

Thermal stability and pollutant adsorption efficiency of nanocomposites consisted of clay and polymeric quaternary ammonium salts*

P. Natkański^a, P. Kuśtrowski^{a,*}, A. Kochanowski^a, A. Białas^a,
Z. Piwowarska^a, M. Michalik^b

^a Faculty of Chemistry, Jagiellonian University, Ingardena 3,
30-060 Kraków, Poland

*tel. +48-12-6632006; fax: +48-12-6340515; e-mail: kustrows@chemia.uj.edu.pl

^b Institute of Geological Sciences, Jagiellonian University, Oleandry 2a,
30-063 Kraków, Poland

Polymer/layered silicate nanocomposites based on polymeric quaternary ammonium salts (ionenes) intercalated into the interlayer galleries of montmorillonite were synthesized. Zeta potential measurements were conducted to determine the amount of ionenes required to neutralize the negative charge of clay. The composition and structure of the obtained nanocomposites were examined by elemental analysis, ATR-FTIR and XRD. High dye sorption capacity was observed for the composite containing ionene 6,2.

1. INTRODUCTION

In recent 20 years, research into polymer/layered silicate (PLS) nanocomposites has become a very interesting field of material engineering and chemistry of polymers. These materials are mainly used for car and packaging production, but they are also tested as drug carriers [1] and water pollutant adsorbents [2]. In industrial effluent dyes are particularly harmful substances [3] and cresol red is one of their examples [4].

*This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65th birthday

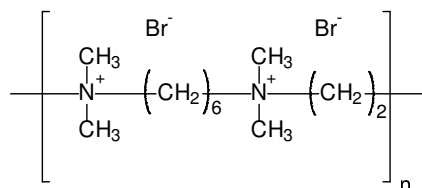
Layered silicates can be generally classified on the basis of the layer type. Phyllosilicates, which are usually applied to the preparation of PLS nanocomposites, belong to the group 2:1. Such minerals consist of the layers built of a two-dimensional sheet containing trivalent cations, octahedrally coordinated by two hydroxyl groups and four oxygen atoms, sandwiched between two other sheets of silicon atoms tetrahedrally coordinated by oxygen [5]. Some ions in both the tetrahedral and octahedral positions are substituted by ions with lower charge, e.g. Si^{4+} by Al^{3+} in tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral sites. These substitutions result in negative charge of the layers, which is counterbalanced by interlayer cations such as Na^+ , K^+ , Ca^{2+} or Mg^{2+} . The inorganic interlayer cations can be easily exchanged by larger ones, e.g. metal oligocations [6] or alkylammonium ions [7].

PLS nanocomposites with the intercalated, flocculated or exfoliated structure of layered silicate [8,9] can be obtained by various techniques. For example, clay can swell in a monomer solution or liquid monomers, which polymerize in the interlayer galleries [10-12]. Another method - the melt intercalation involves annealing a mixture of the clay modified with an organic compound (e.g. intercalated with alkylammonium ions) with polymer at the temperature higher than the polymer softening point [13]. Intercalation of a soluble polymer or prepolymer into the interlayer space can be also applied [14]. This method has been used in the presented work for the introduction of polymeric quaternary ammonium cations, known as ionenes, into natural Wyoming montmorillonite. As a result the nanocomposite with high sorption capacity of cresol red was obtained.

2. MATERIAL AND METHODS

2.1. Synthesis

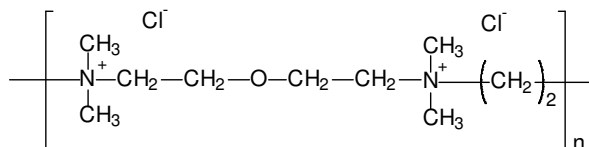
2.1.1. *Ionenenes*. Two different ionenes (6,2 and 2-O-2,2) were prepared by polyquaternization of N,N,N',N'-tetramethylethylenediamine (TEMED) with 1,6-dibromohexane or bis(2-chloroethyl) ether, respectively [15]. For synthesis of ionene 6,2,



the equimolar amounts (0.15 M) of 1,6-dibromohexane (Koch-Light Laboratories Ltd.) and TEMED (BDH Chemical Ltd.) were dissolved in 200 mL of the mixture of 80% N,N-dimethylformamide (DMF) and 20% water (v/v), and

stirred at 60°C for 6 h. The final product was dried in a vacuum drier at room temperature for 4 days.

