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Study on Exfoliation of Layered Materials and their Application in Nanocomposites

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References

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Abstract

The presented work deals with the preparation and characterization of layered materials from the group of layered metal organophosphonates and double layered hydroxides. These materials are investigated in terms of the possibility of preparing their nanoform using the liquid-based exfoliation process. Their subsequent application for the preparation of polymer nanocomposites is evaluated. An important part of the work is the study of the process of exfoliation itself and the development of a methodology for a reproducible preparation and evaluation of the exfoliated materials. Furthermore, methods of dispersion of the prepared fillers into polymer systems, distribution of the particles in the polymer matrix and the influence of the presence of the fillers on the utility properties of the nanocomposite are studied.

Abstrakt

Předkládaná práce se zabývá přípravou a charakterizací vrstevnatých materiálů ze skupiny vrstevnatých organofosfonátů kovů a podvojných vrstevnatých hydroxidů. Tyto materiály jsou zkoumány z hlediska možnosti přípravy jejich nanoforem pomocí procesu exfoliace v kapalinách s následným uplatněním pro přípravu polymerních nanokompozitů. Významnou část práce tvoří studium procesu samotné exfoliace a vypracování metodiky pro reprodukovatelnou přípravu a hodnocení exfoliovaných materiálů. Dále jsou studovány způsoby dispergace připravených plniv do polymerních systémů, distribuce částic v polymerní matrici a vliv přítomnosti plniv na užitné vlastnosti nanokompozitu.

Key words

Exfoliation, layered materials, layered metal organophosphonates, layered double hydroxides, nanofiller, nanosheets, nanocomposite

Klíčová slova

Exfoliace, vrstevnaté materiály, vrstevnaté organofosfonáty kovů, podvojné vrstevnaté hydroxidy, nanoplnivo, nanodesky, nanokompozit

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Introduction

Intensive research in the field of nanotechnology especially development in nanoparticles synthesis and characterization brings new possibilities to combine nanoparticles with traditional materials and enhance material properties in this way. Objects with dimensions in the order of nanometers show different behavior than bulk materials of the same composition, which implies that in some cases it is advantageous to replace these bulk materials.

For the nanostructure’s preparation, procedures based on either molecular precursors (bottom-up methods) or bulk material (top-down methods) have been developed and described. Two-dimensional structures are difficult to synthesize directly, so exfoliation as a top-down approach seems more advantageous. In general, it is a process of disintegration of a layered material in which thin sheets of the material are separated from the bulk. The essence of the process lies in overcoming the attractive forces which hold the layers together by an external action. The most popular method nowadays is the so-called „Liquid based exfoliation” [1], where mechanical forces are combined with chemical interactions between layered particles and molecules of solvent and possibly also other auxiliary agents.

Among materials, which can be exfoliated and subsequently incorporated into a polymer matrix in a form of 2D nanosheets, belong hybrid organic-inorganic particles of layered metal organophosphonates or layered double hydroxides.

Aims of the thesis

The principal aim of this work was to study the exfoliation process of layered materials, in order to prepare nanosheets for subsequent application in polymer nanocomposites. To achieve this goal, effort was divided into three secondary objectives.

The first objective was to synthetize layered particles from the groups of layered metal phenylphosphonates and layered double hydroxides and to characterize their physical-chemical properties.

The second objective was focused on the exfoliation process. The intention was to find a suitable exfoliation method for the above-mentioned material groups and to develop methodology for evaluation of the effectiveness of the exfoliation process based on characterization of the exfoliated material.

The third objective was to find suitable method for incorporation of the obtained particles and nanosheets into a polymer matrix and to analyze influence of the presence of the fillers to the nanocomposite properties.

