



Structural Studies (FTIR, XRD) of Sodium Carboxymethyl Cellulose Modified Bentonite

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Abstract

The study investigates the effect of the organic compound representing the cellulose derivative - sodium salt of carboxymethyl cellulose (CMC/Na) on the structure of the main component of bentonite (B) - montmorillonite (MMT). Structural analysis revealed that the CMC/Na of different viscosity interacts with the mineral only via surface adsorption, causing at the same time partial or full delamination of its layered structure. This was confirmed by the XRD diffraction tests. Such polymer destructive influence on the structure of the modified main component of the bentonite limits the use of its composites as an independent binder in moulding sand technology, but does not exclude it from acting as an additive being a lustrous carbon carrier. According to the IR spectra of the B/CMC/Na materials, it can be stated that the interaction between the organic and inorganic parts is based on the formation of hydrogen bonds. That kind of the interpretation applies especially to the MMT modified in the bentonite with a lower viscosity polymer. The characteristics of the main IR absorption bands for composites with a higher viscosity polymer indicates the formation of less stable structures suggesting the random nature of the hydrogen bonds formation.

Keywords: Montmorillonite, Carboxymethyl cellulose, Composite, Adsorption, Structural tests

1. Introduction

To improve the castings surface quality the carbon-containing additives such as: coal dust, carbon black, graphite, synthetic resin and mixtures from crude oil processing are added to the bentonite-bonded moulding sands (green sands) [1]. The quantitative share of coal in the moulding sand composition must be controlled and stay within a certain range, because its excess may also adversely

affect the final characteristics of castings [2,3]. It is also important to control the structure and the texture of the resultant carbon [4]. In addition to the beneficial effect, carbon additives are also a source of an increased emission of highly harmful gaseous compounds (VOC, PAH, BTEX). The products of their high-temperature pyrolysis released while pouring the mould with liquid metal get into the atmosphere and remain in the structure of the waste moulding sands, being a threat during their storage or recycling of the circulating moulding sand in the foundry [5].

Few attempts to develop the effective and ecological substitutes for commonly used carbon additives in the synthetic moulding sands have been made so far [4,6].

The harmfulness problem of carbon additives in moulding sands with bentonite is indirectly related to the main challenges posed to the modern chemistry of the macromolecular compounds aiming at the development of biodegradable polymeric materials for the use in various industries. Polymer-supported technologies of moulding sands are a difficult part of the foundry industry to replace. Phenol-formaldehyde and urea-furfuryl resins have an established position. To limit the toxicity of the synthetic resins, two-component moulding binders are used, in which a part of them is replaced by biodegradable materials, usually polysaccharides [7]. Native starch is used in the foundry industry as an additive to the synthetic moulding sands to increase their strength properties and reduce the tendency to sand grains friable into the mould cavity. However, a modified form of starch in the form of carboxymethyl starch (CMS) is most often used [8]. It is characterized by a better solubility in cold water and increased adhesive properties. It turns out that the carboxymethyl starch in the form of a sodium salt (CMS-Na) with an appropriate high degree of substitution (DS), defined as the average number of substituted hydroxyl groups in each glucopyranose ring (Williamson synthesis), can act as a main foundry binder, giving the moulding sand suitable strength properties and meeting the requirements in concern of the economy and the ecology of the process [9,10].

Cellulose, especially its derivatives, is another example of the polysaccharide, but definitely less frequently used in the foundry practice. Each cellulose molecule consists of the glucose units in the 4C_1 -chair configuration linked together by oxygen-ether bridges between the 1 and 4 carbon atoms, known as β -1,4-linkage, forming long, straight and unbranched chains organized into microfibrils (Fig. 1a). The glycosidic linkages of cellulose result in a stiff molecule capable of forming fibrils by hydrogen bondings [11]. Cellulose can be characterized by biodegradability, thermal and chemical stability, but also is known as carbon fiber (CF) precursor material [12]. However, similarly to starch, due to its insolubility in water and in organic solvents, cellulose undergoes various modifications. Cellulose ethers have the greatest practical application. The simplest and the most advantageous for economic reasons one is the production of carboxymethyl cellulose (CMC). CMC is an anionic polymer, which contains a hydrophobic polysaccharide backbone and numerous hydrophilic carboxyl groups, hence showing an amphiphilic characteristic (Fig. 1a). It is a non-toxic and soluble in both cold and warm water polymer having also good binding properties [13]. The exact functional properties of CMC depend on the degree of substitution (DS) of cellulose structure as well as the chain length of the cellulose backbone. The DS of CMC usually varies in the range of 0.60–0.95 derivatives per monomer unit [14].

