Organic modification of layered silicates for use as barrier pigments in coating systems

J. Lommes, J.Kromalicki, G. Patzelt, V. Stenzel, A. Hartwig

Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM

joshua.lommes@ifam.fraunhofer.de

Abstract

Functional coatings and the barrier pigments they contain are an indispensable part of corrosion or product protection. The frequently used layered silicates in their pure form often do not achieve a sufficient protection of the components or products. The barrier effect of the silicates can be significantly improved through targeted organic modification. The general use of commercial (unmodified) silicates leads to an improvement in the barrier of about 20 %. In contrast, the use of modified silicates achieves an improvement of up to 80 % [1], due to the extent of the diffusion path [2]. Decisive for the diffusion path and therefore for the subsequent functionality of the barrier is the exfoliation and orientation of the silicates, which depends on the compatibility with the coating system. Due to the large number of coating systems and the associated binder classes, the silicates should be specifically adapted to the respective polymer by being modified with reactive groups, which represents the main focus of this work. As a first polymer system an epoxy matrix was chosen. Thus, commercial silicates were modified by an epoxy-oligomer matrix based on 1,4-butanediol diglycidyl ether. The produced silicates were examined with the aid of scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The expansion of the layers and the attachment of the organic molecules were investigated using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

1   Introduction

Diffusion of moisture and gases is an undesirable process in many applications. The process promotes corrosion, and thus, the failure of the component. Corrosion causes a total annual damage of 4 % of the gross national product. This puts corrosion as a cause of damage on a par with the wear of materials [3, 4]. However, diffusion does not only play a decisive role in the protection of components. In the area of food packaging, barriers also serve to protect the packaged product from water penetration and to prevent odours from escaping. This is because moisture has a decisive influence on the shelf life and quality of the food. Many properties, such as texture, shelf life or even degradation through oxidation, depend on the water absorption of the biological materials. Thus, the nutritional quality is also a function of the moisture content [5, 6]. That's why the reduction of diffusion by barrier pigments has already been investigated by using layered silicates in polymer nanocomposites [7-11]. Due to the large number of different matrices and coating systems, targeted organic modification of natural layered silicates can lead to better compatibility with the system, and thus, to an improved barrier [12-15]. *Fig. 1* shows a model of a barrier coating with pigments. The pigments aligned parallel to the surface are completely exfoliated and therefore extend the diffusion path enormously. Gases and moisture cannot directly reach the object to be protected and the protection is guaranteed for a longer period of time. This property is quantified by the so-called flow rate (Q) through the layer. The ratio of the flow rates without ($\dot{Q}_0$) and with ($\dot{Q}_N$) pigments can be taken from equation (1).

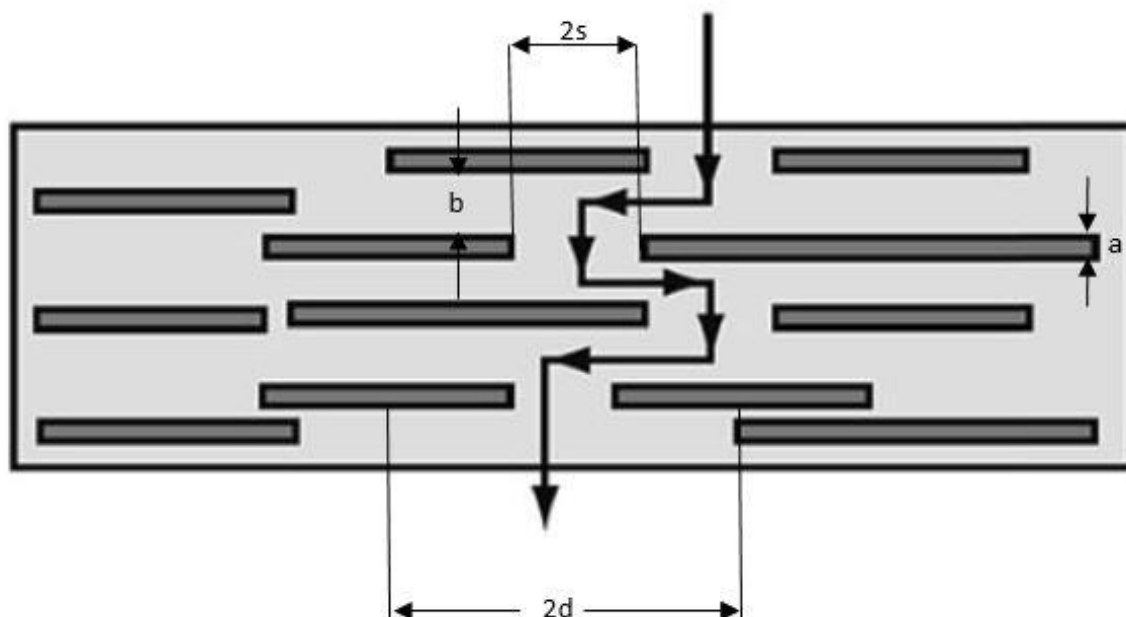*Fig. 1: Model of platelet-shaped pigments in a coating [11]*

