with the aim to optimize the reaction conditions, to increase the yield of product and to increase the degree of substitution (DS) [7]. Starch is unique raw material resources due to high biocompatibility and annual renewability (potatoes (5%), corn (82%), wheat (8|%), etc.) that distinguish it from cellulose derived from wood, which period of maturing is 18-20 years for fast-growing wood [2, 8-9]. Starch is a carbohydrate consisting of linear and helical amylose molecules and branched amylopectin molecules with general chemical formula $(C_6H_{10}O_5)_n$ [10-12].

Starch was the first polymer reagent used for the drilling muds in 1939 [13]. However, with the introduction of polymer reagents based on cellulose ethers widespread use of starch started to reduce. This was primarily due to the need to use bactericides and low thermostable starch reagents [2].

Currently, the natural starch is not used in drilling fluids. Instead of it, the following types of modified starch such as carboxymethyl, hydroxyethyl, as well as oxidized starch are applied to regulate the filtration and rheological characteristics of drilling muds. The chemical modification of cornstarch is performed to overcome the insolubility in water, hardly controlled viscosity after gelatinization, the turbidity of aqueous solutions [14]. Carboxymethylated starch (CMS) is the most commonly used material among the modified starch reagents. It is a starch derivative in which the –OH groups is partially substituted by ether group (-O-CH_2COOH) [15]. It is characterized by good resistance to high content of salt, high durability to thermal and bacteriological affect [16]. The CMS has a wide applicability due to water-solubility, high viscosity and stability as a fluid loss reducing agent in drilling fluid [10, 17]. The application of CMS in enhanced oil recovery is also growing [18].

The main objective of this work is to synthesize and characterize CMCS with potential application as additives in water-based drilling fluids. These materials were also evaluated regarding their thermal resistance and rheological behavior in the presence of various salts. Starch is a perspective material from practical point of view because it is non-toxic, contains easily modifiable functional groups and is ecologically friendly [19].

Experimental part

Materials

Cornstarch was purchased from LLP "Zharkent Starch-Factory". Sodium monochloroacetate (Na-MCA) $ClCH_2COONa$ was obtained from Merck-Schuchardt (Hohenbrunn, Germany). The chemical reagents used in this investigation (NaOH, CH_3CH_2OH, NaCl, KCl, $MgCl_2$, $CaCl_2$, HCl, LiBr, d_6-DMSO, and d_1-TFA were purchased from Sigma Aldrich (Finland) and used as received.

Synthesis of carboxymethylated cornstarch (CMCS)

Modification of cornstarchwas carried out in two steps [19]. Firstly, alkalization was performed by mixing of 0.4 g cornstarch, 1.2 mL ethanol and 0.28 mL aqueous 11.5 M NaOH solution at 25ºC, the mixture was stirred for 20 min. In the second step, 0.28 g Na-MCA was added and the reaction mixture was heated to 58ºC and stirred during 100 min. The precipitated in ethanol CMCS was filtered and dried under vacuum at 50ºC.

Methods

^{1}H NMR of cornstarch and CMCS were recorded on a Bruker Avance III 500 spectrometer at 70ºC according to procedure [20]. The viscosity-average molecular weights of the cornstarch and CMCS were determined by Mark-Kuhn-Houwink equation, $[\eta]=K_\eta \cdot M^a$, where M_η is the viscosity-average molecular weight and the parameters K_η and a are related to local stiffness of the polymer and depend on the nature of polymer, solvent and temperature. The Fourier Transform Infrared (FTIR) spectra of the starch samples were registered by FTIR spectrometer Carry 660 (Agilent, USA).The viscosity of cornstarch and CMCS solutions was measured by Ubbelohde viscometer at 25±0.1 °C. The rheological behavior of CMCS solutions was monitored with the help of Rheolab QC, Anton Paar (Austria). The thermal characteristics of samples were determined with the help of DSC 131 EVO Setaram and TGA «Labsys EVO» Setaram (France). The samples were heated from 25 to 500 ºC at heating rate 10ºC/min. The size and ζ-potential of CMSC was determined with the help of Dynamic Light Scattering (DLS) device Malvern Zetasizer Nano ZS90 (UK). Scanning electron micrographs were obtained with the help of SEM (Jeol JSM-6490LA, Japan). Static shear stress (SSS) measurements after 1 min and 10 min (SSS_1 and SSS_{10}) were performed by means of the instrument SNS-2 (Russian Federation). Water yield of the drilling muds (W) was determined by VM-6 instrument (Russian Federation). The thickness of the filter cake (δ) was measured by the instrument WIKA IV-2 (Russian Federation).

