Studies of Poly(Acrylic Acid-*co*-Maleic Acid) Sodium Salt Intercalated Montmorillonite

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Abstract

The intercalation into interlayer spaces of montmorillonite (MMT), obtained from natural calcium bentonite, was investigated. Modification of MMT was performed by the poly(acrylic acid-*co*-maleic acid) sodium salt (*co*-MA/AA). Efficiency of modification of MMT by sodium salt co-MA/AA was assessed by the infrared spectroscopic methods (FTIR), X-ray diffraction method (XRD) and spectrophotometry UV-Vis. It was found, that MMT can be relatively simply modified with omitting the preliminary organofilisation – by introducing hydrogel chains of maleic acid-acrylic acid copolymer in a form of sodium salt into interlayer galleries. A successful intercalation by sodium salt of the above mentioned copolymer was confirmed by the powder X-ray diffraction (shifting the reflex (001) originated from the montmorillonite phase indicating an increase of interlayer distances) as well as by the infrared spectroscopy (occurring of vibrations characteristic for the introduced organic macromolecules). The performed modification causes an increase of the ion exchange ability which allows to assume that the developed hybrid composite: MMT-/maleic acid-acrylic acid copolymer (MMT-*co*-MA/AA) can find the application as a binding material in the moulding sands technology. In addition, modified montmorillonites indicate an increased ability for ion exchanges at higher temperatures (TG-DTG, UV-Vis). MMT modified by sodium salt of maleic acid-acrylic acid copolymer indicates a significant shifting of the loss of the ion exchange ability in the direction of the higher temperature range (500–700°C).

Keywords: Foundry, Hybrid materials, Montmorillonite, Intercalation, Lustrous carbon

1. Introduction

The interest of obtaining modified aluminosilicates of special properties, including improved mechanical parameters, decreased combustibility, increased chemical resistance and higher barrier level, still remains. Aluminosilicates of a laminar structure – such as montmorillonite (MMT) – are the most important for the technology. Montmorillonite has the laminar structure 2:1 type. Each MMT layer is composed of octahedric (O) aluminooxide sublayer ($Al_{3,0-4,0}$ $Mg_{0-1,4}$ $Fe^{3+}_{0-1,4}$) between two tetrahedric (T) silicaoxide sublayers ($Al_{0-0,8}$ $Si_{7,2-8,0}$). The lack of a total compensation of the layer charge causes an appearance of a negative charge excess in the structure. This charge is equalized due to the presence of compensating metal cations (among others: Ca^{2+}, Mg^{2+}) in interlayer spaces (apart from water particles). These cations can be relatively easy substituted by other cations by means of the ion exchange, which is changing the MMT properties. The characteristic lamellar charge and variability of

compensating cations determine the surface and colloidal MMT properties, such as the free swelling capacity (FSC) and cation exchange capacity (CEC) [1–3].

The MMT modification can be performed by means of exchanging interlayer ions into hydrated inorganic or organic cations, including quaternary ammonium salts, oxonian, sulphonian and phosphonian salts and other cationic complexes such as methylene blue and cationic dyes [4–6]. The majority of ionic substitutions in montmorillonites occurs in octahedric layers. Intercalation reactions, being direct or indirect introduction of determined molecules into the interlayer spaces, cause the formation of hydrogen bonds of various durability, between the reactive groups of the mineral and the introduced particles. Thus, montmorillonite reacts with organic substances by electrostatic influences (e.g. ion exchange), secondary bonds (e.g. adsorption of neutral particles) or by covalence bonding (e.g. vaccination) [7–9]. In addition, the presence of interlayer aqueous spaces causes that – apart from the surface adsorption – MMT is able to absorb water particles, which is displayed by swelling (changes of cross-linking intervals) [10–12]. Lamellar aluminosilicates as inorganic nanofillers found applications in synthesis of materials, of flocculent properties such as (co)polymer acrylamide/montmorillonite [13]. Such copolymers can be obtained by the heterophasal polymerisation method of the type: water in oil in the presence of MMT particles [13, 14]. It was found, that due to wetting of the acrylamide copolymer (PAAm) chain with a particle/particles of inorganic filler the flocculation efficiency of the hybrid increases. Copolymers PAAm with MMT as a nanofiller allow to decrease the flocculent addition while maintaining the comparable flocculation efficiency. Their additional advantage is a possibility of selective removal of contaminations, e.g. toluene from the aqueous environment. The method of obtaining hybrid materials of the starch/montmorillonite type in a form of thin polymer foils for packing food-stuffs, was also developed [13]. Organically modified aluminosilicates constitute the interesting group of organic-inorganic hybrid materials, on account of their potentially wide application in synthesis of polymer nanocomposites and as modifiers of rheological properties of paints, inks and cosmetics as well as absorbers of toxic gases or medicine carriers [13, 15–17].

