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X-ray scattering and calorimetric studies of organoclays obtained by ion-exchange

Summary — Structure and thermal behavior of organoclays has important influence on properties of clay-based polymer nanocomposites. Depending on starting materials, *i.e.* the mineral and amphiphilic compounds, one can obtain organoclays differing in properties. Therefore the careful choice of substrates is the way to predict and tailor ability to accommodate molecules in the interlayer spaces, catalytic activity or thermal stability of these complexes. In this paper, we present results of structural and calorimetric studies of the systems obtained of the synthetic silicate called SOMASIF modified with stoichiometric amounts of three different quaternary alkylammonium salts. SAXS studies clearly indicate that interlayer spacing (d_{001}) of silicate, calculated from the main diffraction maximum, grows strictly linearly with the length of long aliphatic chains bonded to quaternary nitrogen atoms. Further analysis of the diffractograms leads to the conclusion that the ion exchange results in formation of a mixture of three phases with different values of interlayer spacing (d_{001}). Results of DSC measurements suggested that, despite being adsorbed on the surface of silicates, quaternary ammonium cations may undergo phase transitions similar to the moieties in the bulk. The temperature range of these transitions was however found to be distinctly shifted towards lower values in comparison to the alkylammonium salts alone. Thermogravimetric analysis (TGA) was applied to estimate thermal stability as well as the coverage of silicate surface with amphiphilic molecules.

Keywords: organomontmorillonite, structure, SAXS, DSC.

BADANIA KALORYMETRYCZNE I RENTGENOGRAFICZNE ORGANOMONTMORYLONITÓW OTRZYMANYCH NA DRODZE WYMIANY JONOWEJ

Streszczenie — Struktura i charakterystyka termiczna organofilizowanych glinokrzemianów warstwowych (rys. 1, tabela 1) ma istotny wpływ na właściwości nanokompozytów polimerowych otrzymanych z udziałem tego typu napełniaczy. Decydujący wpływ na właściwości takich napełniaczy ma dobór związków amfifilowych (takich jak czwartorzędowe sole amoniowe) stosowanych do modyfikacji glinokrzemianów. Przedstawiono wyniki badań: termograwimetrycznych, kalorymetrycznych i rentgenograficznych układów otrzymanych na drodze organofilizacji syntetycznej fluoromiki o handlowej nazwie SOMASIF, za pomocą trzech homologicznych, czwartorzędowych bromków alkiloamoniowych. Pomiary SAXS wykazały, że wymiana jonowa przeprowadzona przy użyciu stechiometrycznej (w stosunku do pojemności jonowymiennej minerału) ilości soli prowadzi do powstania układu złożonego z trzech faz odznaczających się różnymi odległościami międzypłaszczyznowymi (d_{001}) (rys. 2—4). W przypadku fazy dominującej, wartość d_{001} jest liniowo zależna od długości najdłuższego łańcucha alkilowego związanego z atomem azotu. Zależność taka sugeruje, że cząsteczki soli amoniowych w obrębie galerii wykazują uporządkowaną strukturę o charakterze parakrystalicznym. Badania przeprowadzone metodą mikrokalorymetrii skaningowej (DSC, rys. 5) dostarczyły danych wskazujących, że układy takie mogą ulegać przemianom fazowym zbliżonym do topnienia i krystalizacji. Skutkiem interkalacji cząsteczek soli do dwuwymiarowych galerii montmorylonitu jest znaczne obniżenie wartości temperatury przejść fazowych. Stabilność termiczną uzyskanych układów oraz stopień obsadzenia powierzchni materiału amfifilowymi cząsteczkami soli oceniano na podstawie pomiarów termograwimetrycznych (tabela 2).

Słowa kluczowe: organomontmorylonit, struktura, SAXS, DSC.

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INTRODUCTION

One of the cheapest and most easily available sources of the nanoparticles are smectic clays such as montmorillonite. At certain conditions, primary particles of smectites can be intercalated with polymer macromolecules or delaminated to form a dispersion of individual flat particles thus forming systems referred to as nanocomposites [1]. By tuning the interactions between polymer and particles by use of well selected surface modifiers as *e.g.* ammonium salts, as well as controlling composition of the systems, one can facilitate formation of nanocomposites with desired supramolecular architecture [2].