Results and Discussion.

Modification of cornstarch

The carboxymethylation of cornstarch proceeds by two steps:

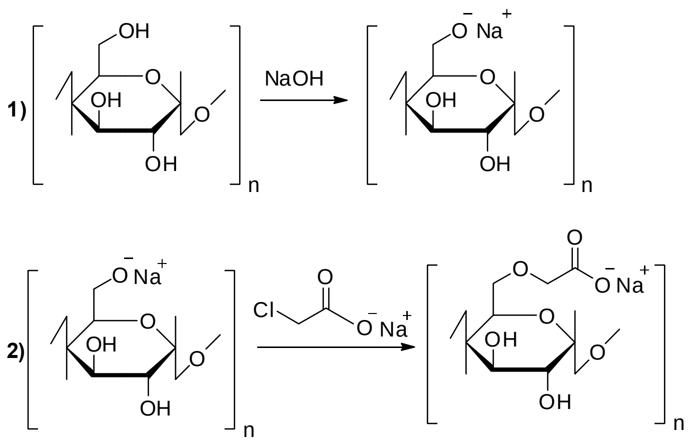


Figure 1 -Modification of corn starch with sodium monochloroacetate

In the first step (1) the OH groups are transformed to $O^{-}Na^{+}$, then on the second step (2) the Na^{+} ions are eliminated by chlorine of sodium monochloroacetate by the following reaction:

— $O^{-}Na^{+}$ + Cl-CH_2COONa → —O-CH_2COONa + NaCl

As a result a fully water-soluble carboxymethylated cornstarch (CMCS) with DS = 80% was obtsined.

Identification of the CMCS structure by H^1 NMR and FTIR spectroscopy

^{1}H NMR spectrum of CMCS registered at 70 ºC is shown in Figure 2.