$$\frac{\dot{Q}_0}{\dot{Q}_N} = 1 + \alpha^2 \frac{\phi^2}{1 - \phi} \tag{1}$$

This ratio depends on the aspect ratio of the pigments α, which is the ratio of the thickness of the pigments to the surface area. Furthermore, the degree of filling ϕ of the coating has an enormous influence on the flow rate of the coating because a high aspect ratio in combination with a high degree of filling leads to a low permeation through the coating [2, 16-18]. This effect and the suitability of silicates for use was already described by Cussler (1988) et al. in 1988 for use in diffusion inhibiting coatings due to the large aspect ratio leading to a large lateral expansion at low thickness [16-18].

Silicates are esters and salts of silicic acid (Si(OH)$_4$). If these are arranged in a layered structure, they are called phyllosilicates or layered silicates. Macroscopically, the structure can be understood as thin layers lying on top of each other, which are called stacks. The individual layers have a negative partial charge. Between the individual layers of silicates are positively charged sodium atoms as counter ions. *Fig. 2* shows both the macroscopic (left) and the atomic structure (right) of layered silicates. At the atomic level, the characteristic structure of oxygen tetrahedral can be seen, which are linked to each other by octahedral. The octahedral contain silicon atoms or other metal ions or other metal ions, such as aluminium or magnesium. The sodium atoms between the layers, which serve to balance the charge, can also be seen here. [19, 20].
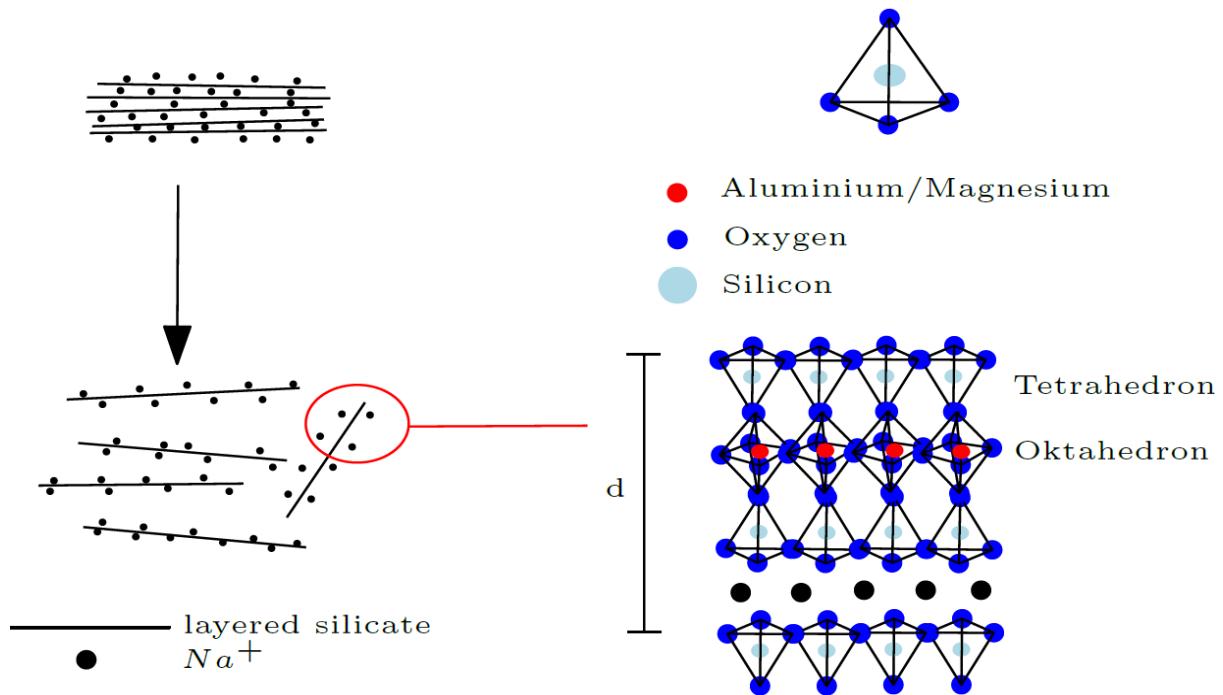

