

Modification and characterization of MBDHTA⁺ intercalated nanoclay

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Highlights:

The purified suspension of montmorillonite was modified with Noranium MB2HT.

Basal spacing of organoclay increased from initial 1.23 nm to 3.91 nm.

The properties of organoclay were characterised.

Abstract

The modification of montmorillonite (totally quartz and impurities free) was performed using methylbenzyl di-hydrogenated tallow ammonium chloride (Noranium MB2HT, MBDHTA) in different synthesis conditions. The influence of quaternary ammonium salt concentration,

temperature and modification duration on the structure and properties of modified montmorillonite was examined.

The intercalation of quaternary ammonium into the interlayer space of montmorillonite resulting in the expansion of basal spacing has been investigated by X-ray diffraction (XRD). The maximum basal spacing d_{001} of 3.92 nm was determined for montmorillonite modified at 70 °C temperature and surfactant-clay (w/w) ratio 1:1. The thermal analysis (TG/DTG) revealed that the quantity of intercalated modifier grew with increasing of MBDHTA loading and synthesis temperature. The presence of MBDHTA⁺ in the interlayer space of modified montmorillonite, bond character and the arrangement of surfactant ions were identified by Fourier transform infrared (FTIR) spectroscopy. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images demonstrated that MBDHTA⁺ packing in the interlayer space of organoclay assumed regular arrangement with increment of surfactant loading. Modifier intercalation was found to decrease the montmorillonite specific surface area and pore volume as calculated by nitrogen adsorption-desorption isotherms.

Keywords: montmorillonite, quaternary ammonium, modification, structure, characterization.

1.Introduction

Physical (thermal treatment) and chemical modification (acid activation, intercalation of organic molecules, ammonium salts) of clays has been used to produce materials for various practical applications (Bergaya et al., 2006). Organically modified clays generated interest because of their wide application in industry and environmental protection (He et al., 2010; Borisover et al., 2012). Montmorillonite is frequently used in preparation of organoclays because of its disposition for intercalating organic compounds, interlayer swelling capability and low cost (He et al., 2014). The modification of clays transforms the silicate surface from hydrophilic to organophilic and consequently improves the compatibility with less polar matrices. Generally organoclays are prepared by modifying natural or sodium saturated nanoclays with a cationic surfactants – quaternary ammonium salts (quats), e.g. Arquad 2HT-75 (Sarkar et al., 2011),

hexadecyltrimethylammonium bromide (He et al., 2006); surfactants with different alkyl chain lengths (Hu et al., 2013; Xi et al., 2007) and various structure (de Paiva et al., 2008). There is information about modification of clays with non-ionic surfactants, e.g. polypropylene glycol, and amphiphilic phospholipid, e.g. lecithin, (Quellet-Plamondon et al., 2014). The properties, microstructure and morphology of modified clays depend on the surfactant loading, their alkyl chain lengths and molecule structure (de Paiva et al., 2008; Shah et al., 2013; Palkova et al., 2011). For environmental protection quaternary alkylammonium ions are preferred to primary alkylammonium ions because hydrolysis is absent, and desorption of free alkylamine is strongly reduced. Quats has not lost its relevance due to extensive use and some unresolved issues so far (He et al., 2014). There is still a lack of studies on the modification of clays with methylbenzyl di-hydrogenated tallowammonium (MBDHTA⁺, Noranium MB2HT), therefore the investigation of modification and characterization of MBDHTA⁺ intercalated nanoclay is needed.

In this study Noranium MB2HT was used for the preparation of organomontmorillonite as long alkyl chain and branchy structure cationic modifier. X-ray diffraction (XRD), thermal analysis (TG/DTG), Fourier transform infrared spectroscopy (FTIR), scanning electron (SEM) and transmission electron (TEM) microscopy, Brunauer, Emmett, and Teller (BET) methods were employed to characterize the modified montmorillonite.

2. Materials ant methods

2.1. Materials

The purified suspension of montmorillonite (totally quartz and impurities free) and organic modifier methylbenzyl di-hydrogenated tallow ammonium chloride (Noranium MB2HT, CECA S.A. France) for experiments was supplied by Laviosa Chimica Mineraria S.p.A. (Livorno, Italy). Hydrogenated tallow is consisting of approximately 65 % C₁₈H₃₇, 30% C₁₆H₃₃ and 5% C₁₄H₂₉ (Lertwimolnum and Vergnes, 2005). The properties of montmorillonite suspension: concentration of sodium exchanged montmorillonite 3.9 %, impurity content is less than 1 %, CEC 105 meq/100 g, specific surface area of dried material (BET method) – 9.9 m²/g. Montmorillonite is a hydrophilic

smectite clay with chemical formula $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O})$. Properties of Noranium MB2HT (quaternary ammonium salt): active material 83.77 %, the average molecular weight 640 g/mol, pH – 7.5.

2.2. *Synthesis of organoclay*

Noranium MB2HT was used for modification of montmorillonite suspension. Modifier does not have an accurate molecular weight due to the presence of homologs, so for this reason, the calculation of exact amount of the modifier was not possible to explain in terms of montmorillonite CEC. Accordingly the modifier-montmorillonite (w/w) ratios of 0.6:1; 0.8:1; 1:1, and 1.2:1 (denoted as 0.6Nor_BNa⁺, 0.8Nor_BNa⁺, 1.0Nor_BNa⁺ and 1.2Nor_BNa⁺, respectively) were used. The organoclays were prepared in a cation exchange reaction at 60 and 70 °C temperature for 0.25–7 hours by mechanical (1800 rpm) mixing. The materials were heated to the reaction temperature and only then were mixed. The modified nanoclay was filtered, then dried at 70 °C for 24 h and ground in an agate mortar, grit on 200 meshes (sifted through the 200 mesh grid) and used without any purification. The powders were stored in desiccators.

The modified montmorillonite, prepared by cation exchange reaction in montmorillonite suspension, was separated from mixture by filtration and solution was analyzed. The concentration of quaternary ammonium ions (NH₄⁺) in the filtrate was determined spectrophotometrically using Nessler reagent (Merc, Germany). Measurements were made with spectrophotometer Varian Cary 50 at wavelength 400-425 nm. Also the determination of NH₄⁺ ions by titration with 0.002M solution of sodium tetraphenylborate in the presence of 2,7-dichlorofluorescein indicator was performed (Metcalf, 1984).

2.3. *Characterization*

The XRD analysis of original and modified nanoclays were performed on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with Ni 0.02 mm filter to select the CuK_α wavelength. Diffraction patterns were recorded in a Bragg-Brentano geometry using a fast counting

detector Bruker LynxEye based on silicon strip technology. The specimens of nanoclays were scanned over the range $2\theta = 1\text{--}70^\circ$ at a scanning speed of 6° min^{-1} using a coupled two theta/theta scan type.

Thermal analysis (TG/DTG) was performed on a Linseis STA PT1600 instrument for evaluation of the thermal properties and phase transformation of modified nanoclays. About 15-17 mg of finely ground sample was heated in a Pt-Rh crucible from 25 to 900 °C at a heating rate of 15 °C/min under dry nitrogen atmosphere (flow rate 4.5 l/h). The differential thermogravimetric curve (DTG) was derived from TG curve. The modifier loadings in the organoclay were determined by using TG and DTG curves in the temperature range of 200–480 °C.