Nanocomposite materials of polyamide 6, epoxy resins and unsaturated polyesters with hydrofobised bentonite were also developed [18]. Investigations contained methods of montmorillonite modifications and utilising its organoderivatives in water soluble epoxide coatings compositions and as adsorbents of styrene vapours [19]. In addition, it was shown that there is a possibility of improving nanocomposite properties with isotactic polypropylene and montmorillonite in the double worm extrusion process [20–22].

Montmorillonite in a pure form is not applied in the casting technology. The montmorillonite modification is performed in natural bentonite (i.e. calcium) by means of ion exchange (calcium cations into sodium cations). Bentonite – modified by sodium cations – indicates a better ability of binding mineral matrix grains, which is essential in its application as the material binding matrix grains in the moulding sands technology [23–29]. Green moulding sands are widely applied in the casting technology. More than 70% of the world casting production is performed in this technology, moreover it occurs that only the addition of carbonic or polymer materials to the modified bentonite warrants that castings without defects are obtained. This addition improves technological properties of green moulding sands, increases binding forces of matrix grains and decreases sand friability. The component containing carbon introduced in proper amounts constitutes a carbon carrying material (the so-called lustrous carbon carrier), which improves the casting surface quality. As the literature data indicate the proper addition of carbon compounds (graphite) and organic compounds (resins, polymer mixtures) warrants obtaining sound castings. Lustrous carbon carriers present in the moulding sand during the mould pouring with liquid metal undergo thermal degradation at a decreased oxygen access. During the thermal decomposition the so-called pyrolytic carbon, being a mixture of amorphous and lustrous carbon, is formed. The lustrous carbon carrier in a classic meaning is a coal dust. Organic mixtures (resin mixtures) are also used. The composition of a green moulding sand – in dependence of bentonite properties – contains 5–10% of bentonite (montmorillonite content above 75%), 2–5% of water, 3–8% of carbon carrying material and 85–95% of mineral matrix [24–27]. However, carbon carriers – mainly coal dusts – introduced together with bentonite generate the new problem, this time the environmental one. The presence of carbon carriers during the mould pouring with liquid metal alloy causes an increased emission of harmful substances, including aromatic hydrocarbons. Because of that, the investigations aimed at the development of technologies with new or modified carbon carriers, leading to decreasing their negative influence on the environment, are carried out [28–31].

The results of analytical investigations (XRD, FTIR, TG–DTG, UV-Vis) of montmorillonite separated from calcium bentonite and its modified form, are presented in the hereby paper. The aluminiumsilicate modification was performed by the MMT intercalation by the poly(acrylic acid-*co*-maleic acid) sodium salt (*co*-MA/AA). It was done not only for improving its ion exchange ability but mainly for introducing, into interlayer spaces, an organic compound (carbon-forming material), which could become the lustrous carbon precursor during the high-temperature process of the mould pouring with liquid metal. Polar carbonyl groups (>C=O) and sodium cations are present in copolymer *co*-MA/AA (Fig. 1). This fact is important in forming hydrogen bonds in the interlayer spaces as well as in ion exchanges (activation by sodium cations). In addition, *co*-MA/AA is a hydrophilic polymer of a significant fraction of carbon atoms in its structure, and thus can become an efficient precursor of lustrous carbon during the mould pouring with liquid metal.
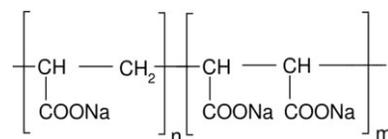

Fig. 1. Unit structure of sodium salt copolymer of maleic acid-acrylic acid

The effectiveness of the performed intercalation was confirmed by using the powder X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) as well as spectrophotometry UV-Vis. In addition, the thermo-stability of the obtained modifier MMT-*co*-MA/AA (TG–DTG), was determined. Knowledge achieved from the performed investigations will become necessary in the next research stage directed to determine the technological properties of green moulding sands prepared with fractions of MMT-*co*-MA/AA and for the confirmation the legitimacy of the modification method selection, in the context of the functionality of the hybrid material obtained for the casting technology, i.e. for obtaining sound castings.

