INTERCALATION AND GRAFTING OF VERMICULITE WITH OCTADECYLAMINE USING LOW-TEMPERATURE MELTING

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Abstract—Octadecylamine (ODA) was used to intercalate a fine-grained and a coarse-grained fraction of natural Mg-vermiculite (VER) using a low-temperature melting procedure. Mixtures of Mg-vermiculite fractions and powdered ODA in the molar ratios of 2:1, 1:1, 1:2 and 1:6 were homogenized and heated for 1, 3, 15 and 30 h at 80ºC to prepare intercalated samples. X-ray powder diffraction analysis of intercalated samples was combined with molecular modeling to investigate their interlayer structure. Significant amounts of non-intercalated vermiculite and diffuse peaks with very low intensity and basal spacings close to 29 Å were identified when the lowest concentration (molar ratio VER:ODA = 2:1) was used. According to molecular modeling, this indicates the initial stage of a one-layer arrangement of distorted ODA molecules in the interlayer. If the concentration of ODA molecules and treatment time were increased, a two-layer arrangement of ODA molecules with a different ODA chain-disorder and interlayer-space saturation was identified. Interlayer ODA molecules were inclined to the vermiculite basal plane with an inclination angle for two-layer arrangements that ranged from 76 to 95º. Experimental basal spacings with these two-layer arrangements varied from 52 to 58 Å and were in agreement with molecular modeling results. A fully-saturated 58 Å two-layer ODA arrangement was identified when higher ODA concentrations (VER:ODA = 1:2 and 1:6) and 15 and 30 h treatment times were used. There was no significant difference between ODA-intercalated samples prepared using fine-grained and coarse-grained Mg-vermiculite fractions. A grafted ODA-chain nano-layer with a 49.6(2.1) Å average height was observed on the surface of thin ODA-intercalated micro-flakes using atomic force microscopy. Grafted ODA chains not only created an homogeneous surface nano-layer, but also variable-width channels between the ODA molecules.

Key Words—Atomic Force Microscopy, Intercalation, Low-temperature Melting, Molecular Modeling, Octadecylamine, Vermiculite, X-ray Powder Diffraction.

INTRODUCTION

The intercalation of organic species into the interlayer space of smectites and vermiculites has been studied extensively because the resulting intercalates have interesting properties and they are useful for many industrial applications (*e.g.* as catalysts, adsorbents, thixotropic agents in lacquers and paint, sensors, and as a part of polymer/clay nanocomposites). Organic species can be introduced into the interlayer space as neutral molecules or as cations (see *e.g.* Lerf, 2000; Theng, 1974; Lagaly, 1981, 1987). If neutral molecules are intercalated into an interlayer space, the interlayer cations remain in the space between layers. An interlayer structure depends on the interlayer cations, concentration of guest molecules, the host-guest and guest-guest interactions and, in addition, on the ion-dipole interaction between the guest molecules. Intercalation of organic cations into interlayer space is based on the ion-exchange reactions, which in turn depend on the density of the layer charge, degree of exchange, type of organic cations (*e.g.* on the length of the alkyl chain) as well as on the host-guest and guest-guest interaction energy.

The intercalation processes have usually been studied by solid-liquid or solid-gas reactions, while the so-called solid-solid reaction between powdered clay and organic compound in the solid stage has not been studied much.

Solid-liquid intercalation of various organic compounds (*e.g.* lysine, L-ornithine, piperidine, cetylpyridinium bromide, benzidine and aniline) into vermiculite has been used for preparation of organic complexes of vermiculite. Investigation of their structures based on single-crystal X-ray diffraction (XRD) analysis provides important information about the arrangement of organic molecules in the interlayer space (Iglesias and Steinfink, 1974; Raupach *et al.*, 1975; Rausell-Colom and Fornes, 1974; Slade *et al.*, 1978; Slade and Raupach, 1982; Slade and Stone, 1983). The quality of intercalated crystals is the limiting factor for the accuracy of the XRD analysis and Vahedi-Faridi and Guggenheim (1997, 1999a, 1999b) showed that it is possible to prepare very good-quality periodic vermiculite crystals intercalated with mono-, di- and tetramethylammonium and tetramethylphosphonium. The X-ray analysis of single crystals also provides very good-quality data for three-dimensional refinement of their structures.

The X-ray powder diffraction method was used by Sutherland and MacEwan (1961) for analysis of vermiculite intercalated with different chain-length

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amines. They prepared intercalates using the solid-liquid reaction between vermiculites and amines in the neutral and ionic form and reported relationships between the interlayer spacings and the number of C atoms in the chains. Linear relations between basal spacings and chain lengths for neutral molecules showed that basal spacings varied from 26.5 to 56.3 Å when the number of C atoms increased from 6 to 20. The slope of the relation is ~2.3 Å per C atom, suggesting that the chains may be perpendicular to the layers. A similar linear relationship was observed for the ionic complexes, though the slope of the corresponding relation was less (~1.5 Å per C atom), suggesting that the chains may be inclined.