Fig. 2: (left) Schematic of the layered structure of silicates (right) Idealised structure of a layered silicate using the example of montmorillonite [19, 20].

In aqueous medium, exfoliation of the layered silicates takes place. The water molecules enter the interstices of the layers and swell the silicates apart. The particles are no longer present as agglomerates and can develop a distinct barrier. In non-aqueous media, there is no swelling, and thus, no exfoliation and sufficient barrier effect. Through targeted organic modification, pigments can be synthesised that exfoliate even in solvent-containing environments [15, 21]. *Fig. 2* shows on the left side the exfoliation of stacked silicates in water. After the intercalation of the solvent, a disorder and a broader layer spacing of the layered structures can be observed.

By means of an ion exchange reaction, the sodium atoms can be exchanged for other cations. Through this exchange, organic cations get between the silicates, and thus, increase the distance between the layers. *Fig. 3* shows this reaction schematically using the example of a reaction with an organic, protonated epoxy oligomer. Due to the widening of the layer distance, the silicates are in an intercalated state. The organic modifiers prevent the re-agglomeration of the particles into their stacks. Furthermore, this allows solvents and polymer molecules to enter the interlayers more easily and promote exfoliation, and thus, the barrier. The driving force for this reaction is entropy. The significantly increased conformational freedom and increasing intercalation provide positive entropy during the reaction. In addition, the increasing hydrophobicity of the particles and the resulting inhomogeneity at the surface lead to the entropic driving force of ion exchange [22-24].
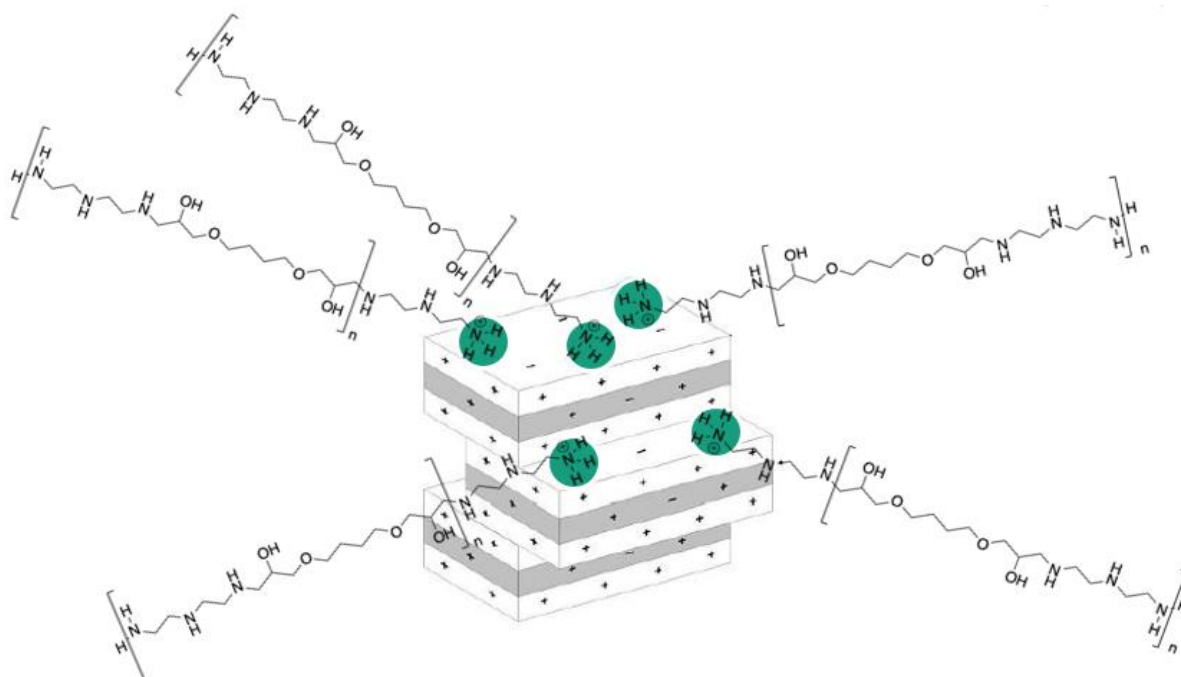

