Carboxymethyl Starch/Montmorillonite Aqueous Dispersions: The Effect of Components and Mixing Method on Rheoviscometric Characteristics

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ABSTRACT: The rheoviscometric properties of low and high substituted carboxymethyl starch (CMS) 2 wt% aqueous solutions and their dispersions with sodium, calcium, and organomodified montmorillonite (MMT) have been investigated. The influence of MMT type and content on viscosity of CMS (degree of substitution, DS, 0.90)/sodium MMT aqueous dispersions, their stability, and transparency during storage up to 18 months has been investigated. Moreover, the methods of MMT dispergation in low substituted CMS solutions (DS 0.15), that is, mechanical stirring or mechanical and ultrasonication stirring on viscosity have been compared. It resulted in higher viscosity when using the latter mixing procedure (7000 and 9250 mPa·s, respectively, at 1 rpm for CMS (DS 0.15)/7 phr calcium MMT). In addition, thermal resistance of native starch and both CMS with different DS values has been investigated. The results are important as far as commercial applications of CMS solutions or dispersions with MMTs are concerned. © 2013 Wiley Periodicals, Inc. Adv Polym Technol 2013, 32, 21353; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21353

KEY WORDS: Carboxymethyl starch, Montmorillonite, Nanostructure, Viscosity, Water-soluble polymers

Introduction

There is an increasing interest in modifying the biodegradable and renewable polymers to obtain materials with different properties. Chemical modification of starch has been performed to overcome the shortcomings of native starch, such as insolubility in cold water, excessive or uncontrolled viscosity after heating, and tendency to retrogradation.[1] The water solubility could be improved by introducing ionogenic groups into starch macromolecules, for example, via carboxymelthylation.[2] The properties of carboxymethyl starch (CMS) solution (viscosity, dissolution rate, etc.) are determined mainly by the total degree of substitution (DS).[3] However, the commercially available CMS materials often exhibit low DS up to 0.3.[4] It has found application mainly in nonfood industry: as a disintegrant and coating in pharmaceutical industry,[5] thickening and sizing agent in textile industry,[6] or colloidal agents.[7] In addition, CMS has been used in the oil drilling industry as a fluid loss reducer for all types of water-based mud (changing its flow properties as well as thixotropy) as it is more efficient and has higher temperature stability than native starch.[8,9] A precise control of flow properties is important because of their effect on the drilling rate, hole cleaning, and gas entrapment, etc.[10]

Montmorillonite (MMT) has a stacked platelet structure with each platelet having a thickness of approximately 1 nm with a hydrophilic layer between each platelet.[11] MMT has been used as a thickening and thixotroping agent in paint and mineral oil industry, as an antifriction agent in building industry, and as an emulsion stabilizer in pharmaceutical industry.[12]

There are no literature data on CMS/MMT aqueous dispersion characteristics. However, limited sources on other carboxymethylated polysaccharide/MMT systems including relevant derivatives of cellulose or chitosan are accessible.[13–17]

Benchabane and Bekkour[13] investigated rheological behavior of aqueous calcium MMT/carboxymethyl cellulose (CMC) suspensions. They found that CMC (DS 0.65–0.85) coated the clay particles and prevented the reorganization of the agglomerates without enlargement of the MMT interlayer spacing caused by CMC. It means that the polymer additive acts only on the external surface of the clay particles (or aggregates) by coating them, therefore preventing further particles' interaction.

Amorim et al.[14] studied the influence of ionic strength on the viscosity of sodium MMT using low viscosity CMC (DS 0.85, M 70,000 g/mol) in CaCl$_2$ and MgCl$_2$ dispersions. The authors concluded that (i) CMC acted as the deflocculant of the system and (ii) the viscosity of CMC/MMT systems was only slightly affected by the salinity.