Another polymeric quaternary ammonium salt, ionene 2-O-2,2,



was synthesized by stirring the mixture of 200 mL of the DMF solvent with 0.3 M bis(2-chloroethyl) ether (BDH Chemical Ltd.) and 0.3 M TEMED (BDH Chemical Ltd.) at 80°C for 6 h. The obtained polymer was dried in a vacuum drier at room temperature for 7 days.

2.1.2. Polymer/montmorillonite nanocomposites

Natural Wyoming montmorillonite was initially pre-treated with a NaCl aqueous solution in order to exchange pristine interlayer cations by Na⁺. 100 g of the clay was suspended in 4 L of 1 M NaCl solution. The slurry was stirred at 70°C for 24 h, then the precipitate was isolated by filtration and washed several times with distilled water to remove Cl⁻ ions. This exchange procedure was repeated three times. Finally, the obtained solid was dried at 60°C overnight. Determined according to the method described by Bergaya and Vayer [16], the cation exchange capacity (CEC) of sodium-exchanged montmorillonite (MMT-Na) was equal to 100 meq/100 g.

The prepared Na montmorillonite was used for the intercalation of polymeric quaternary ammonium salts. 3 g of the clay was suspended in 300 mL of distilled water. Subsequently, 7.45 (sample denoted as MMTI-1-10) or 10.15 mL (MMTI-1-50) of the 5 wt.% aqueous solution of ionene 6,2 was added to the suspension. Analogously, 5.60 (MMTI-2-10) or 7.65 mL (MMTI-2-50) of the 5 wt.% aqueous solution of ionene 2-O-2,2 were used for the synthesis. The suspension was stirred at 70°C for 4 days, then the precipitate was filtered and washed with distilled water. The modified clays were dried in a vacuum drier at room temperature for 4 days.

2.2. Characterization

The zeta potential measurements were carried out using a Malvern Instruments Zetasizer Nano-ZS. 1 mL aliquots of an aqueous ionene solution were gradually dosed to the 100 mL of the suspension containing 0.25 g of MMT-Na in water.

The content of carbon, nitrogen and hydrogen in samples was determined by elemental analysis performed in an EA 3000 Euro Vector instrument. A Philips X'PERT APD diffractometer equipped with a Cu anode ($\lambda = 1.54056 \text{ \AA}$) was used for structural studies. The powder X-ray diffraction (XRD) patterns were recorded in the 2θ range of $2-64^\circ$ at a scanning rate of 0.02° . The infrared spectra were recorded with a Perkin Elmer Spectrum 400 FTIR (Fourier transform infrared) spectrometer equipped with ATR (attenuated total reflectance) accessories. The measurements were carried out in the wavenumber range of $400-4000 \text{ cm}^{-1}$ with 2 cm^{-1} resolution using the diamond crystal plate. The decomposition of the samples was studied in a Mettler Toledo 851e thermoanalyzer. The TG measurements were conducted in air (a flow rate of 80 mL/min) from 30 to 1000°C at a heating rate of $10^\circ/\text{min}$.

Sorption of cresol red dye was performed at 30°C . The initial concentrations of cresol red solutions varied in the range between 1×10^{-5} and $1 \times 10^{-4} \text{ M}$. 100 mL of the dye solution was contacted with 0.1 g of the adsorbent for 4 days. After attaining sorption equilibrium, the amount of the adsorbed dye was determined measuring absorbance at 433 nm with a Merck Spectroquant Pharo 100 VIS spectrophotometer. The dye amount deposited on the studied adsorbent (q_e) was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where: C_0 is the initial concentration of a dye solution (mol/L), C_e is the concentration of the dye solution at equilibrium (mol/L), V is the volume of a dye solution (L), and m is the mass of an adsorbent (g).