Fig. 3: Schematic representation of the attachment of long-chain organic molecules to the silicate surface by an ion exchange reaction

2   Materials and methods

2.1   Materials

The layered silicate Cloisite Na+ was purchased from BYK Additives & Instruments. The other chemicals for the synthesis were acquired from Sigma Aldrich. 1,4-butane-diol diglycidyl ether (1,4-BDDGE) was purchased with a purity of ≥95%. Diethylene triamine (DETA) were delivered with a purity of 99%. Hydrochloric acid with 37% was used.

2.2   Methods

2.2.1 Preparation of the modified layered silicates

To prepare the oligomerised epoxy resin, which should modify commercial silicates later on, 1,4-butanediol diglycidyl ether (1,4-BDDGE) and diethylene triamine (DETA) had to react. For this purpose, 23.8 g DETA (0.231 mol) were dissolved in 25 g ethanol within a round bottom flask and heated to 54 °C with stirring. After cooling the solution, 15.54 g (0.768 mol) of 1,4-BDDGE was added in ten equal portions via a dropping funnel. The reaction mixture was then kept at 60 °C for 2 h. The solution was then stored at room temperature overnight. The solution was stored at room temperature overnight while stirring. The next day, the ethanol was distilled off using a rotary evaporator leading to the oligomeric epoxy resin.

After that, two precursors were prepared for the synthesis of the modified layer silicates. 5g of the oligomer epoxy resin was protonated with different ratios of hydrochloric acid (HCl) (1:1; 1:2; 1:4; 1:6; 1:8 and 1:10) by dissolving 100 mL of the oligomer in distilled water combined with HCl in the respective ratio for one hour at RT. Moreover, 20 g of the unmodified silicate were first suspended in 400 mL distilled water and then stirred for 1 h at 80 °C. The two solutions were then combined and stirred for a further hour at moderate temperature. The protonated oligomer exchanges the sodium atoms at the surface of each silicate particle. The modification with long chain molecules leads to a wider spacing layer and prevents an agglomeration of the particles. The modified layered silicates could then be filtered and dried.

2.2.2 Characterisation

The modification of the oligomer was checked by FTIR spectroscopy (Bruker Alpha-II Platinum ATR) with a resolution of 2 cm^{-1} and 32 scans per measurement in a range of 4000 – 400 cm^{-1}.

The X-ray photoelectron spectroscopy (XPS) investigations were carried out with an Escalab Xi+ system. Parameters: Magnetic lens mode, acceptance angle of the photoelectrons 0 °, monochromatic AlKα excitation, Constant Analyser Energy mode (CAE) with 150 eV pass energy in overview spectra and 40 eV in energetically high-resolution line spectra, analysis area: 0.65 mm. The neutralisation of electrically non-conductive samples is carried out by a combination of low-energy electrons and low-energy argon ions.

For the subsequent application as barrier pigments, the exfoliation of the modified silicates had to be determined in order to make sure the silicates are able to reduce the permeation of moisture and harmful gases. Thus, X-ray diffraction (XRD) was used to determine the layer spacing of the silicates. The diffractograms were recorded using the MiniFlex 600 from Rigaku. The excitation was carried out with Cu-Kα radiation in a measuring range of 2 – 80 ° with a step size of 0.03 ° and a measuring time per angle of 5 s.

