

Carboxymethyl Cellulose Modified by a Titanium Tetrachloride Solution¹

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Abstract—The modifying effect of a titanium tetrachloride solution in hexane on carboxymethyl cellulose in the sodium salt and free acid forms was studied. The features of the structure, morphology, and thermal behavior of the modified carboxymethyl cellulose were revealed by IR spectroscopy, thermogravimetry, and X-ray diffraction analysis, as well as by scanning electron microscopy.

Keywords: carboxymethyl cellulose, titanium tetrachloride, hexane, modification, adsorption

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In recent years, good progress in development of technologies for creation of new inorganic-organic polymer composites attractive for application in nanotechnology [1, 2] and in polymer chemistry has been made by researchers around the world. Amongst matrices considered for designing such composites are polysaccharides, nontoxic biodegradable polymers derived from renewable resources. Individual structural features of polysaccharides (degree of branching of the structure, mono- or polyfunctionality of the macromolecules, polydispersity, molecular weight) have an effect on their properties: viscosity, gelling ability, hardness, density, swelling degree, solubility [3], etc.

Cellulose occupies a special place among polysaccharides. It is relatively sensitive to chemical modification, whereby it undergoes degradation (to short-fibered, powdered cellulose and nanocellulose), and to functionalization leading to a number of ethers and esters. Also, high surface area of cellulose is successfully modifiable by spraying, impregnation, or treatment with oxides, alkoxides, oxohalides, or halides of Ti, Fe, Zn, and some other elements. From a practical perspective, inorganic-cellulose composites containing nanodispersed particles of the above-

mentioned metal oxides are of interest [4–8]. The resulting products are highly reactive, display sorption and antimicrobial properties [9, 10], and find application as medicines, membranes, thickeners, sorbents, and catalysts [11, 12].

More efficient bonding of inorganic particles with cellulose can be provided via introducing reactive functional groups, e.g., carboxy or carbonyl groups able of forming chemical bonds with the inorganic component, into the cellulose macromolecule. This is achieved by oxidation [13] or by degradation of the cellulose macromolecule [14], as well as by the incorporation of molecular spacers, e.g., polycarboxylic acids, promoting the formation of ester linkages between cellulose and metal oxide particles [15]. An alternative approach is based on the use of matrices consisting of cellulose ethers and esters, whose properties differ from those of the initial cellulose fiber due to the presence of grafted functional groups. Many cellulose ethers/esters were used for the synthesis of film or fibrous polymer composites containing nano- or microstructured inorganic components bonded to the polymer matrix by various types of intermolecular forces. For example, hydrophilic nanocomposite hybrid films containing silicon and titanium compounds facilitating the removal of various organic pollutants (dyes, solvents) from aqueous and aqueous-organic solutions were

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synthesized from ethyl cellulose by the sol-gel technique [16], specifically, by hydrolytic polycondensation of Si and Ti alkoxides in a solution of cellulose ether in tetrahydrofuran. A highly efficient sorbent capable of CO₂ capturing, concentrating, and removing was prepared from cellulose acetates and titanium compounds [17]. Template synthesis of celluloses modified by carboxymethyl, cyanoethyl, and amidoethyl groups yielded alumina- and titania-based composite materials with the structural and morphological properties adjustable by functionalization and supramolecular reorganization of the cellulose matrix [18, 19].