Montmorillonite samples as received and modified were characterized by Fourier transform infrared spectroscopy (FTIR). FTIR spectra in the $4000 - 550 \text{ cm}^{-1}$ range were recorded by spectrophotometer Bruker Tensor 27 with ATR-A537 (ZnSe) and detector TE-DLaTGS with a resolution of 4 cm^{-1} .

For TEM analysis, small drops of diluted suspension of 0.1 g of the modified nanoclay in 5 ml of distilled water were placed on Cu mesh grids which had been coated with a thin carbon film. The grids were dried at 25 °C prior to the insertion into the instrument. The samples were examined in a FEI TecnaiTM G² F20 transmission electron microscope operated at an accelerating voltage of 200 kV and images were fixed with GATAN Orius CCD camera. The interlayer spacing of organoclays was measured directly from the high resolution TEM images.

The surface morphology of the modified montmorillonite was examined by SEM. Small amounts of the dried powders were placed on carbon tape and sputter coated with a thin conductive layer of gold. The samples were examined with a scanning electron microscope ZEISS EVO MA10 the resolution of which 3.5 nm and accelerating voltage 30 kV.

Nitrogen adsorption–desorption isotherms were plotted at 77K with a Quantachrome Instrument Autosorb – iQ. Prior to adsorption, the samples were out gassed with He in a vacuum for 12 h at 95 °C. The relative pressure (P/P_0) between 0.05 and 0.35 was used for the calculation of BET

(Brunauer Emmett and Teller method) surface areas. The pore size distribution of organoclay was calculated by quenched solid density functional theory (QSDFT) model applied on the desorption branch of the isotherm with slit equilibrium kernel in micropores range.

3. Results and discussion

3.1. XRD characterization

The XRD pattern of unmodified sodium exchanged montmorillonite shows the interplanar d_{001} 1.23 nm spacing characteristic for Na- montmorillonite (Figure 1, curve 5).

The methylbenzyl di-hydrogenated tallow ammonium chloride (Noranium MB2HT) was selected for the modification of montmorillonite due to (regarding) structure of molecule with the long chain and branched molecule which lead to a larger interlayer spacing.

Modification temperatures 60 °C and 70 °C of montmorillonite have been chosen taking into account the melting point of modifier which value approximately equal 53 °C was determined by TG/DSC analysis (the curves are not present).

The XRD analysis of modified montmorillonite revealed the successful gradual intercalation of Noranium MB2HT into the gallery (001) of nanoclay interlayer space dependent on the concentration (amount) of modifier (Figure 1a and 1b, curves 1-4). The value of montmorillonite d_{001} spacing at modification temperature of 60 °C gradually increases from ~3.56 nm up to ~3.91 nm (diffraction peak 001 shifts to lower 2-theta angles) when the ratio of modifier to nanoclay changes from 0.6:1 to 1.2:1 (w/w) (Table 1). This result suggests that a progressive packing of organic ions occurs in a gallery of montmorillonite from the lateral (when the alkyl chains lying is parallel to the montmorillonite (001) layer) to the paraffin type arrangement (when the alkyl chains attempt to locate perpendicular to the montmorillonite (001) layer) (Hu et al., 2013). Value of basal reflection ~3.92 nm obtained in the last case remains unchanged during further increment of modifier to montmorillonite ratio from 1.2 to 1.5 (w/w) (results are not depicted in the paper) thereby verifying about reaching the final largest expansion of gallery between montmorillonite TOT layers. The maximum obtained interplanar spacing value (3.92 nm) is not a simple sum of the

thickness of the TOT layer and the largest dimension of modifier molecule (Ref.) which confirms about the formation of paraffin type two layers.

Moreover, the broadening of 001 basal peak decreases and intensity of that peak increases with increasing the above mentioned ratio (Figure 1a and 1b, curve 1-4). This indicates that the straight-chain molecules of modifier are more regularly ordered in the gallery of montmorillonite and a less different arrangement types of intercalated quaternary ammonium cations occur. Presence of higher orders of diffraction peaks, such as d_{002} and d_{003} , in the XRD patterns of organoclay (Figure 1a and 1b, curves 1, 2) indicates a regular arrangement of alkyl chains of modifier in the interlayer space of montmorillonite.

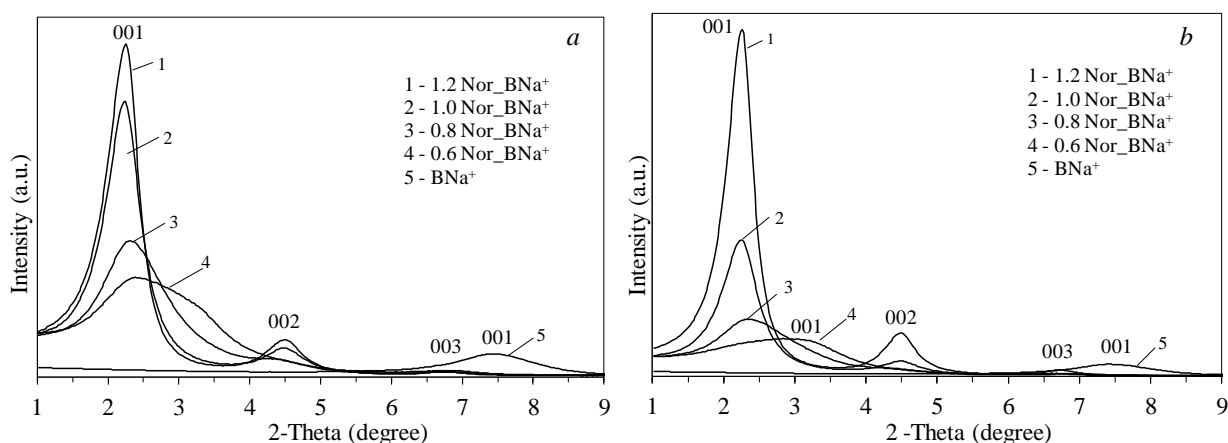


Fig.1. XRD patterns for montmorillonite modified for 0.5 h at 60 °C (a) and at 70 °C (b).

Nearly identical structural changes occur in the case of modification at temperature 70 °C (Figure 1b, curves 1-4). The value of d_{001} spacing gradually increases from 3.00 nm up to ~ 3.92 nm when the ratio of modifier to bentonite changes from 0.6: 1 to 1.2:1 (w/w). The interplanar spacing's obtained at 70 °C temperature and concentrations of 0.8, 1.0 and 1.2 (w/w) are slightly larger than those obtained at 60 °C (Table 1). As evident from the dependence of the basal d_{001} spacing on concentration of the modifier (Table 1), the optimal mass ratio of surfactant to montmorillonite 1:1 (w/w).

Table 1

The dependence of basal spacing between the (001) lattice planes of modified montmorillonite on the concentration of modifier.