3 Results and discussion

The result of the IR spectroscopy of the produced oligomer 1,4-BDDG-DETA is shown in *Fig. 4* In the reaction between the diglycidyl ether and the multifunctional amine, the oxirane ring reacts in an addition reaction with the amine group to form a hydroxide group. The spectrum of the 1,4-BDDGE shows the vibrations of the saturated CH- and CH_2-groups at wavenumbers between 2750 cm^{-1} and 3050 cm^{-1}. The band shortly above 3000 cm^{-1} can be explained by the ring tension. Furthermore, the ether structure is clearly visible with a vibration at 1096 cm^{-1}. The characteristic oxirane band appears at a wavenumber of 910 cm^{-1}. The spectrum of the reaction product also shows the characteristic oscillations of the CH_2 and CH_3 groups at the same wavenumbers. Furthermore, there is a broad band between 3500 cm^{-1} and 3000 cm^{-1}, which was identified as
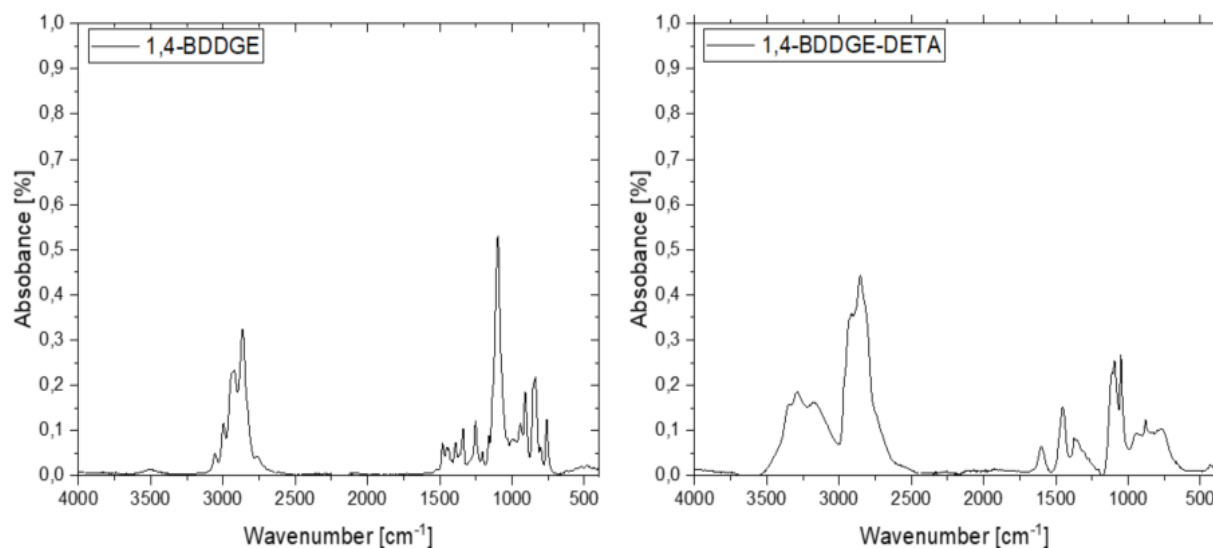
an OH vibration. Together with the decrease of the oxirane vibration at 910 cm^{-1}, a sufficiently complete reaction can be observed here. In addition, the carbon-nitrogen oscillations at 1052 cm^{-1}, which are located directly next to the occurring C-O band can be clearly identified.

Fig.4: IR spectra of the reactant 1,4-butanediol diglycidyl ether (1,4-BDDGE) and the reaction product with diethylenetriamine (1,4-BDDGE-DETA)
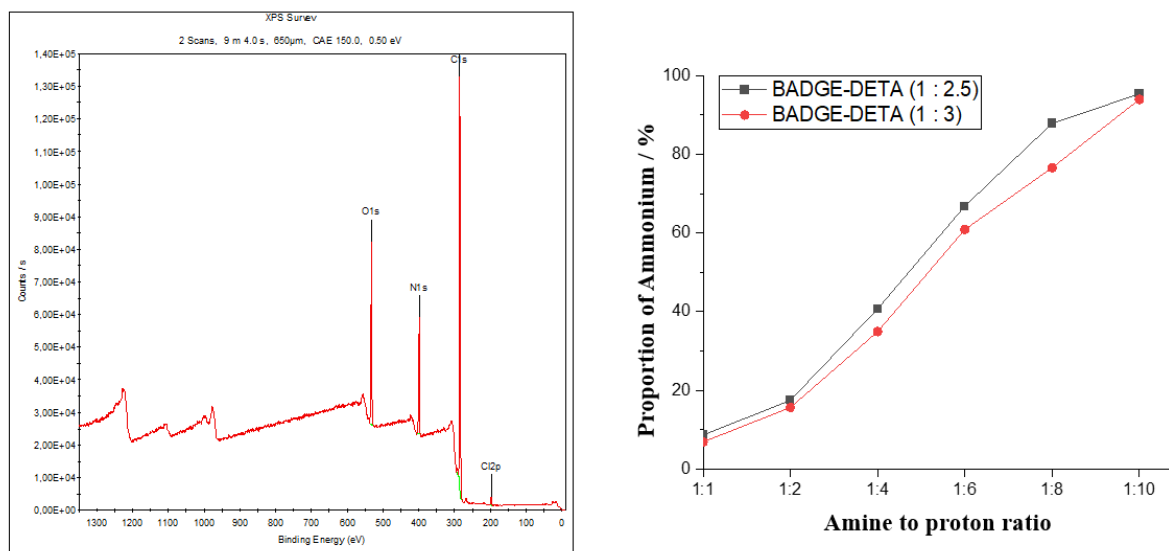

