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SILANE MODIFICATION OF LAYERED SILICATES AND THE MECHANISM OF
NETWORK FORMATION FROM EXFOLIATED LAYERS

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ABSTRACT

The edges of a synthetic layered silicate, Laponite XLG, was successfully modified with various amounts of ethoxytrimethylsilane, a monofunctional silane compound. The occurrence of the reaction was confirmed with various methods. Thermogravimetric measurements and the Fourier-transform infrared spectroscopy (FTIR) analysis of both the treated filler and the reaction medium yielded a saturation like correlation as a function of the amount of the silane used for treatment. The analysis of the bonded amount of silane by FTIR spectroscopy showed that a side reaction takes place during modification. Although the expected dimerization did not occur, the silane hydrolyzed, thus systematically changing the amount of bonded silane determined from the absorption of oxygen containing groups. Only vibrations related to the absorption of the $-\text{SiCH}_3$ group can be used for quantitative analysis. X-ray diffraction (XRD) measurements proved that the silane is bonded onto the surface of the silicate and it does not enter the interlamellar space. Approximately 50 mg silane is bonded to 1 g silicate corresponding to almost complete reaction of the surface $-\text{OH}$ groups. The results of the measurements were supported by model calculations and extremely good agreement was found between the calculated and the measured values. Surface modification did not hinder the formation of a house-of-card structure showing that the generally accepted mechanism of network formation needs revision. An explanation was offered based on the release of hydroxyl ions from the $-\text{MgOH}$ moiety of the silicate. The

modification of the edges of layered silicates may facilitate exfoliation or help functionalization, but does not prevent network formation and cannot be used for the control of rheological properties.

Keywords: laponite, edge modification, functional silane, surface coverage, gallery structure, house-of-card structure

1. INTRODUCTION

A few years ago layered silicate nanocomposites generated considerable interest in both academia and industry. Intensive research was done to prepare such composites for practical applications. Layered silicate fillers were claimed to create large interfaces resulting in significant reinforcement at small filler content. The condition of reinforcement is the complete, but at least large extent of exfoliation of the clay and the even dispersion of the platelets in the polymer matrix. Unfortunately, large exfoliation and homogeneous structure was rarely achieved in spite of numerous claims. A complex structure formed in most composites prepared from layered silicate fillers, which consisted of individual silicate layers, but also intercalated stacks or tactoids, large original particles and occasionally a silicate network. Since structure could not be controlled and properties tailored to the requirements of specific applications, the interest in layered silicate nanocomposites ebbed somewhat in recent years.

Since the cohesive forces among the layers of the silicate are strong, the exfoliation of neat, unmodified silicates is difficult or outright impossible. Surface modified silicates are used in the composites practically always. Surface modification is claimed to improve the compatibility between the hydrophobic polymer matrix and the hydrophilic clay [x], but in fact, it facilitates exfoliation. Two kinds of surface modifications can be used for layered silicates. The most often the inorganic cations located among the silicate layers are exchanged for organic cations, usually long chain amine salts. These long chain aliphatic amines located among the layers increase gallery distance and decrease the strength of interactions among the layers. However, this treatment alone usually do not result in large extent of exfoliation and often a compatibilizer is need as well to achieve reasonable properties [x].

The other approach to modify the surface characteristics of layered silicates is to coat them with organic silanes. Quite often various clays are modified with organofunctional silanes and considerable success was claimed in some cases, often without sufficient proof or explanation. Silicates can be modified with mono- or trialkoxy silanes. The latter usually leads to the formation of a polysiloxane layer on the surface of the silicate, which decreases surface energy, but can hinder exfoliation significantly [Herrera, JMC]. Contrary to long chain aliphatic amine salts, silanes can react chemically with the hydroxyl groups located at the edges of the silicate platelets. Reaction

with monoalkoxy silanes covers the edges of the particles with aliphatic groups, and decrease their surface energy and the strength of interactions. Such a modification may facilitate exfoliation and in the case of functional groups, it can result in the coupling of the polymer and the silicate [x]. Several groups studied the chemistry of such silane modification and also its consequences. Daniel et al. [x] modified laponite with n-octyldimethylsilane and studied the effect of reaction and settling time, as well as sonic treatment on the amount of bonded silane. They found that the maximum amount of silane bonded onto the surface was 0.08 mmol/g, while Herrera et al. [x] could attach 0.5 mmol/g γ -metacryloxy dimethyl methoxysilane to the surface of laponite. The reason for the one order of magnitude difference was not explained; and is not clear, since the size of the silane molecules or the difference in the surface area of the silicate does not justify it. The possible effect of this modification on structure formation in layered silicate nanocomposites was not discussed, and remains a question to be answered later.

A large extent of exfoliation often leads to the formation of a silicate network, frequently called house-of-card or scaffold structure. The formation of such a structure is the result of electrostatic interactions between the negatively charged lateral surface of the plates and the positively charged edges. The formation of such a structure was confirmed also in layered silicate nanocomposites by a number of groups

[Reichert1,2, Okamoto, Wagener, Karger, Zhang]. The exact influence of the network structure on composite properties is not known; both disadvantageous and beneficial effects were mentioned. The presence of the house-of-card structure increases melt viscosity and melt elasticity [Reichert1,2, Okamoto, Wagener], which is disadvantageous for the processing of the material. The sensitivity to shear and changing structure might be disadvantageous as well; both strong shear thinning [Wagener] and shear-thickening [Okamoto] behavior was observed depending on the conditions of the study or processing. On the other hand, beneficial effect was reported in elastomers, very good anti-collapsing behavior was observed in silicon elastomers at medium high temperature [Zhang], while strong reinforcement, large stiffness and strength in natural rubber vulcanizates [Karger]. If the accepted mechanism of the formation of the silicate network is true, the silane modification of the edges of silicate platelets should change also the development of such structure and consequently the properties of the composites.

The goal of the present study was to modify the edges of a layered silicate, laponite, with a monoalkoxy silane in order to replace silanol groups with an organic moiety. The reactions, including side reactions, taking place during the modification are investigated in detail by the analysis of the modified silicate and the reaction medium. Surface coverage is determined in different ways and the results are compared to model calculations. The effect of surface modification on the

formation of a house-of-card structure is investigated by rheology. A model is proposed for the mechanism of network formation, and the possible consequence for practice is briefly mentioned in the final section of the paper.