No data on the CMC use as an independent binding material for mineral matrix grains in moulding sand technology has been reported so far. However, using the unique physicochemical properties of bentonite or rather its main component, montmorillonite (MMT) (layered structure, highly chemically reactive surface) (Fig. 1b), CMC can be used as a material modifying its properties in terms of eliminating the need for the

separate carbon additives in synthetic moulding sands. Considering cellulose as one of the carbon fibers precursors, its derivative (CMC) can be a potential source of the desired carbon structure determining the surface quality of castings. Long CMC chains can intercalate between the montmorillonite packages or adsorb onto its surfaces, changing its crucial for foundry industry properties.

Modification of montmorillonite was carried out in the calcium bentonite (unmodified) using the obtained sodium salt of carboxymethyl cellulose (CMC/Na) due to the benefits of the presence of sodium ions in the mineral structure, i.e. better swelling and binding capacities.

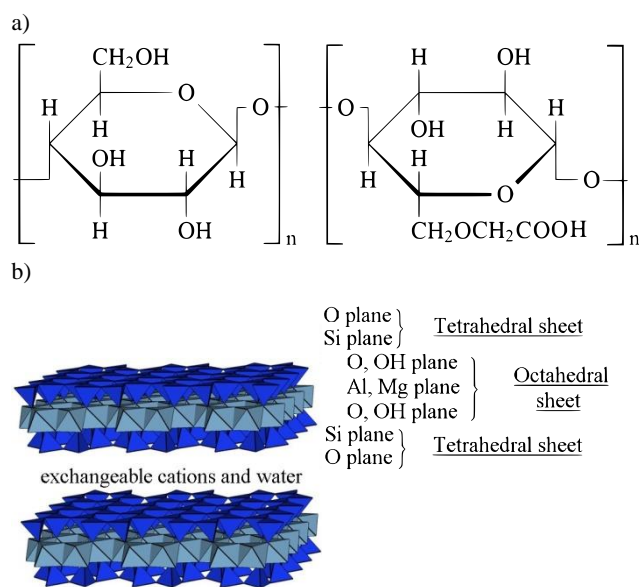


Fig. 1. Scheme of: a) the molecular structure of cellulose (left) and the carboxymethyl cellulose (CMC) – DS = 1.0 (right), b) montmorillonite crystal structure in bentonite

The conducted structural analysis is the first stage (preceding the thermal analysis and the strength tests of moulding sands and the survey of the surface quality of castings received with the use of prepared materials) in determining the possibility of obtaining a full-value binder binding mineral matrix grains in moulding sands with bentonite.

2. Experimental

2.1. Materials

Calcium bentonite used in this study was supplied by the ZGM Zębiec S.A. (Poland). It is characterized by the cation exchange capacity determined by the Cu(II)-TET adsorption method 65.3 meq/100 g clay, MMT content 69.2% and swelling index 8 cm³/2 g. Modifications were carried out using aqueous solutions of two types of carboxymethyl cellulose purchased from CMC S.A. (Poland):

- POLOFIX[®] LV (CMC_{LV}), being a low-viscosity variation of the technical carboxymethyl cellulose salt with a degree of substitution (DS) of 0.6, pH of a 2% water solution 5.5 and a viscosity of 20.3 mPa·s;
 - Pollocel[®] AS-2/170 (CMC_{HV}), being a technical carboxymethyl cellulose sodium salt with a degree of substitution (DS) of 0.6, pH of a 2% water solution 9.0 and viscosity 120.5 mPa·s;
- and high purity sodium carbonate, Na₂CO₃ (Merck KGaA), forming the following systems: CMC_{LV}/Na and CMC_{HV}/Na.