Fig. 5: XPS spectrum of the protonated oligomer (left) and proportion of protonated nitrogen at the different amine to proton ratios (right)

Because of there viscosity properties two oligomers with an amine to epoxy ratio from 1:2.5 and 1:3 were produced and investigated in the following. The degree of protonation of the oligomers and the ion exchange at the silicate were investigated using XPS. To check the completeness of the exchange, the proportions of sodium in particular were used by evaluating the nitrogen peak in the spectrum. The diagram in *Fig.5* shows an XPS overview spectrum of the oligomer with its peaks. From this, the different degrees of protonation of the amine were determined and plotted against the amine to HCl ratio. It can be clearly seen that as the supply of protons increases, the degree of protonation also increases. The more protons the solution contains, the more amine is protonated in the chain of the oligomer. The oligomers produced in this way show only a slight difference compared to one another.

The amine content and the degree of protonation of both resins are comparable. With an

Tab. 1: Atomic composition of the layered silicates before and after modification with the respective oligomers

Content / at%	Unmodified layered silicate	CNa⁺-1,4-BDDGE-DETA (1 : 2.5) 8x HCl	CNa⁺-1,4-BDDGE-DETA (1 : 2.5) 10x HCl	CNa⁺-1,4-BDDGE-DETA (1 : 3) 8x HCl	CNa⁺-1,4-BDDGE-DETA (1 : 3) 10x HCl
C	1,5	10.3	8.8	9.2	7.8
Si	23,2	19.3	19.3	19.3	19.5
O	60,1	58.0	59.7	59.0	59.6
Na	3,1	0,0	0,0	0,0	0,0
N (total)	0,1	2.5	2.3	2.5	2.5
NH₄⁺	0,0	1.8	1.8	1.8	1.9
org. N	0,1	0.7	0.5	0.7	0.6

amine to HCl ratio of 1:8 and 1:10, protonation degrees of up to 96 % could be achieved. These precursors were then selected for the ion exchange reaction.

The control of the exchange reaction was also carried out with the XPS. *Tab. 1* shows the fractions of selected atoms in percent. The unmodified layered silicate has a sodium content of 3.1 atomic percentage (at%). The atomic percentage describes which percentage of one type of atoms is contained in the substance in relation to all atoms. In the modified phyllosilicates, no more sodium could be detected, which is why it can be assumed that the sodium has been completely replaced. Furthermore, one can see the increase in carbon and nitrogen, which is also an indication of the exchange reaction that has taken place. The content of silicon and oxygen decreases slightly. This is due to the higher total number of atoms, which on the one hand is influenced by the different addition of hydrochloric acid and on the other hand increases due to the exchange reaction. In general, there is no clear difference between the individual modifications. Both the ratio of the reactants and the amine to acid ratio have only a minimal influence on the addition to the silicate.