Carboxymethyl cellulose in the sodium salt and free acid forms is the polymer that is most extensively used and most widely produced among cellulose ethers. In the free acid form carboxymethyl cellulose is traditionally applied as a thickener and filler in the cosmetic, food, and building industries and also as a viscosity modifier and water-retaining agent in the petroleum industry. Water-soluble sodium salt of carboxymethyl cellulose is used as a plasticizer, thickener, and sorbent in various industry sectors. The presence of two types of reactive groups (hydroxy, carboxy in the alkyl substituent of the macromolecule) in the carboxymethyl cellulose structure, together with the above-mentioned features, make carboxymethyl cellulose a promising candidate for the development of composite materials, including those filled with inorganic compounds. Carboxymethyl cellulose proved itself as an effective stabilizer in the preparation of metal nanoparticles and compounds, including superparamagnetic iron oxide nanoparticles and silver nanoparticles [20]. An antibacterial carboxymethyl cellulose-hydrogel-ZnO-nanocomposite was prepared by carboxymethyl cellulose crosslinking with polycarboxylic acids using zinc salts [21]. A polyaniline/carboxymethyl cellulose/TiO₂ nanocomposite effective in adsorption of organic dyes from aqueous solutions [22] was synthesized by polymerization of aniline in a carboxymethyl cellulose solution containing TiO₂ and other reagents. Titania gives a number of specific properties to its composites with polysaccharides, in particular, chemical and thermal stability, photocatalytic and biological activity, and superhydrophilicity [23, 24]. By imparting new features to carboxymethyl cellulose through modifying its surface or structure with titanium compounds it will be possible to provide new application areas to this cellulosic polymer in addition to the traditional ones

(e.g., titanium-containing sorbents, films resistant to oils, lubricants, and organic solvents and heterogeneous catalysts in organic synthesis). At the same time, for predicting the practical suitability of inorganic-organic materials being developed it is essential to study their structural, morphological, thermal, and other physicochemical properties is essential.

One of TiO₂ precursors is titanium tetrachloride. The effect of its solutions on various cellulosic and lignocellulosic materials was examined previously [25–27] with the view of preparing powdered titanium-containing composites.

The aim of this study was to carry out modification of carboxymethyl cellulose in the free acid and salt forms by treatment with TiCl₄ solutions and to evaluate the effect of the carboxymethyl groups on the extent of modification, structural features, morphology, and thermal behavior of titanium-containing composites. For comparison, data on modification under comparable conditions were given for mercerized pulp acting as a precursor in the preparation of carboxymethyl cellulose.

Treatment in a TiCl₄ solution leads to modification of carboxymethyl cellulose fibers, as evidenced by the Ti(IV) content of 1.14–1.39 mmol/g in the samples (see the table), corresponding to the consumption of 55–67% of the initial TiCl₄ contained in the solution. The highest Ti(IV) levels were revealed for the samples based on the salt form of carboxymethyl cellulose. This indirectly influenced the change in mass of the samples, which increased by 21.4 and 24.8% relative to the weighed samples of untreated CMC-Na-0.3/TiCl₄ and CMC-Na-0.9/TiCl₄, respectively. Close Ti(IV) levels were revealed for the SBC-M/TiCl₄ sample based on mercerized softwood pulp.

The increment of the mass of the samples depends on the degree of hydrolytic transformations of TiCl₄ or, alternately stated, on the number of available water molecules participating in the reaction not only during treatment but also during air-drying of the samples. The gaseous reaction byproducts which are partially adsorbed on the highly developed fiber surface also have an effect on the change in mass, being specifically responsible for its increasing disproportionately to the titanium content in the samples.

Tightly coating the carboxymethyl cellulose fiber surface, titanium compounds form a film which gets cracked due to release of gaseous products (mainly

Characterization of the samples examined

Sample	Ti(IV) content, mmol/g		Mass increment, %	$P(\text{H}_2\text{O})$, % ^a
	in solution	in the sample		
CMC-Na-0.3	–	–	–	53
CMC-Na-0.9	–	–	–	98
CMC-Na-0.3/TiCl ₄	2.09	1.39	21.4	35
CMC-Na-0.9/TiCl ₄	2.09	1.39	24.8	47
CMC-H-0.3/TiCl ₄	2.09	1.27	19.9	*
CMC-H-0.9/TiCl ₄	2.09	1.14	19.7	*
SBC-M/TiCl ₄	2.09	1.34	20.3	*

^a $P(\text{H}_2\text{O})$ is the water solubility; an asterisk (*) indicates poor solubility in water of the water-soluble organic low-molecular-weight compounds resulting from cellulosic component degradation.