2. Experimental

2.1. Materials and apparatus

The following materials and reagents were used in the tests:
- calcium bentonite (natural), ZGM "Zębiec" (Table 1),
- sodium salt copolymer of maleic acid-acrylic acid from BASF, pH = 8, 40% aqueous solution, Brookfield viscosity 2800 mPa·s (23°C), 70,000 g/mol,
- triethylenetetramine from Aldrich,
- copper (II) sulfate from Merck,
- potassium bromide from Acros Organics,
- distilled water from POCH company.

Table 1.
Selected properties of the bentonite

CEC, mmol/100g	64
pH	7
Water content, %	12
Montmorillonite content, %	65

The research involved the use of apparatus laboratory equipment:
- Philips X'Pert Pro MD diffractometer,
- Spectrometer Digilab Excalibur FTS 3000 Mx with detector DTGS by Bio-Rad,
- Thermal Analyzer produced by Jota,
- Spectrophotometer VIS ODYSSEY DR/2500 by HACH,
- Ultrasound device Sonic-3's POLSONIC: frequency – 40 kHz, ultrasonic power (max/period) – 2×160 W,
- MPW-350 laboratory centrifuge,
- Hei-TORQUE Value 400 agitator,
- universal dryer with an electronic temperature controller and forced air circulation type SUP-65 WG by WAMED,
- SNOL-7.2/1300 laboratory furnace.

2.2. Examinations

The analytical methods were used in the research:
(1) X-ray diffractometry – for the purpose of the measurement, a X'Pert Pro diffractometer from Philips (now PANalytical)

was used. The X'Pert Pro is two-wheel diffractometer with 240 mm diameter goniometer. During the measurement, the system worked in the Bragg–Berntano geometry. X'Pert Pro diffractometer was equipped with Cu anode X-ray tube which allows linear focus beam. The radiation beam was monochromatized ($K_{\alpha1}$=1.5406 Å) with Johansson's mirror. The sample holder allowed measurements on samples with amounts not exceeding 1 mg. When performing measurements in the range of 5–30 deg. a program with the following parameters was used: step size 0.016 deg, scan speed – 0.012110 deg/s, slit – 1/8" and time per step 8 s.

(2) Fourier transform infrared spectral analysis – were carried out by means of the spectrometer Digilab Excalibur FTS 3000 Mx with detector DTGS, electrically cooled. This spectrometer is equipped with two attachments: ATR with ZnSe crystal for multiple reflection and the transmission attachment. Potassium bromide mixture (about 200 mg) with the sample (about 2 mg) was formed with the use of a hydraulic press under the 8 tons pressure in a special matrix. Transmission spectra of the samples were recorded in a range: 4000–400 cm^{-1}, at the resolution of 4 cm^{-1}. Number of scans was selected in dependence on the level of the obtained signal (within 32 scans). The correction of the obtained spectra base line was performed by means of the Merlin (FTS 3000) software,

(3) UV-Vis spectrophotometry – to sample of bentonite (200 mg) has been added to the water (35 ml). Then, obtained system was ultrasonically dispersed. To the suspension was added 10 ml of 0.01 mol solution of Cu(II)-triethylenetetramine and filled up with water to a volume of 50 ml. The whole mixture was centrifuged until a clear solution required in the photometric measurement. Spectrophotometric tests of the prepared solution was carried in the quartz square cell with an optical path length of 10 mm at a wavelength of 620 nm. Distilled water was used as the reference sample (blank test),

(4) Thermogravimetry – the thermal examinations were performed by using thermal analyser. The temperature range of test was 20–1000°C and a heating rate was of 10°C/min
in oxygen atmosphere.