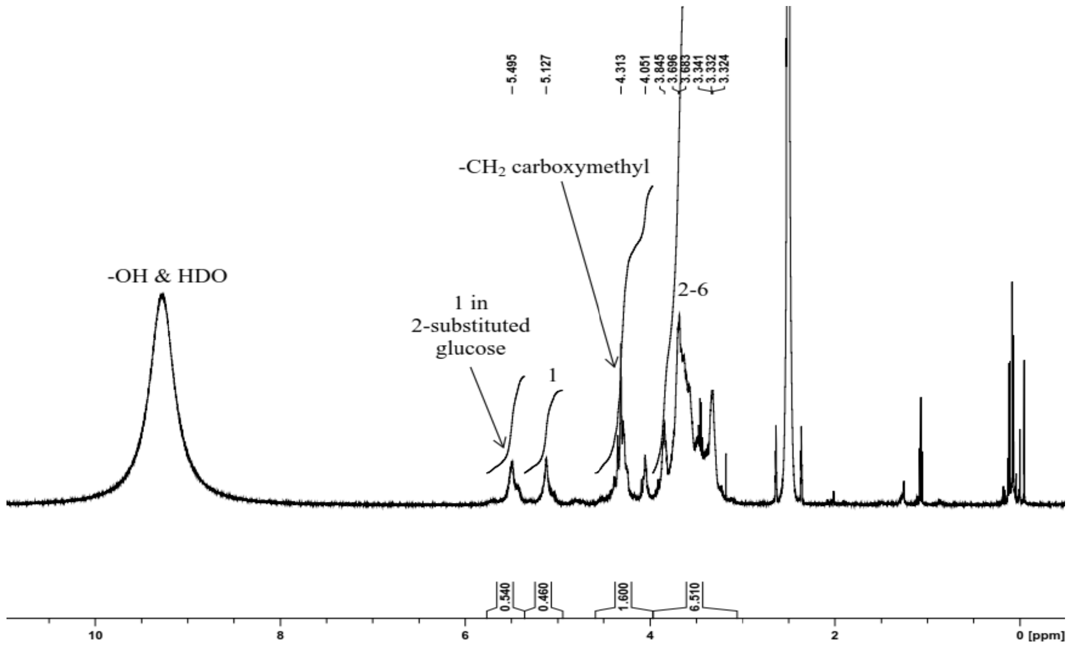


Figure 2 - ^{1}H NMR spectrum of CMCS in d_6-DMSO

The substitution degree of CMCS determined from the methylene signal of the carboxymethyl substituent (4.31 ppm) and the anomeric protons of glucose (5.13 and 5.50 ppm) was equal to 80%.

FTIR spectra of pristine and modified cornstarch are compared in Figure 3.

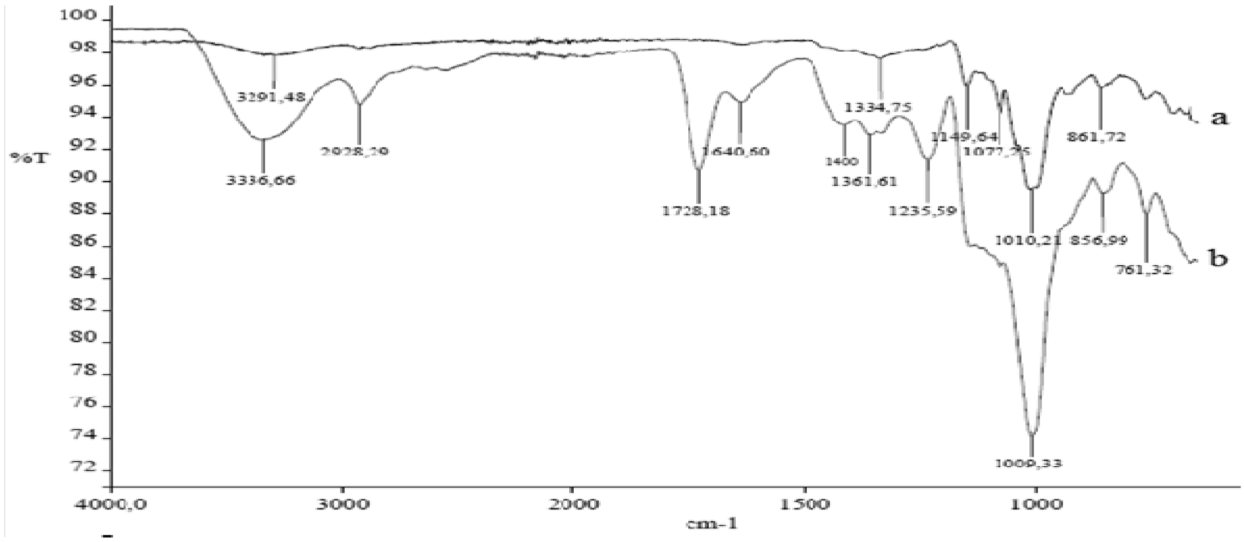


Figure 3 - FTIR spectra of cornstarch (a) and CMCS (b)

The broad bands between 3336 and 3291 cm^{-1} is assigned to OH stretching vibrations due to hydrogen bonding between the hydroxyl groups. The band around of 2928 cm^{-1} belongs to CH_2 symmetrical stretching vibrations. A new peak at 1728 cm^{-1} is specific for ester groups, the bands at 1640 and 1400 $cm^{-1}$are related to asymmetric and symmetric vibrations of carboxylate ions (COO^-). At 1200-1360 cm^{-1} the vibrations of CH_2, CH, and C-OH groups are observed. An absorption band at 1009 cm^{-1} corresponds to stretching vibrations of ether groups -OCH-O-CH_2. Low intensive bands in the range of 860-760 cm^{-1} correspond to out-of-plane vibrations of OH-group of glucopyranose ring. Thus, both H^1 NMR and FTIR spectra of CMCS reveal that the modification by Na-MCA takes place to obtain the water-soluble derivatives of cornstarch.