HCl) into the interfacial space (voids between the cellulose surface and titanium compounds). In sites of most abundant accumulation of inorganic particles they give a contrasting color, which is also true of the SBC-M/TiCl₄ fibers. However, the latter are distinguished by a small quantity of surface cracks, indicating less active gas release. The quantity of cracks, depending on the thickness of the inorganic layer being formed, the presence of through holes for gas release, and the moisture content of the initial samples, was 7.8–12.9% in the case of carboxymethyl cellulose and 5.4% in the case of mercerized softwood pulp. It should be noted that, prior to modification, the fibers of the samples examined have similar appearance.

Cellulose drying to a constant weight worsens the results of modification in a TiCl₄ solution and affects the degree of degradation of the cellulose macromolecules during preparation of powders [27]. The accessible water molecules on the fiber surface are involved in hydrolytic transformations of TiCl₄. This is accompanied by evolution of hydrogen chloride exerting a destructive effect on the fibers, leading to their embrittlement and breaking down into shorter fragments, which is also true of the SBC-M/TiCl₄ sample. A similar effect was observed for the CMC-H-0.3/TiCl₄ and CMC-H-0.9/TiCl₄ samples based on carboxymethyl cellulose in the free acid form.

In the case of the sodium salt of carboxymethyl cellulose, treatment with TiCl₄ caused less profound degradation of the fibers due to the competing ion exchange reaction between HCl and the sodium salt of carboxymethyl cellulose. This is confirmed by a 1.5–2 fold decrease in water solubility of CMC-Na-0.3/

TiCl₄ and CMC-Na-0.9/TiCl₄ relative to the corresponding unmodified samples (see the table). Qualitative analysis of the modified samples by means of energy-dispersive X-ray spectroscopy (EDX) revealed the presence of the following elements: titanium, chlorine, and oxygen, as well as of sodium in the case of the carboxymethyl cellulose salt. Elemental mapping for CMC-Na-0.3/TiCl₄ and SBC-M/TiCl₄ taken as examples indicates distribution of these elements over the entire surface of the samples analyzed.

Changes in the functional composition of the samples, caused by modification with the TiCl₄ solution, were also detected by means of IR spectroscopy. For example, a pronounced asymmetry of the broad band of the stretching vibrations of the OH groups participating in intra- and intermolecular hydrogen bonding was observed in the 3100–3700 cm⁻¹ region of the IR spectra of carboxymethyl cellulose, by contrast to those of the mercerized softwood pulp. A blue shift (from 3414 to ~3440 cm⁻¹) of the maximum of this band is also observed. These features evidence the formation of a structure with weaker hydrogen bonds in carboxymethyl cellulose, which fact does not contradict the published data [28]. A stronger asymmetry of the band associated with the stretching vibrations of the OH groups, revealed for the CMC-Na-0.9 sample, is due to its higher degree of substitution.

Upon modification of carboxymethyl cellulose in the salt and acid forms no uniformity was observed in the change of intensity of the bands associated with the stretching vibrations of the OH groups (near 3400 cm⁻¹) and of the C–H bond (near 2900 cm⁻¹). The revealed anisotropy of polarizability of these bonds is explained

by the influence of the nature, electrostatic field, and degree of substitution of the cellulosic objects and of the electronic structure of the atom (sodium, hydrogen). Treatment with the TiCl_4 solution caused decline in intensity of the absorption band in the region of $1000\text{--}2400\text{ cm}^{-1}$. Decreased absorption intensity in the region below 1600 cm^{-1} is attributable [29] to the ability of the oxygen atom to withdraw electrons from the less electronegative neighboring carbon atom in the molecule, which is enhanced by the presence of the titanium compounds. This leads to steric hindrance of the C–O groups and to the observed changes of the IR absorption bands.

Analysis of the modified carboxymethyl cellulose samples in the free acid form using the example of the CMC-H-0.3/ TiCl_4 sample indicates partial interaction of Ti(IV) with carboxy groups. Treatment of CMC-H-0.3 with the TiCl_4 solution leads not only to decline in intensity of the absorption bands at 1738 , $1290\text{--}1180\text{ cm}^{-1}$ but also to the appearance of a weak band at 1628 cm^{-1} [30]. The contour of the IR spectrum of CMC-H-0.3 in the $1430\text{--}1370\text{ cm}^{-1}$ region, associated with in-plane bending vibrations of the C–O–H groups, remains unchanged after the modification, suggesting the lack of chemical interaction between TiCl_4 and OH groups.