1. Theoretical part

1.1. Layered materials

Layered metal organophosphonates are a class of materials which exhibit a hybrid character by their nature. They are generally defined as salts of phosphonic acids with general formula RPO_3H_2 (R = alkyl or aryl group) with metals. Many different types of layered metal organophosphonates have been prepared. The exact structural arrangement is characteristic of each particular material, but in general, there are metal atoms in the center of the layer, which are surrounded on both sides by phosphonates. The organic ligand then goes into the interlayer space. The type of organic substituent determines how the layered material will interact with the environment and what added properties the structure acquires, e.g., zirconium sulfophenylphosphonates are intensively investigated for use as a proton conductor [2]. Some materials can be synthesized in a combined form, where various organic substituents are incorporated in the structure. It is the diversity of these materials that brings their enormous potential for application in many branches of human activity, but due to their higher price, which is mainly due to the price of raw materials, not due to the complexity of the preparation itself, they are not studied so intensively. In this work, the attention has been focused on calcium phenylphosponate dihydrate with general formula $CaC_6H_5PO_3{\cdot}2H_2O$ (CaPhP) and series of newly-prepared and characterized materials which combine phosphonate groups with phosphite ($Ca(C_6H_5PO_3)_x(HPO_3)_{1-x}{\cdot}nH_2O$) or phosphate groups ($Ca(C_6H_5PO_3)_x(HPO_4)_{1-x} \cdot nH_2O$).

Layered double hydroxides (LDHs) represent a large group of layered solids with general formula $[M_{1-x} M'_x(OH)_2]^{a+}(A^{n-})_{(a/n)} \cdot bH_2O$, where M is typically a divalent metal cation, M' is a trivalent metal cation, and (A^{n-}) represents n-valent anion. The structure of LDH is similar to that of clays, but its layers consist of metal hydroxide sheets which are charged positively. This charge is compensated by anions accommodated between these sheets. Owing to their structural similarity to clays they are nicknamed "anionic clays". The properties for which double layered hydroxides are intensively investigated are mainly: (a) their high anion exchange capacity, which can be adjusted as intended during the synthesis using a correctly selected ratio of starting metals; (b) regularity in the arrangement of layers, which also brings an even distribution of charge; (c) chemical diversity; (d) and for some applications (e.g. targeted drug delivery) their solubility in acidic media is also advantageous [3–5]. In this work, LDHs of zinc-aluminum type with four different anions were synthetized and characterized.

1.2. Exfoliation

Exfoliation in general is a process of disintegration of a layered material when thin sheets of a material are completely separated from the bulk. In other words, exfoliation is one of the top-down methods for the preparation of nanomaterials. To delaminate the bulk to obtain the individual sheets, it is necessary to overcome the cohesive forces between the adjacent layers. In principle there are two options [6]: It is possible to “tear” the layers apart by a perpendicular force or to use a shear force, which is parallel to the layers, and slide the layer away from the others. Nowadays, the most popular method is the so called „Liquid-based exfoliation” [1], where the mechanical forces are combined with chemical interactions with molecules of a solvent and a surfactant (e.g., in an ultrasound bath), see Figure 1.

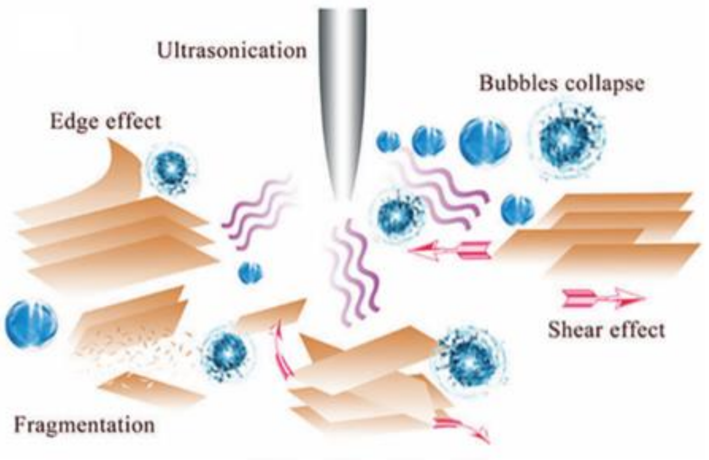

Figure 1 – Schematic illustration of the processes involved during exfoliation with ultrasound treatement [7]

The advantage of delamination in a liquid is the ability to better manage the stability of the resulting individual sheets by selecting a suitable solvent or using surfactants, and thus prevent the regrowth of the layered crystals. Another advantage is in obtaining a suspension of a nanomaterial, which can be directly applied, for example, to polymers in the preparation of composites. This eliminates the dispersion step, which could be challenging for the preparation of nanostructures.