Almasi et al.[15] prepared starch/CMC/MMT films cross-linked with citric acid and plasticized with glycerol. They found the intercalated structure of clay in composite films, which exhibited lower water solubility and higher mechanical properties in comparison with the neat film.

CMS is cheaper, and its production is more environment friendly than that of CMC. For this reason, CMS or CMS/MMT dispersions could replace CMC in many applications.

The goal of this paper is to determine the effect of CMS of low and high DS (0.15 and 0.9, respectively) and pristine and organophilized MMTs in aqueous dispersion on rheoviscometric characteristics of the CMS/MMT aqueous system. Two methods of MMT dispergation in aqueous solutions of CMS have been applied, i.e., mechanical stirring and sonication, to compare their effectiveness and influence on viscosity enhancement. Moreover, stability, transparency, as well as thermal properties, and MMT crystallographic structure changes have been evaluated.

Experimental

MATERIALS

Potato starch (Nowamyl S.A., Nowogard, Poland) as well as CMS of DS 0.15 (Zetpezet, Poland) was applied after controlling the moisture content. Monochloroacetic acid (MCA, a.g.; Chempur, Poland) was used as an etherifying agent, whereas isopropanol (IPA, pure; Chempur) was used as a reaction medium. Sodium hydroxide (microgranules), acetic acid, and copper sulfate penthahydrate were the products of Chempur, murexide and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) of Sigma-Aldrich (Seelze, Germany). Sodium MMT and calcium MMT (technical grade; ZGM Zebiec S.A., Poland) were purified via centrifugation (MLW K23D, 3000 rpm, 10 min) before use. Organophilized MMT ZS1 was a pilot product of ZGM Zebiec S.A.

PREPARATION OF CMS WITH HIGH DEGREE OF SUBSTITUTION

Modification of potato starch was carried out in a batch reactor equipped with a mechanical stirrer, a thermocouple, and a capillary tube supplying nitrogen to the reaction system. Starch (13.6–14 wt% moisture) was etherified in isopropanol/water in a one-step process. In the batch reactor, MCA was dissolved in isopropanol, and then water solution of NaOH was added. When the mixture became white and homogeneous, starch and remaining NaOH were introduced. Obtained product was filtered, neutralized with glacial acetic acid, washed five times in 80 wt% methanol aqueous solution, and then washed once again in methanol and dried in the air.

DETERMINATION OF DS

DS was measured according to method described by Kessel.[18]

The CMS sample was moisturized by 1 mL of ethanol and dissolved in 50 mL of distilled water. Subsequently, buffer was added (NH_4Cl aqueous solution, 20 mL), neutral pH was adjusted, and then the whole mixture was poured into a measuring
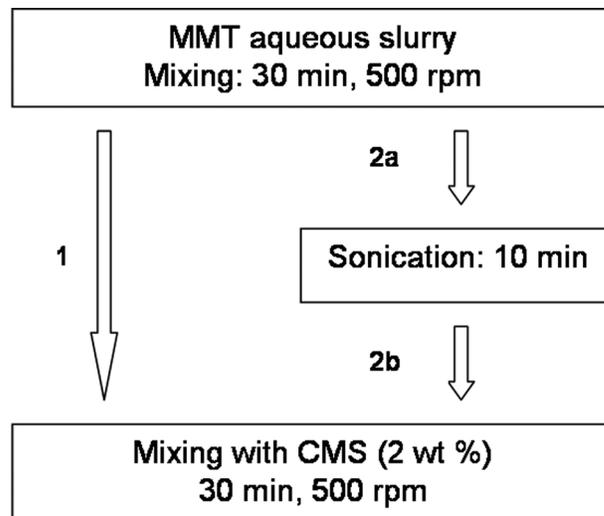
FIGURE 1. Scheme of CMS/MMT aqueous dispersions preparation.

flask (250 mL) with 50 mL of $CuSO_4$ solution. After 15 min, the measuring flask was filled up with water and the whole content was filtered. Filtrate was titrated with EDTA solution using murexide as an indicator.