2. EXPERIMENTAL

2.1. Materials

Laponite XLG obtained from Byk Additives and Instruments was used as the layered silicate studied. Its density is 2.53 g/cm³, cation exchange capacity 55 meq/100 g and a specific surface area of 388 m²/g was measured for it by nitrogen adsorption using the BET method. The surface area of the completely exfoliated clay is 906 m²/g as determined by the methylene blue approach [x]. According to the producer, the diameter of the individual platelets is 25 nm and its thickness 0.92 nm. The ethoxytrimethylsilane (ETMS) used for the surface modification of the silicate was purchased from the Tokyo Chemical Industry Co. Ltd. with a purity of > 98 %. Hexamethyldisiloxane (HMDS) was used as reference compound to check the occurrence of side reactions during surface modification; it was a product of 98 % purity obtained from the Tokyo Chemical Industry Co. Ltd. Toluene used as solvent was purchased from Molar Chemicals Ltd. with a purity of 99.99 %. All reagents were used as received without further purification. The experiments were done at room temperature (25 °C) and atmospheric pressure.

2.2. Surface modification

Surface modification was carried out in a toluene suspension of 120 g/dm³ concentration. 6 g silicate was weighed into the reaction flasks and 50 ml ETMS solution with various silane concentrations was added. The reaction was continued for two days under continuous stirring with a magnetic stirrer. The amount of silane changed from 0 to 800 mmol/100 g silicate in 12 steps.

After two days, the suspension was let to settle and then the clear solution was filtered using a PTFE filter with 0.45 μm pore diameter. The filtrate was washed three times with toluene to remove the physically adsorbed silane. The supernatant and the washing solution were put aside for further characterization. The silicate removed from the beaker—and finally dried. The amount of dissolved ETMS was determined by Fourier-transform infrared spectroscopy (FTIR) with the help of calibration.

2.3. Characterization

The solution decanted from the suspension and the dried silicate were analyzed by FTIR spectroscopy. The spectra were recorded with a Bruker Tensor 27A apparatus in the 4000 and 400 cm^{-1} wavenumber range with 2 cm^{-1} resolution and 64 scans. Solutions were studied in a KBr cuvette of 118 μm optical path, while powders were characterized in KBr pastilles containing 1

mg sample in 250 mg KBr.

Thermal gravimetric measurements (TGA) were carried out using a Perkin Elmer TGA 6 instrument. The measurements were done on samples of 15-20 mg weight in oxygen atmosphere. The temperature program consisted of three steps: thermostating at 30 °C for 1 min, heating up to 800 °C with a rate of 10 °C/min and then maintaining this temperature for 10 min.

The gallery structure of filtered and dried silicates was characterized by X-ray diffraction. The measurements were carried out using a Phillips PW 1830/PW 1050 equipment in the range of $2-12^\circ 2\theta$ angles with $\text{CuK}\alpha$ radiation (0,154 nm) at 40 kV and 35 mA anode excitation.

The viscosity of the aqueous suspensions with various concentrations of the neat Laponite XLG and the silicate modified with 100 mmol/100 g silicate ETMS were determined with an Anton Paar Physica MCR 301 rheometer with cone-plate geometry (CP25-1) at 0.1 s^{-1} shear rate. The gap was 0.049 mm, and the temperature was maintained at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ using the Peltier system of the rheometer.

3. RESULTS AND DISCUSSION

The results will be discussed in several sections. The modification reaction and the amount of bonded silane are presented first, then the apparent contradiction in the results and possible side reactions are analyzed subsequently. The location of the silane and the gallery structure of the silicate

are discussed next, followed by theoretical considerations; consequences for practice are also mentioned briefly in the last section of the paper.

3.1. Surface modification

The amount of ETMS bonded onto the surface of the silicate was determined with thermogravimetric measurements first. Weight loss measured in the temperature range of 200 and 600 °C results from the evaporation of water and the degradation of the organic compound bonded to the surface. The results obtained on the coated samples were corrected with the weight loss measured on the neat, non-reacted silicate, which loses only water adsorbed on its surface. The weight loss of the silicate samples is plotted against the amount of the silane compound used for modification in [Fig. 1](#). The scatter of the points is considerable and the results might be biased by the fact that organically modified samples bind less water than the neat silicate, but the tendency is clear. A saturation type correlation is obtained indicating that the silane reacts with active hydroxyl groups located at the edges of the silicate, the number of which is limited. According to the results of [Fig. 1](#), saturation concentration is around 2.2 wt% organic content. The molecular weight of the moiety bonded to the surface is 71.25 g/mol, while the molecular weight of the initial silane is 118.25 g/mol, thus this saturation weight corresponds to a surface coverage of 37.3 mg silane/g silicate.

Because of the standard deviation and possible bias of the TGA measurements, the amount of bonded silane was checked by further measurements. The FTIR spectrum of the laponite sample treated with **xxx mmol silane** is presented in **Fig. 2** together with the assignment of the characteristic absorbance peaks. The region containing the vibration of the $-\text{SiCH}_3$ group is shown in the inset with larger magnification for the neat silicate and two samples treated with different amounts of silane. The spectra clearly prove that the reaction takes place indeed (the silicate was washed to remove the unreacted silane) and the saturation character of the reaction as well. For quantitative characterization the OH bending vibration appearing at 653 cm^{-1} ($\delta\text{Mg}_3\text{OH}$) was used as internal standard. The relative peak area of the $-\text{SiCH}_3$ vibration is plotted against the amount of silane used for treatment in **Fig. 3**. The concentration dependence of the relative peak area of a vibration, which should not change as an effect of surface modification is also plotted in order to verify the procedure. We can see that the intensity of this latter, the relative peak area of the combined vibration of the Si-O-Mg and Si-O-Si bending bands appearing at 464 and 449 cm^{-1} does not change at all during modification. On the other hand, the relative peak area of the characteristic vibration of the methylsilane group shows the same tendency as that obtained by the TGA measurements. Although the scatter of the points is considerable again because of the small intensity of this vibration, the tendency is unambiguous. Nevertheless, the

results give only a qualitative picture about the effect of surface modification, and because of the large standard deviation of the determination, we need further data to determine the amount of bonded silane and surface coverage quantitatively.