2.2. Preparation of B/CMC/Na materials

Two series of samples based on the calcium bentonite with different type (low and high viscosity) of polymer were prepared: B/CMC_{LV}/Na and B/CMC_{HV}/Na.

Calcium bentonite (20 g) was dispersed into 50 ml of CMC_{LV}/Na and CMC_{HV}/Na aqueous solutions. The polymer concentration at constant sodium carbonate content in these carboxymethyl cellulose/sodium carbonate systems was 5, 25 and 50% by weight of bentonite. The amount of sodium carbonate used to produce the sodium form of polymers corresponded to the ion-exchange capacity (IEC) of mineral. The B/CMC_{LV}/Na and B/CMC_{HV}/Na composite materials divided additionally into I_{LV} , 2_{LV} , 3_{LV} and I_{HV} , 2_{HV} , 3_{HV} , respectively, due to the variation in the polymer content (e.g. I_{LV} corresponds to the B/CMC_{LV}/Na with a 5% polymer content), were stirred at 20°C for 12 hours and then allowed to react for a week (adsorption and/or intercalation combined with ion exchange). After drying to constant weight at 105°C, the samples were milled in an agate mortar for structural tests.

2.3. Structural studies

The interaction between montmorillonite in bentonite and CMC/Na solution was assessed on the basis of the structural analysis results: Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

The FTIR spectroscopy was performed in the mid infrared (MIR) regions (4000 – 400 cm⁻¹) with the use of Bruker Company Vertex 70v spectrometer. Standard transmission technique (with KBr pellets) was used. The spectrum was recorded at 4 cm⁻¹ resolution with 64 recorded sample scans. To perform the X-ray diffraction (XRD) measurements the Panalytical Empyrean diffractometer with a PIXcel3D detector and CuK α radiation source was used.

3. Results and discussion

3.1. Fourier Transform-Infrared Spectroscopy analysis

The IR spectra of unmodified calcium bentonite displays the presence of the functional groups typical for its main

component (MMT) (Fig. 2). The characteristic absorption peak of the hydroxyl group associated with Al³⁺ cations of octahedral MMT layers is observed at a wavenumber of 3631 cm⁻¹. This maximum is also the first of three modes of water molecules vibrations (ν_1 , symmetrical stretching vibrations). The other modes of H₂O vibrations correspond to the absorption peaks recorded at 3437 cm⁻¹ (ν_2 , asymmetric stretching vibrations) and 1641 cm⁻¹ (ν_3 , bending vibrations). The most intense peak at 1043 cm⁻¹ corresponds to Si–O stretching vibrations in the tetrahedrons forming the outer layers of aluminosilicate packages of MMT, while the band with a maximum at 796 cm⁻¹ is associated with Si–O stretching vibrations indicating the presence of quartz in the sample (confirmed in the XRD test). The observed IR peaks below 1000 cm⁻¹ are attributed to Al–Al–OH (916 cm⁻¹) and Al–Mg–OH (845 cm⁻¹) bending vibrations. The maximum absorption band of layered aluminosilicates in the 600 – 200 cm⁻¹ wavenumber range represents Si–O bending vibrations: 625, 523 and 465 cm⁻¹ [15,16].

For the samples of carboxymethyl cellulose, CMC_{LV} and CMC_{HV}, the presence of a strong maximum at 1598 cm⁻¹ and 1604 cm⁻¹ respectively, indicates the presence of carboxyl group –COO⁻ (Fig. 2). The broad absorption band at 3425–3437 cm⁻¹ for both of polymers represents the stretching vibrations of –OH group. The C–H stretching peaks are observed at 2916 cm⁻¹ (CMC_{LV}) and 2922 cm⁻¹ (CMC_{HV}). The bands at ~1420 cm⁻¹ can be assigned to –CH₂ scissoring vibrations as well as to the symmetric stretching vibrations of the carboxyl group in the form of salt (–COO⁻). The IR peaks maximum appeared at 1326 and ~1060 cm⁻¹ indicates the presence of –OH bending and C–O–C stretching vibrations respectively [17,18].