PREPARATION OF CMS/MMT DISPERSIONS

The CMS/MMT slurries were prepared by dispersing an appropriate amount of MMT in distilled water (25°C). The clay suspension was then mixed mechanically (the mechanical method) or first stirred mechanically and subsequently using ultrasonication (the sonication method). After preparation of MMT dispersion, CMS powder was added (2 wt%) and the system was mechanically mixed until homogeneity was achieved. The scheme of CMS/MMT dispersions preparation methods are presented in Fig. 1.

Mechanical Method

The clay suspension was mechanically stirred for 30 min. Subsequently, CMS powder was added slowly (2 wt%) and the system was mechanically mixed for 30 min.

Sonication Method

The clay suspension was mechanically stirred for 30 min and subsequently by sonication for 10 min (Hielscher, UP200, 200 W, 24 kHz) using various amplitude/period parameters: 30%/0.5 h, 50%/0.5 h, or 60%/0.5 h. Next, CMS was added (2 wt%) and the system was mechanically mixed for 30 min.

A list of all investigated CMS/MMT systems is given in Table I.

VISCOSITY MEASUREMENTS

The rheoviscometric characteristics of 2 wt% aqueous CMS solutions as well as CMS/MMT dispersions were determined 30 min after preparation at 25°C using a Brookfield RV rheoviscometer. In addition, the rheoviscometric stability tests

TABLE I ◼

Investigated CMS/MMT Aqueous Systems

CMS	MMT		Mixing Method
	Type	Concentration on Dry CMS [phr]	
DS 0.15	MMT-Ca	0	Mechanical
		3	Sonication
		5	
		7	
DS 0.8	MMT-Na	0	Mechanical
		2	
		5	
	MMT-Ca	7	Sonication
	OMMT ZS 1	2	Mechanical
		5	
DS 0.9	MMT Ca	0	Mechanical
		7	Sonication

were performed after 72 h, 1 and 3 months, as well as 1.5 years after dispersion preparation.

INSTRUMENTAL METHODS

For gel permeation chromatography (GPC) analysis, a Shodex OHpak SB-806M MQ column with Shodex OHpak SB-G precolumn in a Merck Hitachi liquid chromatograph (pump L-7100, interface D-7000) with a RI detector (Merck Lachrom RI L-7490) was used. Dextran standards for the column calibration and chromatography eluent, sodium nitrate solution 0.1 M, were applied (at a flow rate of 0.5 cm^3/min).

Dispersion of MMTs in the modified polysaccharide matrix was investigated with X-ray diffraction analysis (diffractometer X'pertPro, PANalytical operated at the Co Kα wavelength 1,514 Å). CMS/MMT dispersions were poured out into polystyrene Petri dishes and dried in vacuum at 60°C for 24 h. Obtained composite films were grounded.

Thermal properties were determined using thermogravimetric analysis (TGA Q-500; TA Instruments) in the air atmosphere; samples in platinum pans were scanned in a temperature range of 40–900°C with a heating rate of 10°C/min.

Fourier transform infrared (FTIR) spectra of the samples were recorded by Nexus (ThermoNicolet) using the ATR (Golden Gate) technique. For each sample, 32 scans were taken from 4000 to 400 cm^{-1}.

The dispersion transparency was determined by evaluating the transmittance of 2 wt% aqueous solutions of CMS and its composition with MMTs using a spectrophotometer UV-vis (SPEKOL 11) at the wavelength of 470 nm.