The analysis of the reaction solution can yield the amount of bonded silane quantitatively. After calibration, the amount of silane can be determined in the reaction medium and in the washing solution and the difference of added silane and the amount found in the two solutions gives the quantity of silane bonded to the surface of the silicate. The silane compound used for the surface modification of laponite has several characteristic peaks, which can be used for quantitative analysis. The dependence of the amount of retained ETMS determined from two vibrations on the amount of silane used for modification is shown in **Fig. 4**. Rather surprisingly two different correlations are obtained; in fact, the six correlations determined can be divided into two well-defined groups. The absorbance of vibrations belonging to the $-\text{SiCH}_3$ group appearing at 1259, 1251 and 842 cm^{-1} shows saturation tendency similarly to the results obtained by the TGA measurements and the FTIR characterization of the silicate powder. On the other hand, the intensity of the groups containing oxygen, i.e. the $-\text{SiO}-$ (1165 cm^{-1}), $-\text{SiOC}-$ (1108 cm^{-1}) and the $-\text{OCH}_2\text{CH}_3$ (947 cm^{-1}) groups, is considerably larger and increases continuously. The results also clearly show that the scatter of the points determined from the vibration of the $-\text{SiCH}_3$ group is

much larger than in the second case, for the groups containing oxygen. The dissimilarity needs explanation and the contradiction must be resolved in order to be able to carry out the further analysis of the results.

3.2. Side reactions

One possible explanation for the discrepancy mentioned in the previous paragraph is the occurrence of a side reaction or side reactions. The modification of the silicate with the silane used in our experiments theoretically should proceed according the reaction presented in [Scheme 1](#). We can safely assume, as the scheme shows, that a silane platelet can react at two positions, one above the other, at its edges (see also later) resulting in the formation of ethanol. On the other hand, two side reactions can also take place during modification, the hydrolysis of the silane and its dimerization as shown by [Scheme 2](#).

According to the [Scheme 2](#), the number of the $-\text{SiCH}_3$ groups is equivalent in the trimethylsilanol and the stoichiometrically forming hexamethyldisiloxane compound. Accordingly, the concentration of this group does not change in the reaction medium, even if these side reactions take place. On the other hand, the oxygen containing groups analyzed ($-\text{SiO}-$, $-\text{SiOC}-$, $-\text{OCH}_2\text{CH}_3$) can be found only in the ethoxytrimethylsilane compound thus if side reactions take place, their number decreases in the solution. A smaller amount of a group in the reaction medium indicates larger amount of silane bonded to the silicate surface.

In order to check the possibility of dimerization, the spectrum of the dimer was recorded and the peaks appearing in the spectrum were assigned to the corresponding groups. In **Fig. 5**, the spectrum of HMDS is compared to that of the silane reagent, ETMS, and **the reaction solution, which contained originally xxx mg/g silane, after the reaction**. Only the siloxane contains the -Si-O-Si- moiety and the comparison of the spectra presented in **Fig. 5** clearly shows that the vibration of this group is absent in the spectrum recorded on the reaction medium, and naturally, it cannot be found in the spectrum of ETMS either. This result clearly shows that the side reaction, which takes place during the surface modification of the silicate by the silane, is not the dimerization of the latter.

The other possible side reaction presented in **Scheme 2** is the hydrolysis of the silane used for surface modification. The reaction products, both the silanol compound and ethanol, of this side reaction absorb in the wavelength range above 3500 cm^{-1} . The corresponding range of the spectrum of the reaction medium is plotted in **Fig. 6** together with the FTIR spectrum of ethanol. The comparison clearly proves the presence of both compounds in the reaction medium, the absorbance of the silanol group at 3639 cm^{-1} overlaps with the -OH group of ethanol appearing at 3600 cm^{-1} . The spectra in **Fig. 6** confirm that the hydrolysis of the silane takes place during surface modification leading to the consumption of the reagent and thus indicating larger amount of bonded silane. Further analysis confirmed that the amount of

bonded silane calculated from vibrations related to the $-\text{SiCH}_3$ group is always smaller than that derived from the vibrations of oxygen containing groups. This conclusion is important, since in one case the absorbance of the $-\text{OCH}_2\text{CH}_3$ group was chosen as reference, when the reaction medium was used for the quantitative determination of the amount of bonded silane [N16].

After the identification of the vibrations, which can be used for quantitative analysis, we could calculate the maximum amount of bonded silane. We obtained 50 mg/g, which differs about 20 % from the value determined by TGA. However, because of the small weight losses measured by TGA led to large standard deviation and the possible bias of the dissimilar water absorption of the treated and the neat filler, we regard the value determined with FTIR analysis as more relevant. The validity of this value will be further checked by theoretical considerations.

3.3. Gallery structure, location

The structure of layered silicates treated with organofunctional silane compounds can be quite complicated. Silanes having two and especially three alkoxy groups usually form polysiloxanes on the surface of the silicate, the structure and properties of which depend very much on the chemical character of the organofunctional group. We used a monofunctional silane, which cannot polymerize, but only reacts with the active hydroxyl groups located at the edges of the

silicate platelets. Although polymerization cannot occur, the silane can adsorb on the plane surface of the silicate and can also diffuse into the space among the plates, it can be located in the gallery space. Accordingly, we checked this latter possibility and characterized the silicate with X-ray diffraction measurements.

The traces recorded on silicates treated with different amounts of the silane are presented in **Fig. 7** in the range of the silicate reflection. The reflection is rather diffuse indicating less order than in the case of montmorillonite, for example. Nevertheless, the peak of the silicate can be identified unambiguously in each case. Compared to the neat, untreated silicate, the peak shifts towards smaller 2θ angles corresponding to larger gallery distance. This could indicate the diffusion of the silane among the layers. However, we must call the attention here to the fact that the layer distance of the silicate that went through the surface treatment procedure, but only with the solvent (toluene) without any silane, is also larger than that of the neat filler. We must assume that the solvent diffused into the galleries, and could not be removed completely during drying thus increasing layer distance.