3. RESULTS AND DISCUSSION

The procedure applied to the synthesis of ionenes resulted in obtaining the solid products with the C/N and C/H molar ratios of 5.70 and 0.38 for ionene 6,2 and 4.53 and 0.36 for ionene 2-O-2,2 (cf. Table 1), which are close to the expected ones. The argentometric titration (Mohr method) revealed that the polyquaterization yield was equal to 74% and 75% for the synthesis of ionene 6,2 and 2-O-2,2, respectively. The prepared polymeric quaternary ammonium salts were used for the synthesis of organically modified layered silicates (OMLS) nanocomposites.

Prior to the intercalation, the measurements of zeta potential were performed for MMT-Na in the presence of ionenes. The determined zeta potential of MMT-Na vs. an ionene dose is presented in Figure 1. As seen the isoelectric point (IP)

was achieved after adding 0.1125 g and 0.0851 g of ionene 6,2 and 2-O-2,2, respectively, in regard to 1 g of MMT-Na. The differences in the measured IP values could be explained by the various molecular mass and chemical nature of the reacting ionenes. It is most likely that the C-O-C linkage in ionene 2-O-2,2 molecules can interact with montmorillonite layers via hydrogen bonding.

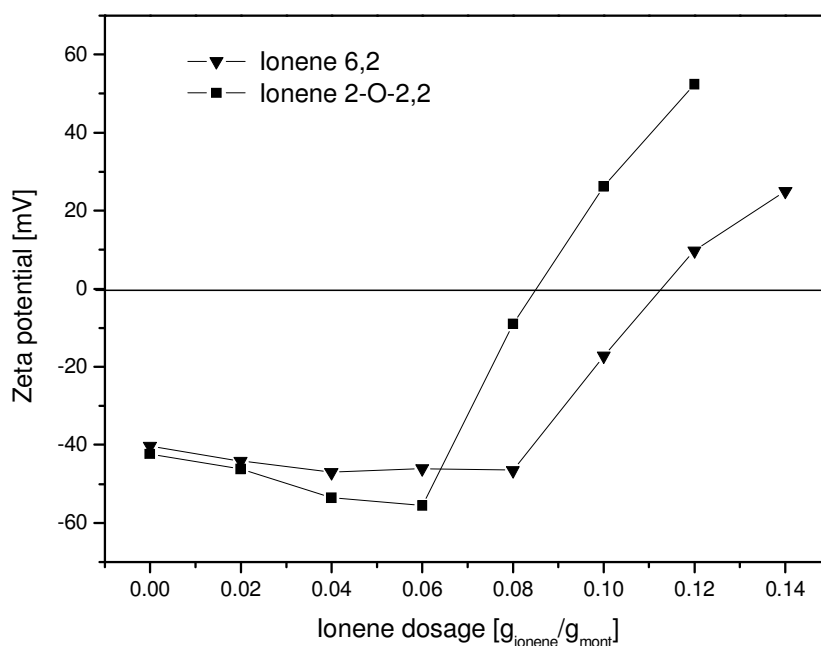


Fig.1. Changes in zeta potential of MMT-Na after dosing ionenes.

The zeta potential experiments enabled to determine the real amounts of polymeric quaternary ammonium salts necessary to neutralize the layer negative charge. During the further modification of MMT-Na, a 10% or 50% excess of ionenes in relation to the amount needed to attain the IP values was used.

The structure of Na-montmorillonite and the synthesized nanocomposites was examined by powder X-ray diffraction. The collected patterns, shown in Figure 2, confirm the successful intercalation of ionenes' chains into the interlayer spaces of MMT-Na. The (001) diffraction line observed for the Na-exchanged sample at 9.1° is significantly shifted to lower 2θ angles after the modification of clay with polymeric quaternary ammonium salts. This effect can be attributed to an increase in the interlayer distance caused by the introduction of larger cations compared to Na^+ ones. The d-spacing increased by ca 4.3-4.4 Å (Table 1) regardless of the type and amount of the ionene used. Furthermore,

observing the intensity of the (001) diffraction peak one can find that the layers of the modified clays are well ordered.