Results and Discussion

FTIR SPECTROSCOPY

The introduction of carboxymethyl groups can be evidenced by FTIR spectroscopy (Fig. 2). The CMS carboxylate (—COO—) gives the strong bands at about 1650 and 1400 cm^{-1}.[19] The ab-
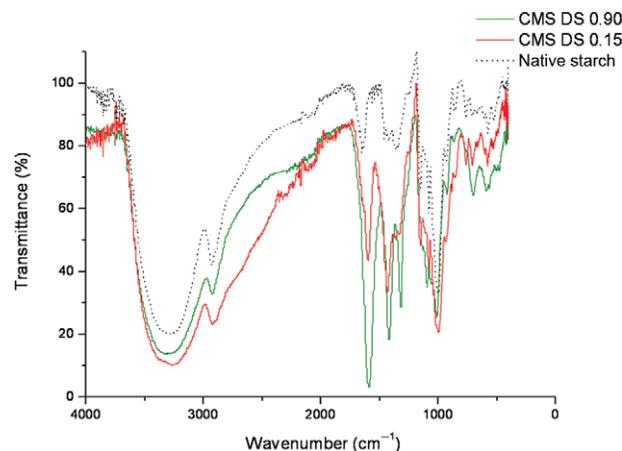
FIGURE 2. FTIR spectra of native potato starch and CMS derivatives with DS = 0.15 and 0.9.

sorption band at about 1650 cm^{-1} increases with the DS value due to the higher concentration of the carbonyl group.[20] The broad band between 3600 and 3000 cm^{-1} is assigned to OH stretching and that at 2900 cm^{-1} to CH_2 symmetrical vibrations.[21] By carboxymethylation, the intensity of the bands at about 3400 and 2900 cm^{-1} decreased.

RHEOVISCOMETRIC CHARACTERISTICS OF CMS SOLUTIONS AND CMS/MMT DISPERSIONS

The rheoviscometric patterns of 2 wt% solutions for both carboxymethyl starches are presented in Fig. 3. The CMS aqueous solutions are non-Newtonian liquids—their viscosity decreased with an increase in the shear rate. A higher viscosity value at 1 rpm exhibited CMS with a higher DS value (0.9) of 14,000 mPa·s whereas that with DS 0.15 of 2,000 mPa·s only. This was caused by the higher density of negatively charged carboxymethyl groups and therefore greater electrostatic repulsion between polysaccharide chains for the DS 0.9 derivative, resulting in a higher viscosity value. Similar results were reported by Tatongjai and Lumdubwong[22] where 5% w/v fluid of moderately substituted carboxymethyl rice starch (0.6) exhibited higher yield stress and apparent viscosity when compared to a low substituted material (0.2). Similarly, Sangseethong et al.[6] reported an increase in the apparent viscosity when DS of cassava starch increased from 0.4 to 0.7.
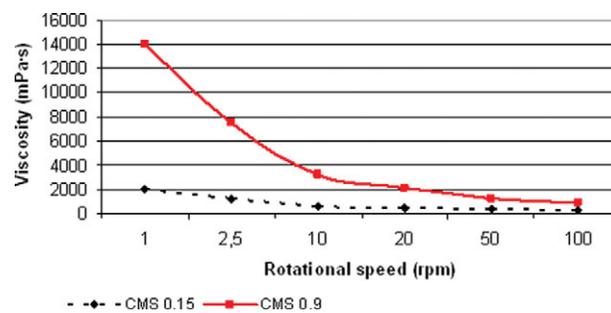
FIGURE 3. Rheoviscometric patterns of CMS aqueous solutions with DS 0.15 and 0.9.
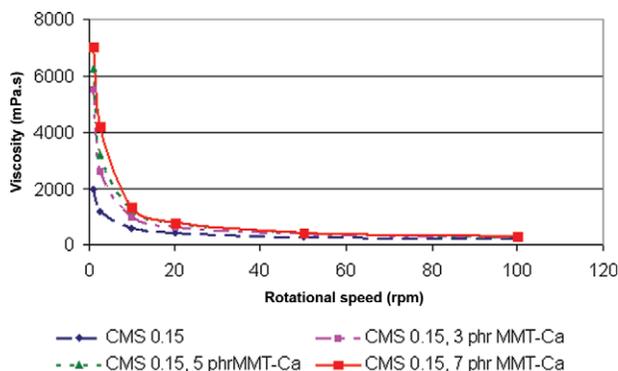
FIGURE 4. Effect of the clay content on the viscosity of aqueous CMS (DS= 0.15) dispersion with MMT-Ca prepared by mechanical mixing.