2.3. Montmorillonite sample preparation and modification

The separation of the pure montmorillonite fraction from calcium bentonite was carried out based on the known methodology [32] as follows:
- 50 g of calcium bentonite were added to 1000 ml of distilled water,
- the prepared mixture was dispersed in an ultrasonic device for 5 min,
- the mixture was kept for 72 h at room temperature in a closed vessel,
- by decanting water was poured from the resulting suspension,

- the centrifugation process was carried out (24 min, 5,000 rpm),
- after centrifugation from the bottom of the vessel, the material was collected and dried to a constant mass in a laboratory dryer at a temperature of 80°C,
- after drying, the material was mechanically ground and then modified.

Modification of montmorillonite with sodium salt of maleic acid/acrylic acid copolymer was carried out by making a ternary mixture consisting of: montmorillonite, distilled water and 40% aqueous solution *co*-MA/AA while maintaining in a weight ratio: 1:25:2. (based on US Patent 6274527 B). First, the montmorillonite was mixed with distilled water and then the *co*-MA/AA was introduced into the system. All ingredients were mixed together for 3 h using a Hei-TORQUE Value 400 agitator (100 rpm). The resulting dispersion was allowed to stand for 12 h. The centrifugation was then carried out using a laboratory centrifuge (3 min, 4,000 rpm). The obtained substance was dried (100°C, 12 h). Then, material was ground in a mortar and analytical tests were subjected.

Sample preparation consisted in the heating, continuously to the set temperature in the SNOL-7.2/1300 laboratory furnace, with the heating rate about 10°C/min. The samples of montmorillonite before and after modification (10 g) were heated in a laboratory furnace at the following temperatures: 168, 465, 700 and 778°C. The temperature values were verified on the basis of thermal analysis results (TG–DTG). It was decided that the heating time in the oven would be 5 minutes. This is the time that ensures deactivation of MMT above 600°C [5, 25, 27, 28].

3. Results and discussion

3.1. Structural investigations

Structural investigations, in order to confirm the modification efficiency of MMT separated from bentonite by means of sodium salt of copolymer: maleic acid-acrylic acid, were carried out as the first research stage. Two analytical methods: XRD and FTIR were applied.

Powder diffraction patterns, recorded for montmorillonite separated from natural bentonite (MMT) before and after the modification by sodium salt of copolymer *co*-MA/AA, are presented in Figure 2. The performed modification was confirmed on the basis of shifting of the observed reflex (d_{001}), characteristic for the MMT phase. The observed effect proves the successful intercalation of polymer chains into interlayer spaces of montmorillonite. The partial delamination of aluminosilicate layers occurred together with the intercalation, which is indicated by the decreased intensity and widening of the reflex (d_{001}). The presence of diffraction lines corresponding to other crystalline phases occurring in natural bentonite (d_{100}, 19.9) can be seen in the recorded XRD patterns. A relatively large intensity of reflexes allows to identify the presence of quartz ($d_{011}/26.6$) and albite ($d_{201}/23.6$).

The chemical compositions of MMT and MMT-*co*-MA/AA are presented in Table 2. On the basis of the oxide composition shown in the Table 2, it can be stated that the MMT modification

by means of the intercalation of the copolymer *co*-MA/AA by sodium salt led to the ion exchange. Calcium and magnesium cations were substituted by sodium cations, which is shown by their decreased percentage fraction (in counting for oxides) in the obtained hybrid material.
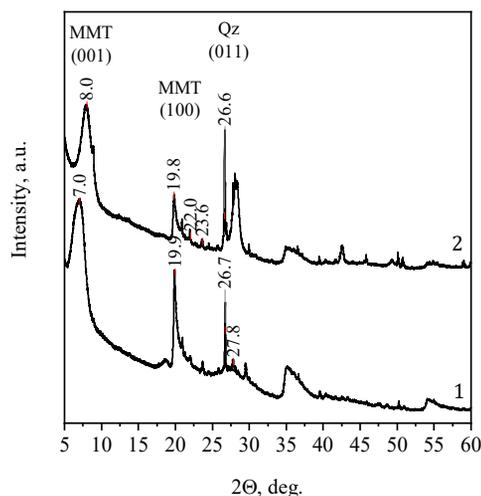

Fig. 2. XRD diffractograms of 1) MMT, 2) MMT-*co*-MA/AA

Table 2.
Chemical properties of the MMT and MMT-*co*-MA/AA

Contents, %	MMT	MMT-*co*-MA/AA
SiO_2	66.553	65.528
Al_2O_3	22.209	22.189
MgO	3.788	3.093
CaO	2.919	1.201
Fe_2O_3	2.341	2.329
Na_2O	0.818	4.252
K_2O	0.799	0.755
TiO_2	0.157	0.155
MnO	0.120	0.116
P_2O_5	0.057	0.052
ZnO	0.008	0.008
LOS[*]	0.231	0.322

[*] The low content of associated minerals in the sample

In addition, based on the Bragg's rule, interlayer distances were calculated (Tab. 3). It was found that the performed modification increased interlayer distances (d_{001}) in MMT.