Viscosity-average molecular weight (M_η) of CMCS

The viscosity-average molecular weight (M_η) of the CMCS was calculated by the Mark-Kuhn-Houwink relationship $[\eta]=K_\eta \cdot M^a$ taking into account that $K_\eta=2.0 \cdot 10^{-4}$ and a=0.75 for a standard starch in 0.1 M aqueous NaCl at $25^{\circ}C$ [2].

The viscosity-average molecular weights (M_η) of cornstarch and CMCS were found to be $2.15 \cdot 10^3$ $g \cdot mol^{-1}$ and $2.75 \cdot 10^5$ $g \cdot mol^{-1}$ respectively. A significant increase in the M_η of the cornstarch after carboxymethylation is due to the presence of bulkier carboxymethyl groups in modified cornstarch.

Viscosity measurements

The influence of temperature on solution behavior of CMCS is shown in Figure 4.

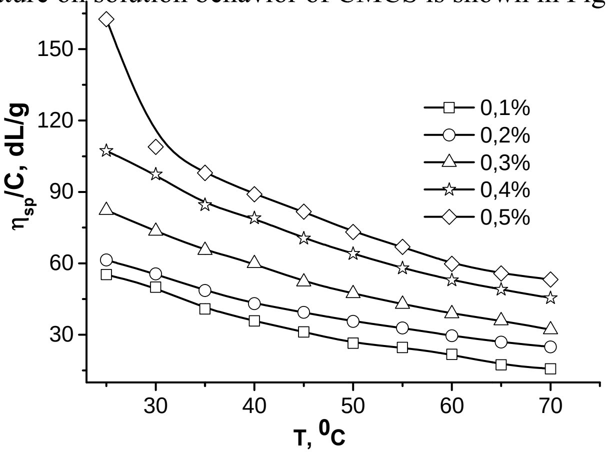
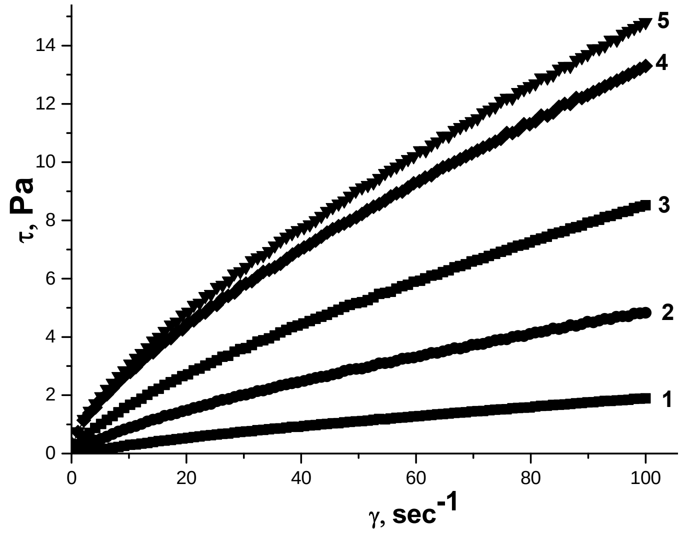


Figure 4 – Temperature dependent reduced viscosity of aqueous solutions of CMCS

The reduced viscosity of aqueous solutions of CMCS gradually decreases with increasing of the temperature. This may be connected with a gradual disaggregation of macromolecular associates due to destruction of hydrogen bonds.

Rheological characteristics of CMCS solutions

Rheological properties are considered as important parameters to evaluate the applicability of the CMCS as drilling fluids. The CMCS solutions represent the pseudo plastic liquids and are suitable for the formulation of drilling fluids.