Gallery distance was calculated from Bragg's law and it is plotted against the amount of silane used for treatment in **Fig. 8**. Layer distance does not change with increasing amount of the silane. The scatter of the points seems to be considerable, but it is smaller than 0.1 nm, which is less than the distance of

one C-C bond, thus we can conclude that the compound used for surface modification does not diffuse into the gallery space, but reacts with the edges of the platelets. We must remind the reader here to the fact that the silicate was thoroughly washed with toluene, thus unreacted, physisorbed silane molecules were completely removed before the measurements.

3.4. Discussion, consequences

The amount of silane, which theoretically can be bonded to the surface of a laponite platelet, was estimated also by model calculations. The basis of the calculation was the reaction presented in [Scheme 1](#). The geometry optimization of the attached silane molecule was carried out with the Avogadro software. The space occupied by a silane molecule was approximated with a sphere with a radius, which corresponds to the distance of the Si2 atom and the farthest hydrogen in the molecule (see [Fig. 9a](#)). This distance was calculated as 0.55 nm. For the dimensions of a laponite platelet, we used the values given by the producer (see [Fig. 9b](#)). The thickness of the silicate platelets is 0.92 nm thus we assumed that it is sufficiently large to bind two silane molecules one above the other as [Scheme 1](#) shows. Subsequently, we calculated the number of molecules that the edge of the platelets can accommodate in a single or a double row. According to the calculations, 51 mg silane can react with 1 g silicate because of geometric reasons. This value slightly exceeds the number derived from the TGA measurements (37.3 mg),

but closely corresponds to that obtained from the FTIR study (50 mg). Consequently, silane molecules are located only at the edges of the platelets indeed in accordance with the results of the XRD measurements. The results also indicated that the edges of the platelets are practically completely covered with silane molecules, thus the modification of the silicates must influence their possible interactions and allow obtaining more information about silicate/silicate interactions.

A house-of-card structure forms, if a layered silicate is dispersed in water in sufficiently large amount. The lateral surface of the platelets has negative charge in water, while below a certain pH, the average charge of the edges is positive. Opposite charges attract each other and the silicate network forms. The house-of-card structure should not develop when we block the interactions of the active hydrogens of the silicate -OH groups by replacing them with an aliphatic moiety, since only weak van der Waals bonds can form between the edges and the surface of the platelets. The formation of the silicate network can be detected by rheology both in suspension and in nanocomposite melts [x]. The viscosity of suspensions is plotted against silicate concentration in **Fig. 10**. The formation of the silicate network is clearly indicated by the steep increase of viscosity above a certain silicate content. Quite surprisingly, practically the same correlation is obtained for the silicate treated with 100 mmol ETMS/g silicate, i.e. the silicate network forms even though the -OH groups were reacted with the silane.

Since several experiments confirmed the reaction of the silicate and the silane, as it was shown above, the accepted scheme of network formation must be revisited.

The surface of the silicate layers is negatively charged because in the octahedrally coordinated magnesium oxide layer surrounded by the two parallel silica layers a certain number of the Mg^{2+} ions are equivalently exchanged to lithium ions having a single positive charge. The free negative charges of the layers are compensated by sodium ions, which dissociate from the surface in water leaving negatively charged surfaces behind. Because of their limited size, the edges of the layers are closed by $-Si-OH$ and $-Mg-OH$ groups. At certain pH values, the $-Si-OH$ groups are deprotonated in water, thus the edge becomes negatively charged that would not allow the formation of the house-of-card structure. On the other hand, $-Mg-OH$ groups release hydroxyls in water leaving behind $-Mg^+$ moieties, i.e. a positively charged surface. Accordingly, the source of positive charge at the edges of the silicate platelets are not the $-Si-OH$, but the $-Mg-OH$ groups. Consequently, in spite of the reaction of the $-Si-OH$ groups with the silane and the elimination of active hydrogens, the positive charge of the edges is maintained and the silicate network forms. Obviously, silane treatment does not hinder the elimination of the hydroxyl ions and the much stronger electrostatic interactions overwhelm the weak dispersion interaction of the $-SiCH_3$ groups. The explanation is presented graphically in [Fig. 11](#) and it is verified by the results shown

in **Fig. 10**. Accordingly, the edges of silicate platelets can be modified with functional silanes to achieve coupling or some other function, but modification is superfluous if we want to avoid the formation of the house-of-card structure to control the rheology of a suspension or a nanocomposite melt.

4. CONCLUSIONS

The edges of a synthetic layered silicate, laponite, were successfully modified with a monofunctional silane compound. The occurrence of the reaction was confirmed with various methods and surface coverage was determined. Thermogravimetric measurements and the FTIR analysis of both the treated filler and the reaction medium yielded a saturation like correlation as a function of the amount of silane used for treatment. The determination of the bonded amount of silane by FTIR analysis must be carried out with care, since side reactions take place during modification. Although the expected dimerization of the silane did not occur, it hydrolyzed during treatment systematically changing the amount of bonded silane determined from the FTIR absorption of oxygen containing groups. Only vibrations related to the absorption of the $-\text{SiCH}_3$ group can be used for quantitative analysis. XRD measurements proved that the silane is bonded onto the surface of the silicate and it does not enter the gallery space. According to the FTIR measurements, approximately 50 mg silane is bonded to 1 g silicate corresponding to almost complete surface coverage. The results

of the measurements were supported by model calculations and extremely good agreement was found between the calculated and measured values. Surface modification did not hinder the formation of a house-of-card structure showing that the generally accepted mechanism of network formation needs revision. An explanation was offered based on the release of hydroxyl ions from the -Mg-OH moiety of the silicate. Modification of the edges of layered silicates may facilitate exfoliation or help functionalization, but does not prevent network formation and cannot be used for the control of rheological properties.