Sample code	d_{001} , nm	
	60 °C	70 °C
BNa ⁺	1.23	1.23
0.6 Nor_BNa ⁺	3.56	3.00
0.8 Nor_BNa ⁺	3.75	3.76
1.0 Nor_BNa ⁺	3.91	3.92
1.2 Nor_BNa ⁺	3.90	3.91

Modification temperature 60 °C has been chosen for the further investigations because the intensity of basal diffraction peak 001 of montmorillonite is larger at this temperature when the modifier to clay mass ratio was 1:1 and 0.8:1(w/w) (Figure 2).

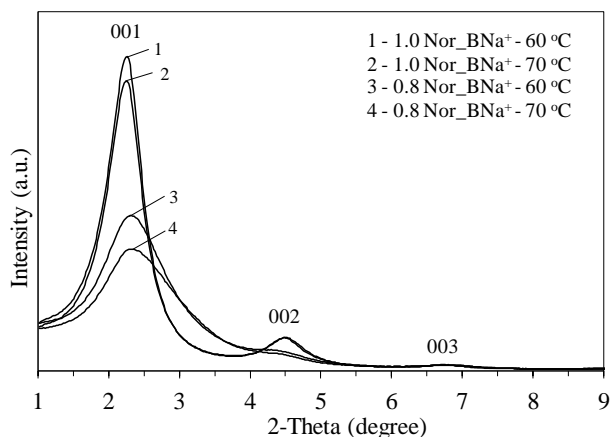


Fig.2. Comparison XRD patterns of montmorillonite modified for 0.5 h at 60 °C and at 70 °C.

The duration time for montmorillonite modification have been found from variation of interplanar spacing d_{001} of montmorillonite modified for 0.25 –7 h at 60°C when mass ratio of modifier to clay was 0.8:1 (w/w) (Figure 3). The maximum intensity of diffraction peak 001 and the largest expansion of basal spacing d_{001} have been obtained during modification of montmorillonite for 0.5 h (Figure 3b).

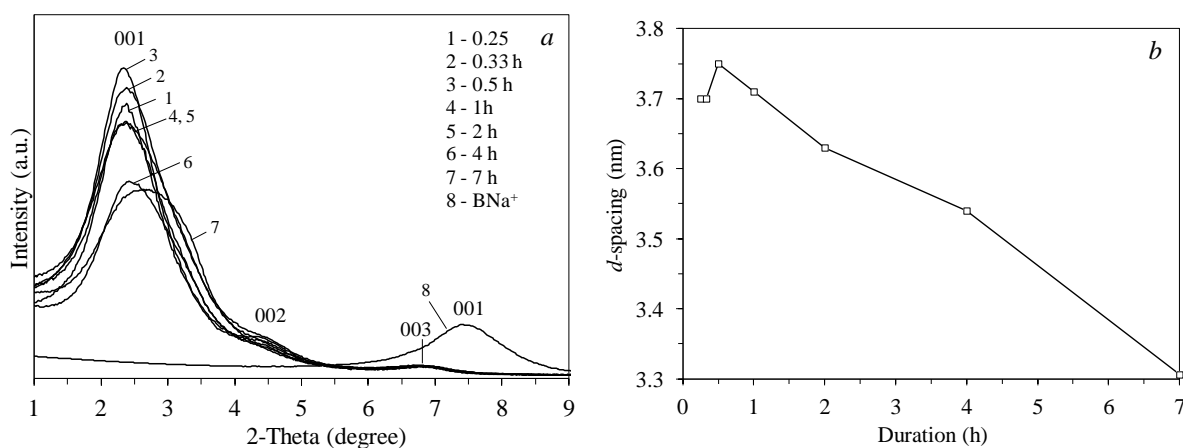


Fig.3. XRD patterns of montmorillonite modified at 60 °C in mass ratio of modifier to clay 0.8:1 (w/w) (a) and the dependence of basal spacing d_{001} of montmorillonite on the modification duration (b).

However, it is difficult to get the detailed information on the arrangement of modifier molecules in the interlayer of montmorillonite based on XRD results. For further characterization of the state (arrangement) of the surfactant in the clay, the samples of modified montmorillonite as well as original materials were analyzed using TG/DTG method.

3.2. TG/DTG of unmodified and modified montmorillonite

Simultaneous thermal analysis (TG/DSC) of methylbenzyl di-hydrogenated tallow ammonium chloride (curves are not presented) exhibited 5 endothermic reactions. The first one is related with melting of material (point of reaction 41 °C, T_{\max} = 53.7 °C), the second – evaporation of solvents, the third (peak maximum 185 °C), the fourth (peak maximum 321 °C) and the fifth (peak maximum 414 °C) indicated the destruction of modifier. This finding was confirmed by the DTG curves of the sample (Figures 4b and 5 b; curve 6).

For modified montmorillonite, significant mass losses occur from 200 °C to 480 °C (Figure 4 a and b, curves 2-5) which is higher than that for pure montmorillonite (Figure 4 a and b, curve 1). This result is related with the formation of new bonds of modifier and nanoclay also due to location of modifier between the layers of MMT that limit the decomposition rate of surfactant and determine higher decomposition temperature.

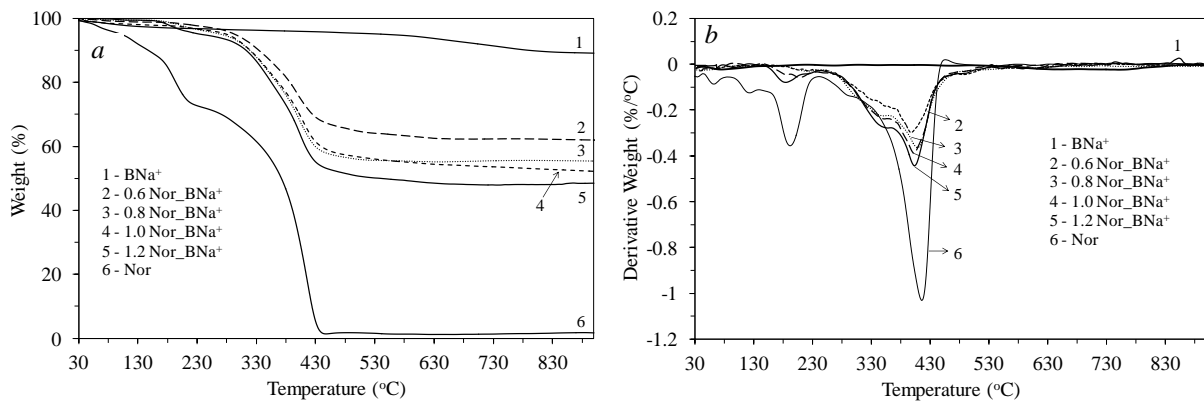


Fig.4. TG (a) and DTG (b) curves of montmorillonite modified 0.5 h at 60 °C

The onset decomposition temperatures, the maximum mass loss rate temperatures for each degradation step and the amount of modifier intercalated in the montmorillonite during 0.5 h at 60 °C are shown in Table 2. Evolution of organic materials was determined from the weight loss between 200 and 480 °C.