(1) 0.25, (2) 0.5, (3) 1, (4) 2, (5) 1.5 wt.%
Figure 5 – Concentration dependent shear stress-shear rate curves of aqueous solutions of CMCS

As the polymer concentration increases the solution viscosity increases as well. However, increasing of the polymer concentration higher than 1.5 wt.% is not efficient. Therefore it is expected that the optimal concentration of CMCS for shear rate is 1.5 wt.%.

Dependences of shear stress on shear rate for CMCS solutions in the presence of NaCl, KCl, $MgCl_2$ and $CaCl_2$ are shown in Figure 6.

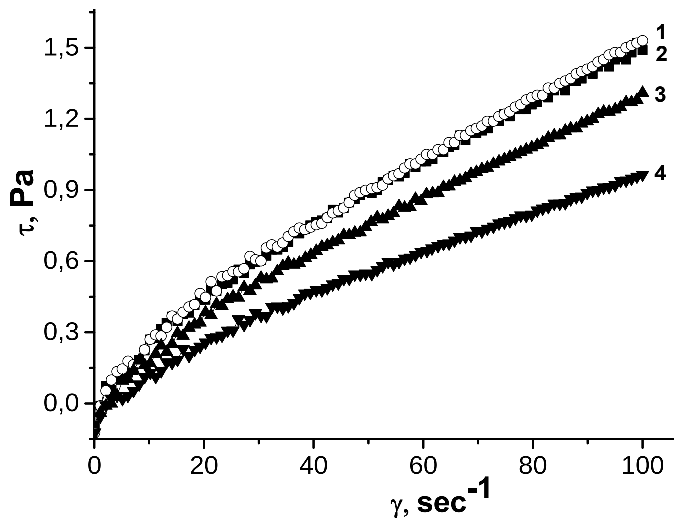


Figure 6 - The shear stress-shear rate curves of 0.5% wt.% CMCS solutions at the ionic strength of μ=0.01 adjusted by NaCl (1), KCl (2), $MgCl_2$ (3) and $CaCl_2$ (4)

Aqueous solutions of CMCS behave polyelectrolyte character that is suppressed upon addition of low-molecular-weight salts. The viscosity resistant behavior of CMCS in saline water provides the stability of drilling muds in a wide range of salt concentrations.

Thermal characteristics of cornstarch and CMCS

Thermal properties of cornstarch and CMCS derived from DSC are shown in Figure 7. The appearance of exothermic peaks at 80.2 and 83.3 ºC is probably due to removal of residual moisture. The broad endothermic peaks at the interval of temperature 285.85-392.77 and 251.3-326.87 ºC probably reflect the crystallization of cornstarch and CMCS, respectively.

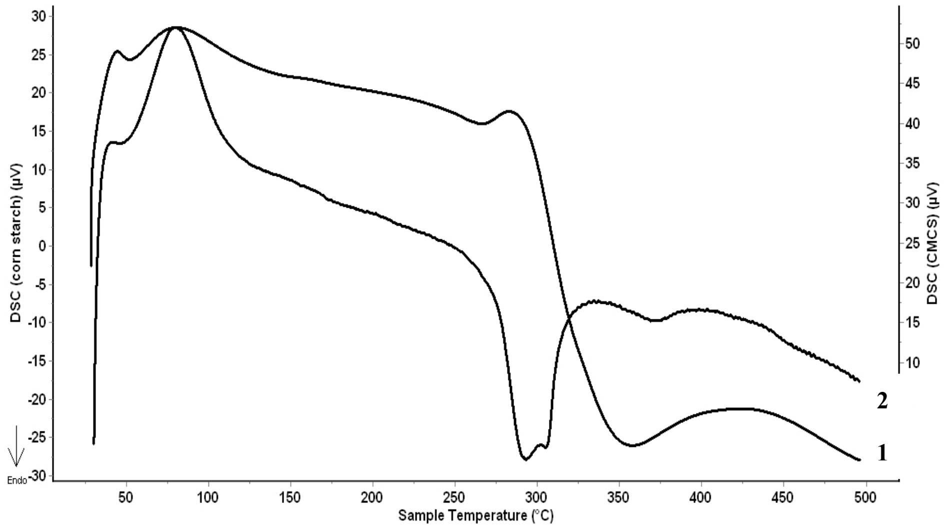


Figure 7 - DSC curves of cornstarch (1) and CMCS (2)