Table 3.
Interlayer spacings calculated for MMT and MMT-*co*-MA/AA

Sample	Interlayer spacings		
	d_{001}, Å	d_{100}, Å	d_{011}, Å
MMT	11.09	4.48	3.34
MMT-*co*-MA/AA	12.52	4.46	3.33

A better inspection of the montmorillonite structure – before and after the modification – was achieved by means of the infrared spectroscopy. The obtained IR spectra for the MMT and MMT-*co*-MA/AA samples are presented in Figure 3. Bands characteristic for stretching vibrations of OH groups, present in silane groups (Si–OH) (3625 cm^{-1}), were observed in montmorillonite. Bands corresponding to asymmetric stretching vibrations in SiO tetrahedrons (1047 cm^{-1}) are also seen. The band at 795 cm^{-1} confirms the quartz presence in tested materials. The bands at 795 cm^{-1} and 536 cm^{-1} can be assigned to Si–O–Al and Mg–Al–OH vibrations, respectively.
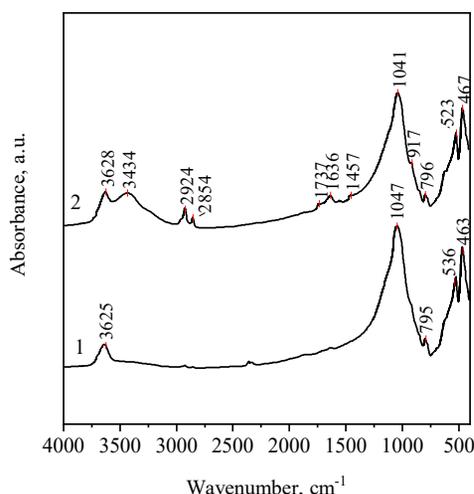

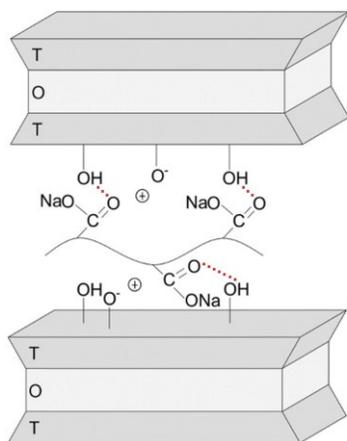Fig. 3. IR spectra of: 1) MMT, 2) MMT-*co*-MA/AA

Fig. 4. Hydrogen bonds in the MMT-*co*-MA/AA hybrid system

In the IR spectrum, recorded for the obtained hybrid mineral-polymer MMT-*co*-MA/AA material (spectrum 2) bands typical for the montmorillonite structure (bands: 3628 cm^{-1}, 1041 cm^{-1}, 796 cm^{-1}), as well as originated from the polymer part: 2924 cm^{-1} (C–H stretching), 2854 cm^{-1} and 1457 cm^{-1} (C–H deforming), were seen. The wide band corresponding to stretching O–H vibrations occurs within wavenumbers 3500–3000 cm^{-1}, indicating the hydrogen bonds occurrence (Figs. 3–4).

The band originated from stretching and bending H–OH vibrations in water particles adsorbed on the aluminosilica surface at 1636 cm^{-1}, can be also observed in spectrum 2 (Fig. 3). The adsorption maximum at 1737 cm^{-1} was assigned to C=O stretching vibrations [8, 9, 32, 33]. All characteristic bands for the MMT and MMT-*co*-MA/AA samples are gathered in Table 4.