In the case of the CMC-Na-0.3/ TiCl_4 sample the characteristic absorption band at 1609 cm^{-1} associated with the stretching vibrations of the C=O bond in the OCH_2COONa group not only declines in intensity but also splits into two components, with the weaker component appearing as a shoulder at 1736 cm^{-1} . This fact confirms partial conversion of the sodium salt of carboxymethyl cellulose to the H-form as a result of ion exchange between HCl and the salt. The absence of new bands in the IR spectra of the modified samples evidences physical adsorption of the titanium compounds during treatment with TiCl_4 .

The structural changes caused in the cellulose samples by the modification were evaluated by X-ray diffraction technique (see supplementary materials, Fig. 1). Analysis of the diffraction patterns of the initial samples shows that, among CMC-Na-0.3, CMC-H-0.3, and mercerized softwood pulp samples, CMC-Na-0.3 has the lowest content of the crystalline phase. These samples exhibit different intensities of the diffuse maximum in the $20^\circ\text{--}21^\circ$ region which characterizes this phase (see supplementary materials, Figs. 1a, 1c, 1e). Modification of carboxymethyl

cellulose caused a decrease in intensity of the reflections in the diffraction patterns. A small though well-defined reflection in the region of small angles appears in a section of the curves of the scattering intensity distribution, recorded for CMC-Na-0.3/ TiCl_4 (maximum at 7.1°) and SBC-M/ TiCl_4 (maximum at 7.4°), indicating the presence of adsorbed titanium compounds on the fiber surface. In the diffraction pattern of the CMC-H-0.3/ TiCl_4 sample this reflection (maximum at 7.6°) is weakly pronounced, as confirmed by a lower Ti(IV) content compared to the other modified samples (see table), as well as by partial involvement of titanium in bonding with the carboxy group.

No crystalline phases attributable to titanium compounds were detected in the X-ray diffraction patterns, suggesting that the colloidal particles coating the cellulose fiber surface during modification are X-ray amorphous. They are formed as a result of partial hydrolytic transformations of TiCl_4 .

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses showed that, compared to the CMC-H-0.3 and mercerized softwood pulp samples, CMC-Na-0.3 exhibits a lower thermal degradation onset temperature (275°C against 291°C) and a lower maximum thermal degradation rate (see supplementary materials, Fig. 2). Reduced thermal stability of the CMC-Na-0.3 sample is attributable to its most loosened structure. When the temperature reaches 600°C , the mass of its carbon residue is the largest, being 19.2% of that of the initial weighed sample taken for the thermal analysis. This is due to the presence of sodium atoms in the macromolecule, forming a mixture of Na_2O and Na_2O_2 oxides during thermal degradation of sodium salt of carboxymethyl cellulose in air.

After treatment with a TiCl_4 solution in C_6H_{14} the thermal stability of all the samples decreases, and the intensive degradation maximum shifts to lower temperatures ($285\text{--}305^\circ\text{C}$ against $303\text{--}325^\circ\text{C}$). It should be noted that, for the CMC-H-0.3/ TiCl_4 sample, the shift of this parameter ($314\rightarrow 310^\circ\text{C}$) is insignificant compared to those in the case of CMC-Na-0.3/ TiCl_4 ($303\rightarrow 285^\circ\text{C}$) and SBC-M/ TiCl_4 ($325\rightarrow 305^\circ\text{C}$). The thermal degradation onset temperature for CMC-H-0.3/ TiCl_4 is higher (by 26 and 10°C , respectively). Such thermal behavior of this sample indirectly confirms partial chemical adsorption of Ti(IV) by

carboxy groups, which, in turn, leads to only insignificant decrease in thermal stability relative to other samples.

For all the modified samples the carbon residue mass by the time of reaching 600°C is greater than the corresponding mass of these samples before treatment with TiCl₄ due to the presence of titanium compounds.