Mass loss percentages for cornstarch and CMCS were calculated from TGA data (Figure 8). TGA studies reveal high heat resistance for CMCS as compared to the cornstarch. CMCS loses 38.47 % of the mass, while cornstarch – 45.83

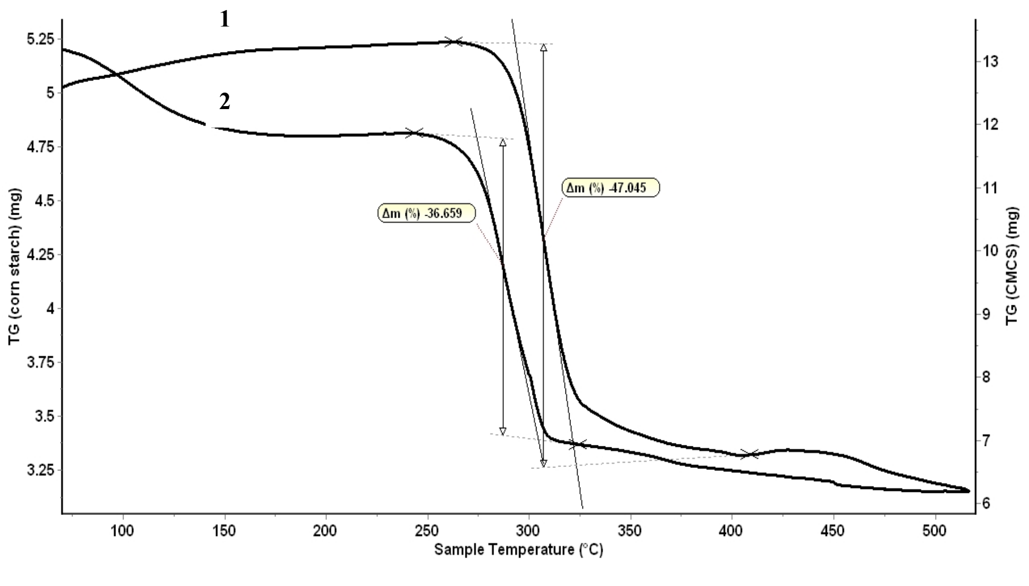


Figure 8 - TGA curves of cornstarch (1) and CMCS (2)

DLS measurements

Table 2 shows the average sizes and ζ-potentials of CMCS. The size distribution of CMCS is varied from 235 nm to 1034 nm. The negative values of the ζ-potentials of CMCS in water confirm the substitution of hydroxyl groups of cornstarch by carboxymethyl moieties.

Table 1 – The average sizes and ζ-potentials of CMCS in water

C, wt.%	Size, nm	ζ-potential, mV
0.1	1034	-85
0.2	633	-60
0.3	235	-56
0.4	487	-50
0.5	552	-53

Morphology of cornstarch and CMCS

The SEM images of cornstarch and the CMCS are compared in Figure 9. SEM showed the carboxymethylation to change the structure of starch granules, compared with native cornstarch. Cornstarch granules are smooth, round in shape with sizes ranging from 5 to 15 µm. After carboxymethylation the granules of cornstarch are bigger in size (400-500 µm) and the granular surface becomes rough and scaly. Probably these changes are due to modification of cornstarch affected by strong alkaline environment and heat treatment.