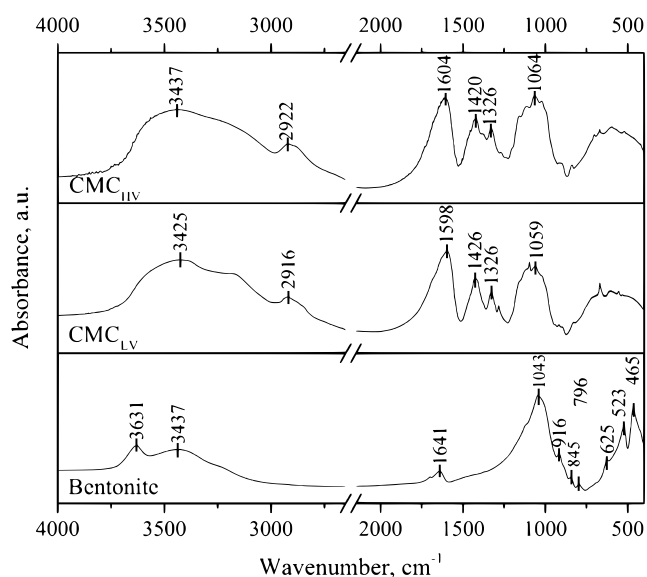


Fig. 2. IR spectra of starting materials used in the preparation of inorganic-organic materials

FTIR technique was also used to study the mineral/polymer interaction, since a shift and a band intensity change in the range of 3300 – 3700 cm⁻¹ indicate the possible way of inorganic-organic materials connection. IR spectra of materials with the lowest polymer content (I_{LV} and I_{HV}) are characterized by the

lower band intensity at 3631 cm^{-1} and the lower band intensity combined with the maximum change position towards higher wavenumber values, i.e. from 3437 to 3448 cm^{-1} for I_{LV} and from 3437 to 3453 cm^{-1} for I_{HV} , in comparison with the spectrum of unmodified bentonite (Figs. 3 and 2 respectively). This is the result of the change in charge of the adjacent polymer and bentonite molecules. In this case, carboxymethyl cellulose, regardless of type, interacts with the MMT surface in the bentonite, but this interaction takes place between the partially laminated MMT and the polymer. The peak position change towards higher values of the wavenumber can be attributed to the weakening of the bonding interaction between the single particles of mineral, therefore this may be an expression of CMC/Na adsorption to the MMT surface in the form of individual three-layer packages.

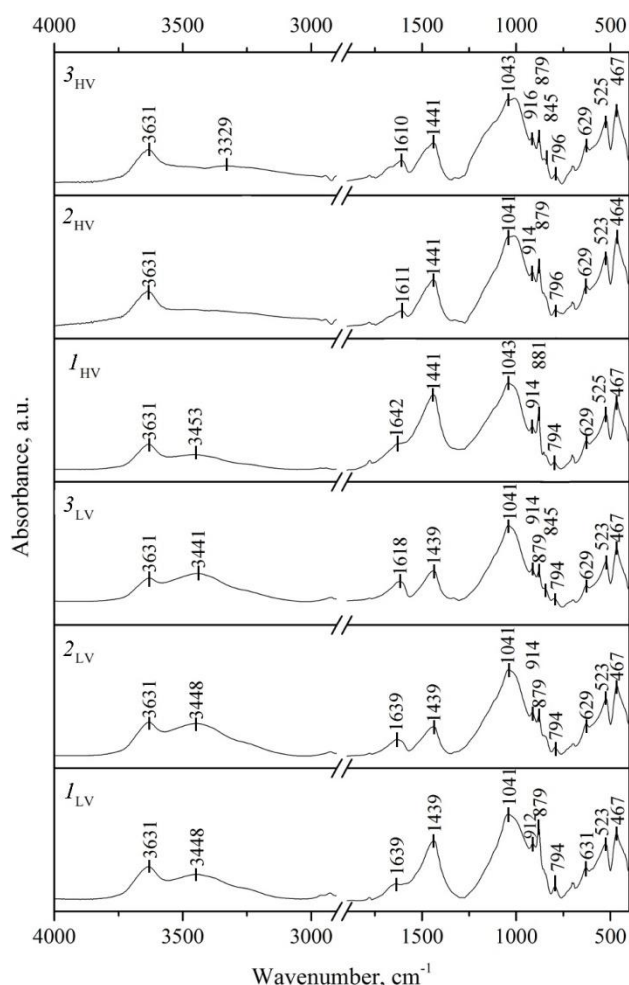


Fig. 3. IR spectra of the B/CMC_{LV}/Na and B/CMC_{HV}/Na materials with distinction into the polymer content: 1 – 5%, 2 – 25%, 3 – 50%