5. ACKNOWLEDGEMENTS

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7. CAPTIONS

- Fig. 1 Dependence of bonded silane on the amount of reactant (ETMS) added determined from the weight loss of silicate samples by TGA measurements.
- Fig. 2 FTIR spectrum recorded on a silicate sample reacted with **xxx mmol silane** and the assignation of the most important vibrations. Changes in the intensity of the $-\text{SiCH}_3$ band with increasing silane treatment.
- Fig. 3 Increase in the amount of bonded silane ($-\text{SiCH}_3$ at 1257 cm^{-1}) with increasing amount of ETMS added. The intensity of vibrations not influenced by the treatment remain constant (Si-O-Mg and Si-O-Si at 464 and 449 cm^{-1} , respectively). The analysis was done on powder samples in KBr pastille.
- Fig. 4 Determination of the amount of bonded silane from the reaction medium by FTIR analysis. Symbols: (O) $-\text{SiCH}_3$

at 842 cm^{-1} , (\square) $-\text{SiO}-$ at 1165 cm^{-1} .

Scheme 1 Scheme of the primary reaction taking place during the modification of laponite with ETMS.

Scheme 2 Possible side reactions occurring during the surface modification of the silicate with the monofunctional silane (ETMS).

Fig. 5 Comparison of the FTIR spectra of the dimer, ETMS and the reaction medium, **which contained xxx mmol silate**, after the reaction. Absence of the characteristic $-\text{Si}-\text{O}-\text{Si}-$ vibration of the dimer in the latter.

Fig. 6 Confirmation of the hydrolysis of the silane during surface modification. Detection of the expected reaction products by FTIR spectroscopy.

Fig. 7 X-ray diffraction patterns recorded on the silica samples reacted with various amounts of ETMS. The trace of the neat silicate and that subjected to the same treatment, but without ETMS. The amount of ETMS increases from 0 to 800 mmol from bottom to top.

Fig. 8 Independence of the layer distance of the silicate of the amount of silane used for treatment. The separate point indicates the neat laponite.

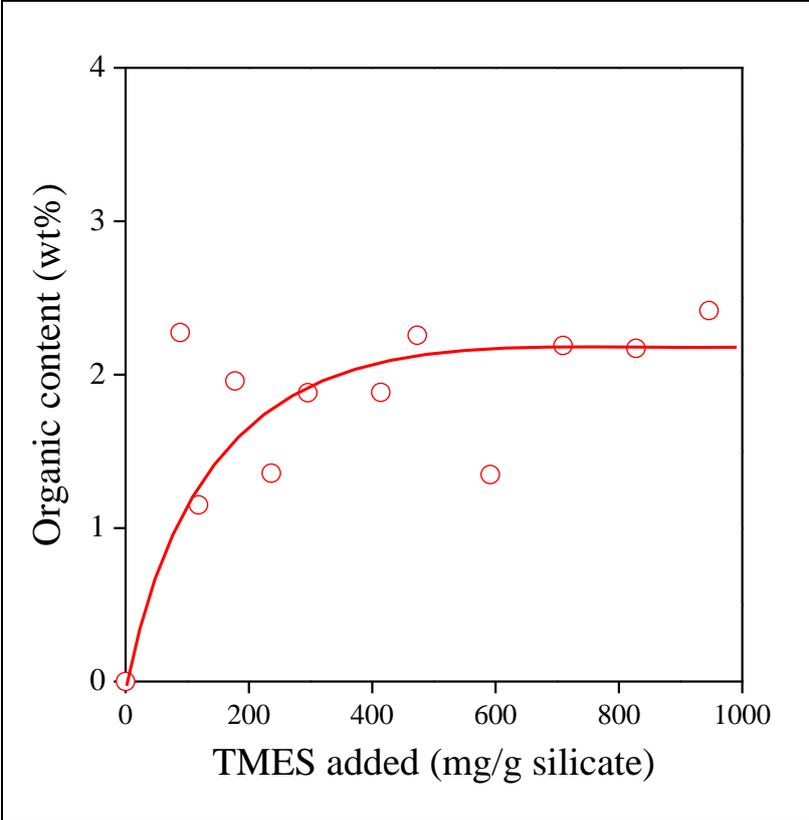
Fig. 9 Optimized geometry of the silane molecule (a) and the dimensions of a laponite platelet (b).

Fig. 10 Development of a house-of-card structure independently of the surface modification of the silicate. Viscosity plotted against the amount of silicate in the

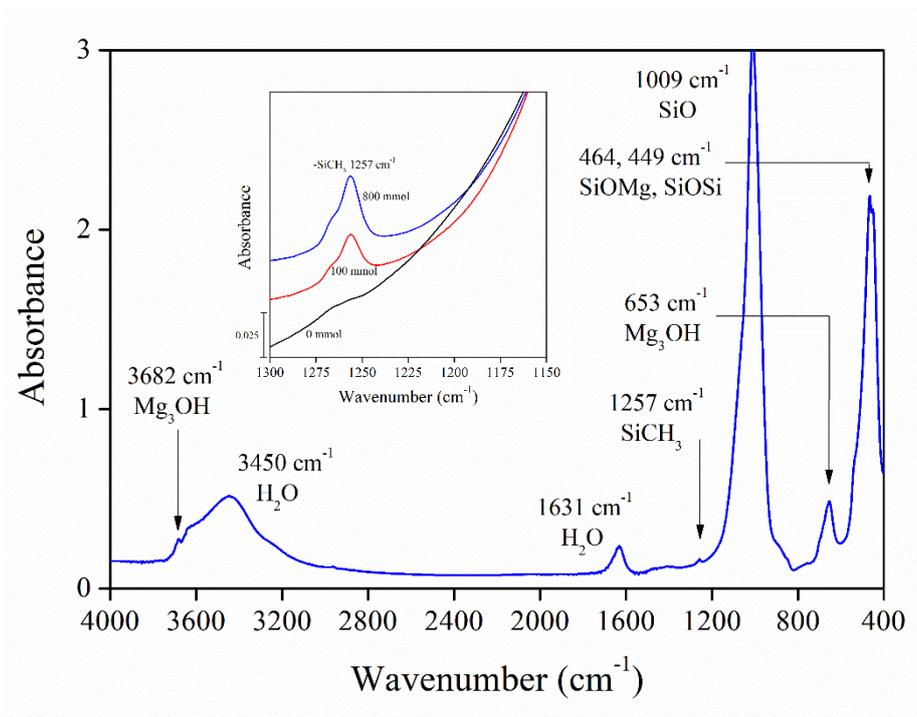
suspension. Symbols: (\square) 0 mmol, (\circ) 100 mmol ETMS/g silicate.