Brindley (1965) calculated the amine-chain inclination in the interlayer space of intercalated vermiculite using the experimental data of Sutherland and MacEwan (1961). His calculation showed that neutral amine-chains inclined at ~65° to the (001) plane, assuming fully extended amine molecules in two layer chains and amine groups closely associated with pairs of silicate oxygen. Brindley (1965) also predicted the basal spacing for amine-intercalated vermiculites with different numbers of C atoms in the chains using the same experimental data and calculated the amine-chain inclination angle. The agreement between predicted and observed basal spacings was relatively good for the number of C atoms in the chains ranging from 6 to 16. The disagreement appeared for vermiculite intercalated with octadecylamine (the predicted and observed values of the first basal spacings were 54.8 and 52.4 Å, respectively). However, octadecylamine used for the experiment was not pure. Johns and Sen Gupta (1967) prepared 4, 6, 8, 10 and 12 carbon-alkylammonium-vermiculite complexes using solid-liquid intercalation. The basal spacings ranged from 14.75 Å to 28.13 Å and the one- and two-layer arrangement of alkyl chains in the interlayer of hexylamine-vermiculite (20.79 Å) and octylamine-vermiculite (28.13 Å), respectively, using single-crystal XRD data and one-dimensional Fourier analysis, were reported. Based on the 00*l* reflections of the alkylammonium–vermiculite complexes, authors predicted the alkyl chain (with 4, 6, 8, 10 and 12 C atoms) inclination at ~55±5° to adjacent silicate surface. Generally, the following arrangements of alkylammonium chains in the interlayer of vermiculite can be recognized as monolayer, bilayer and paraffin-type complexes (Lagaly and Weiss, 1969; Lagaly, 1982). In the monolayer (13.7 Å) and bilayer (17.7 Å) complexes, the long axis of the alkylammonium molecules is parallel to the clay surface. In paraffin-type alkylammonium complexes, the long axis of the alkylammonium molecules is nearly perpendicular to the clay surface.

Solid-solid reaction is based on effective diffusion and penetration of organic species from the outer surfaces of guest solid into the interlayer space (Rastogi *et al.*, 1977). Solid-solid intercalation of organic guest species into the interlayer space of smectites has been reported by Patil *et al.* (1984), Toda *et al.* (1987), Ogawa *et al.* (1989, 1990a, 1990b, 1991, 1997). Bujdák and Slosiariková (1992) compared the results of solid-solid and low-temperature (low-*T*) melting intercalations of octadecylamine into montmorillonite. They concluded that solid-solid reaction caused the formation of intercalated compounds, though the thermal treatment of the mixture of powdered octadecylamine and montmorillonite produced a greater amount of intercalated montmorillonite. The low-*T* melting intercalation of organic compounds into vermiculite has not been reported previously.

Marcks *et al.* (1989) reported a technique for preparing vermiculites for examination by high-resolution transmission electron microscopy (HRTEM) and obtained the high-resolution lattice images of octylammonium-vermiculite. The observations showed a perpendicular arrangement of the alkyl chains with a paraffin-type orientation to the silicate layers and an average distance of 4.5 Å between the chains.

The aim of the present paper was to prepare intercalated vermiculites with a low energy of exfoliation for potential use in polymer-clay nanocomposites and, therefore, octadecylamine with long chain molecules was chosen. The low-*T* melting procedure was used for intercalation of vermiculite with octadecylamine. In the present study, computer molecular modeling combined with the X-ray powder diffraction analysis was used to investigate the structure and energy characteristics of organically modified vermiculite. Atomic force microscopy (AFM) was used for analysis of the surface of thin vermiculite micro-flakes after low-*T* melting.

EXPERIMENTAL

The Mg-rich vermiculite (VER) was collected from a weathered ultrabasic zone at Letovice, Czech Republic. The following structural formula was calculated from chemical analysis using a basis of 10 structural O and two OH and total negative charge equal to 22 per formula unit: $(Mg_{0.35}K_{0.02}Ca_{0.01})(Mg_{2.39}Fe^{3+}_{0.51}Fe^{2+}_{0.02}$ $Al_{0.08})(Si_{2.64}Al_{1.33}Ti_{0.03})O_{10}(OH)_2 \cdot 4.97H_2O$ (Weiss *et al.,* 1994). Octadecylamine, $CH_3(CH_2)_{17}NH_2$, obtained from Aldrich (97% pure; the melting point, 55–57ºC) was used as an intercalant. In order to ascertain the influence of the particle size of the vermiculite on the reactivity with octadecylamine, two grain-size fractions were chosen: The fine-grained fraction A (arithmetic mean particle diameter of 42.7 µm) with 94 vol.% of particles <100 µm, and coarse-grained fraction B (arithmetic mean particle diameter of 194.4 µm) with 41 vol.% of particles <100 µm. The laser Fritsch Particle Sizer Analysette 22 was used for particle-size analysis.

Four mixtures of fine-grained Mg-vermiculite fraction (VER-A) and powdered octadecylamine (ODA) were prepared by mixing VER-A and ODA in the molar

ratios of 2:1, 1:1, 1:2 and 1:6. Individual mixtures were homogenized with an agate mortar and pestle for a few minutes under laboratory conditions (RH = 65±5% and 25ºC) and then heated for 1, 3, 15 and 30 h at 80ºC to investigate not only the influence of ODA concentration but also the time of thermal treatment on the intensity of intercalation using low-T melting. The same procedure was applied to the coarse-grained Mg-vermiculite fraction B (VER-B) and samples with the molar ratios of VER-B:ODA = 2:1, 1:1, 1:2 and 1:6 were prepared.

X-ray powder diffraction patterns of intercalates were obtained using XRD powder diffractometer INEL equipped with the curved position-sensitive detector CPSD120 (reflection mode with a Ge monochromator and CuKα_1 radiation). A mixture of Si and Na dodecylsulfate was used as a calibration standard for CPSD120. Samples were examined after 1 h of cooling under laboratory conditions, pressed into the flat rotation holder and exposed under the same experimental conditions (2000 s, 35 kV and 15 mA).

The surface of micro-flakes selected after intercalation of coarse-grained VER-B intercalated with ODA was investigated by an AFM method (AFM-Explorer[TM], ThermoMicroscopes), at the contact mode with 8 µm Z-linearized dry scanner, silicon probe 1520-00.