FIGURE 5. Effect of sonication parameters on the viscosity of aqueous CMS (DS = 0.15) dispersion with 7 phr MMT-Ca prepared by the combination of mechanical mixing and sonication.

Introducing calcium MMT (mechanically mixed slurry—method 1) into the aqueous CMS (DS 0.15) system resulted in higher viscosity (Fig. 4). The more MMT-Ca was added, the higher viscosity at the lower shear rate was observed: 5500, 6250, and 7000 mPa·s for 3, 5, and 7 phr, MMT-Ca at 1 rpm, respectively. Increasing the shear rate resulted in the viscosity drop to the similar value ca. 400 mPa·s for 100 rpm, despite the MMT-Ca content.

In a case of sodium MMT dispersions based on higher substituted CMS, the nanofiller content effect was less pronounced (Table II), although the level of viscosity was substantially higher than that for the calcium MMT modified systems. Similar viscosity levels were obtained despite various nanoclay concentrations in CMS/MMT-Na dispersions (2 and 5 phr). As molecular weight (M_w) of CMS with high DS determined by GPC was ca. 940,000 g/mol, polysaccharide chains could cause coating of clay particles resulting in a limited dispergation of MMT platelets, similar to the polyanionic cellulose/MMT systems.[14]

Also the kind of MMT used had a significant effect on rheoviscometric characteristics of CMS/MMT systems. Applying sodium MMT resulted in an almost double viscosity increase at 1 rpm from 14,000 up to ca. 26,000 mPa·s (2 phr MMT-Na). On the contrary, when organophilized montmorillonite (OMMT) (with hydroxyl groups in modifying ammonium alkyl and aryl substituents: C_{12-14} alkyl, trishydroxymethyl, and o-cresyl) was used, only a slight effect was noticed (little or no change of viscos-

ity) (Table II). The cationic modifier content in the ZS1 nanofiller was about 40 wt%. Its electrostatic interactions with clay platelets caused lowering of the hydrophilicity of MMT particles and restricted access of hydrophilic CMS molecules. As a result, some levels of reagglomeration of clay platelets is possible, resulting in lowering of the viscosity of CMS/OMMT dispersion as compared to that of CMS/MMT-Na. A minor influence of OMMT on the viscosity of the aqueous CMS/OMMT system could play the interaction between anionic carboxylate groups and cationic ammonium charges if the molecules of the latter are present on the outer layer of OMMT particles. As a result, partial precipitation of CMS/quaternary ammonium salt with a long aliphatic chain (above C_{12}) complexes could be considered, similar to the systems of CMC/long aliphatic chain cationic surfactant.[23]

The stability of CMS solution and CMS/MMT dispersions has been evaluated by the measurements of viscosity and transmittance after some time of storage (up to 1.5 year) (Table II). The viscosity of CMS aqueous solution or dispersion with MMT as a rule has decreased with time, with the exception of the systems with OMMT ZS1.

CMS solutions as well as its aqueous dispersions with sodium MMT exhibited a gradual viscosity decrease up to 30%–40% after 1.5 years, as compared with the freshly prepared

TABLE II

Effect of MMT Type and Content on CMS (DS = 0.8)/MMT Aqueous Dispersion Viscosity and Stability