The IR spectra of the 2_{HV} sample in the analyzed wavenumber range suggests the polymer destructive effect on the mineral layered structure (Fig. 3). However, a decrease in the band intensity resulting from the valence vibrations of –OH groups

forming MMT octahedrons (3631 cm^{-1}) with a simultaneous increase in the band intensity corresponding to the vibrations of –OH groups from interlayer water of the mineral for 2_{LV}, 3_{LV} and 3_{HV} materials compared to the calcium bentonite spectra was observed (Figs. 3 and 2 respectively). This correlates with the involvement of some –OH octahedron groups in the formation of hydrogen bonds with CMC/Na. Accordingly, the overall band intensity with a maximum at 3631 cm^{-1} weakened while the band at $\sim 3440\text{ cm}^{-1}$ strengthened. Formation of classic hydrogen bonds (between the polymer chains and the MMT interlayer water molecules) associated with an intensity decrease, elongation and shift of stretching vibration bands at $\sim 3440\text{ cm}^{-1}$ towards lower frequencies was observed for the composite with the highest polymer content of higher viscosity (Fig. 3, 3_{HV}).

Increasing gradually the absorption band associated with the vibrations of atomic groups characteristic for CMC at 1598 and 1604 cm^{-1} for CMC_{LV} and CMC_{HV} respectively (Fig. 2) and corresponding to the vibrations of the carbonyl group for all the composite materials an increasing concentration of the polymer in tested structure may be indicated (Fig. 3). The shift of these bands towards higher wavenumbers, but also the decrease in their intensity as the polymer content increases in the sample (especially evident in the case of the bentonite modified with higher viscosity polymer) can be observed. The maximum shift towards higher frequencies, but also the decrease in band intensity are observed at 1426 cm^{-1} for CMC_{LV} (1439 cm^{-1} for composites 1_{LV}, 2_{LV} and 3_{LV}) and 1420 cm^{-1} for CMC_{HV} (1441 cm^{-1} for composites 1_{HV}, 2_{HV} and 3_{HV}). This can be associated with a growing share of carbonyl groups, mostly substituted with sodium ions during the reaction with sodium carbonate, in the formation of hydrogen bonds with the surface functional groups of MMT (Fig. 4). However, this formation is limited because of the presence of adsorbed (condensed) Na⁺ ions, which decrease the effective charge density of the polymer [19].

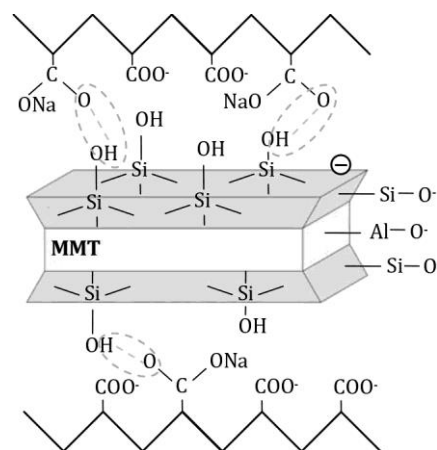


Fig. 4. Scheme of the interaction between the main component of bentonite (MMT) and CMC/Na

In the range of low wavenumbers (below 1100 cm^{-1}) no changes in the position of absorption bands in relation to the peak maximum of unmodified bentonite spectrum for the obtained inorganic-organic materials were observed (Figs. 2 and 3). This is a direct consequence of the mineral content dominance,

regardless of the content of the polymer itself and its physicochemical characteristics.

Table 1 summarizes the details of the specific identification of characteristic absorption bands for the IR spectra of starting

materials (unmodified bentonite with both types of CMC) and obtained inorganic-organic composite materials.

Table 1.