MOLECULAR MODELING

The initial model of Mg-vermiculite for molecular simulations was built according to structure data published by Shirozu and Bailey (1966), with the cell parameters of the 2:1 layer a = 5.34 Å, b = 9.23 Å. In order to create a super-cell of a reasonable size for modeling (see also Čapková $et\ al.$, 1999), we had to simplify the structure formula of $2a \times 2b \times 1c$ super-cell to the form: $Mg_3(Mg_{19}Fe_4^{3+}Al_1)(Si_{21}Al_{11})O_{80}(OH)_{16}$ with the negative layer charge equal to 6. The starting super-cell parameters A = $2a$ = 10.68 Å, B = $2b$ = 18.46 Å, β = 97.68º were used for the calculations; however, the starting value of the C parameter in the initial model was set up according to basal spacing obtained from the X-ray powder diffraction data (14.35 Å). In any case, the C parameter was variable during energy minimization together with the angles β and α. The 2:1 layer was treated as rigid units during energy minimization. The rigidity of the layers required the following constraints for the energy minimization: the cell parameters A, B and γ were kept fixed. The series of initial models has been created with different concentrations of the ODA molecules and results of simulations were compared with experimental data. Molecular simulations were carried out in a Cerius[2] modeling environment (Cerius[2] documentation, 2000; Comba and Hambley, 1995).

The first 500 steps of minimization were run under an external pressure of 10 GPa. Afterwards the pressure was released and a new minimization was started. After the energy minimization using the Universal force field (Rappé $et\ al.$, 1992), quench dynamics were started in an NVT ensemble at T = 300 K. In quench dynamics, periods of dynamics were followed by a period in which the structure was minimized (100 steps of dynamics between quenches and 500 steps of minimization in quenches). The temperature was kept constant using a Berendsen thermostat (Berendsen $et\ al.$, 1984). A dynamic time step was 0.001 ps. The vermiculite layer was kept fixed during dynamic simulations. After the dynamics run for 75 ps, the system was again minimized under conditions mentioned above. The energy minimization was performed using the Minimizer module in Cerius[2]. The Ewald summation method was used to calculate the Coulomb energy in a crystal structure (Karasawa and Goddard, 1989). The Ewald sum constant was 0.5 Å^{-1} and the minimum charge taken into the Ewald sum was 0.00001 e. All atom pairs with separations <10 Å were included in the real-space part of the Ewald sum and all reciprocal-lattice vectors with lengths <0.5 Å^{-1} were included in the reciprocal part of the Ewald summation. Charges in the crystal were calculated in Cerius[2] using the QEq method (charge equilibrium approach) (Rappé and Goddard, 1991). For van der Waals energy, we used the Lennard-Jones functional form, with the arithmetic radius combination rule. A non-bond cut-off distance for van der Waals interactions was 7.0 Å.

RESULTS AND DISCUSSION

Molecular modeling

The results of molecular mechanics and dynamics simulations showed that the one-layer arrangement of guests in the interlayer of Mg-vermiculite can exist up to the concentration of 10 ODA molecules per $2a \times 2b \times 1c$ super-cell. The calculated basal spacing for this maximum concentration ODA in one layer is 36 Å. When the concentration of ODA molecules is lower, the one-layer is not fully saturated and the ODA chains are disordered. As an example, the side view of the model of the interlayer structure with one-layer arrangement of 8 ODA molecules per $2a \times 2b \times 1c$ super-cell (molar ratio VER:ODA = 1.5) and with the calculated basal spacing 30.6 Å is given in Figure 1.

Molecular modeling also showed that for concentrations >10 ODA molecules per $2a \times 2b \times 1c$ super-cell, the guests start to form a two-layer arrangement. As an example, the model of the interlayer space of intercalated vermiculite structure with two-layer arrangement of 16 ODA molecules per $2a \times 2b \times 1c$ super-cell (molar ratio VER:ODA = 0.75) and with the calculated basal spacing 52.5 Å is given in Figure 2. One can see that the two-layer structure in the interlayer is not perfectly developed; ODA chains are distorted and inclined at ~76º to the basal plane. If the concentration of ODA molecules increased, the basal spacing and inclination angle of ODA chains also increased. The model of the
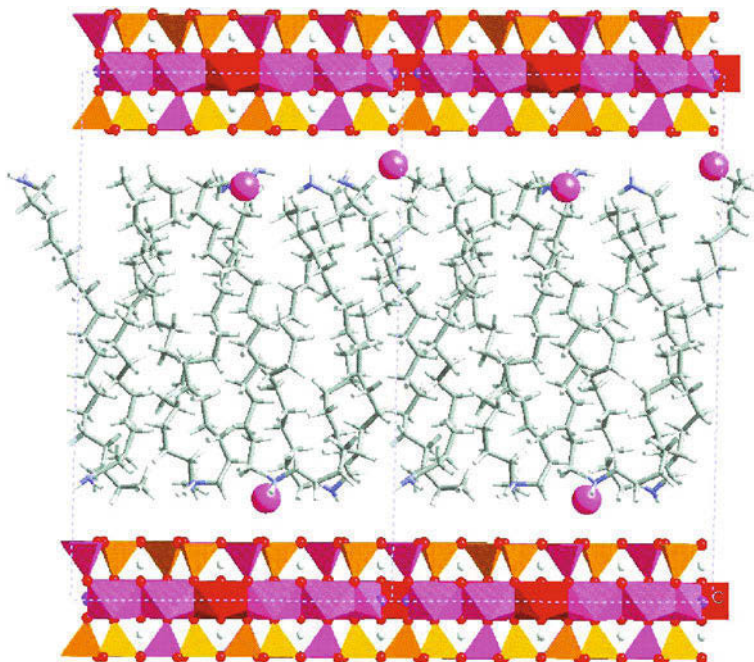
Figure 1. The side view of the structure of Mg-vermiculite intercalated with 8 octadecylamine molecules in a $2a \times 2b \times 1c$ super-cell obtained from molecular modeling after energy minimization (model VER/ODA-8). Three super-cells are visualized with Mg^{2+} cations in the interlayer as spheres.
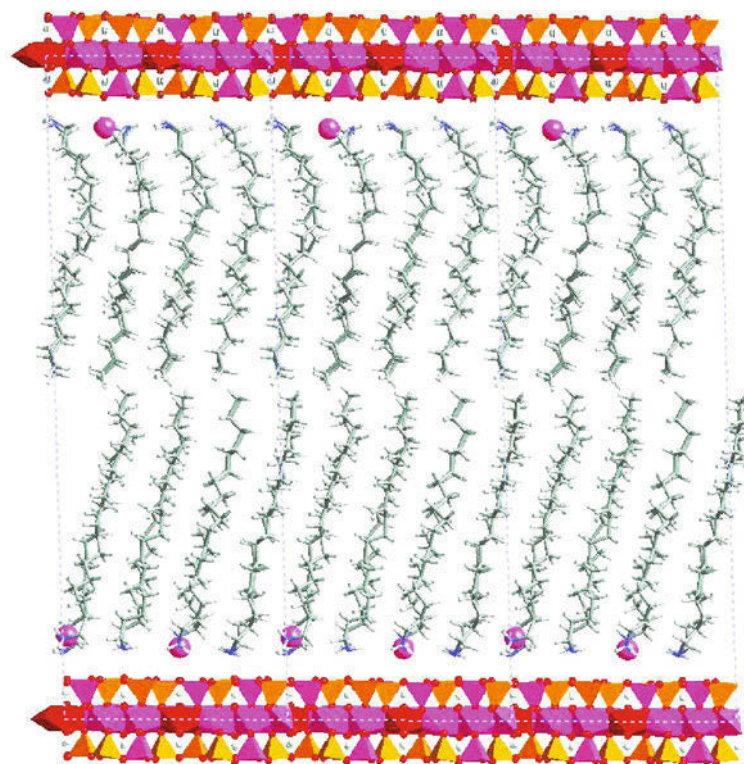