Table 4.
Characteristic bands in the IR spectra [8, 9, 32, 33]

Band position, cm^{-1}		Assignment
MMT	MMT-*co*-MA/AA	
3625	3628	Stretching vibrations of inner Al(OH) groups
–	3434	O–H stretching vibration
–	2924	Asymmetric C–H stretching vibration
–	2854	Deforming C–H stretching vibration
–	1737	C=O stretching vibration
–	1636	H–O–H bending vibration
–	1457	Deforming C–H bending vibration
1047	1041	Si–O–Si stretching vibration
–	917	Si–O–Si stretching vibration
795	796	Si–O–Al, Mg–Al–OH
536	523	Si–O–Al bending vibrations
463	467	Si–O–Si bending vibrations

It can be stated, on the basis of the structural analysis (XRD and FTIR) that the MMT modification was efficiently performed (Fig. 5). For the MMT-*co*-MA/AA sample the shift of d$_{001}$ reflex and a decrease of its intensity (XRD) as well as changes observed in IR spectra indicate that *co*-MMT/AA was introduced into the interlayer space. The bonding influence between montmorillonite and copolymer occurred due to forming secondary bonds (adsorption of neutral particles) and hydrogen bonds (band: 3434 cm^{-1}). In addition, the increased interlayer distances caused – that apart the surface adsorption – MMT was able to increase the absorption of water particles (band 1636 cm^{-1}). Due to the intercalation, bands 1047 cm^{-1} and 536 cm^{-1} were shifted in the direction of lower wavenumbers while bands 463 cm^{-1} in the direction of higher wavenumbers, in the IR spectrum (Fig. 3 spectra 1 and 2). These bands are related to Si–O–Si vibrations, which indicates changes in the MMT structure caused by the modification process.

3.2. Thermoanalytical investigations

When montmorillonite in bentonite is in contact with liquid metal of a temperature of approximately 600°C, it starts losing its binding force. The reason of this effect constitutes the isothermal deactivation of montmorillonite, including sorption properties [25, 27, 28]. In order to determine the temperature influence on the MMT thermal degradation before and after its modification, as well as to indicate the temperature range in which deactivation occurs, the thermal analysis (TG–DTG) was performed.
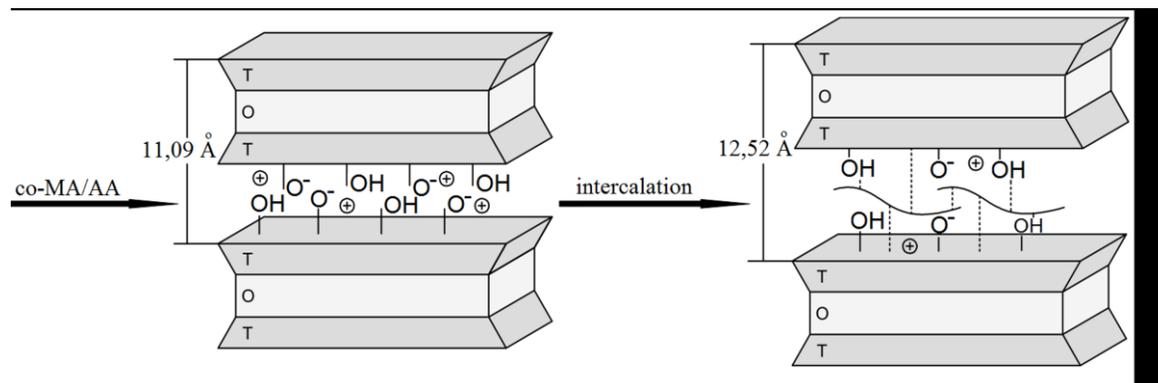
Fig. 5. Synthesis route of *co*-MA/AA intercalated MMT hybrid

Finding the temperature value, in which the montmorillonite deactivation occurs is also essential with regard to the recycling process of green moulding sands. These moulding sands after making the casting (i.e. spent sands) are treated as wastes. They are subjected to recycling by the so-called rebounding process, during which the active montmorillonite amount is properly supplemented in the moulding sand composition. The amounts of active montmorillonite remained in spent green moulding sands is – at present – mainly analysed by means of the spectrophotometric UV-Vis method, determining the cation exchange capacity.

Thermoanalytical investigations (TG–DTG and UV-Vis) were performed in order to determine the temperature range within which significant mass losses of MMT, before and after its modification, occurred. These information allowed to find the modification influence on the MMT thermostability. The obtained MMT-*co*-MA-AA hybrid material was verified from the point of view of retaining its cation exchange capacity within the determined temperature range (on the bases of TG–DTG curves), including sorption properties [25, 27, 28].