1.3. Polymer nanocomposites

Nanocomposites [8] are composites which contain fillers with their size in the range of nanometers. According to the nanomaterial form, three types of nanocomposite can be distinguished: (a) 0D nanocomposites which contain isolated nanoparticles, (b) 1D nanocomposites which contain nanofibers or nanotubes and (c) 2D nanocomposites which contain plate-like particles with their thickness below 100 nm. The properties of the resulting nanocomposite depend not only on the type and shape of the nanofiller used, but also on its concentration, the quality of the dispersion, and especially on its interaction with the polymer matrix. Nanoparticles are characterized by a significantly larger specific surface area compared to the conventional microstructures, which increases the possibilities of contact of the filler surface with the macromolecules of the polymer system. Thus, in the case of nanofillers, a much lower filling load should be sufficient to influence the properties of the polymer matrix. However, this presupposes a high-quality and homogenous distribution of the nanofiller within the polymer matrix, which is not trivial to obtain.

2. Experimental part

2.1. Materials and methodology

Layered materials were prepared via coprecipitation method from water soluble precursors. Calcium phenylphosphonate and mixed calcium phenylphosphonate-phosphites and phenylphosphonate-phosphates were synthetized by reaction of calcium chloride with the appropriate acids under the basic pH. The molar ratio of the reacting components corresponded to a molar ratio Ca:P 1:1. Layered double hydroxides were prepared by a reaction of nitrate salts of appropriate metals in the presence of selected anion. Basic pH was ensured by the presence/decomposition of urea. The molar ratio of Zn:Al in the reaction mixture was 2:1.

Exfoliation of layered materials was performed in the best suitable solvent (for the details about the solvent selection see chapter Results and discussion) by means of sonication or shear forces. Sonication was performed in an ultrasound bath (FP11 201 Fisherbrand) with frequency 37 kHz and sweep function turned on. During sonication, samples were cooled by ice cubes. For the exfoliation by shear forces, a high-shear homogenizer IKA T10 Standard Ultra-turrax® (IKA®-Werke GmbH & Co. KG, Germany) equipped with a dispergation tool S 10 D-7 G-KS-65 was used.

Polymer composites were prepared by dispersing the unexfoliated or exfoliated filler into the polymer matrix using a shaft stirrer with a dispersing disc. In the case of unexfoliated particles, a three-roll milling was used for further homogenization. The prepared polymer dispersions were mixed with an appropriate hardener by hand. Then the free films were prepared on polypropylene plates using a gap-applicator or the samples were cast into molds. The samples were cured one day at a laboratory temperature and then thermally cured in an oven following the curing protocol (see Table 1).

Table 1 - Overview of the polymer systems used in this work and their curing conditions

Resin	Hardener	Curing protocol
Epoxy CHS-520	Jeffamine D230 Jeffamine D2000	1 day l. t. → 1 h 40 °C → 3 h 60 °C → 12 h 80 °C
Epoxy CHS-200 V	Telalit 180	1 day l. t → 2 h 50 °C → 2 h 80 °C
LV CC 220	LV BU 45 N	7 days l. t.

2.2. Characterization techniques

Powder X-ray diffraction (XRD)

Measurement by powder X-ray diffraction was performed on a D8-Advance diffractometer (Bruker, AX, Germany) with Bragg-Brentano geometry (40 kV, 30 mA) θ-θ using CuKα radiation. Diffraction angles were measured at room temperature from 2 to 65 ° (2θ) in 0.02 ° increments and a 10 s signal acquisition time for each step.

Atomic force microscopy (AFM)

Atomic force microscopy measurements were performed on a Dimension Icon (Bruker) in percussion mode using ScanAssyst-AIR tips (k = 0.4 N / m). The samples for analysis were prepared on atomic smooth mica using the spin-coating method and dried at 60 ° C for 24 h.

Scanning electron microscopy + Energy dispersive X-ray spectroscopy (SEM+EDX)

Analyzes were performed on a JEOL JSM-55000 LV device with an accelerating voltage of 20 kV, equipped with a GRESHAM Sirius 10 EDX detector (JEOL, USA Inc.).

Transmission electron microscopy (TEM)

Transmission electron microscope images were taken on a JEOL NeoARM 200 equipped with a 200 kV Schottky electron emitter. A few drops of the sample were applied to a carbonized copper grid.