Figure 2. The side view of the structure of Mg-vermiculite intercalated with 16 octadecylamine molecules in a $2a \times 2b \times 1c$ super-cell obtained from molecular modeling after energy minimization (model VER/ODA-16). Three super-cells are visualized with Mg cations in the interlayer as spheres.
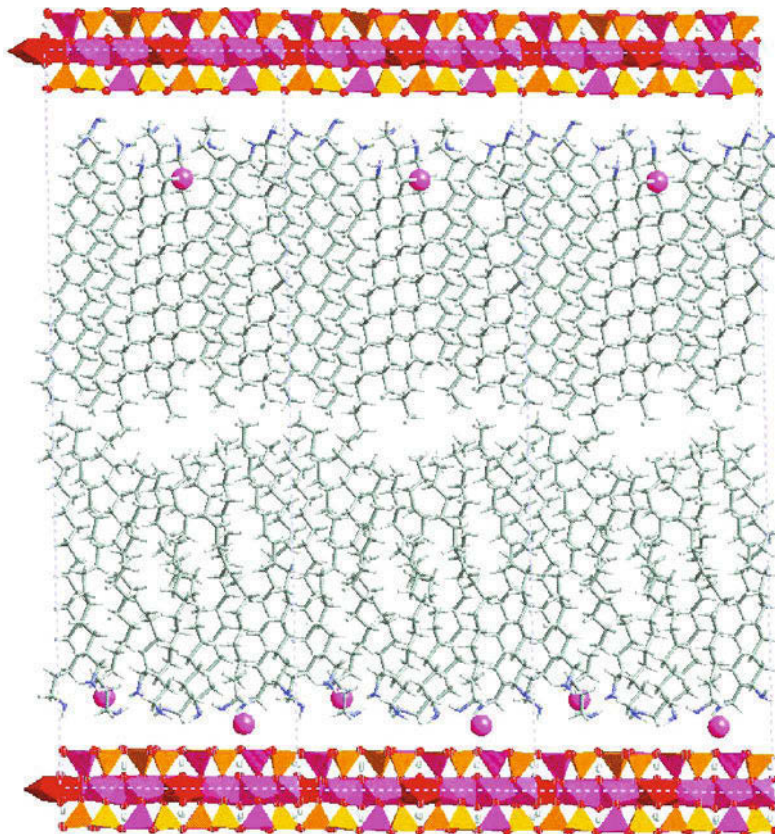
Figure 3. The side view of the structure of Mg-vermiculite intercalated with 20 octadecylamine molecules in a $2a \times 2b \times 1c$ super-cell obtained from molecular modeling after energy minimization (model VER/ODA-20). Three super-cells are visualized with Mg cations in the interlayer as spheres.

interlayer space with two-layer arrangement of 20 ODA molecules per $2a \times 2b \times 1c$ super-cell (molar ratio VER:ODA = 0.6) showed (Figure 3) that the calculated basal spacing reached 57.7 Å and partial distortion ODA chains (lower layer). Relatively ordered ODA chains in the upper layer are inclined at ~85° to the basal plane and there is a tendency to incline ODA chains at ~95° in the lower layer. A similar but more ordered zigzag arrangement in the two-layer sequence with different inclination angle of lower and upper ODA chains was observed in the fully saturated montmorillonite with the basal spacing 58 Å (Pospíšil *et al*., 2002). Our models, as well as the low-T melting procedure, are based on intercalation of neutral molecules, and therefore the interlayer Mg-cations remain in the interlayer space near the silicate layer in all calculated models.

The calculated energy characteristics for individual models described above are given in Table 1. The results show the increasing sublimation energy per super-cell including its van der Waals and electrostatic contributions with increasing stability of intercalates and guest concentration. The two-layer arrangement has greater sublimation energy and stability than the one-layer arrangement.