Two mass losses were observed in the TG curve for MMT: 11.07% and 3.96% (Fig. 6a). The first one occurred when a temperature reached 220°C. At this temperature the bonded water (zeolitic) is released, and the sample mass decreases by 11.07%. At this temperature the changes in the DTG curve were also seen. The second mass loss (3.96%) was recorded at a temperature of app. 600°C. At this temperature a smaller change in the DTG curve, related to the structural degradation, was seen. At a temperature of app. 778°C the change related to the sodium presence in the material, is seen in the DTG curve.

In case of the TG–DTG curve recorded for MMT-*co*-MA/AA (Fig. 6b) two mass losses were observed: 6.02% and 4.55%. The first one, noticed at a temperature of app. 160°C, is related to freeing the constitutional water. This loss is accompanied with a significant change in the DTG curve. The second mass loss was noticed at a temperature of app. 700°C. At this temperature the significant change, related to the structural MMT degradation, was also observed in the DTG curve.

In addition – within the considered temperature range – the MMT mass remained at the level of 84.97%, while the mass of the obtained hybrid material MMT-*co*-MA/AA remained at a higher level (89.43%). This indicates that in the hybrid MMT-*co*-MA/AA material, due to its thermo-destruction, the carbonized fraction was formed.

a)
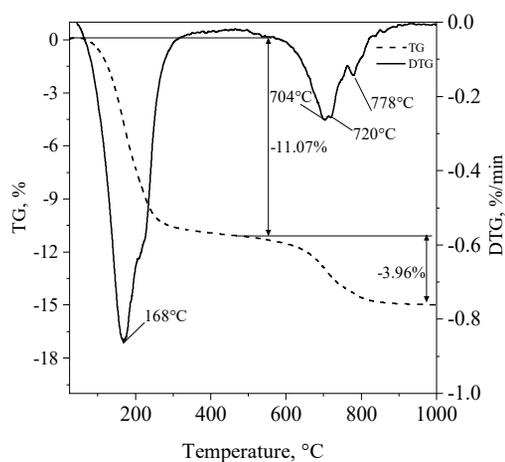
b)
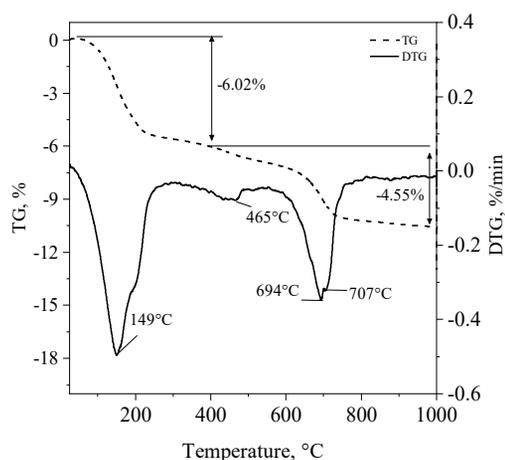
Fig. 6. TG–DTG curves of MMT (a), MMT-*co*-MA/AA (b)

This fact is important for the further verification of the obtained composite material in the green moulding sands technology, since

this material contains the potential carbon carrying material [25, 27, 28].

A sample of the MMT actually completely decomposes up to the temperature of 1000°C (remaining sample mass equals 29.7%). Information obtained by analysing the TG–DTG curves for the MMT and MMT-*co*-MA/AA is presented in Table 5.

Table 5.
The analysis of TG–DTG curves

Stage	Temperature range, °C		Δm, %		Temp. of maximum rate of weight loss, °C	
	MMT	MMT-co-MA/AA	MMT	MMT-*co*-MA/AA	MMT	MMT-*co*-MA/AA
I	20-457	20-401	12.9	11.6	110	116
II	457-1000	401-1000	23.1	21.1	300	293