Table 2

Values of thermal analysis for montmorillonite and modifier

Sample code	Onset decomposition temperature from TG °C	Maximum mass loss rate temperature from DTG (°C)	Maximum mass loss from TG (200-480°C), %
BNa^+	—	—	1.5
Nor	177/301/380	192/321/414	98.6
0.6Nor_BNa ⁺	187/295/372	213/317/401	30.7
0.8Nor_BNa ⁺	182/310	199/ double ~ 401	39.0
1.0Nor_BNa ⁺	164/331	197//double ~ 400	43.1
1.2Nor_BNa ⁺	155/305/372	197/340/403	45.0

The maximum mass loss rate temperature of the modified montmorillonite was higher at lower surfactant –clay (w/w) ratio, i.e. 0.6 and 0.8 (Table 2). Supposedly, the higher temperature is related with the stronger interaction between modifier and nanoclay (Quellet-Plamondon et al., 2014).

Arrangement of modifier molecules in the interlayer have changed at higher surfactant concentration and the less energy was required for its destruction.

This effect of the variation of decomposition temperature with increased intercalated modifier concentration proved that an interaction between quaternary ammonium ion and oxygen of the montmorillonite has occurred. Overlapping peaks in DTG analysis (curves 2–5) have indicated the different structures within the organoclays. The positions of peaks of reaction maximum depend on the arrangement of molecules in the interlayer space which is more regular for 1.2Nor_BNa⁺ montmorillonite, modified 0.5 h at 60 °C, resulting in much less broadened diffraction peak (Figure 1 a) and higher decomposition temperature of third peak, i.e. 403 °C (Figure 4 a and b).

Thermal analysis (TG/DTG) of montmorillonite modified 0.5 h at 70 °C temperature for the evaluation of thermal properties and phase transformation of nanoclays was accomplished (Figure 5, a and b).

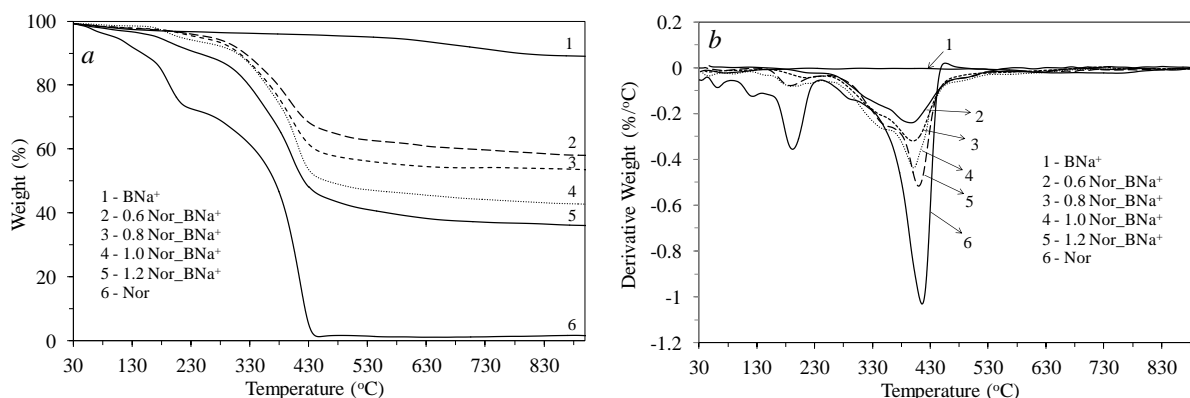


Fig. 5. TG (a) and DTG (b) curves of montmorillonite modified 0.5 h at 70 °C

Relative mass changes of modified montmorillonite depend on the modifier-clay ratio – the higher materials ratio, the more of modifier is intercalated to interlayer space or absorbed by the nanoclay. Maximum amount of modifier, i.e. 48 %, was reached in 1.2Nor_BNa⁺ montmorillonite (Figure 5 a and b, curve 5). The DTG patterns of the modified nanoclay showed three characteristic weight loss steps (Figure 5b, curves 2-5). Supposedly, the first weight loss occurs at 184–204 °C due to decomposition of unreacted modifier, the second at 331–344 °C corresponds to decomposition of the modifier bound to their neighboring molecules, the third peak at 395–410 °C occurs due to the

loss of modifier bounded to the montmorillonite. Decomposition temperature of intercalated modifier is higher than that of the as received material due to formation of new bonds. This effect of the change of decomposition temperature with increased intercalated modifier concentration has proved that an interaction between quaternary ammonium ion and oxygen of the montmorillonite has occurred. The positions of reaction maximum peaks depend on the arrangement of molecules in the interlayer space. The results of investigations indicated broad destruction peak at 395 °C (modifier-clay w/w ratio 0.5:1) related with decomposition of modifier molecules, disorderly arranged in the interlayer space (Figure 1 b, broad diffraction peak). The arrangement of molecules in the interlayer space is more regular for 1.2Nor_BNa⁺ bentonite, resulting in much less broadened diffraction peak (Figure 1 b) and higher, i.e. 344 and 410 °C, decomposition temperature (Figure 5 b). There is a direct dependence on the order of arrangements of modifier in the interlayer and modifier-clay (w/w) ratio (Figures 4, 5).

Supposedly, the first DTG peak at 187–199 °C temperature is related with the destruction of modifier and evolution of benzene, the second two at 343–346 °C and 395– 418 °C – with the destruction of alkenes (Cervantes-Uc et al., 2007).

3.3. FTIR analysis

FTIR spectroscopy can be used for determination of molecular conformation also organic and inorganic components of the chain. The changes of structure of organically modified montmorillonite using FTIR spectroscopy were investigated (Figure 6). The peaks that appear at the 3000-2800 cm⁻¹ region are the signature of CH₂ symmetric and asymmetric stretching vibration and CH₂ bending vibration of organic material (Figure 6). The wavelength and the width of these bands are very sensitive to the packing density and interaction between methylene groups (Sarkar et al., 2010). As shown in Figure 6, the CH₂ asymmetric stretching vibration appeared at 2919.7 (curve 4) and 2917.7 cm⁻¹ (curves 2 and 3) wave number for the modifier and modified montmorillonites, whereas CH₂ symmetric stretching vibration was observed at 2851.7 and 2849.8 cm⁻¹ wave number, accordingly. The appearance of the absorption bands of methylene groups confirms the presence of

exchanged modifier in the montmorillonite (curves 2 and 3). The intensities of the peaks depend on the amount of modifier in organoclay. It was observed that asymmetric stretching vibration of CH_2 groups shifted towards a lower wave number (from 2919.7 to 2917.8 cm^{-1}) when amount of modifier increased. In general, the shifts of peak to lower wave number are characteristic of ordered arrangement of alkyl chains in the interlayer space of organoclays (Chen et al., 2001). It was also observed from the results of XRD analysis (see Figure 1, a). The FTIR spectra of modifier (curve 4) and modified montmorillonite (curves 2 and 3) show absorption bands at 1643 cm^{-1} characteristic for aromatic group (Freeman, 2006). Also absorption peaks at 1467 cm^{-1} and 1375 cm^{-1} in the modified montmorillonite (curves 2 and 3) arise from the bending vibration at 2961.7 cm^{-1} – stretching vibration of the methylene units. Absorption band at 1299 cm^{-1} (Sarkar et al., 2011), characteristic for wagging vibration of the methylene units of modifier (curve 4), was not identified clearly in the samples of modified montmorillonite due to overlapping of two peaks – 1299 and 1375 cm^{-1} .