The authors of numerous papers related to polymer-layered silicate nanocomposites reported application of either commercially available clay fillers such as Cloisite [3], Nanofil [4], Dellite [5] or the organoclays being prepared in the course of the study by treating silicates with (sometimes partly aromatic) alkylammonium or alkyphosphonium amphiphilic compounds [6—8]. The goal of such process is to exchange of alkali metal ions residing in the interlayer regions (also referred to as galleries) of the silicate with the organic compounds to render the clay organophilic and enable intercalation or exfoliation of the clay in polymer matrix. In most cases, an excess of organic compound is used in order to ensure the completeness of ion exchange and to maximize the value of basal spacing and thus the volume of interlayer region [1, 6, 9].

Interestingly, although the filler preparation plays a key role in successful intercalation or exfoliation of the clay particles in the polymeric matrices, and therefore is absolutely vital for successful preparation of nanocomposites, in the literature one can hardly find a paper where the preparation of organoclay is treated with appropriate care. Usual approach for obtaining organoclay involves a generally accepted, versatile synthetic protocol adapted from some preceding literature. This step is immediately followed by formation of nanocomposite, which actually is the main point of most works. Only just in several papers formation of the organoclays for application in polymer systems is treated with due diligence. An important point to consider is the choice of proper amphiphilic compound and the appropriate synthetic procedures [2, 9]. For instance it is known, that ammonium salts, commonly used for silicate modification, at elevated temperatures decompose due to Hoffmann elimination that results in releasing tertiary amines to the polymer [10]. This very adverse phenomenon, being one of main reasons of thermal instability of organoclays, can be reduced by removing the excess of amphiphilic compounds or replacing ammonium with phosphonium or other salts [8, 11]. In 2004 Pukánszky *et al*. published very interesting results, showing how the structure and properties of intercalated polypropylene nanocomposites depend on the conditions of organoclay preparation [12]. The Authors concluded that intercalation may occur only above certain critical gallery distance that corresponds to the doubled cross-sectional dimension aliphatic chain. In one of our previous works [7] we demonstrated that the modification of clay with alkylammonium salts may affect mutual orientation of structure units in the nanocomposites made of semicrystalline polymers and organoclays. All these examples clearly indicate that the thorough knowledge of properties and structure of organoclays has strong implications for tailoring polymer nanocomposites.

In this paper, we present results of structural and calorimetric studies of model systems obtained of the synthetic layered silicate — SOMASIF ME100 — modified with simple quaternary alkylammonium salts. Using X-ray diffraction technique we demonstrate that the structure of resulting organoclays is more complex than usually reported — the study leads to the conclusion that ion exchange does not result in products with only single interlayer spacing. The results are discussed in terms of consistency with earlier research and generally accepted models. Additionally, to find out more about thermal properties and arrangement of molecules on the silicate surface, the systems are investigated by means of DSC and TGA methods.

EXPERIMENTAL

Materials

— Synthetic sodium layered silicate SOMASIF® ME100 (M) with cation exchange capacity of 1.1 meq/g [13] and specific surface 900 m^2/g was provided by CO-OP Chemical Japan.

— For ion-exchange reactions three alkyltrimethylammonium bromides were used: didodecyldimethylammonium (**1C12**), hexadecyltrimethylammonium (**1C16**) and octadecyltrimethylammonium bromide (**1C18**). All these compounds were purchased from Aldrich and used as received.

The ion-exchange reactions

The ion-exchange reactions were performed as follows: 5.0 g of SOMASIF ME100 was dispersed in 200 ml of deionized water and vigorously stirred for 1 h at 80 °C in a 0.5 dm^3 glass reactor. After this time, a solution of 5.575 mmol of ammonium salt in 100 ml of deionized water heated to 80 °C was slowly added to the dispersion of the clay. In the next step, the suspension was stirred for an additional one hour at 80 °C and then filtered hot on heated sintered disc filter funnel followed by repeated washings of the filter cake with hot deionized water. The concentration of Br$^-$ was tested using 0.1 mol/dm^3 $AgNO_3$ solution. After ion-exchange, the organoclays were thoroughly washed with ethanol then air-dried, ground into fine powder in an agate mortar and finally vacuum dried at 50 °C to a constant weight. The products of ion exchange reactions are abbreviated here as **M1C12**, **M1C16**, **M1C18** for **1C12**, **1C16** and **1C18** salts, respectively.