Thermogravimetry (TG)

Thermogravimetric measurements were performed on two devices: an in-house built TG analyzer using a computer-programmable furnace and a Sartorius BP210 S analytical balance and a commercial TGA Q500 instrument (TA Instruments). The measurements were performed in air with a heating rate of 5 ° C / min.

Optical microscopy (OM)

The samples were scanned using an Olympus BX51 optical microscope equipped with a DP70 digital recording system.

Dynamic light scattering (DLS)

Particle size was measured by a light scattering method on a 90Plus / BI-MAS instrument (Brookhaven Instruments Corporation, USA).

UV-Vis spectroscopy (UV/Vis)

The optical properties of the samples were measured using an HP 8453 UV-Vis spectrometer (Perkin Elmer).

Dynamic mechanical analysis (DMA)

DMA measurements were performed using a Discovery DHR2 hybrid rheometer (TA instruments).

3. Results and discussion

3.1. Synthesis and characterization of layered materials

3.1.1. Metal organophosphonates

The synthesis of *calcium phenylphosphonate (CaPhP)* has been described previously [5]. In this work the synthesis conditions were revised in order to investigate possibility to transfer it into a larger-scale. There are two points that need to be highlighted. First, the role of pH is crucial. It is important to maintain pH>9 in the whole reaction volume during the whole reaction time. Thus, it is recommended to start rather at pH = 10 than pH = 9 when working with higher volumes. Second, it is appropriate to add the whole volume of calcium chloride solution in one portion. In the case of a drop-by-drop addition, which was also tested, the already formed particles act as a substrate for new lamellas and larger aggregates are formed rather than new separate particles.

In this work, series of *new materials* which combine *phosphonate* groups with *phosphite* ($Ca(C_6H_5PO_3)_x(HPO_3)_{1-x}\cdot nH_2O$) or *phosphate* groups ($Ca(C_6H_5PO_3)_x(HPO_4)_{1-x}\cdot nH_2O$) were also prepared and characterized. The molar ratio of phenylphosphonic acid to phosphorous or phosphoric acid varied from 3:1 to 3:1. The overview of the prepared samples is in Table 2 and Table 3. The prepared materials were characterized by means of XRD, SEM, EDX and TG.

Table 2 - List of mixed calcium phenylphosphonate-phosphites

Sample	Ratio H_2PhP: H_3PO_3	Basal spacing (Å)	Chemical composition
CaPhP	1:0	15.05	$CaC_6H_5PO_3\cdot 2H_2O$
CaPhP-HPO_3_3:1	3:1	14.95	$Ca(C_6H_5PO_3)_{0,94}(HPO_3)_{0,06}\cdot 1.32H_2O$
CaPhP-HPO_3_2:1	2:1	14.86	$Ca(C_6H_5PO_3)_{0,93}(HPO_3)_{0,07}\cdot 1.68H_2O$
CaPhP-HPO_3_1:1	1:1	14.66	$Ca(C_6H_5PO_3)_{0,68}(HPO_3)_{0,32}\cdot 1.33H_2O$
CaPhP-HPO_3_1:3	1:3	14.95 7.25	Not determined
$Ca(HPO_3)$	0:1	7.25	$Ca(HPO_3)\cdot H_2O$

Table 3 - List of mixed calcium phenylphosphonate-phosphates

Sample	Ratio H_2PhP: H_3PO_4	Basal spacing (Å)	Chemical composition
CaPhP-HPO_4_3:1	3:1	15.0	$Ca(C_6H_5PO_3)_{0,62}(HPO_4)_{0,38}\cdot 1.18H_2O$
CaPhP-HPO_4_1:1	1:1	15.26	Contains $Ca_5(PO_4)_3(OH)$
CaPhP-HPO_4_1:3	1:3	7.58	$Ca(HPO_4)\cdot H_2O$
$Ca(HPO_4)$	0:1	7.6	$Ca(HPO_4)\cdot H_2O$