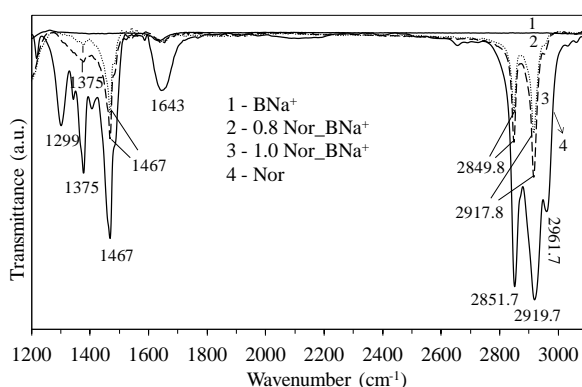


Fig.6. Selected FTIR absorption spectra of montmorillonite modified 0.5 h at $60\text{ }^{\circ}\text{C}$.

According to the results of FTIR analysis of organoclays, the largest amount of modifier was determined in the samples of montmorillonite 1.0Nor_BNa^+ modified 0.5 h at $60\text{ }^{\circ}\text{C}$ temperature.

The concentration of unreacted modifier – quaternary ammonium ions (NH_4^+) – in filtrate was measured with spectrophotometer or by titration in order to determine the optimal ratio of modifier and montmorillonite, when all amount of modifier take part in ion exchange reaction (Table 3).

Table 3

Ammonium ions concentration in filtrate of reaction products

Sample code	Concentration of NH_4^+ in filtrate, mg/l
0.8Nor_BNa ⁺	0
1.0Nor_BNa ⁺	11.4
1.20Nor_BNa ⁺	89.6

When modified montmorillonite was prepared without surfactant excess (1.0Nor_BNa⁺), inconsiderable amount of modifier in filtrate was detected (Table 3).

3.4. SEM ant TEM analysis

SEM images (Figure 7, images a – c) indicated the significant morphological differences among the unmodified and modified montmorillonites. It was observed a small amount of flakes and visible aggregated particles in the structure of unmodified montmorillonite (Figure 7, image a).

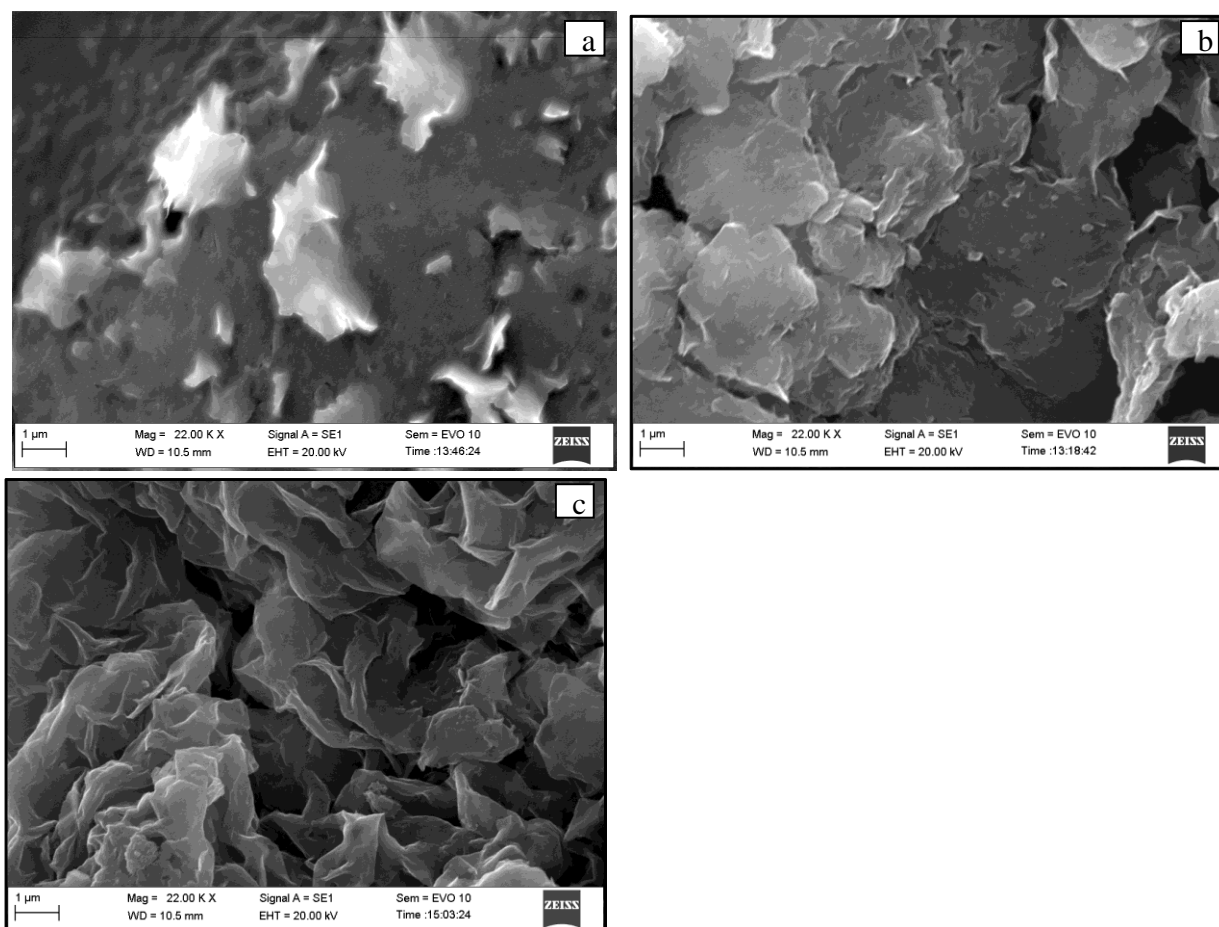


Fig. 7. SEM images of montmorillonite: a – unmodified, b – modified 0.5 h at 60 °C, modifier-bentonite (w/w) ratio 0.6:1; c - modifier-montmorillonite (w/w) ratio 1:1.

Organoclays are characterized by large amount of curled flakes with reduced aggregation of the particles (Figure 7, image b). Moreover, packing density of layers decreases with increasing of modifier content, whereas the interlayer spacing and dimension of flakes increase (Figure 7, image c). TEM images show the lamellar structure built of curved and randomly intercalated layers (Figure 8, images a-d) as well as individual regularly intercalated platelets of montmorillonite (Figure 8, images e, f). Furthermore, some regularly intercalated layers occur only in a small area.