The exfoliation energy (important for nanocomposite technology) was calculated as the total interaction energy per super-cell between the two neighboring guest layers (including the ODA molecules and Mg cations). In the case of one-layer arrangement of guests, the exfoliation energy was calculated as the interaction energy between the guests anchored to the lower and to the upper vermiculite layer. The dramatic decrease of the exfoliation energy can be seen in Table 1 for the two-layer guest arrangement in the vermiculite interlayer. The same effect was observed for montmorillonite

Table 1. Results of molecular modeling for three models VER/ODA-8, VER/ODA-16 and VER/ODA-20 with different guest concentrations of 8, 16 and 20 ODA molecules per $2a \times 2b \times 1c$ super-cell, respectively.

Model	Calculated d (Å)	E_{subl} (kcal/mol)	E_{exfol} (kcal/mol)
VER/ODA- 8	30.6	1152	162
VER/ODA-16	52.5	2815	17
VER/ODA-20	57.7	2935	19

E_{subl} = sublimation energy; E_{exfol} = exfoliation energy; both are related to one super-cell

intercalated with ODA molecules (Pospíšil *et al.*, 2002). However, the exfoliation energy for the fully saturated two-layer arrangement of ODA in montmorillonite (E_{exfol} = 38 kcal/mol) is greater than in vermiculite (E_{exfol} = 19 kcal/mol).

X-ray diffraction

The XRD pattern of the untreated Mg-vermiculite contains a set of basal reflections with *d* values of 14.35, 7.18, 4.77, 3.59 and 2.88 Å and relative intensities of 100, 7, 13, 28 and 25%, respectively. The XRD pattern of the powdered ODA sample obtained at a room temperature contains the regular set of reflections in the range 1–10°2θ (Figure 4). No changes in the XRD pattern of the ODA sample were observed after thermal treatment for 1, 3, 15 and 30 h at 80ºC and after subsequent cooling under laboratory conditions for one hour.

The low-*T* melting at 80ºC produced a series of VER/ODA intercalates with different XRD patterns when the ODA concentration and time of treatment were changed. Therefore, the concentrations of ODA and the treatment time in the low-*T* melting procedure are crucial factors in the development of the intercalated structure. A low concentration of ODA appears to have little effect on the XRD pattern of Mg-vermiculite (Table 2). For example, in the XRD patterns of intercalated samples with molar ratio VER:ODA = 2:1 and with the treatment time exceeding 1 h, a significant amount of non-intercalated vermiculite was identified. However, in addition to vermiculite reflections, the diffuse peak with very low intensity and *d* value close to 29 Å was also observed (Figures 5a and 6a). It could indicate the early stages of a one-layer arrangement of distorted ODA molecules in the interlayer of vermiculite, similar to arrangement in the VER/ODA-8 model (Table 1). If the treatment time is equal to or <1 h, the XRD pattern contains only non-intercalated Mg-vermiculite reflections.

The XRD pattern of intercalated sample with molar ratio VER:ODA = 1:1 and 1 h treatment time also contained only non-intercalated Mg-vermiculite reflec-

tions. The significant amount of non-intercalated vermiculite was identified when the 3, 15 and 30 h treatment times were used. After 3 h of treatment, the diffuse peak with low intensity and *d* value close to 29 Å in addition to vermiculite reflections was observed. The XRD patterns of samples treated for 15 and 30 h exhibited three low-angle peaks with *d* values of the first basal reflection equal to 54.7 and 55.8 Å, respectively (Figures 5b and 6b). This indicates the development of a disordered two-layer arrangement of ODA molecules in interlayers which are not fully saturated.

The XRD patterns of intercalated samples with molar ratio VER:ODA = 1:2 exhibit significant changes in comparison with the patterns of non-intercalated Mg-vermiculite (*e.g.* Figures 5c and 6c). The basal spacing of intercalated samples varied from 51.5 to 58.3 Å when the treatment time changed from 1 to 30 h (Table 2). The profile fitting analysis of XRD patterns of those samples showed that sets of new low-angle basal reflections with a different degree of the regularity of the d_{00l} values and with a different distribution of intensity of basal reflections appeared in the samples treated for 1, 3, 15 and 30 h at 80ºC. To characterize the degree of regularity of the d_{00l} values, the coefficient of variation (CV) was used. Bailey (1982) defined CV = $100s/<x>$, where $<x>$ is the mean of the individual observed $l \times d_{00l}$ values, and *s* is the standard deviation for a small sample. In the ideal case of 'single-phase' crystals CV = 0, and according to Bailey (1982), the coefficient of variation should be <0.75 to demonstrate adequate regularity of alternation of layers in the regularly interstratified structures. The XRD patterns of the samples treated for 1 and 3 h exhibit rather non-integral d_{00l} values (CV = 1.8 and 1.2, respectively) with the *d* value of the first basal reflections equal to 51.5 and 52.9 Å, respectively. It indicates the early stages of the disordered two-layer arrangement of ODA molecules in the interlayer, like the arrangement in the VER/ODA-16

Figure 4. XRD pattern of octadecylamine, $CH_3(CH_2)_{17}NH_2$ (from Aldrich, 97% pure).

Table 2. Observed *d* value of the first basal reflection (*d*, in Å) obtained from XRD analysis of intercalated Mg-vermiculite (VER) samples with octadecylamine (ODA) using low-*T* melting. Fine-grained and coarse-grained fractions (VER-A and VER-B, respectively) of Mg-vermiculite were intercalated with ODA in the molar ratios 2:1, 1:1, 1:2 and 1:6 and heated for 1, 3, 15 and 30 h at 80ºC.