Akronim Sample	Viscosity at 25°C, 1 → 100 rpm (mPa·s)					Transmittance (%)		
	After 0.5 h	After 72 h	After 1 month	After 3 Months	After 1.5 Year	After 72 h	After 3 Months	After 1.5 Year
CMS (DS 0.8)	14,000 → 830	n.d.[a]	n.d.[a]	10,000 → 670	9,000 → 625	71.7	74.0	76.3
CMS-MMT-Na 2 phr	26,500 → 985	25,000 → 1000	21,000 → 940	19,000 → 720	16,000 → 525	57.2	58.5	53.7
CMS-MMT-Na 5 phr	26,000 → 900	23,000 → 900	21,000 → 890	18,000 → 660	21,000 → 600	38.4	38.0	37.0
CMS-ZS1 2 phr	15,200 → 900	16,000 → 925	16,000 → 940	15,200 → 870	13,500 → 700	18.4	27.0	32.1
CMS-ZS1 5 phr	14,500 → 830	14,700 → 640	15,500 → 890	17,000 → 940	17,000 → 775	6.9	7.9	10.9

[a]n.d.: not developed.
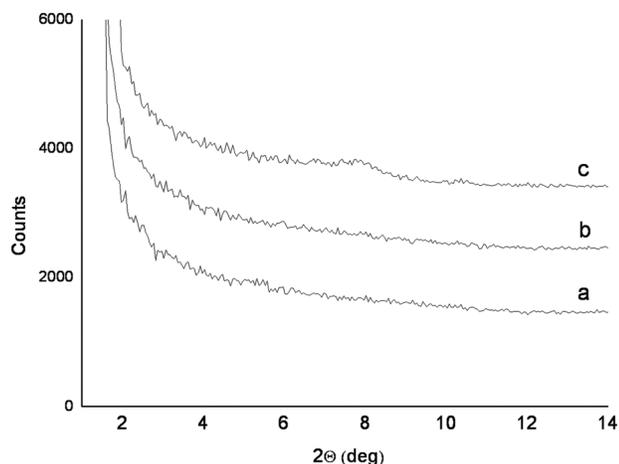
FIGURE 6. XRD patterns of CMS/7 MMT systems. (a) MMT-Ca aqueous slurry prepared by mechanical mixing; (b) prepared by the combination of mechanical mixing and sonication (60/0.5); and (c) CMS (DS = 0.9)/7 phr MMT prepared by the combination of mechanical mixing and sonication (60/0.5).

systems (Table II; at 1 rpm). In the case of CMS/OMMT dispersions, viscosity changes during storage were different: slow decrease (ca. 10%) or even some increase (ca. 18%) for 2 and 5 phr OMMT in the system. Generally, aqueous dispersions of MMT-Na and OMMT with CMS did not exhibit visual ten-

dency to environmental degradation during storage (no mold formation).

The presence of clay influenced the transmittance of CMS/MMT systems, more noticeable in a case of OMMT (Table II), which may be the result of the interaction between anionic charges of CMS and cationic ammonium groups of the clay modifier, containing a long aliphatic chain, causing partial turbidity of the dispersion,[23] as mentioned earlier. The stability tests allow assuming that MMT-Na could work as an efficient thickener and suspension stabilizer.[24]

For CMS (DS 0.15) dispersion prepared with rather high calcium MMT content (CMS/MMT-Ca 7 phr) via a combined method of clay dispersion, that is, by mechanical mixing followed by sonication (method 2), interesting results have been obtained (Fig. 5). When lower sonication amplitude was applied (30% and 50%), the viscosity was lower than that for a similar system mixed only mechanically, 5000, 5500, and 7000 mPa·s at 1 rpm, respectively. However, when more severe conditions were applied, the viscosity jumped up to 9250 mPa·s at 1 rpm. The explanation of these data could be due to the better clay platelets dispersion using the latter method, thus giving more efficient intercalated/exfoliated CMS/MMT hybrids.