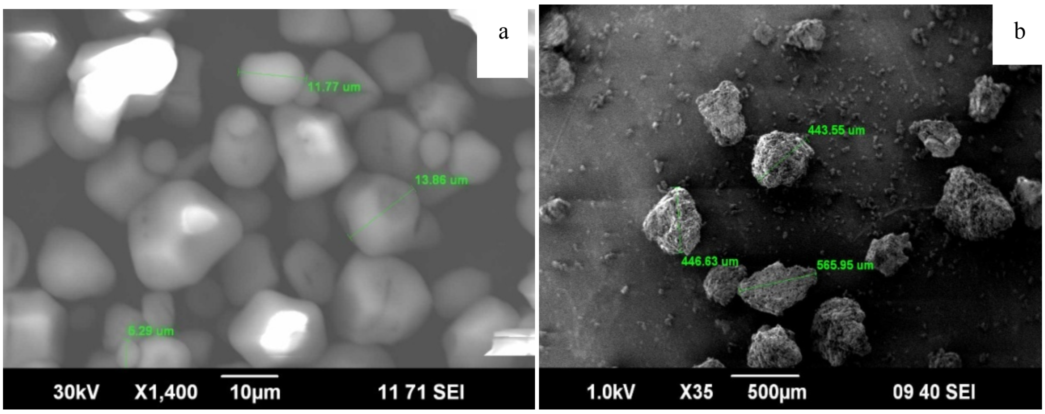


Figure 9 - SEM images of cornstarch (a) and CMCS (b)

Formulation of drilling fluids

The drilling fluids (DF) composed of gellan, xanthan, CMCS, Polyanionic cellulose (PAC), KCl and bentonite were formulated to obtain an appropriate DF with optimal solution density (ρ), relative viscosity (η_{rel}), dynamic shear stress (DSS), fluid loss indicator (W), thickness of mud cake (δ), and ratio of static shear stress (SSS_1/SSS_{10}).

Properties of drilling fluids

The structural-mechanical, filtration and filter cake forming properties of model system, consisting of 0.1% gellan, 0.2% xanthan, 0.25-0.35% CMCS at the interval of pH 9.2-10.0 are summarized in Table 2. Analysis shows that all drilling fluids based on CMCS possess good structural-mechanical and filtration characteristics. The thickness of filter cake may be increased by adding 4 wt.% of bentonite. The thixotropic characteristics of drilling fluids are improved with increasing of CMCS concentration. Moreover, the CMCS with high DS due to good water-solubility and high viscosity is more beneficial than industrial starch that is applied for formulation of drilling fluids.

Table 2 – Composition and characteristics of drilling fluids

№	Ratio DF*, %						pH	ρ, g/cm^3	η_{rel}, sec	DSS, Pa	W, cm^3	δ, mm	SSS_1/SSS_{10}, dPa
	gellan	xanthan	CMCS	PAC	KCl	bentonite							
1	0.1	0.2	1**	0.5	0	4	10	1.03	54	1.2	5	0.4	8/15
2	0.1	0.2	1**	0.5	1	4	9.8	1.04	52	1.4	5	0.4	7.5/14
3	0.1	0.2	1**	0.5	3	4	9.6	1.05	52	1.7	5	0.4	7/13
4	0.1	0.2	0.25	0.5	0	1	9.2	1.02	33.6	1.7	6	0.4	3.3/5.3
5	0.1	0.2	0.25	0.5	0	2	9.4	1.06	35.7	1.7	5.5	0.4	5/7
6	**0.1**	**0.2**	**0.25**	**0.5**	**1**	**4**	**9.6**	**1.08**	**32.8**	**1.6**	**5**	**0.5**	**9.8/11.5**
7	**0.1**	**0.2**	**0.35**	**0.5**	**2**	**4**	**9.7**	**1.08**	**35.3**	**1.5**	**5**	**0.5**	**12.3/13.9**
*The rest is water													
** Industrial CMCS													

Samples No. 6 and 7 containing gellan, xanthan, CMCS and PAC in the presence of 4% bentonite exhibit the best SSS_1/SSS_{10} characteristics that are applicable as drilling fluids [21].

Conclusion

Water-soluble CMCS were prepared by carboxymethylation of cornstarch. The introduction of carboxymethyl groups into the structure of cornstarch was detected by FTIR and H^1 NMR spectroscopy. The viscosity-average molecular weight of CMCS is much higher than unmodified cornstarch. Aqueous solutions of CMCS show a high viscosity that decreases upon increasing of temperature and salt addition. The thermal, morphological and rheological properties of CMCS have been evaluated. Water-based optimal drilling fluids composed of various polysaccharides, salt and bentonite have been formulated and suggested for application.