Methods of testing

— Structure of the obtained systems was investigated using SAXS technique on Rigaku Ultima IV X-ray diffractometer fitted with 2 kW X-ray (CuKα, λ = 0.154184 nm) tube operated at 40 kV and 30 mA, slit collimation system forming a parallel beam and a scintillation counter. The instrument was working in a transmission, asymmetric scanning mode. Data were collected in 0.01° steps within 2θ range of 0.1 to 7.0°.

— TG measurements were performed on a Mettler-Toledo TGA/SDTA 851^{e} instrument within a temperature range of 25—900 °C. Samples were heated at a rate of 10 deg/min under nitrogen atmosphere.

— DSC investigations were done using a Mettler-Toledo DSC 821^{e} apparatus coupled with Thermo-Haake cooler. Samples were heated from 25 up to 100 °C at a rate of 10 deg/min and then cooled to 25 °C at the same ramp.

RESULTS AND DISCUSSION

Dimensions of alkylammonium molecules were estimated from quantum-mechanical modeling done at semi-empirical level (am1) using HyperChem for Windows software. For the sake of simplicity, for long alkyl chains, straightened all-trans conformation was assumed. The molecules were then approximated with cylinders and cones (to impart rotational symmetry to the objects) circumscribed over Van der Waals diameters of the moieties, according to the geometrical construction presented in Fig. 1. The geometrical parameters of the investigated ammonium salts are gathered in Table 1.

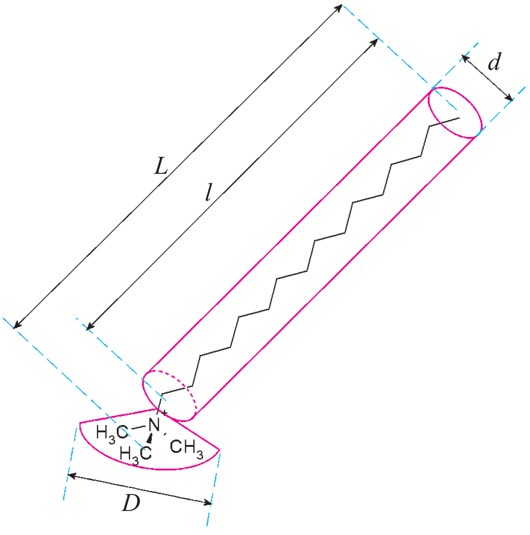

Fig. 1. Geometrical construction employed for a description of alkylammonium salts used in the study

T a b l e 1. Geometrical parameters of alkylammonium salts molecules derived from molecular modeling

Compound	*L*, nm	*l*, nm	*D*, nm	*d*, nm
1C12	1.832	1.620	0.47	0.296
1C16	2.341	2.131	0.47	0.296
1C18	2.597	2.374	0.47	0.296

T a b l e 2. Results of TG analysis of the organosilicates

Compound	Weight loss at 700 °C wt. %	Decomposition temperature[a], °C	Ion exchange ratio mmol/meq	Molecular packing nm^2/molecule
M1C12	19.5	278	0.91	1.42
M1C16	23.8	252	0.96	1.36
M1C18	24.9	269	0.92	1.42

[a] The temperature of 3 % weight loss.

Results of thermogravimetric measurements performed for the investigated organosilicates indicate a high degree of ion exchange (Table 2). The decomposition temperatures, defined as points where weight loss of 3 % was recorded, were found by approx. 30—60 °C higher than those reported for organoclays obtained with the excess of ammonium compound [14].

The scattering patterns shown in Fig. 2 clearly indicate that apart from the main maximum there are also weak maxima located on both sides of the main reflection. Although in the case of M1C12 system these peaks are barely over the noise level, generally one can say that there are three diffraction peaks corresponding to three different interlayer spacings (*d*). All these peaks are located at *s*-values lower than the original peak recorded for the anhydrous M (s_{max} = 1.04 nm, data not shown) and, considering the structure of the organoclays, they may only be a result of a diffraction of X-rays on the crystalline planes parallel to (00*l*) [15].