Characteristic bands in the IR spectra of the studied calcium bentonite, CMC_{LV}, CMC_{HV} and B/CMC/Na materials [15–18]

Sample									
Bentonite	CMC _{LV}	CMC _{HV}	<i>I</i> _{LV}	<i>I</i> _{LV}	<i>I</i> _{LV}	<i>I</i> _{HV}	<i>I</i> _{HV}	<i>I</i> _{HV}	Bands assignment
Wavenumber, cm ⁻¹									
3631	–	–	3631	3631	3631	3631	3631	3631	ν -OH stretching vibrations of OH groups from the outer layers of MMT
3437	–	–	3448	3448	3441	3453	–	3329	ν (H–O–H) stretching vibrations from water molecules in the interlamellar space of MMT
–	3425	3437	–	–	–	–	–	–	–OH stretching vibrations
–	2916	2922	–	–	–	–	–	–	–CH aliphatic stretching vibrations
1641	–	–	–	–	–	–	–	–	Al–OH, Si–OH stretching vibrations
–	1598	1604	1639	1639	1618	1642	1611	1610	–COO [–] asymmetric stretching vibrations of carboxyl group
–	1426	1420	1439	1439	1439	1441	1441	1441	–CH ₂ bending vibrations or –COO [–] symmetric stretching vibrations of the carboxyl group in the form of salt
–	1326	1326	–	–	–	–	–	–	C–O–H bending vibrations or –COO [–] twisting vibrations
–	1059	1064	–	–	–	–	–	–	C–O–C stretching vibrations
1043	–	–	1041	1041	1041	1043	1043	1043	ν (Si–O) stretching vibrations in SiO ₄ tetrahedrons or ν -OH stretching vibrations associated with an adsorbed water
916	–	–	912	912	914	914	914	916	δ (Al–Al–OH) in-plane bending vibrations
845	–	–	–	–	845	–	–	845	Al–Mg–OH bending vibrations
796	–	–	794	794	794	794	796	796	ν (O–Si–O) stretching vibrations (presence of SiO ₂) or δ (Mg–Al–OH) bending vibrations
625	–	–	631	629	629	629	629	629	Al–O, Si–O out-of-plane vibrations
523	–	–	525	523	523	525	523	525	δ (Al–O–Si) bending vibrations
465	–	–	467	467	465	465	464	467	δ (Si–O–Si) bending vibrations

3.2. X-ray diffraction analysis

To increase the MMT interlamellar spacing, bentonite was modified with cellulose derivative. CMC varying with viscosity and content in prepared B/CMC/Na materials was used as a modifier of mineral structure. Figure 3 shows the XRD diffraction patterns of bentonite before and after modification.

The XRD pattern of unmodified bentonite displays a typical diffraction peak at $2\theta = 6.2^\circ$, corresponding to the basal spacing between MMT packages, d_{001} , of 1.44 nm (Fig. 5). The variation

in this reflex position, thus in the interlayer distance of mineral, is clearly evident for modified bentonite samples. The visible shift towards higher values of 2θ and even disappearance of the XRD peak position around $2\theta = 6.15^\circ$ indicate the destructive effect of the polymer on the MMT layered structure in the bentonite [17]. The long CMC chains, regardless of the concentration and viscosity, cause the partial or even full delamination (exfoliation) of MMT packages. It may be related to the electrostatic repulsion between carboxyl groups and negatively charged clay surfaces or to the main structural feature of the cellulose and its derivatives,

i.e. the rigidity of the glucose rings and the rotation impossibility around the C–O–C bonds between the adjacent rings because of β -1,4-linkage. Both of the factors determine the rigidity of the chain backbone [19]. This is not necessarily a sign of the uselessness of these materials (B/CMC/Na composites) in the foundry technology, but it should already be noted that such type of a structure will adversely affect certain technological properties of moulding sands containing these additives, e.g. swelling or permeability.