To summarize the results, it is possible to obtain mixed layered calcium phosphonate-phosphite and phosphonate-phosphate structures if the molar ratio of $H_2PhP:H_3PO_3 \geq 1$ or $H_2PhP:H_3PO_4 > 1$. In other cases, a formation of $Ca(HPO_3)\cdot H_2O$, $Ca(HPO_4)\cdot H_2O$ and $Ca_5(PO_4)_3(OH)$ occurs. The basal spacing of $Ca(C_6H_5PO_3)_x(HPO_3)_{1-x}\cdot nH_2O$ decreases with the content of the phosphite groups. On the contrary, the basal spacing of the $Ca(C_6H_5PO_3)_{0,62}(HPO_4)_{0,38}\cdot 1.18H_2O$ particles is the same as for CaPhP. Thermal degradation of the prepared materials follows the same pattern as for CaPhP (see Figure 2). There are two main steps. First one between 25 – 200 °C belongs to the dehydration, which occurs in two less distinct steps. The dehydrated form is stable until 500 °C, when organic part is decomposed and $Ca_2P_2O_7$ is formed.

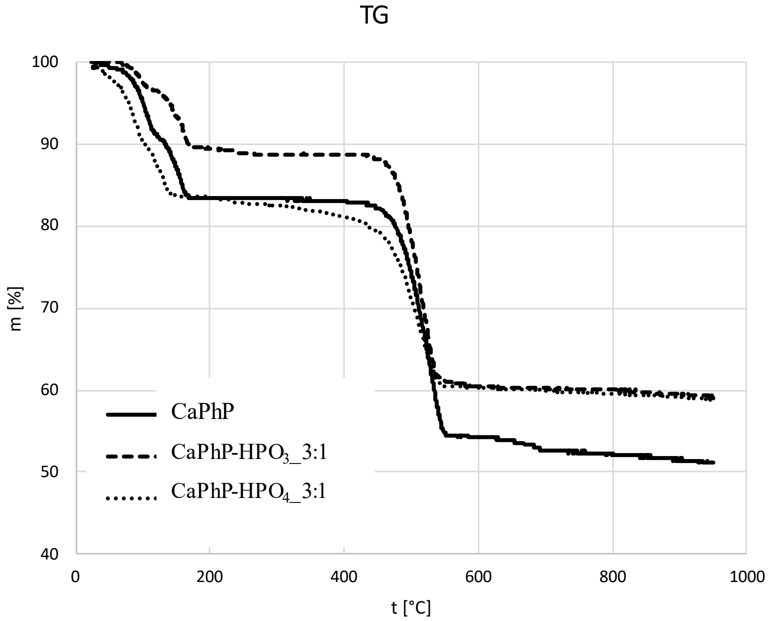

Figure 2 - Thermal degradation of prepared calcium phenylphosphonates

3.1.2. Layered double hydroxides

In this work, hydrotalcites of zinc-aluminum type with four different anions were successfully synthetized and characterized by means of XRD, EDX and SEM. Obtained results are summarized in Table 4. These materials were synthetized by a modified urea method [9] with exception of ZnAl-PBISA-1 and ZnAl-PBISA-3 samples, which were obtained by intercalation of 2-phenyl-5-benzimidazolsulphonic acid into the carbonate form of LDH. All prepared materials are white powders, but morphology of the particles differs with type of the charge compensation anion (see Figure 3). The basal spacing increases in a row $ZnAl\text{-}CO_3$ < ZnAl-LAC < ZnAl-PBISA< ZnAl-DDS. In the case of ZnAl-PBISA it is advantageous to use an intercalation approach than the direct synthesis, because it is possible to accommodate into the LDH structure higher amount of PBISA by intercalation.

Table 4 - List of synthetized LDHs and their properties

Sample	Anion	Zn/ Zn+Al	Al/ Zn+Al	S/Al	Basal spacing [Å]
ZnAl -DDS	dodecylsulphate	0.608	0.392	0.396	25.85
ZnAl-LAC	lactate	0.602	0.398	-	14.46
ZnAl-CO_3	carbonate	0.61	0.39	-	7.62
ZnAl-PBISA-1	2-phenyl-5-benzimidazolsulphonate	0.61	0.39	0.68	21.77
ZnAl-PBISA-2	2-phenyl-5-benzimidazolsulphonate	0.60	0.40	0.56	21.68
ZnAl-PBISA-3	2-phenyl-5-benzimidazolsulphonate	0.61	0.39	0.74	21.76