Vermiculite fraction	Treatment time (h)	VER:ODA (molar ratio)			
		2:1	1:1	1:2	1:6
VER-A	1	–*	–*	51.5	51.7
	3	29[†]	29[†]	52.9	53.6
	15	29[†]	54.7	58.3	58.4
	30	29[†]	55.8	58.3	58.4
VER-B	15	29[†]	54.4	58.2	58.3
	30	29[†]	55.2	58.3	58.4

* Only non-intercalated vermiculite reflections are present
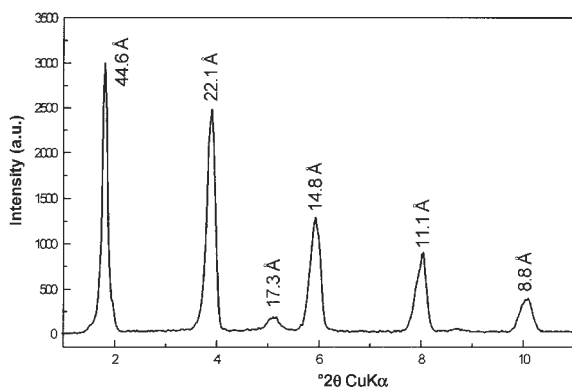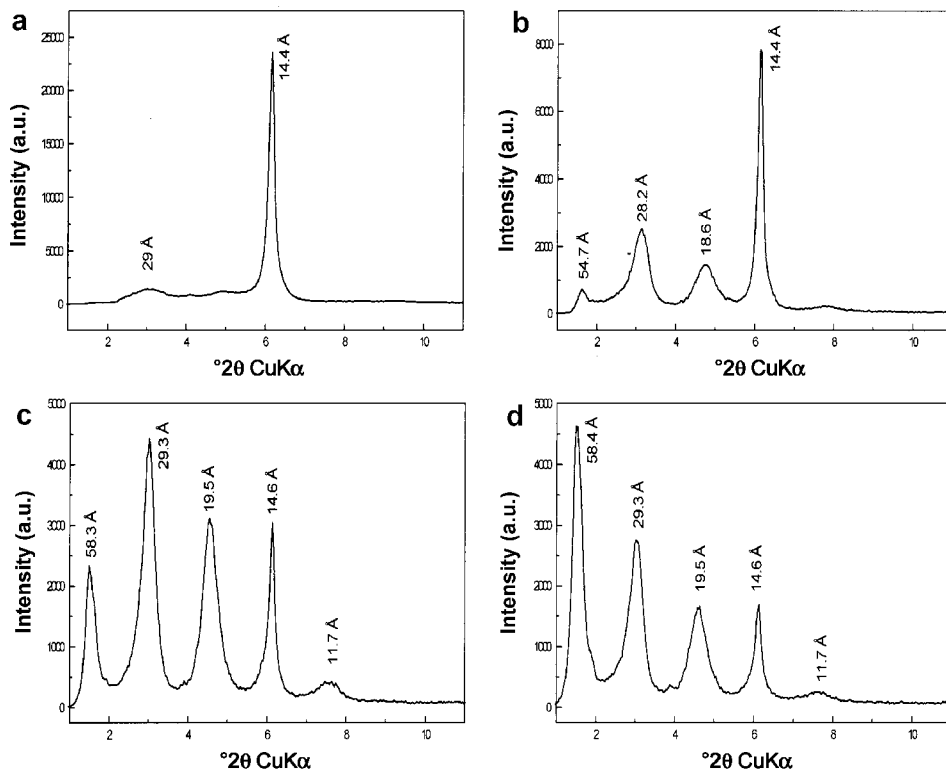[†] Diffuse peak with very low intensity

Figure 5. XRD patterns of Mg-vermiculite (VER) intercalated with octadecylamine (ODA) in molar ratios VER:ODA equal to 2:1 (a), 1:1 (b), 1:2 (c) and 1:6 (d) using low-*T* melting at 80ºC for 15 h.
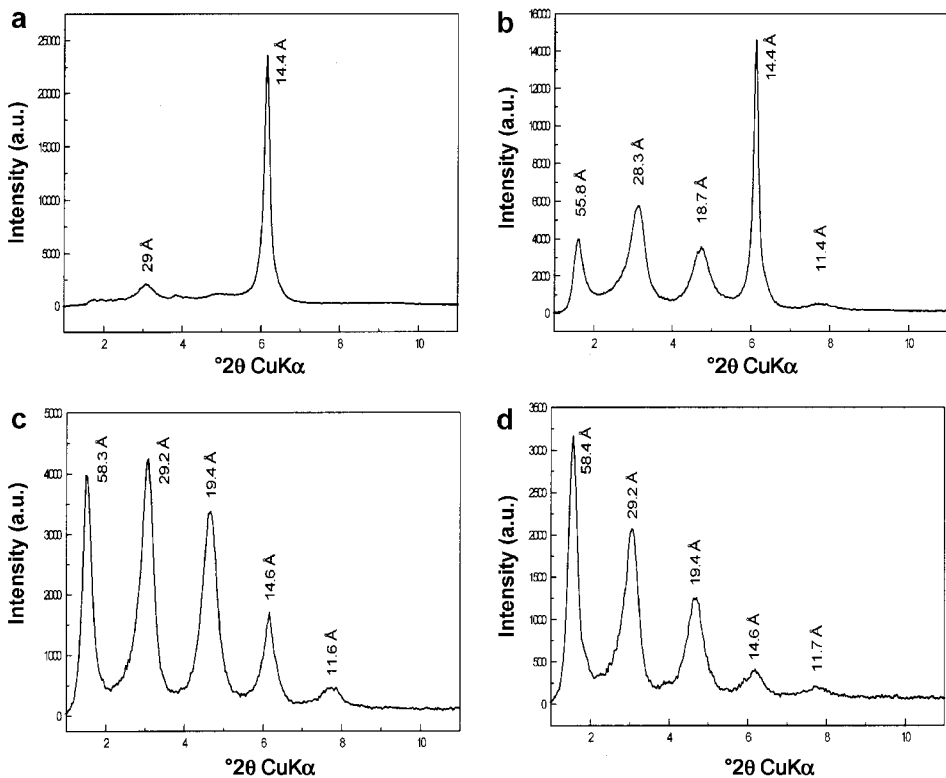