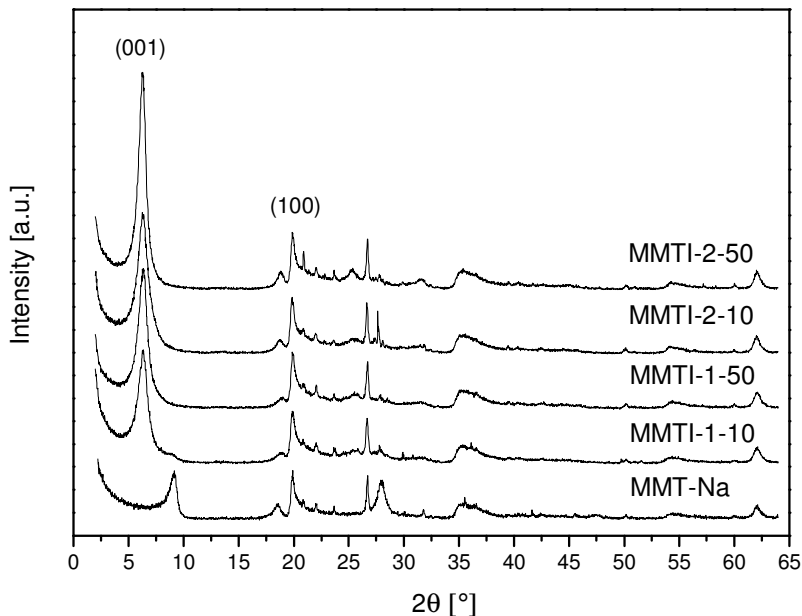


Fig. 2. XRD patterns of MMT-Na and ionene-intercalated montmorillonites.

The presence of organic species in the prepared samples was also confirmed by elemental analysis. After the modification of MMT-Na with ionenes, noticeable amounts of C, H and N were detected (cf. Table 1). The comparison of the C/N molar ratios for pure ionenes and the corresponding OMLS nanocomposites shows that their values were similar. For ionene 6,2 the C/N molar ratio value was 5.70, for MMTI-1-10 – 6.78, whereas in the case of MMTI-1-50 – 5.55. Similarly, for the series of materials based on ionene 2-O-2,2: pure ionene – 4.53, MMTI-2-10 – 4.35, MMTI-2-50 – 4.52. One therefore can conclude that the chosen conditions of the modification resulted in obtaining the expected OMLS nanocomposites. Moreover, the 10% excess of ionene with respect to the measured IP was found to be sufficient to achieve successful intercalation.

Tab. 1. Interlayer distance (d_{001}), mass loss and composition of ionenes, MMT-Na and corresponding nanocomposites.

Sample	d-spacing [Å]	Mass loss [wt.%]		Elemental analysis [wt.%]		
		Total	Ionene decomposition	C	H	N
Ionene 6,2	–	100.0	80.5	31.77	6.92	6.50
Ionene 2-O-2,2	–	100.0	86.5	42.15	9.76	10.86
MMT-Na	9.68	7.4	–	–	–	–
MMTI-1-10	14.02	15.2	4.3	5.01	1.69	0.86
MMTI-1-50	13.97	15.2	4.3	4.28	1.57	0.90
MMTI-2-10	14.05	14.1	4.2	4.11	1.44	1.10
MMTI-2-50	14.12	15.5	4.5	5.03	1.64	1.30

The FTIR spectra, collected in Figure 3A and 3B, prove the presence of ionenes' chains in the montmorillonite gallery. MMT-Na is characterized by bands at 3620 cm^{-1} (stretching vibrations of $-\text{OH}$), 3430 cm^{-1} (hydrogen bonds), 990 cm^{-1} and 1115 cm^{-1} (asymmetric stretching vibrations of SiO_2 tetrahedra), 915 cm^{-1} (bending vibrations of Al-OH), 798 cm^{-1} (stretching vibrations of Al-O tetrahedra), and 515 cm^{-1} (bending vibrations of Si-O) [17, 18]. FTIR spectra of ionenes show characteristic absorptions in the range of $3000\text{--}2860\text{ cm}^{-1}$ and $1490\text{--}1395\text{ cm}^{-1}$ corresponding to the stretching and deformation vibrations of C-H bonds, respectively. The characteristic C-H bending vibrations of the CH_3 and CH_2 groups connected with ammonium cations are observed at 1485 cm^{-1} and 1472 cm^{-1} [19]. The band at 1390 cm^{-1} probably corresponds to the C-H bending vibrations of CH_2 in the alkyl part of the ionenes' chain. The broad absorption peaks in the range of $3100\text{--}3650\text{ cm}^{-1}$ can be attributed to the stretching band of the OH groups, which indicate hydrophilic nature of ionenes. In the case of ionene 2-O-2,2, the peaks observed at 1114 cm^{-1} and 1082 cm^{-1} correspond to the presence of ether bonds.