In the related literature there are at least two different general models describing the structure of alkylammo-

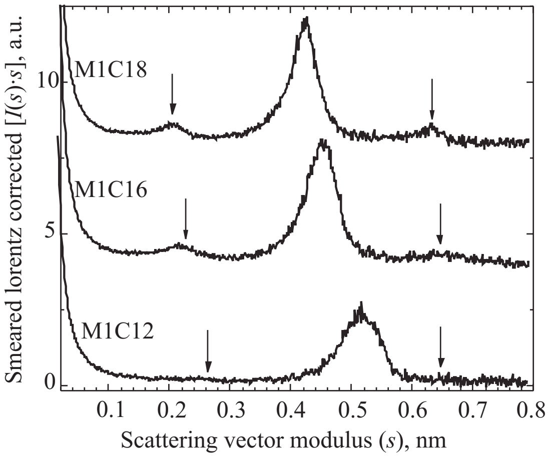

Fig. 2. SAXS patterns recorded for M1C12, M1C16 and M1C18 complexes

nium salts-clay complexes. According to the conventional approaches, intercalated alkylammonium cations create paraffin-like structures inside the galleries of the silicate [16]. More recently, several authors proposed liquid-like arrangement of the long alkyl chains within the galleries of the silicate [17]. Although these views are contradictory, both of them found many followers. Here however both the approaches have an important disadvantage — they do not explain why in the recorded diffractograms there are three maxima in the region where (00*l*) peaks are expected, since in these models the existence of a single phase is assumed. An attempt to explain complexity of diffractograms recorded for SOMA-SIF-based intercalates is made by Gilman *et al.* [18]. On the basis of experimental results and simulations they suggested that occurrence of the small maximum preceding a main basal reflection is due to Peierls-like distortion of the clay lattice in the direction perpendicular to the (00*l*) planes. In this model it is assumed that silicate platelets are stacked in pairs of platelets separated by a certain distance d 1 while the pairs within a single stack are separated by distance equal to $2 \cdot d_1$. The Authors of [18] speculate that this remarkable assembly may be a result of either the occurrence of tubular structures or 1:1 silicate apart from main 2:1 component or the effect of different charges of alternating sides of mineral layers. However, they do not give any strong experimental proofs to confirm any of this ideas.

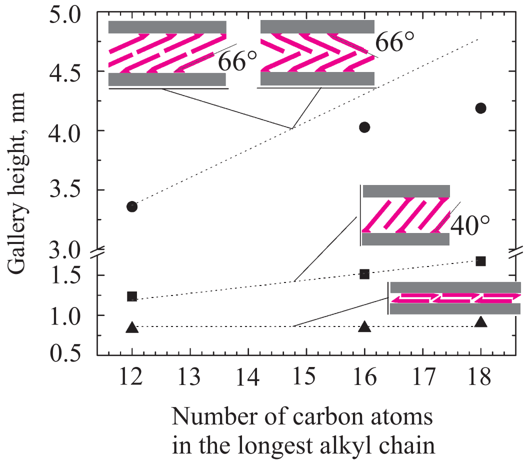

Fig. 3. Measured (points) and expected (lines) gallery heights for different arrangements of the amphiphilic molecules inside the galleries

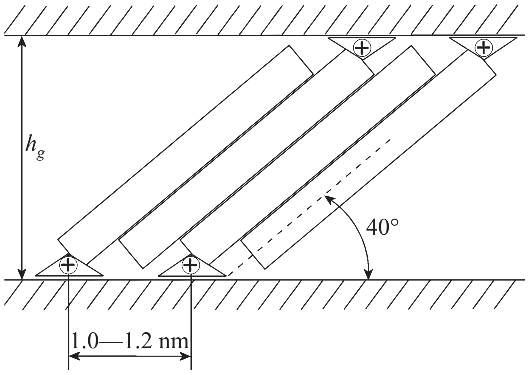

Fig. 4. Paraffin-like structure of amphiphilic molecules packed inside the gallery of the silicate

In an attempt to explain the structure of the investigated complexes we decided therefore to use conventional approach. Firstly, using known structural parameters [15] of the silicate, the values of interlayer distances calculated from peak positions (s_{max}) were transformed into gallery heights (h_g) by subtracting the value of 0.68 nm, corresponding to the thickness of single platelet of the silicate. Secondly, the values of h_g were plotted against the number of carbon atoms in the amphiphilic compounds used in the study (Fig. 3).