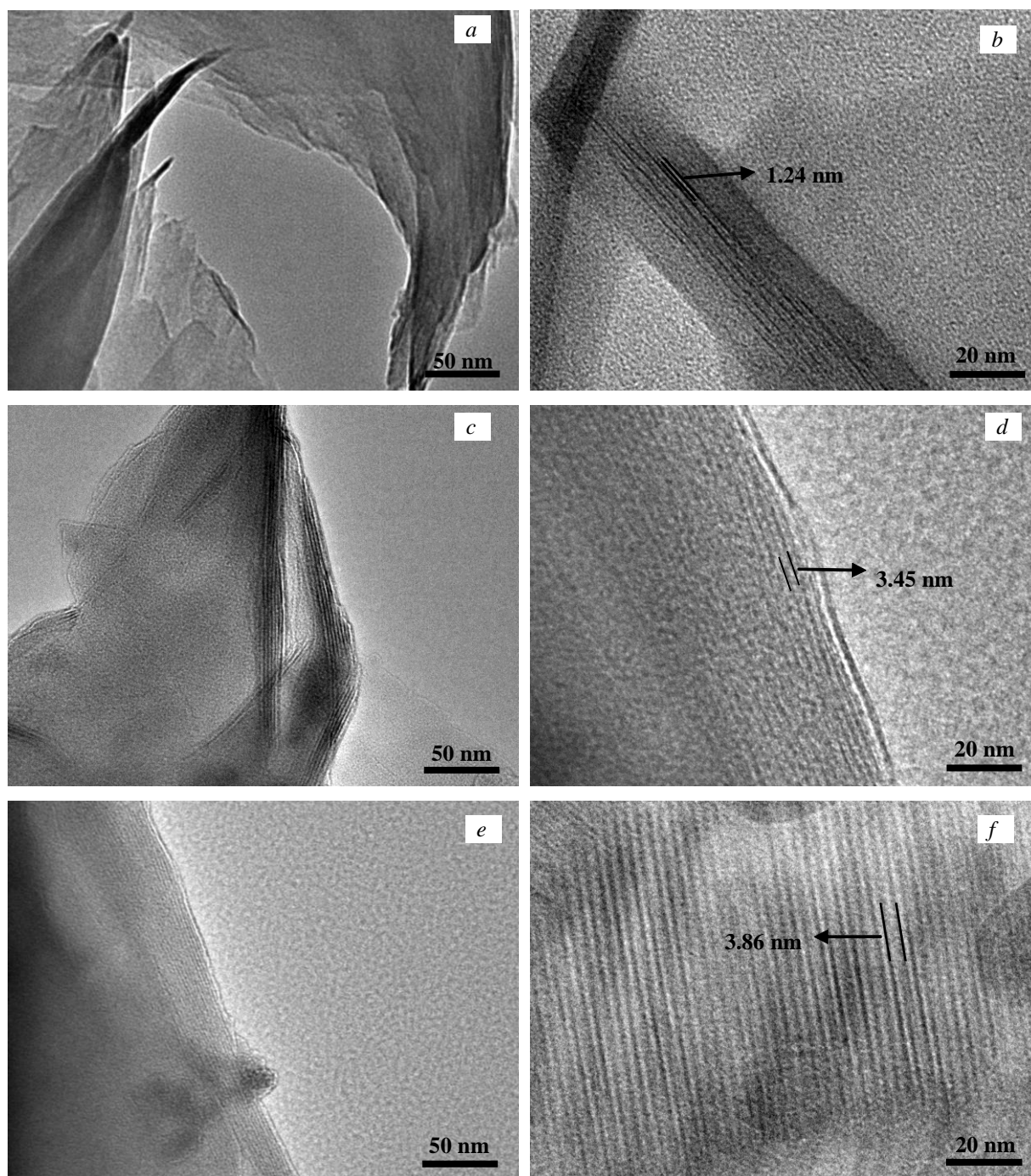


Fig.8. TEM images of montmorillonite: a, b – unmodified, c, d – modified 0.5 h at 60 °C, modifier-bentonite (w/w) ratio 0.6:1; e, f - modifier-montmorillonite (w/w) ratio 1:1.

Generally, montmorillonite is composed of regular layers with regular layer-to-layer distances remained about 1.24 nm. Many curved layers were founded with regular basal distances.

The interlayer spacing measured by TEM analysis was about 1.24 nm, 3.45nm and 3.86 nm for as received (images a and b) and modified 0.6Nor_BNa⁺ (images c, d) as well as 1.0Nor_BNa⁺ montmorillonite (images e, f), respectively, which are in agreement with the XRD results.

Organomontmorillonites show the interlayer spacings of 3.45 nm and 3.86 nm, which are slightly smaller than 3.53 nm and 3.9 nm as measured by XRD. These discrepancies could be explained by the difference of analysis methods: the interlayer spacing measured by XRD is an average of all (001) basal spacings, whereas the TEM results are based on the determination of particular interlayer spacing.

3.5. Structure of the organomontmorillonite

Thermal degradation of organoclay was performed for purpose to highlight thermal stability and structural peculiarities of the organomontmorillonite. X-ray diffraction patterns of 1.0Nor_BNa⁺ organoclay thermally affected for 0.5 h at 200, 330, 410 and 500 °C are shown in Figure 9.

Temperatures of thermal treatment of organoclays were chosen according to the results of their thermal analysis. Changes of basal spacing d_{001} and the amount m of destructed modifier in the thermally treated organoclay are presented in Table 4.

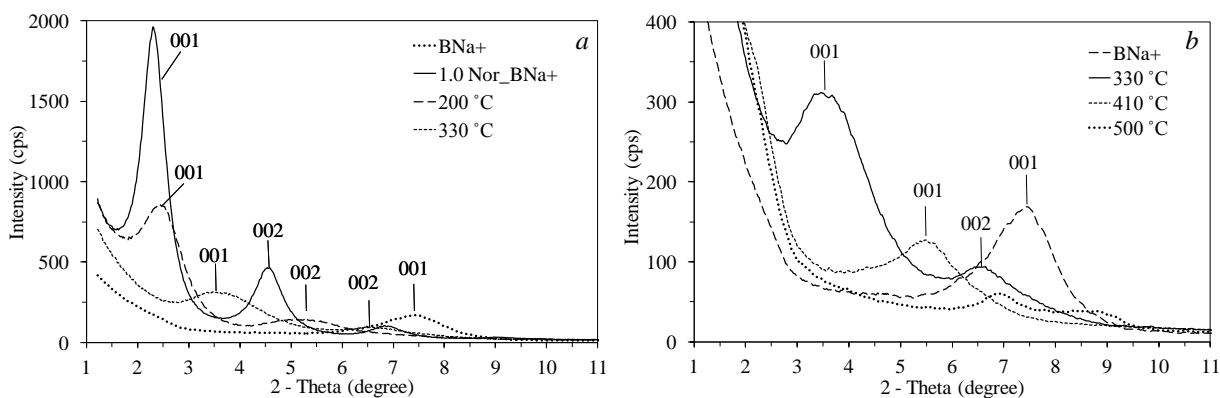


Fig.9. XRD patterns for 1.0Nor_BNa⁺ montmorillonite heated for 0.5 h at 200, 330, 410 and 500 °C temperatures.