In the FT-IR spectra of the synthesized nanocomposites, some characteristic bands of ionenes are invisible due to overlapping with the very intensive bands characteristic of montmorillonite. Only weak bands ascribed to the bending vibrations of CH_2 and CH_3 groups are distinguished, as shown in the insets in Figure 3. Low intensities of these bands suggest the presence of ionene chains between montmorillonite layers attenuating the IR signal. The interaction between the montmorillonite layers as well as the interlayer water molecules and

the positively charged polycations slightly change the position and intensity of vibrations characteristic of functional ionene groups.

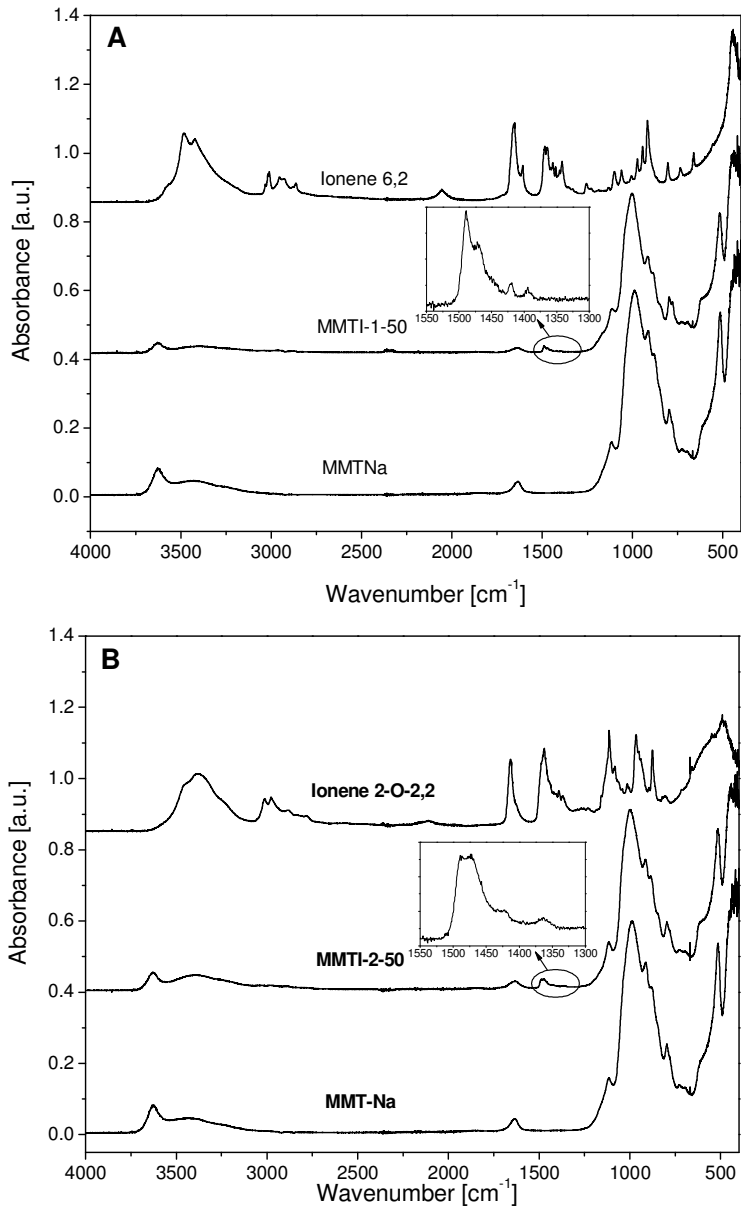


Fig. 3. FTIR spectra of nanocomposites containing ionene 6,2 (A), ionene 2-O-2,2 (B) as well as MMT-Na and a non-modified polymer.