After drying the modified silicates, they were further examined using XRD and the layer distance was determined. With the help of the reflex, the layer distance of the particles can be determined in the Bragg equation. The spectra in *Fig.6* show a shift of the first reflex to smaller theta values. When inserted into the equation, this results in a widening
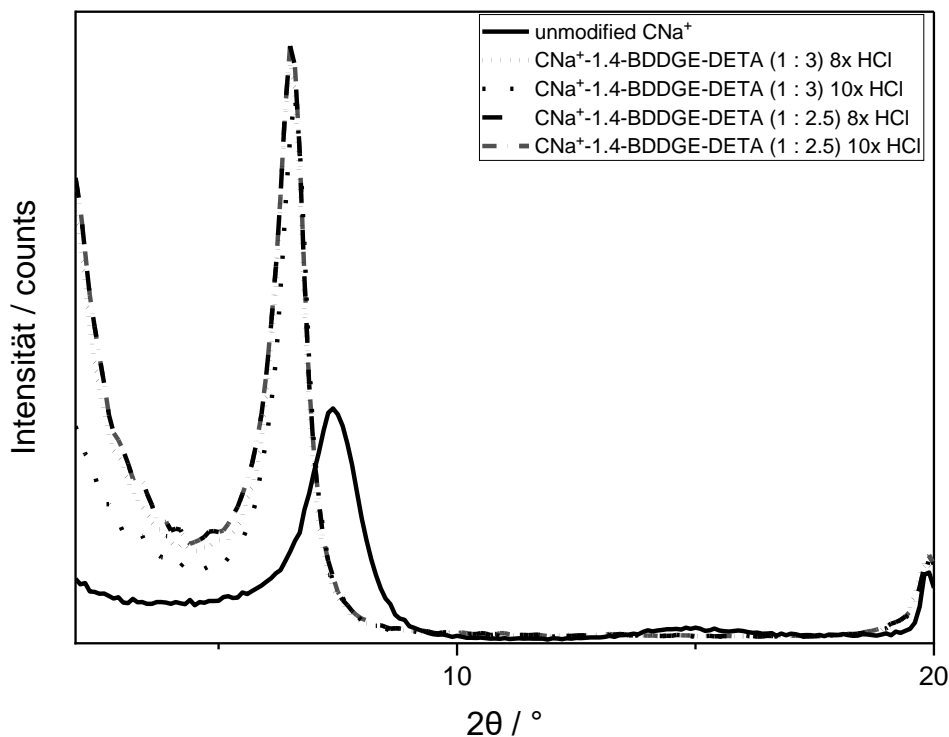

Fig.6: XRD spectra of the layered silicates in the unmodified and modified state

of the layer spacing of the silicate particles. The unmodified silicate has a layer spacing of 2.40 nm. The modified variants show an increase in the distance between the particles of around 10 %.

The maximum distance here is 2.73 nm for the CNa^+-1,4-BDDGE-DETA (1:2.5) 10x HCl variant. The other modifications show a layer distance of 2.69 nm. These measurements suggest that the oligomers are not arranged on the layer silicate as shown in *Fig. 3*. If this were the actual conformation of the oligomers on the silicate, a significantly larger widening of the spacing would have been expected. More likely is an arrangement of an oligomer molecule around the layered silicate. The oligomer molecules were enclosed, and the positive charges occupied the free places of the sodium on the particle. The layered silicate produced in this way is now present as an intercalate. This facilitates the exfoliation in the subsequent coating system and the use as a barrier pigment in non-aqueous media.

4 Conclusion

Within the framework of this work, an oligomer was successfully produced which serves as an organic modifier for layer silicates. The reaction could be verified with FTIR spectroscopy. The characteristic oxirane band at 910 cm^{-1} could not be detected in the product. However, in the range from 3500 cm^{-1} to 3000 cm^{-1} the oscillation of the formed OH group could be observed. Furthermore, different variants of the oligomer could be protonated to different degrees with the help of protons. Thus, an adjustment of the degree of protonation of the organic molecules is possible. The XPS results showed a degree of protonation of 96 % with an addition of 8 and 10 parts of protons per part of amine. The protonated oligomers were successfully bound to the silicate by an ion exchange reaction and the widening of the layer spacing could be demonstrated. The sodium detected by XPS in the unmodified variant was completely removed from the system. At the same time, the increase in carbon and nitrogen in the system also indicates the feasibility of this exchange reaction. The organically modified layered silicates produced showed a 10 % increase in layer spacing in the XRD. This widening is intended to enable the intercalated layer silicates produced in this way to be used as barrier pigments in coating systems.

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Author adress

Joshua Lommes M.Sc.

Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM

Wiener Straße 12

28359 Bremen

Phone: +49 421 2246 684

E-Mail: joshua.lommes@ifam.fraunhofer.de