Heating of organoclay at 200 °C caused considerable decrease of (001) Bragg reflection (Figure 9) but the basal spacing decreased marginally – the initial value of d_{001} ~3.9 nm changed to d_{001} =3.54

nm. TG curves of thermal analysis (Figure 10) similarly showed insignificant difference between initial and treated at 200 °C organoclays (Figure 10 a and b, curves 2 and 3).

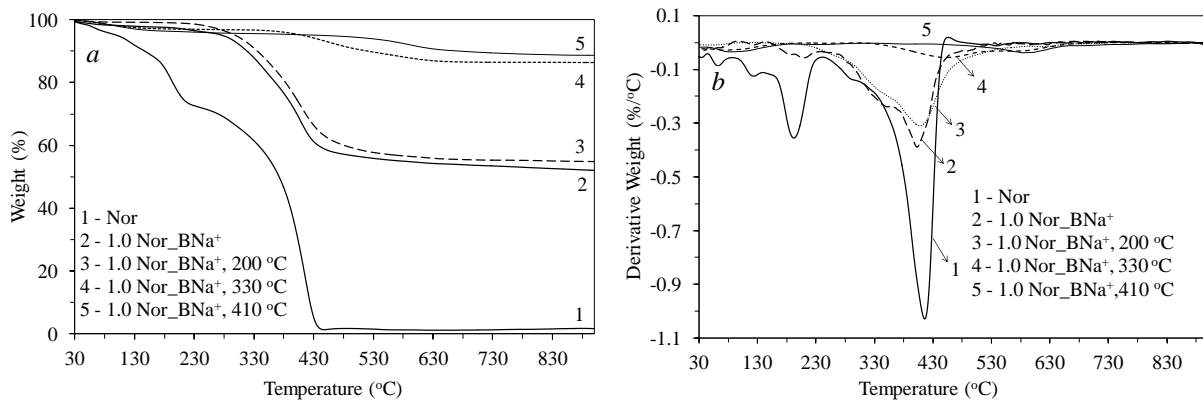


Fig.10. TG (a) and DTG (b) curves of modified montmorillonite 1.0 Nor_BNa⁺ (curve 2). Modified montmorillonite heated 0.5 h at: 3 - 200 °C, 4 – 330 °C, 5 – 410 °C; curve 1- modifier.

The decrease of basal spacing by magnitude of 0.36 nm which is of benzene molecule dimension order confirmed the incoming destruction of modifier and evolution of benzene. The decrease of basal spacing intensity of organoclay thermally treated at 200 °C could be related with the decrease of organoclay crystallite size from 18.3 to 9.6 nm in the <001> direction (Table 4).

Table 4

Effects of thermal treating temperature on the basal spacing d_{001} , mass change m and crystallite size D of organomontmorillonite

Sample No.	Heating T , °C	d_{001} , nm	$\Delta d_{001} = d_n - d_{(n+1)}$, nm	m , %	$\Delta m = m_n - m_{(n+1)}$, %	D , nm
1	20	3.9	0	48	0	18.3
2	200	3.54	0.36	45	3	9.6
3	330	2.45	1.09	14	31	5.8
4	410	1.59	0.86	11	3	6.4
5	500	1.27	0.27	6	5	14.4

The maximum decrease from 3.9 to 2.45 nm of basal spacing d_{001} and maximum mass change $\Delta m = 31$ % occurred during heating of organoclay at 330 °C. Also, crystallite size of

organoclay has obtained minimum value of 5.8 nm at this temperature (Table 4). Those results have indicated that aliphatic chains of modifier have destructed and only the part of modifier connected to silicate layer remained in the gallery of clay.

The last breakup of modifier occurs at 410 °C – the basal spacing decreased to 1.59 nm. The decrease of basal spacing is relatively large ($\Delta d = 0.86$ nm), but the mass change $\Delta m = 3$ % is relatively small. Crystallite size at this temperature increased to 6.4 nm which indicated that montmorillonite layers began to arrange orderly (Table 4).

The thermal treating of nanoclay at 500 °C temperature caused decrease (to 1.27 nm) and splitting of basal spacing. Also mass change is relatively small $\Delta m = 3$ % and the crystallite size increased to 14.4 nm. Those structural changes could be related with the dehydration of montmorillonite (Table 4).

In consequence it could be stated that the performed structural and thermogravimetric study of organoclay indicated that montmorillonite was successfully modified and modifier have obtained a paraffin type arrangement in the galleries of montmorillonite.

Figure 11 presented the N₂ adsorption–desorption isotherms on the as received montmorillonite and organomontmorillonites.

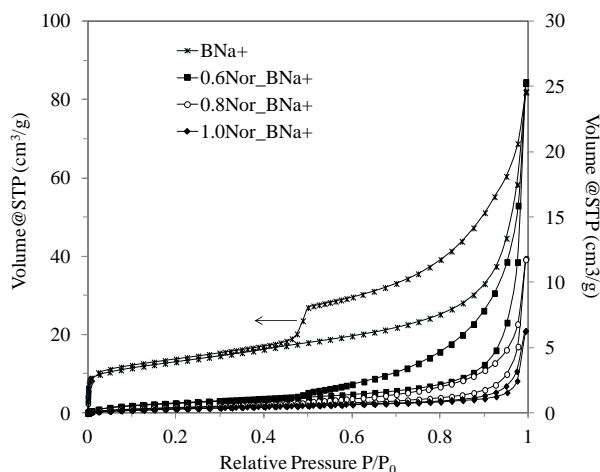


Fig. 11. N₂ adsorption–desorption isotherms on the as received and organomontmorillonites.

The N₂ adsorption of montmorillonite is higher than that of organoclays (Figure 11), and this confirmed about higher specific surface area of as received nanoclay. The N₂ adsorption capacities (specific surface area S_{BET}) of the organomontmorillonites decreased significantly as compared with

the montmorillonite and depend on the MBDHTA⁺ and nanoclay ratio (Figure 11, Table 5).

Decrease of S_{BET} indicated a compact packing of modifier ions in the interlayer space and that the large molecules of surfactant prevent the diffusion of nitrogen molecules to organoclay (Quellet-Plamondon et al., 2014). Also with increase of surfactant loading in modified nanoclay, hysteresis loops become less expressed (Figure 11), which indicated about filling of pore structure by the modifier cations. All desorption isotherms indicated capillary condensation at relative pressure >0.47 furthermore adsorption and desorption curves of samples are not horizontal but sloping over a wide range of relative pressure (Figure 11). This indicated that hysteresis loops most likely to correspond to type H3 by IUPAC (Sing et al., 1988). According to the description, the type H3 loop is characteristic for aggregates of plate-like particles growing to slit-shaped pores, which is typical for the morphology of montmorillonite. Montmorillonite evidently adsorbs N_2 both in the low and high relative pressure range, while the organomontmorillonite adsorbed N_2 mainly in the high relative pressure range. This indicates that nanoclay contains micro-, meso- and macropores, while the organomontmorillonites have meso- and macropores, respectively.