The synthesized materials – a sodium form of montmorillonite and the ionene containing composites – were tested as adsorbents of cresol red dye from aqueous solutions. To compare their effectiveness the sorption isotherm, related to the amount of dye adsorbed on the solid surface at equilibrium, was determined. The equilibrium data obtained from the adsorption studies were fitted by the Langmuir isotherm model, described by the equation:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

where K_L and a_L are the Langmuir constants. The collected results are compared in Figure 4. It was found that montmorillonite showed no adsorption effect under applied conditions. In the presence of the MMTI-2-50 sample a very low amount of cresol red was eliminated from the aqueous solutions. What is more, the solutions intensified their color during sorption. This effect can suggest partial removal of ionene 2-O-2,2 from the studied composite and a direct interaction of free chains of ionene with the dye molecules present in an aqueous solution. Enhancement of sorption capacity was observed for the composite containing ionene 6,2. This material exhibited high stability in an aqueous solution and eliminated a high amount of cresol red.

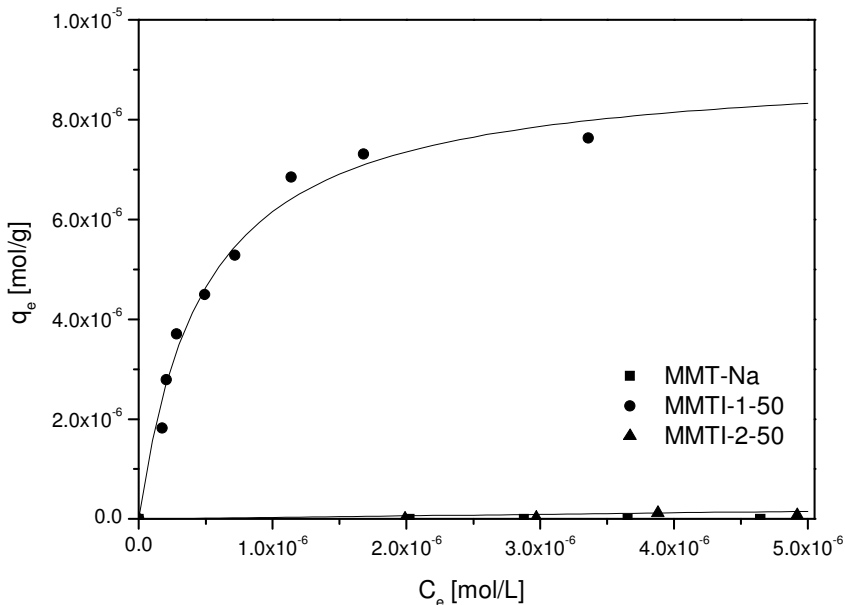


Fig. 4. Dye sorption isotherms for MMT-Na and composites containing ionene 6,2 and ionene 2-O-2,2.

We hope that the synthesized nanocomposites, besides adsorption applications, can be used as precursors in obtaining other PLS materials, especially by the method based on the melt intercalation. In this technique, the thermal stability of the OMLS material is one of crucial parameters. We have therefore studied the behaviour of the synthesized samples at raised temperatures. In Figure 5 the results of thermal analysis of pure ionenes and the PLS nanocomposites are illustrated as TG and DTG curves. The total mass loss and the mass loss related to the organic matter decomposition measured for the studied samples are presented in Table 1.

Both the studied ionenes show similar profiles of mass loss. At relatively low temperatures (below 200°C) DTG peaks assigned to the removal of solvent residues and loosely adsorbed water are observed. Essential decomposition, mainly by oxidation of organic compounds, was revealed in the temperature range of 210-370°C and 200-340°C for ionene 6,2 and ionene 2-O-2,2, respectively. The last decomposition step was detected at temperatures above 450°C. It could be assumed that a part of thermally treated polymeric quaternary ammonium salts is carbonized at medium temperatures, and the formed carbonaceous deposit is burnt even in the temperature range of 450-670°C.