Fig. 11 Scheme showing the mechanism proposed for the formation of the house-of-card structure.

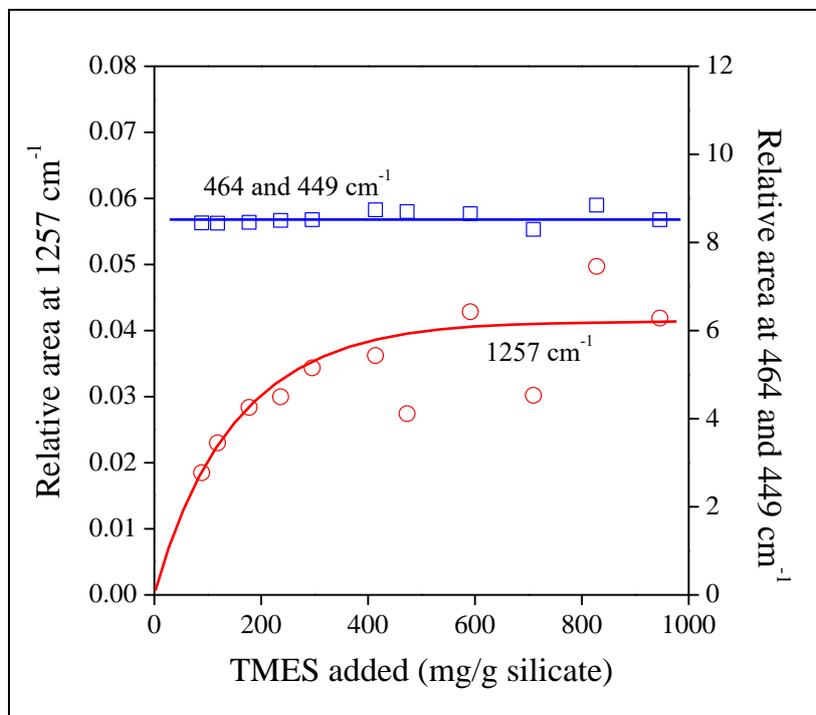
Hegyesei, Fig. 1



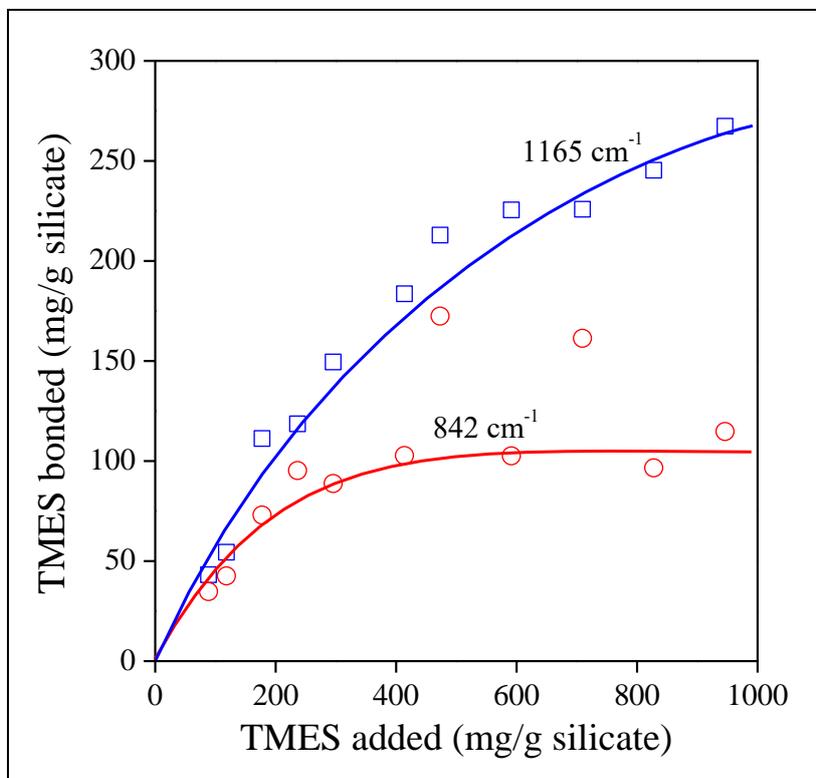
Hegyési, Fig. 2



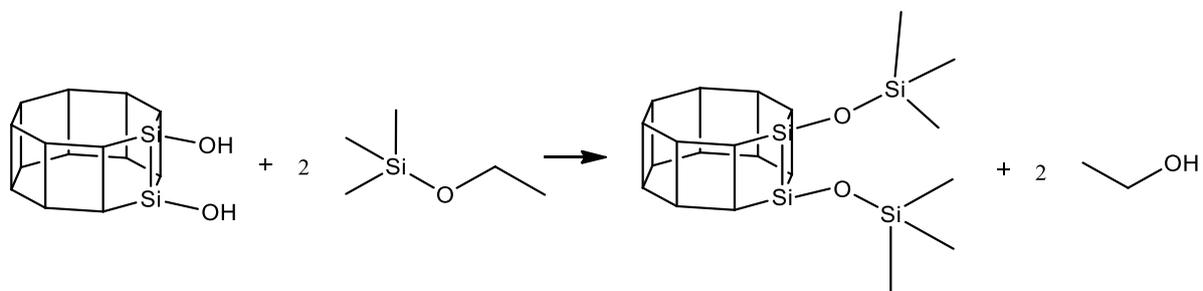
Hegyési, Fig. 3