It should be pointed that increased viscosity after sonication mixing was not observed when higher DS of CMS was used. The reasons could be high viscosity of such a derivative, meaning higher coil sizes as well as more pronounced the electrostatic repulsion effect between MMT platelets and polysaccharide macromolecules than for the low substituted CMS impeding good nanoclay dispersion in a polysaccharide matrix.
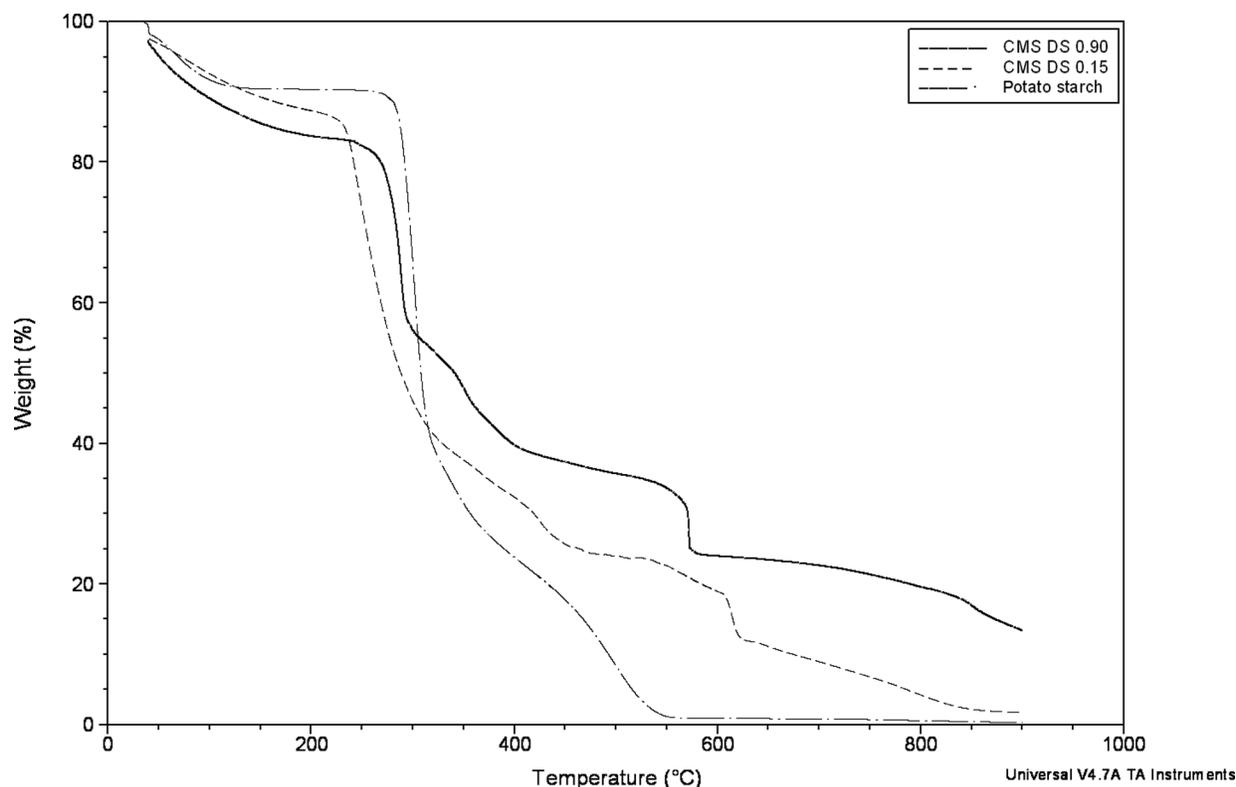
FIGURE 7. TG patterns of native potato starch and CMS derivatives with DS = 0.15 and 0.9.