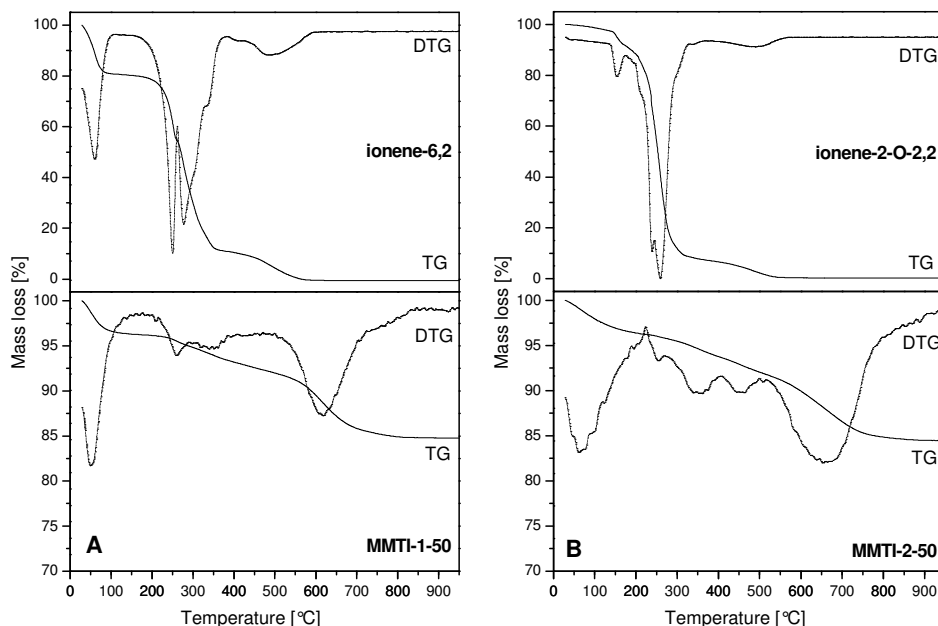


Fig. 5. TG analysis of ionenes (A - ionene 6,2; B - ionene 2-O-2,2) and corresponding nanocomposites.

The addition of montmorillonite led to the appearance of the decomposition steps characteristic of layered silicates. Two additional effects of mass loss can be distinguished. A decrease in sample mass at 50-150°C was caused by dehydration of nanocomposites, whereas the mass loss in the temperature range of 510-750°C was related to dehydroxylation of montmorillonite layers resulting in structural decomposition. Besides these effects, removal of the organic part of nanocomposites is observed at medium temperatures. However, it should be stressed that ionenes intercalated into the interlayers of MMT-Na exhibited higher thermal stability compared to their pure forms.

4. CONCLUSIONS

Polymeric quaternary ammonium salts can be successfully intercalated into the interlayer galleries of natural montmorillonite. Zeta potential measurements seem to be a very helpful method to estimate the amount of organic cations needed to compensate the layer negative charge. The intercalation of ionenes into the interlayers results in an increase in the distance between adjacent layers detected by XRD and the appearance of IR bands characteristic of polycationic chains. It has been found that ionene 6,2-based composites can be applied as highly effective adsorbents of cresol red from an aqueous solution. The thermal stability of all obtained nanocomposites enables their application as precursors in the subsequent syntheses of more complex PLS nanocomposites by melt intercalation.

Acknowledgment. This work was financed by the Polish National Science Centre (grant no. N N507 217640).

5. REFERENCES

- [1] E. Ruiz-Hitzky, P. Aranda, M. Dardera and G. Rytwo, *J. Mater. Chem.*, 20 9306 (2010).
- [2] S. Mishra, R. D. Kulkarni, *Ultrason. Sonochem.*, 16 351 (2009).
- [3] L. Lian, L. Guo, A. Wang, *Desalination*, 249 797 (2009).
- [4] W. Azmi, R. K. Sani and U. C. Banerjee, *Enzyme Microb. Technol.*, 22 185 (1998).
- [5] C. J. B. Mott, *Catal. Today*, 2 199 (1988).
- [6] L. Chmielarz, P. Kuśtrowski, M. Zbroja, A. Rafalska-Łasocha, B. Dudek, R. Dziembaj, *Appl. Catal. B*, 45 103 (2003).
- [7] L. Chmielarz, Z. Piwowarska, P. Kuśtrowski, B. Gil, A. Adamski, B. Dudek, M. Michalik, *Appl. Catal. B*, 91 449 (2009).
- [8] S. Sinha Ray, M. Okamoto, *Prog. Polym. Sci.*, 28 1539 (2003).
- [9] E.P. Giannelis, *Adv. Mater.*, 8 29 (1996).
- [10] K. Xu, J. Wang, S. Xiang, Q. Chen, W. Zhang, P. Wang, *Appl. Clay Sci.*, 38 139 (2007).
- [11] S. G. Starodubtsev, E. K. Lavrentyeva, E. V. Shtykova, K. A. Dembo, V. V. Volkov, *Appl. Clay Sci.*, 46 88 (2009).