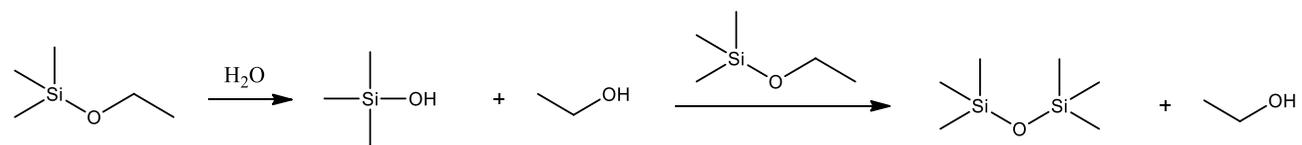
Hegyési, Fig. 4



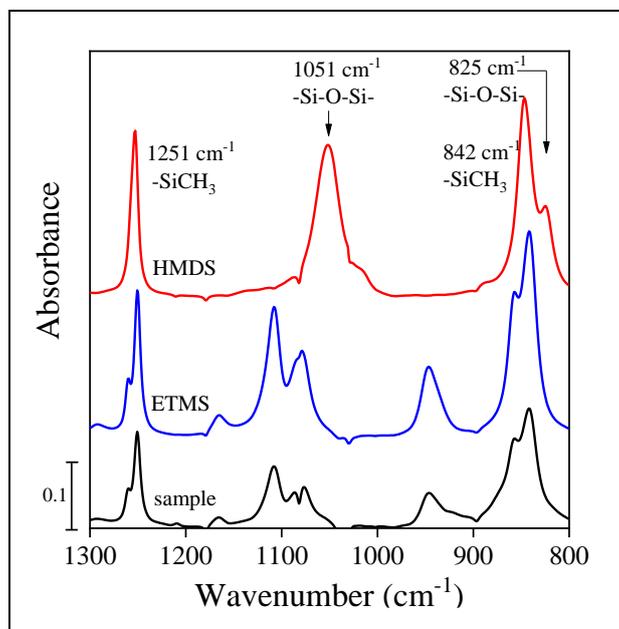
Hegyesi, Scheme 1



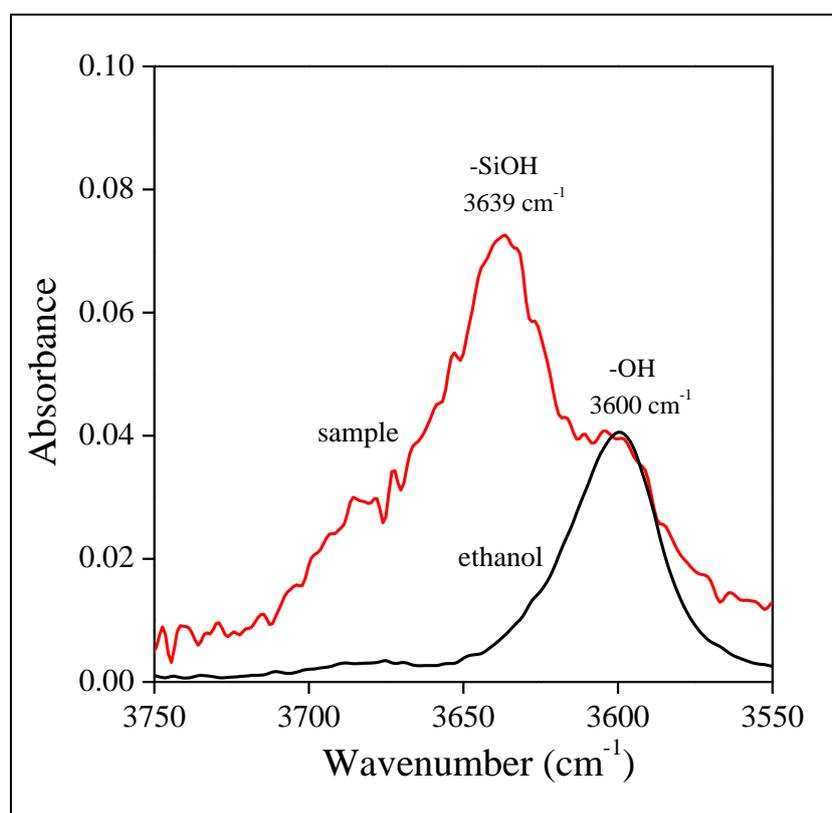
Hegyesi, Scheme 2



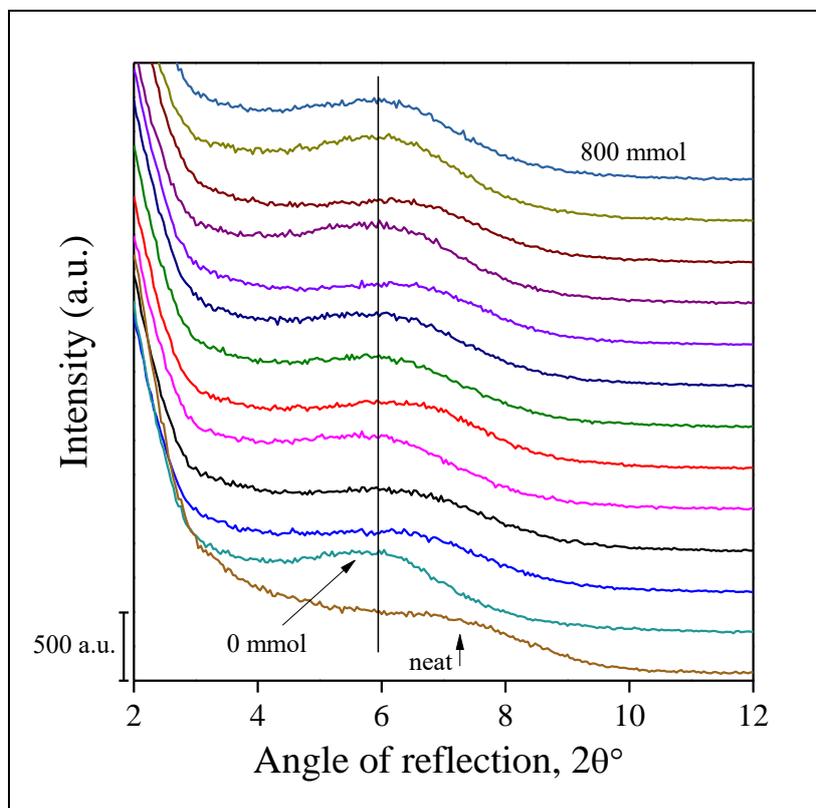
Hegyési, Fig. 5



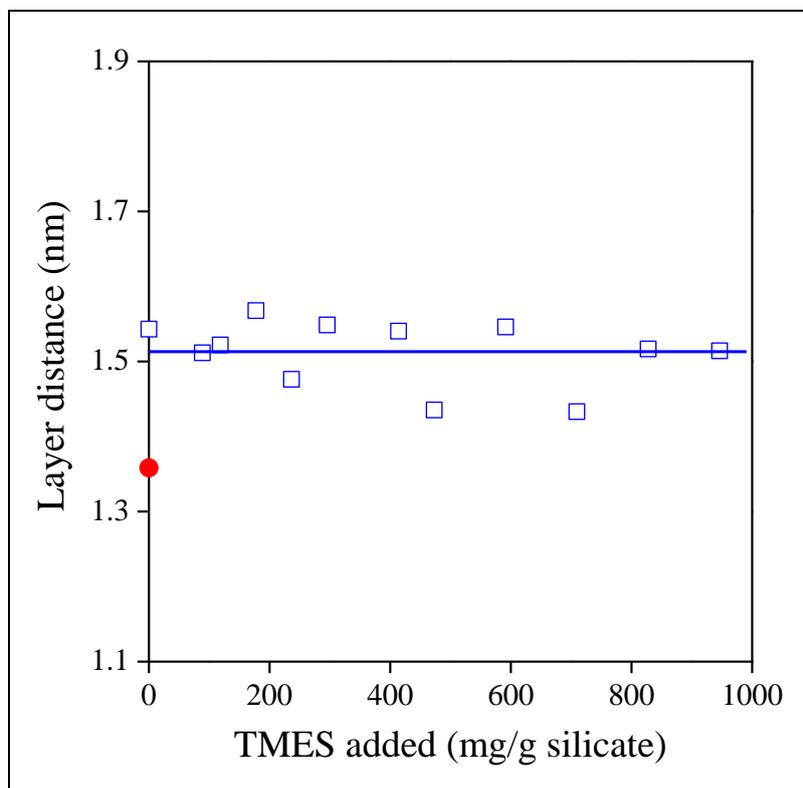