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КАРБОКСИМЕТИЛДЕНГЕН ЖҮГЕРІ КРАХМАЛЫН СИНТЕЗДЕУ ЖӘНЕ СИПАТТАУ

Аннотация. Бұл жұмыстың мақсаты карбоксиметилденген жүгері крахмалын (КМЖК) алу, сипаттау және бұл үлгілерді су негізіндегі бұрғылау ерітінділерінде қолдану мүмкіндігін бағалау болып табылады. Жүгері крахмалын натрий монохлорацетатымен модификациялады. Жүгері крахмалы мен КМЖК құрылысы ЯМР және ИҚ-спектроскопия көмегімен анықталды. ЯМР-спектроскопиясы көмегімен анықталған жүгері крахмалының карбоксиметилдену дәрежесі 80% тең болды. Марк—Кун—Хаувинк теңдеуімен $[\eta]=K_\eta \cdot M^a$ табылған таза жүгері крахмалы мен КМЖК ортамассалық молекулалық массасы (M_η) сәйкесінше $2.15 \cdot 10^3$ г/моль және $2.75 \cdot 10^5$ г/моль тең болды. КМЖК температураға тәуелді тұтқырлығы суда Уббелоде вискозиметрі көмегімен өлшенді, КМЖК реологиялық қасиеттері полимер концентрациясы және ерітіндінің иондық күшіне тәуелділігі реовискозиметрмен бағаланды. Үлгілердің жылу сипаттамалары дифференциалды сканирлеуші калориметрі (ДСК), термогравиметриялық (ТА) және дифференциалды термиялық анализаторы (ДТА) арқылы Eva Setaram (Франция) анықталды. Жүгері крахмалы мен КМЖК морфологиялық қасиеттері сканирлеуші электрондық микроскоп (СЭМ) арқылы зерттелді. Бұрғылау ерітінділерінің құрылымдық – механикалық, фильтрациялық және қабат түзу қасиеттері, КМЖК фильтрация көрсеткіші табылды.

Түйін сөздер: жүгері крахмалы, модификация, карбоксиметилденген жүгері крахмалы, орынбасу дәрежесі, ортамассалық молекулалық масса, тұтқырлық, реология, бұрғылау ерітінділері.

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СИНТЕЗ И ХАРАКТЕРИСТИКА КАРБОКСИМЕТИЛИРОВАННОГО КУКУРУЗНОГО КРАХМАЛА

Аннотация. Целью данной работы является подготовка и исследование карбоксиметилированного кукурузного крахмала (КМКК) для потенциального применения в качестве буровых растворов. Кукурузный крахмал модифицировали монохлорацетатом натрия. Структура кукурузного крахмала и КМКК была установлена с помощью ЯМР и ИК-спектроскопии. Степень карбоксиметилирования кукурузного крахмала, определенная с помощью ЯМР-спектроскопии, была равна 80%. Средневязкостные молекулярные массы (M_η) чистого кукурузного крахмала и КМКК, рассчитанные по уравнению Марка-Куна-Хаувинка $[\eta]=K_\eta \cdot M^a$, равны $2{,}15\cdot10^3$ г/моль и $2{,}75\cdot10^5$ г/моль соответственно. Зависимость вязкости КМКК от температуры измерялась в воде с помощью вискозиметра Уббелоде, а реологические свойства КМКК в зависимости от концентрации полимера и ионной силы раствора оценивались реовискометром. Термические характеристики образцов определялись дифференциальным сканирующим калориметром (ДСК) и термогравиметрическим (ТГА) и дифференциальным термическим анализом (ДТА). Морфологические свойства кукурузного крахмала и КМКК были изучены сканирующей электронной микроскопией (СЭМ). Определены структурно-механические, фильтрационные и коркообразующие свойства буровых растворов и показатели потери жидкости КМКК.

Ключевые слова: кукурузный крахмал, модификация, карбоксиметилированный кукурузный крахмал, степень замещения, средневязкостная молекулярная масса, вязкость, реология, буровые растворы.

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