It was found, on the basis of the performed thermal analysis (TG–DTG), that the copolymer introduced by the intercalation into the MMT structure stabilised thermally the obtained hybrid MMT-*co*-MA/AA material. The pathways of TG–DTG curves indicate that essential changes related to the MMT decomposition occur at temperatures: 168, 700 and 778°C, while related to the MMT-*co*-MA/AA decomposition at temperatures: 465 and 700°C. Taking into consideration the fact, that bentonite – as a binding material of matrix grains – being in contact with liquid metal already at a temperature of app. 600°C starts losing its binding property, due to the montmorillonite thermal deactivation (loss of sorption abilities), the cation exchange capacity was analytically determined (UV-Vis) in the subsequent research stage [25, 27, 28]. The cation exchange capacity is also a measure of the montmorillonite activity in binding matrix grains in green moulding sands. The CEC can be determined by various analytical methods. Currently, the spectrophotometry technique is widely used. This method is based on the spectrophotometric determination – in the presence of a coordinating substance – of the copper cations sorption ability. The results presented in the hereby paper were obtained in the presence of Cu(II)-triethylenetetramine (Cu-TET). When the mineral is in contact with the coordinating substance the adsorption of the Cu-TET complex occurs on the surface of montmorillonite particles [25].

The CEC values obtained for MMT before and after its modification are listed in Figure 7. It results, from the dependence presented in the diagram, that the temperature essentially influences the CEC value. The highest values were obtained for the samples tested in an ambient temperature (20°C) and equaled 86.60 mmol/100g for MMT and 88.38 mmol/100g for MMT-*co*-MA/AA. In both cases these values are of course higher than the CEC value determined for the initial calcium bentonite (Table 1), since natural bentonite, as a combined material, contains the determined MMT amount. It was found that along with the temperature increase the CEC value has smaller and smaller values, which indicates that MMT was losing its sorption ability. It was assumed that the downward trend of the cation exchange ability was connected with structure changes of this mineral caused by the high temperature influence. This decrease of the

ionic exchange ability at higher temperatures is related to the progressing loss of the lamellar structure order (a subsidence of the MMT lamellar structure occurs). However, it was noticed that the obtained hybrid MMT-*co*-MA/AA material is characterised by a higher cation exchange ability than MMT, in the considered temperature range. At a temperature of 465°C MMT-*co*-MA/AA maintains CEC at a higher level (36.06 mmol/100g) than MMT (20.14 mmol/100g), which at a temperature of 700°C completely losses its sorption ability. This fact is essential with regards to the application of modified MMT in the green moulding sands technology. Thus, it can be expected that after the casting knocking out from the mould in the spent moulding sand will be a large fraction of active montmorillonite, which will contribute in lowering costs of the recycling process.
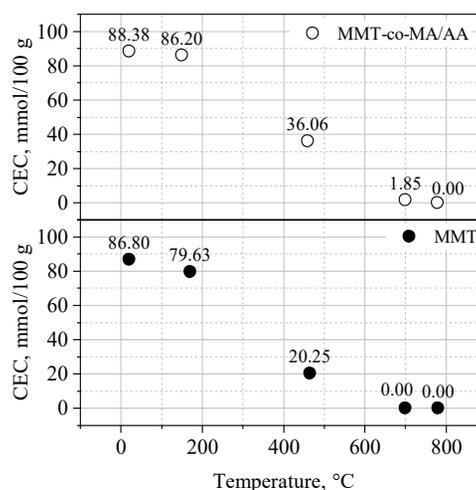

Fig. 7. The ion exchange capacity obtained for samples MMT and MMT-*co*-MA/AA

4. Conclusions

On the basis of the analysis of the presented results it can be concluded that the natural laminar aluminosilicate can be relatively easy modified by introducing polymer chains into its interlayer spaces, with omitting the preliminary organophilization stage. The successful intercalation of montmorillonite was confirmed by the powder X-ray diffraction (shifting the 001 reflex, originated from the montmorillonite phase, indicating increasing of the interlayer distances) and the infrared spectroscopy (occurrence of vibrations characteristic for the introduced organic molecules). It was found, on the basis of the thermal TG–DTG analysis, that the introduction into the montmorillonite structure the sodium salt of copolymer maleic acid-acrylic acid – due to the intercalation – stabilises thermally the obtained hybrid material. In addition, the performed modification causes that the material maintains the sorption ability of Cu (II) cations, present in the coordination compound (Cu-TET), at the higher temperature range. This allows to expect that the developed hybrid material can find applications as

binding material of green moulding sands. This fact is also essential in relation to the possibility of performing more efficient recycling of spent green moulding sands.

Acknowledgement

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