A SEM examination showed that, after the thermal action, the modified samples can preserve the morphology of the destroyed cellulose fiber. The appearance and brittle form of the mineral residue consisting of Ti, O, and, in the case of sodium salt of carboxymethyl cellulose, of Na element as well, evidence structural self-organization of the titanium compounds as a result of treatment of the cellulosic samples with the TiCl₄ solution. Evidently, distribution of the overwhelming majority of the inorganic particles occurs through physical adsorption on the fiber surface. In the interior, the hollow forms of the mineral residue reflect the relief of the burning fiber (irregularities and defects), and in the exterior, twists and kinks. Hollow titanium-containing fibers hold promise for the production of inorganic fibrous sorbents and catalysts.

Thus, treatment of carboxymethyl cellulose with a TiCl₄ solution leads to modification of its fibers. The process of modification consists in physical adsorption of X-ray amorphous titanium-containing particles, resulted from hydrolytic transformations of TiCl₄, on the fiber surface. Carboxymethyl cellulose in the free acid form, alongside physical adsorption, is involved in partial chemical interaction with TiCl₄ via carboxy groups. Modification of carboxymethyl cellulose in the salt form is accompanied by an ion exchange reaction between the sodium salt of carboxymethyl cellulose and HCl, competing with the fiber degradation reaction. The thermal stability of the modified cellulose samples decreases in the series: CMC-H/TiCl₄ > SBC-M/TiCl₄ > CMC-Na/TiCl₄. The difference between the processes of thermal degradation in the case of the titanium-containing derivatives and the corresponding initial cellulose samples is due to those in their functional composition and to the changes in the supramolecular structure.

EXPERIMENTAL

Carboxymethyl cellulose in the free acid and salt forms was synthesized from mercerized softwood

pulp. The latter was obtained by 2-h treatment of bleached softwood kraft pulp (semi-finished product available from Mondi Syktyvkar Forest Industry Complex, Open Joint-Stock Company) in an 18% aqueous NaOH solution, followed by rinsing with distilled water until neutral pH of the washing water was achieved and drying [31]. Sodium salt of carboxymethyl cellulose with various degrees of substitution (CMC-Na-0.3 and CMC-Na-0.9) was prepared by treating mercerized softwood pulp with monochloroacetic acid in isopropanol [28]. Carboxymethyl cellulose in the free acid form (CMC-H-0.3 and CMC-H-0.9) was obtained from the CMC-Na-0.3 and CMC-Na-0.9 samples, respectively, by treatment with 10 M aqueous HCl solution [31]. The moisture contents of the samples examined were 5.4, 12.9, 12.6, 8.6, 7.8% for the mercerized softwood pulp, CMC-Na-0.3, CMC-Na-0.9, CMC-H-0.3, and CMC-H-0.9 samples, respectively. The degree of substitution of carboxymethyl cellulose was determined by the procedure described in [28]. Modification conditions were as follows: air-dry samples of cellulose derivatives were treated with a TiCl₄ solution in hexane at the boiling point (70°C). Next, the cellulose mass was filtered off, brought to air-dry condition, and passed through a sieve with a hole diameter of 200 μm. Commercial TiCl₄ and reagent-grade hexane (Vekton) were used.

The Ti(IV) content in the modified samples was determined photometrically using the calibration curve of the color intensity versus concentration for the Ti(IV) complex with hydrogen peroxide in an acidic medium [32]. Micrographs of the samples were taken on a TESCAN VEGA 3 SBU instrument equipped with an INCA Energy X-ACT energy dispersive X-ray microanalysis system with an accelerating voltage of 20 keV at a field of view of 500, 200, and 50 μm. Carbon tape was used as a substrate. The IR spectra were recorded on a Prestige-21 (Shimadzu) spectrometer equipped with a DRS 8000 A diffuse reflectance attachment in the 4000–400 cm⁻¹ range with a resolution of 4.0 cm⁻¹. X-ray phase analysis was performed on an XRD-6000 (Shimadzu) diffractometer using CuK_α radiation. The diffracted intensity was measured in the range of diffraction angles 2θ of 5° to 40° with a step of 0.05° at the wavelength λ = 0.1542 nm.

Thermal properties of the samples were studied on a NETZSCH STA 409 PC/PG instrument at a heating rate of 5°C/min in the temperature range 25–600°C in air.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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