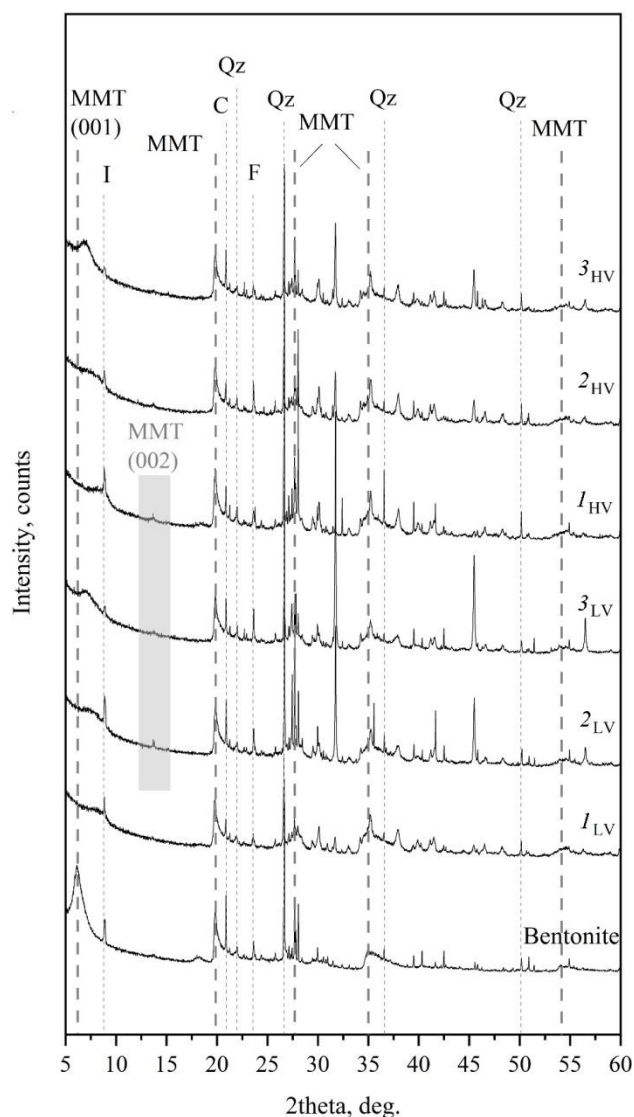


Fig. 5. X-ray diffraction patterns of unmodified bentonite and modified with CMC/Na bentonite with distinction into the polymer content: 1 – 5%, 2 – 25%, 3 – 50%

Other peaks corresponding to the MMT phase in bentonite are observed at 2θ of 20.0° , 27.2° (101), 34.9° (102) and 54.2° (110). The appearance of higher order reflexes like d_{002} -value at $2\theta = 13.6^\circ$ (grey marked place in Fig. 3) suggests that the organic modifier chains are chemically bonded with MMT structure. The

reflexes at 22.0° , 26.8° , 36.7° and 50.1° 2θ angles are associated with the quartz (Qz). Such impurities as feldspar (F , $2\theta = 23.6^\circ$) and calcite (C , $2\theta = 20.9^\circ$) are also present in bentonite and B/CMC/Na composites [20–22].

4. Conclusions

The FTIR and XRD analysis confirmed the preparation of two-component composite materials, which were obtained by modifying the structure of montmorillonite in calcium bentonite with a cellulose derivative - sodium carboxymethyl cellulose of different viscosity. The constituent materials react by the hydrogen bonds formation, which results in the polymer adsorption on the surface of mineral particles.

Based on the conducted research, it can be concluded that bentonite forms a more stable system with the lower viscosity polymer. However, both types of carboxymethyl cellulose caused a partial or full delamination of the MMT structure, which may be related to the similarity of mineral surface and polymer charges or to the rigidity of the polymer chain backbone making it difficult to change its conformation. The interaction between the inorganic and organic parts of the composites takes place through the formation of hydrogen bonds. It can be stated that the carboxyl groups in the form of salt are mainly involved in these weak chemical bonds. Although, their quantity is limited due to the lower effective charge density of COO^- groups resulting from the presence of electrically associated Na^+ ions. It must be noted that the reaction type between CMC/Na and MMT in bentonite depends on many variables, e.g. polarizability, concentration, molecular mass and pH of the polymer, as well as on the properties of the mineral itself, e.g. ion exchange capacity. In addition, the structural analysis of B/CMC/Na materials did not consider the influence of other components (impurities) of bentonite on its reaction with the polymer.

The structural studies of CMC/Na modified bentonite are the first stage of considering its possible use as an independent binder in the synthetic moulding sands technology. Despite the expected insufficient composite strength properties, the thermal studies can still be the source of information about its lustrous carbon formation capacity.

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