Figure 6. XRD patterns of Mg-vermiculite (VER) intercalated with octadecylamine (ODA) in molar ratios VER:ODA equal to 2:1 (a), 1:1 (b), 1:2 (c) and 1:6 (d) using low-*T* melting at 80ºC for 30 h.

model (Table 1). However, the CV values also indicate some irregularities in the sequence of layers (*e.g.* the irregular interstratification of the layers with different degrees of intercalation). If the treatment time increased, the XRD patterns of the samples treated for 15 and 30 h exhibited integral d_{00l} values (CV = 0.2 and 0.3, respectively) with the first basal reflection equal to 58.3 Å (Figures 5c and 6c). This indicates the fully saturated stage with the two-layer arrangement of ODA molecules in the interlayer, similar to the arrangement in the VER/ODA-20 model (Table 1). In both cases, the lower CV values indicate the 'single 58 Å phase' rather than regular interstratification of the layers with different degrees of intercalation.

The XRD patterns of samples intercalated with molar ratios VER:ODA = 1:2 and VER:ODA = 1:6 are quite similar, though some differences appeared in the basal spacings and distribution of intensities of low-angle reflections (compare Figures 5c and 5d, or 6c and 6d). The basal spacings of samples intercalated with molar ratio VER:ODA = 1:6 varied from 51.7 to 58.4 Å (Table 2) if the treatment time was changed from 1 to 30 h. The XRD patterns of the samples treated for 1 and 3 h also exhibit non-integral d_{00l} values (CV = 1.9 and 1.0, respectively) with the *d* values of the first basal reflection equal to 51.7 and 53.6 Å, respectively. This also indicates the early stages of the disordered two-layer arrangement of ODA molecules in the interlayer. The samples treated for 15 and 30 h exhibited integral d_{00l} values (CV = 0.1 and 0.2, respectively) with the *d* value of the first basal reflection equal to 58.4 Å (Figures 5d and 6d). The basal spacing and lower CV values also indicate the fully saturated 'single 58 Å phase' with the two-layer arrangement of ODA molecules.

The low-*T* melting procedure was also used for intercalation of a coarse-grained vermiculite fraction VER-B with ODA in the molar ratios of 2:1, 1:1, 1:2, and 1:6. The XRD patterns (ranging 1–10º2θ) of the intercalated samples treated for 1, 3, 15 and 30 h were very similar to those obtained for a fine-grained fraction of vermiculite VER-A. The basal spacings obtained from a coarse-grained vermiculite fraction treated for 15 and 30 h are given in Table 2.

As mentioned above, Sutherland and MacEwan (1961) published the basal spacing of 52.4 Å for vermiculite intercalated with neutral ODA molecules but the ODA sample was not pure, and therefore, the comparison of that with our results is rather problematic. Brindley (1965) predicted a greater basal spacing (54.8 Å) for ODA-intercalated vermiculites. However, according to our results, such basal spacing corresponds to an interlayer which is not fully saturated with the development of disordered two-layer arrangement of ODA molecules (*cf.* basal spacings of intercalated samples with molar ratios of 1:1 and 1:2 for 15 h treatment time in Table 2). To compare the results for

vermiculite and montmorillonite intercalated with ODA molecules, it follows that the basal spacings of 58 and 57 Å given by Pospíšil *et al.* (2002), and by Ogawa *et al.* (1990b), respectively, for a fully saturated two-layer arrangement of ODA molecules in the interlayer of montmorillonite are close to our results for vermiculite (58 Å). Pospíšil *et al.* (2002) also described the basal spacings which correspond to the one-layer (31–33 Å) and disordered not fully saturated two-layer arrangement (50–55 Å) of ODA molecules in the interlayer of montmorillonite. Comparable results were obtained in our work for a disordered not fully saturated two-layer arrangement of ODA molecules in the interlayer of vermiculite (51–55 Å). Identification of the one-layer arrangement in vermiculite was rather problematic (diffuse peak with very low intensity and *d* value close to 29 Å), while the basal reflections in the XRD patterns of intercalated montmorillonite are clearly visible.

Atomic force microscopy

Using AFM, the grafted nano-layers of ODA chains on the surface of thin micro-flakes selected from intercalated coarse-grained fraction (VER-B) with ODA in the molar ratios 1:2 (treated for 15 h) were observed, and the height of grafted molecular chains was measured. A 3D AFM image of grafted ODA chains is given in Figure 7, for illustration. Grafted ODA chains create not only homogeneous nano-layers but also some channels with different widths. These channels were used to measure the height of grafted ODA chains. Analysis of 15 different micro-surface profiles taken from different micro-flakes showed that the height of grafted ODA chains varies from 40.8 to 59.7 Å and the average height is 49.6(2.1) Å. The width of the channels between grafted chains varies from 21 to 1534 Å, though there are a lot of fields homogeneously covering the micro-flake surface, like nano-layers 7000 × 7000 Å in size and 50 Å in height, approximately.