Purely linear dependences of basal spacing (and therefore h_g-values) recorded for the main diffraction maxima and the one located at approx. 0.65 nm^{-1} are the most striking feature of the plots presented in Fig. 3. In the case of the latter the value of s_{max} is practically independent of the chain length of ammonium salts used for ion exchange. The comparison of the calculated gallery heights with dimensions of molecules studied here indicates that they are flatly arranged on the surface of the silicate creating pseudo-bilayer system. The content of this phase seems to increase with increasing length of alkyl chains from very low (for M1C12 system, the value is unavailable due to poor separation of the peak from background) through 0.067 (M1C16) up to 0.071 (M1C18).

Values of h_g calculated from the main maximum (the basal reflection) increase linearly with increasing length of the longest chains of ammonium salts (Fig. 3.). These data fit the paraffin-like ordering with the chains tilted to the surface by 40 ° (Fig. 3, Fig. 4). This tilting angle is very similar to the value (37 °) found by Minase *et al.* [19] also for paraffin-like bilayer arrangement of densely packed trimethyldococylammonium ions. Such a structure is also very consistent with TG data presented in Table 2. From the one-dimensional (linear) geometric projection (Fig. 4) it is clear that, at this tilting angle centers of ammonium heads are separated by a minimum distance of 1.0—1.2 nm (depending on the conformation of the methyl groups and whether the packing is regular or hexagonal) which is very close to the molecular packing estimated from TGA results (1.2 nm, calculated as the square root of the value of molecular packing, cf. Table 2).

Finally, let us have a look at the peak located at the lowest *s*-values. Its position also decreases with the increasing length of the alkyl tail of ammonium compound, indicating increasing interlayer distance, but in contrast to previously discussed maxima, the growth is nonlinear. For the sake of comparison, the hypothetic structure of paraffin-like bilayer lent to the surface by the angle of 66° is shown in Fig. 3. It is clear that the experimental points do not follow linear dependence characteristic for ordered structures described previously. Also no correlation was found between the length of alkyl chain and the content of

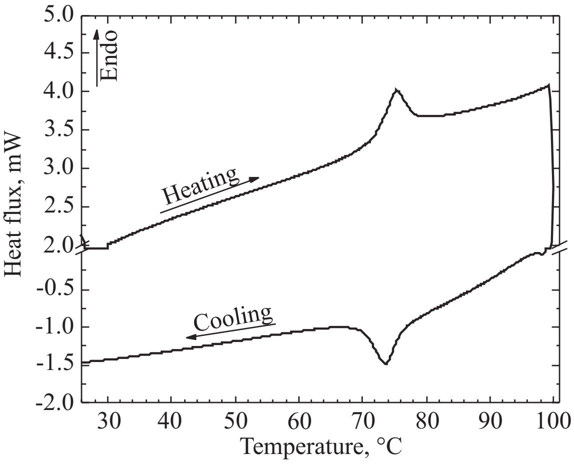

Fig. 5. DSC thermogram recorded for M1C16 intercalation complex

the phase with the highest h_g — the phase content values are: 0.04 (M1C12), 0.17 (M1C16) and 0.10 (M1C18). This may suggest that in this case we deal with either disordered phases as described in [17] or with certain "tethering" of alkyl chains, similarly as pointed out in [19].

Apart from X-ray scattering analysis, we performed DSC investigation of the intercalation complexes. A typical example of the curve recorded for M1C16 system is shown in Fig. 5. Analysis of this curve clearly indicates that within the range of 70—80 °C certain endothermic transition occurs upon heating. Furthermore this transition is fully reversible. Thus, the whole cycle resembles typical melting and crystallization. Since the silicate is completely inert in the abovementioned temperatures, one can assume that the transition is related to structural reorganization of the intercalated molecules. This may suggest, that at the elevated temperatures, the ordered structures of amphiphilic molecules intercalated inside the galleries may undergo reversible process resembling melting or, more generally disordering. However, the recorded "melting point" is located far below the melting point of the respective ammoniums salt and higher then and hydrocarbon corresponding to the alkyl part — *i.e.* in this case the 1C16 salt has a melting point of 237—243 °C while the melting point of hexadecane is 18 °C.