- [12] Y. Xiang, Z. Peng, D. Chen, *Eur. Polym. J.*, 42 2125 (2006).
- [13] H. Baniyasi, A. S. A. Ramazani, S. J. Nikkhah, *Mater. Design.*, 31 76 (2010).
- [14] M. V. Burmistr, K. M. Sukhyy, V. V. Shilov, P. Pissis, A. Spandoudaki, I. V. Sukha, V. I. Tomilo, Y. P. Gomza, *Polym.*, 46 12226 (2005).
- [15] E. Bortel, A. Kochanowski, *Makromol. Chem.*, 188 2019 (1987).
- [16] F. Bergaya, M. Mayer, *Appl. Clay Sci.*, 12 275 (1997).
- [17] M. Sakizci, B. E. Alver, O. Alver, E. Yorukoğullari, *J. Mol. Struct.*, 969 187 (2010).
- [18] M. S. Lakshmi, M. Sriranjani, H. B. Bakrudeen, A. S. Kannan, A. B. Mandal, B. S. R. Reddy, *Appl. Clay Sci.*, 48 589 (2010).
- [19] M. Kozak, L. Domka, *J. Phys. Chem. Solids*, 65 441 (2004).

CURRICULA VITAE



Piotr Natkański. Graduated from the Jagiellonian University (2009). Since 2009 Ph.D. student in Materials Science and Engineering (Institute of Metallurgy and Materials Science Polish Academy of Science and Jagiellonian University) doing research in the Organic Technology Research Group at the Jagiellonian University. Member of Polish Chemical Society. His scientific work is focused on polymer/layered silicates nanocomposites as catalytic precursors and adsorbents dedicated to removal heavy metal cations from wastewater.



Piotr Kuśtrowski. Graduated from the Jagiellonian University (1995). He received Ph.D. and D.Sc. degree in 2000 and 2007, respectively. Since 2008 the head of the Organic Technology Research Group at the Jagiellonian University. Since 2011 university professor. Member of Polish Chemical Society and Polish Catalysis Club. He is a specialist in heterogeneous catalysis as well as in adsorption of air and water pollutants. His research is mainly focused on development of novel catalytic and adsorption systems based on metal oxides, cationic/anionic clays, carbon materials and mesoporous sieves.



Andrzej Kochanowski. Graduated (1974) and Ph. D. (1983) from the Jagiellonian University. He is a specialist in polymer synthesis doing research in the Polymer Chemistry Research Group at the Jagiellonian University.



Anna Białas. Graduated (1994) and Ph. D. (2004) from the Jagiellonian University, deals with environmental catalysis and solid state chemistry. In 2010 began her research in the Organic Technology Research Group, Faculty of Chemistry, Jagiellonian University.



Zofia Piwowska. Graduated from the Jagiellonian University. Research technician in the Environmental Technology Research Group. Specialization: environmental chemistry, catalytic processes for purification of flue gases.



Marek Michalik. Geologist; Graduated from the Academy of Mining and Metallurgy in Krakow (1974). Ph. D. (1985) and D.Sc. (2002) from the Jagiellonian University. Vice-Dean of the Faculty of Biology and Earth Sciences of the Jagiellonian University. Member of the Mineralogical Society of Poland; from 2004 to 2008 President of the Society. Editor of *Mineralogia*; member of the Executive Committee of *Elements*. Main fields of research: mineralogy, environmental mineralogy and geochemistry, petrology.