We suggest that the existence of channels with various shapes and positions can be caused by corrugation of the surface (in nano-scale) and/or by different charge distribution on the surface. Dehydration of Mg-vermiculite after heating at 80ºC causes not only partial reversible collapse of the interlayer structure (the basal spacing decreases from 14.35 to 13.8 Å) but also irreversible nano-scale surface corrugation as we observed on the different flake after heating at 80ºC. The surface corrugation varies from units of Å to thousands of Å as a function of temperature. For example, after heating at 800ºC we observed exfoliation of flakes together with significant corrugation of the surface owing to spontaneous escape of the interlayer molecular water. Therefore, the system 'peak-valley' might be expected to form on the surface of Mg-vermiculite during low-*T* melting, and ODA molecules probably prefer the 'valley' parts in the surface for developing the grafted chains. If the field of the micro-
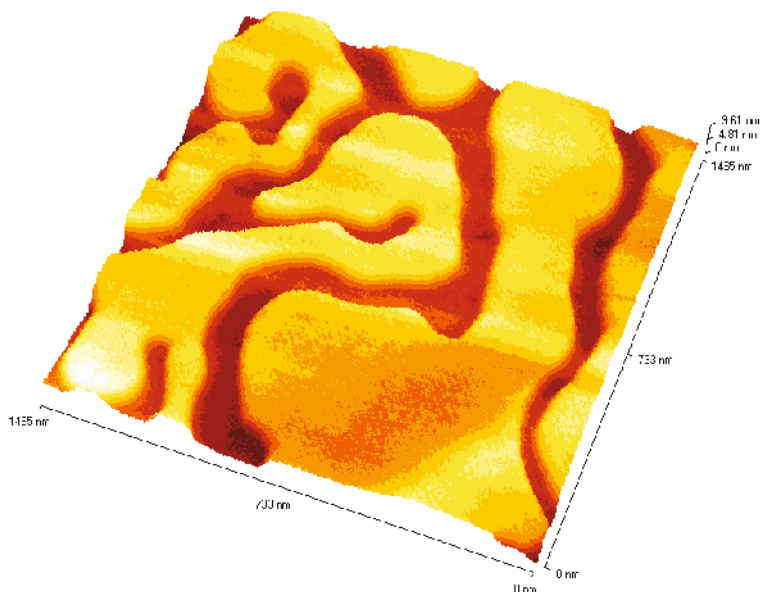
Figure 7. 3D AFM images of grafted nano-layers of ODA chains on the surface of Mg-vermiculite micro-flakes.

flake is non-corrugated the nano-layer of grafted chains covered its surface homogeneously.

CONCLUSIONS

The results of molecular modeling showed that the one-layer arrangement of ODA molecules in the interlayer of Mg-vermiculite can exist up to the concentration of 10 ODA molecules per $2a \times 2b \times 1c$ super-cell (molar ratio VER:ODA = 1.2). The calculated basal spacing for this maximum concentration of ODA in the one-layer is 36 Å. Molecular modeling also showed that for concentrations >10 ODA molecules per one $2a \times 2b \times 1c$ super-cell, the guests start to form a two-layer arrangement and the basal spacing increased significantly. The model of the interlayer space with two-layer arrangement of 20 ODA molecules per $2a \times 2b \times 1c$ super-cell showed (molar ratio VER:ODA = 0.6) that the calculated basal spacing reached 57.7 Å. Relatively ordered ODA chains in the interlayer were inclined to the vermiculite basal plane with an inclination angle for two-layer arrangements that ranged from 76 to 95°. Exfoliation energy of intercalates decreased significantly with increasing guest concentration. Calculated exfoliation energy for the two-layer arrangement (19 kcal/mol) was lower than the energy calculated for the one-layer guest arrangement (162 kcal/mol) in the vermiculite interlayer.

Both the ODA concentrations and the treatment time are important factors in the development of an intercalated structure when the low-T melting procedure is used. Low concentration of ODA (molar ratio VER:ODA = 2:1) had little effect on the XRD pattern of Mg-vermiculite (Table 2). A significant amount of non-intercalated vermiculite and a diffuse peak with very low intensity and d value close to 29 Å were identified when the treatment time was >1 h (Figures 5a and 6a). This could indicate that there was a preliminary stage of one-layer arrangement of distorted ODA molecules in the interlayer. The XRD pattern of the sample contained only non-intercalated Mg-vermiculite reflections when the sample was treated for only 1 h.

The same pattern was observed for intercalated samples with molar ratios VER:ODA = 1:1 and 1 h of treatment. When the treatment time was >1 h (3, 15 and 30 h) the significant amount of non-intercalated vermiculite was identified in corresponding XRD patterns. The first 29 Å diffuse peak with low intensity was observed after 3 h of treatment and three low-angle peaks with d spacings for the first basal reflection of 54.7 and 55.8 Å were observed for the samples treated for 15 and 30 h, respectively (Figures 5b and 6b). This indicates the development of a disordered two-layer arrangement of ODA molecules in the interlayer which was not fully saturated.

The XRD patterns of samples intercalated with molar ratios VER:ODA = 1:2 and VER:ODA = 1:6 are very similar. Some differences appeared in the basal spacing and distribution of intensities of low-angle reflections. The basal spacing of samples intercalated for a treatment time from 1 to 30 h varied from 51.5 to 58.4 Å (Table 2). The XRD patterns of samples treated for 1 and 3 h exhibited non-integral d_{00l} values (the d values of the first basal reflections varied between 51.5 and 53.6 Å). This indicates an early stage of the disordered and not fully saturated two-layer arrangement of ODA molecules in the interlayer. The samples treated for 15 and 30 h exhibited integral d_{00l} values (the d spacing for

the first basal reflections varied between 58.3 and 58.4 Å) (Figures 5c,d and 6c,d). The XRD results indicated a fully saturated 'single 58 Å phase' with the two-layer arrangement of ODA molecules in the interlayer.

Grafted nano-layers of ODA chains with average height of 49.6(2.1) Å were found, using AFM, on the surfaces of thin micro-flakes selected from the inter-calated coarse-grained sample. Grafted ODA chains create not only homogeneous nano-layers on the surface but also channels of different widths (Figure 7). We suggest that the existence of channels with various shapes and positions can be caused by nano-scale corrugation of the surface and/or by different charge distribution on the surface.

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