Table 5

Physical properties of the prepared materials

Sample code	S_{BET} , m^2/g	V_p^a , cm^3/g	D (DFT ^b), nm	d_{001} , nm
BNa ⁺	9.9	0.1271	3.38	1.23
0.6Nor_BNa ⁺	7.1	0.04157	4.04	3.56
0.8Nor_BNa ⁺	6.4	0.03136	4.82	3.75
1.0Nor_BNa ⁺	6.7	0.01886	5.26	3.91

^a BJH desorption cumulative pore volume of pores with diameters less than 320 nm.

^b Pore diameter by QSDFT equilibrium model, slit pores.

Organomontmorillonites with higher modifier amount have more sorption sites and promote the increase of pore diameter and the decrease both surface area and pore volume, accordingly (Table 5).

4. Conclusions

The purified suspension of montmorillonite totally quartz and impurities free was used for the synthesis of organoclay with quaternary ammonium salt – methylbenzyl-di-hydrogenated tallow ammonium chloride (Noranium MB2HT). This organoclay could be applied for the preparation of polymer nanocomposites, in cement based materials and etc. Synthesized organoclay was characterized using the XRD, TG/DTG, FTIR, SEM, TEM and porosity measurement technique.

The XRD analysis of the organoclays revealed that the d_{001} spacing of the organomontmorillonite increased from initial 1.23 nm to 3.91 nm after modification for 0.5 h at 60 °C temperature and 1:1 surfactant-clay (w/w) ratio. The arrangement of modifier molecules in the interlayer space of montmorillonite became more ordered with increasing of surfactant loading.

The TG results confirmed that the intercalation of modifier was achieved in the organoclay samples. The mass loss of modified samples increases from 39 % to 43 %, when modifier-clay (w/w) ratio varies from 0.8:1 to 1:1.

FTIR analysis confirmed the presence of MBDHTA⁺ in organoclay by characteristic peaks 2917, 1849 and 1467 cm⁻¹ indicating that modification of the montmorillonite has occurred. SEM images of modified montmorillonites indicated that, with the increase of modifier content and packing density in the interlayers, the large variously oriented swelled plate-like particles with reduced aggregation begins to dominate. TEM analysis showed that the interlayer expansion of modified montmorillonites depends on the intercalated modifier content, i.e. on the modifier-clay (w/w) ratio and consequently increases with surfactant loading.

The specific surface area S_{BET} of modified montmorillonites decreased from 9.9 to 6.7 m²/g, due to filling of micropores, whereas the pore diameter increased from 3.38 to 5.26 nm.

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References

1. The handbook of clay science: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.) 2006. Handbook of Clay Science, Developments in Clay Science, vol.1, Elsevier, Amsterdam.
2. Lertwimolnum, W., Vergnes, B., 2005. Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix. *Polymer*, 46, 3462–3471.
3. Metcalfe, L.D., 1984. The analysis of Cationic Surfactants. *JAOCS*, 61, 363–366.
4. Sarkar, B., Xi, Y., Megharaj, M., Krishnamurti, G.S.R., Rajarathanam, D., Naidu, R., 2010. Remediation of hexavalent chromium through adsorption by bentonite based Arquad 2HT-75 organoclays. *Journal of Hazardous materials*. 183, 87–97.
5. Chen, G., Liu, S., Chen, S., Qi, Z., 2001. FTIR Spectra, Thermal Properties, and Dispersibility of a Polystyrene/Montmorillonite Nanocomposite. *Macromolecular Chemistry and Physics*. 202, 1189–1193.
6. Cervantes-Uc, J.M., Cauich-Rodriguez, J.V., Vazques-Torres, H., Garfias-Mesias, L.F., Paul, D.R., 2007. Thermal degradation of commercially available organoclays studied by TGA-FTIR. *Thermochimica Acta*. 457, 92–102.
7. Sarkar, B., Megharaj, M., Xi, Y., Naidu, R., 2011. Structural characterization of Arquad 2HT-75 organobentonites: Surface charge characteristics and environmental application. *Journal of Hazardous Materials*. 195, 155–161.
8. Hu, Z., He, G., Liu, Y., Dong, Ch., Wu, X., Zhao, W., 2013. Effects of surfactant concentration on alkyl chain arrangements in dry and swollen organic montmorillonite. *Applied Clay Science*, 75-76, 134–140.
9. Freeman, W.H. *Infrared Spectroscopy*, chapter 16, 2006.

http://bcs.whfreeman.com/hardinger/content/cat_020/ch16.pdf

10. He, H., Frost, R.L., Bostrom, T., Yuan, P., Duong, L., Yang, D., Xi, Y., Klopogge, T., 2006. Changes in the morphology of organoclays with HDTMA⁺ surfactant loading. *Applied Clay Science*. 31, 262–271.
11. Xi, Y., Ray L. Frost, R.L., He, H., 2007. Modification of the surfaces of Wyoming montmorillonite by the cationic surfactants alkyl trimethyl, dialkyl dimethyl, and trialkyl methyl ammonium bromides. *Journal of Colloid and Interface Science*. 305, 150–158.
12. de Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R., 2008. Organoclays: Properties, preparation and applications. *Applied Clay Science*. 42, 8–24.
13. He, H., Ma, L., Zhu, J., Frost, R.L., Theng, B.K.G., Bergaya, F., 2014. Synthesis of organoclays: A critical review and some unresolved issues. *Appl. Clay Sci.*, <http://dx.doi.org/10.1016/j.clay.2014.02.008>.
14. Quellet-Plamondon, C.M., Stasiak, J., Al-Tabbaa, A., 2014. The effect of cationic, non-ionic and amphiphilic surfactants on the intercalation of bentonite. *Colloids and Surfaces A: Physicochem.Eng. Aspects* 444, 330–337.
15. He, H., Ma, Y., Zhu, J., Yuan, P., Qing, Y., 2010. Organoclays prepared from montmorillonites with different cation exchange capacity and surfactant configuration. *Applied Clay Science*. 48, 67–72.
16. Borisover, M., Bukhanivsky, N., Lapides, I., Yariv, S., 2012. The potential of thermally treated organobentonites to absorb organic compounds from water. *Applied Clay Science*. 67–68, 151–157.
17. Shah, K.J., Mishra, M.K., Shukla, A.D., Imae, T., Shah, D.O., 2013. Controlling wettability and hydrophobicity of organoclays modified with quaternary ammonium surfactants. *Journal of Colloid and Interface Science*. 407, 493–499.
18. Palkova, H., Jankovic, L., Zimowska, M., Madejova, J., 2011. Alterations of the surface and morphology of tetraalkyl-ammonium modified montmorillonites upon acid treatment. *Journal of Colloid and Interface Science*. 363, 213–222.

19. Li, Z., Jiang, W-T., Hong, H., 2008. An FTIR investigation of hexadecyltrimethylammonium intercalation into rectorite. *Spectrochimica Acta Part A*. 71, 1525–1534.
20. Sing, K., Everett, D., Haul, R., Moscou, L., Pierotti, R., Rouquerol, J., and T. Siemieniewska, T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Applied Chemistry*. 57, 603–619.