Hegyési, Fig. 6



Hegyési, Fig. 7

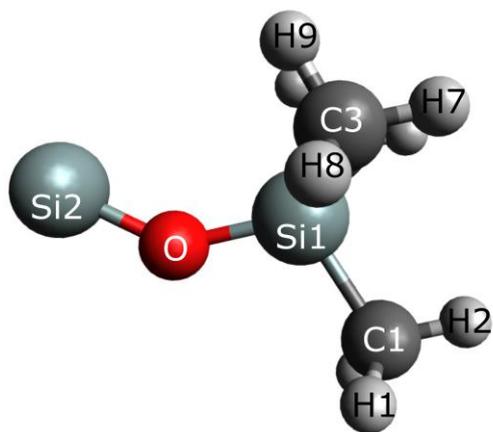


Hegyési, Fig. 8

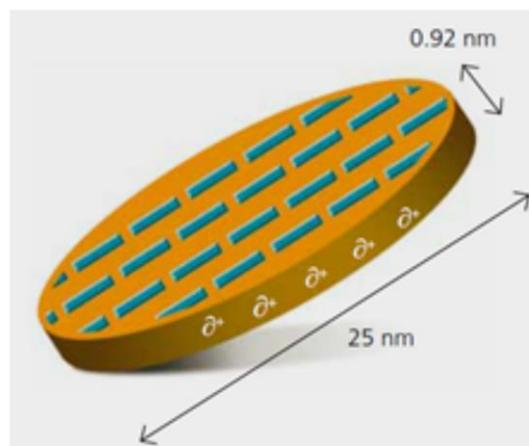


Hegyesi, Fig. 9

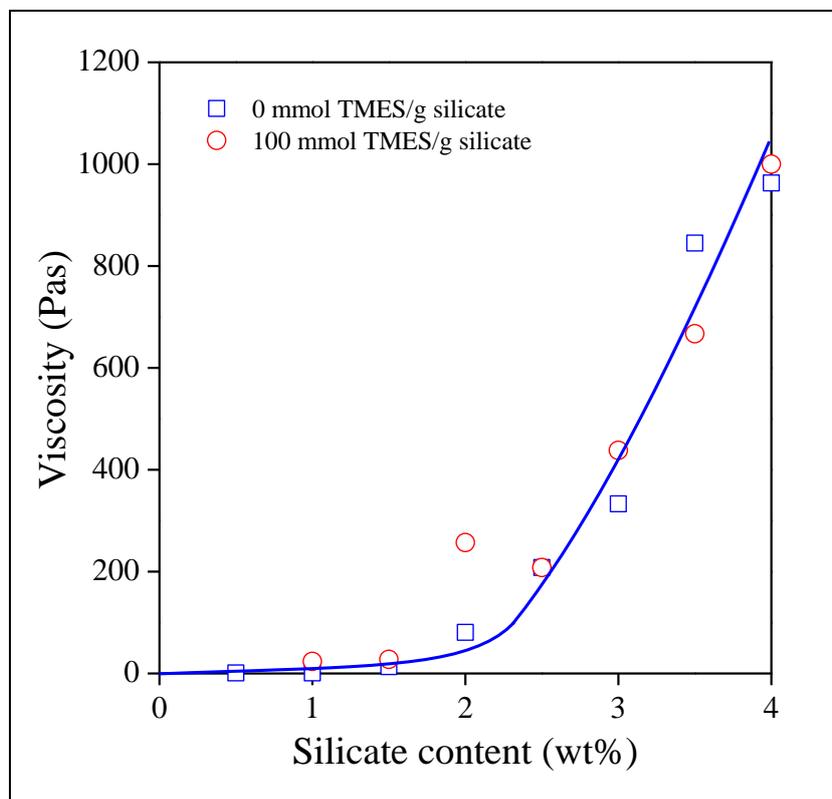
(a.)



(b.)



Hegyési, Fig. 10



Hegyesi, Fig. 11