X-RAY DIFFRACTION MEASUREMENTS

To assess the degree of nanofiller dispersion, X-ray measurements were performed. XRD patterns of nanoclay powders from aqueous CMS/MMT-Ca slurries prepared by various methods are presented in Fig. 6. For sonically prepared CMS (0.15)/MMT-Ca diminishing 2Θ value from ca. 7.8° ($d_{001} = 1.14$ nm) found for MMT-Ca (not shown in Fig. 6) was observed, suggesting to some extent a larger interlayer spacing. No diffraction peak between 3° and 12° was observed, indicating good nanodispersion, that is, practically exfoliation (Fig. 6). However, for the CMS (0.90)/MMT-Ca system, it was a hardly distinguishable diffraction pattern in the range of 7.8°, suggesting worse intercalation/exfoliation in comparison to the CMS systems with lower anionic charge density.

THERMAL PROPERTIES

In Fig. 7, the thermogravimetric patterns of unmodified potato starch and etherified starch with low and high DS value (0.15 and 0.9, respectively) are presented. For all the samples, a weight loss (about 10–15 wt%) at above 100°C was observed, which was affected by free water evaporation. The second step of the weight loss in a range 225–320°C is related to the water evaporation formed during decomposition of starch (from hydroxyl groups of polysaccharide). Subsequently, rapid weight loss was caused by carbonization of the carbohydrate material. Decomposition of unmodified starch started at 300°C (DTG_{max} 302°C; the results are not presented in this paper), and for CMS with DS 0.15 and 0.9, it was started at 250 and 280°C, respectively (DTG_{max} 288°C). Higher stability of higher substituted CMS was an effect of deeper chemical modification, suggesting that the lesser remaining hydroxyls group on the starch, the more stable it was. The third step observed at about 600°C, only for the etherified starch, could be assigned to sodium inorganic compounds resulting from the modification process. In addition, at 500°C the residue of native starch was only about 10% when for CMS 0.15 and 0.9 was 25% and 35%, respectively. The both CMS products started to degrade at lower temperature than unmodified starch; however, CMS decomposition proceeded more slowly than native starch.

Conclusions

The rheoviscometric properties of CMS aqueous solutions depend greatly on its DS. CMS with a high DS value (0.9) exhibited a viscosity of 2 wt% aqueous solutions ca. seven times higher than that for the low DS starch derivative (0.15) at the low shear measurement rate (1 rpm), that is, 14,000 and 2,000 mPa·s, respectively. The dispersions of low DS CMS with increasing MMT-Ca content showed growing viscosities in comparison to the relevant CMS aqueous solution (ca. 3.5 times higher than for 7 phr MMT-Ca, i.e., 7000 and 2000 mPa·s, respectively, 1 phr) when prepared by the simple mechanical mixing. Combined mechanical and sonication methods allowed for an additional viscosity increase (up to 9200 mPa·s, 7 phr MMT-Ca, at 1 rpm). Viscosity differences between the data obtained at higher rotational speed measurements (above 30 rpm) are negligible.

Sodium MMT presence (2–5 phr) in aqueous systems of high-DS CMS (0.8) caused ca. a double increase of viscosity as compared with neat 2 wt% CMS solution (i.e., from 14,000 up to 26,000-26,500 mPa·s, at 1 rpm). However, the introduction of OMMT modified with a long aliphatic chain ammonium salt (with few hydroxyl groups) into CMS solution practically did not thicken the system. On the other side, transparency of the latter dispersions was drastically reduced as compared to those containing MMT-Na. The investigated aqueous dispersions of MMTs s with CMS exhibited stability during the storage over 18 months, while the viscosity fluctuations have been found dependent on the clay type.

Lowly substituted CMS showed lower thermal stability in the temperature range up to 300°C than native potato starch or highly substituted CMS. However, above 400°C, the order of thermal stability was CMS (DS 0.9) > CMS (DS 0.15) > native starch, with residual mass% at 400°C: ca. 40, 30, and 20 wt%, respectively. These results seem important as far as mainly lowly substituted CMS, which are commercially available.

Such CMS/MMT water slurries could find applications as drilling mud additive, electrorheological fluids, binders for foundry, in paper industry, or for nanocomposite film preparations.

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