CONCLUSION

Multiple peaks in the small-angle diffractograms recorded for SOMASIF-based intercalation complexes indicate that the ion exchange leads to formation of phases differing in the arrangement of the amphiphilic molecules intercalated within the galleries. The dominant phase is a well ordered system where the molecules are packed in the way observed in paraffinic hydrocarbons with characteristic tilting angle (40°). With regard to the phase with smaller interlayer distance, the SAXS results indicate formation of flatly arranged pseudo-bilayer system. Its contents seem to increase with the alkyl chain length. Finally, the phase with the highest interlayer distance seems to follow the idea of liquid like disorder of hydrocarbon chains. Although the experimental results presented here do not provide insight into the reasons of formation different phases upon ion-exchange process, it is supposed that this effect may be caused by inhomogeneity of charge distribution on the surface of the silicate.

Independently of the structure of organoclays, it was found that the SOMASIF-based organoclays may undergo fully reversible phase transitions resembling melting and crystallization. Considering the abovementioned molecular arrangement of alkyl chain and the clear, well developed DSC endo- end exotherms the transition is most likely related to the dominant phase of the system.

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REFERENCES

1. Paul D. R., Robeson L. M.: *Polymer* 2008, **49**, 3178.
2. Fornes T. D., Hunter D. L., Paul D. R.: *Macromolecules* 2004, **37**, 1793.
3. Nayak S. K., Mohanty S., Samal S. K.: *Polym.-Plast. Technol. Eng.* 2009, **48**, 976.
4. Santos K. S., Liberman S. A., Oviedo M. A. S., Mauler R. S.: *J. Polym. Sci. B, Polym. Phys.* 2008, **46**, 2519.
5. deGiraldi A. L. F. M., Bizzaria M. T. M., Silva A. A., Mariano C., Velasco J., d'Avila M. A., Mei L. H. I.: *J. Nanosci. Nanotechnol.* 2009, **9**, 3833.
6. Kiersnowski A., Pigłowski J.: *Eur. Polym. J.* 2004, **40**, 1199.
7. Kiersnowski A., Gutmann J. S., Pigłowski J.: *J. Polym. Sci. B, Polym. Phys.* 2007, **45**, 2350.
8. Bruzaud S., Grohens Y., Ilinca S., Carpentier J.-F.: *Macromol. Mater. Eng.* 2005, **290**, 1106.
9. Connolly J., van Duijneveldt J. S., Klein S., Pizzey C., Richardson R. M.: *Langmuir* 2006, **22**, 6531.
10. Xie W., Gao Z., Pan W.-P., Hunter D., Singh A., Vaia R.: *Chem. Mater.* 2001, **13**, 2979.
11. Xie W., Gao Z., Pan W.-P., Hunter D., Koene B., Tan L.-S., Vaia R.: *Chem. Mater.* 2002, **14**, 4837.
12. Pozsagy A., Frŕter T., Szŕzdi L., Müller P., Sajň I., Pukŕnszky B.: *Eur. Polym. J.* 2004, **40**, 27.
13. Kiersnowski A.: PhD Thesis, Faculty of Materials Science and Engineering, Warsaw University of Technology, 2005.
14. Davis R. D., Gilman J. W., Sutto T. E., Callahan J. H., Trulove P. C., DeLong H. C.: *Clays Clay Miner.* 2004, **52**, 171.
15. Hydrous phyllosilicates (exclusive of micas) in "Reviews in Mineralogy" (Ed. Bailey S. W.), 1988, p. 19.
16. Weiss A., Holm C., Platikanov D.: *Colloid. Polym. Sci.* 1993, **271**, 891.
17. Hackett E., Manias E., Giannelis E. P.: *Chem. Mater.* 2000, **12**, 2161.
18. Gelfer M. Y., Burger C., Nawani P., Hsiao B. S., Chu B., Mayu S. Rafailovich M., Panek G., Jeschke G., Fadeev A. Y., Gilman J. W.: *Clays Clay Miner.* 2007, **55**, 140.
19. Minase M., Kondo M., Onikata M., Kawamura K.: *Clays Clay Miner.* 2008, **56**, 49.