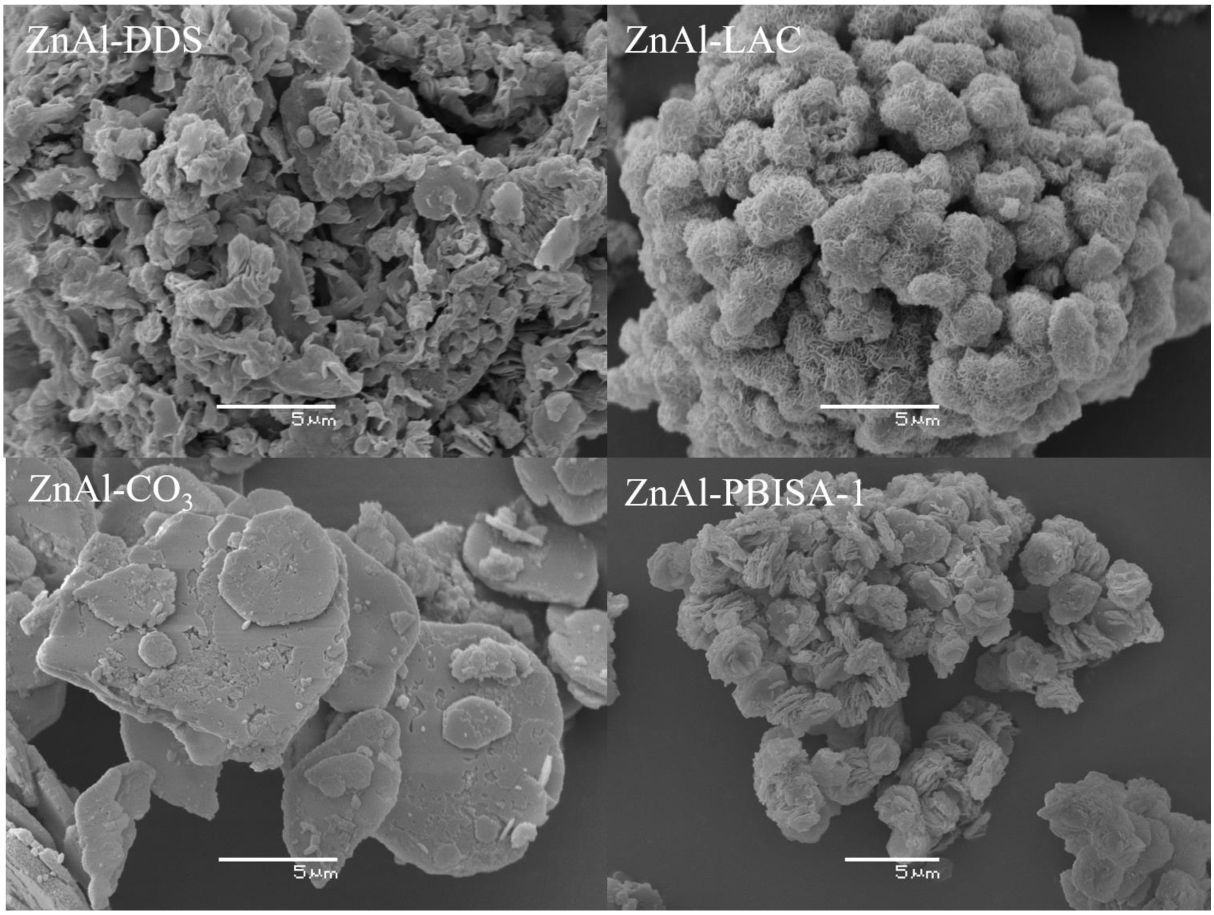

Figure 3 - Morphology of LDH particles

3.2. Exfoliation

3.2.1. Development of a Methodology for Samples Preparation and Characterization

The main part of this work was focused on liquid-based exfoliation. As the number of possible combinations of materials, solvents and technical approaches exceeds real possibilities to include all, it was necessary to establish standard methodology for sample preparation and characterization. Basically, it is possible to divide the process into the three steps: a) Selection of a suitable solvent, b) exfoliation by selected method and c) characterization of the obtained material.

Selection of a suitable solvent is a crucial part for the liquid-based exfoliation approach because molecules of a good solvent can act as an exfoliating agent and especially, they stabilize the obtained exfoliated lamellas and prevent their restacking. For the fast selection, a so-called "vial test" was established, based on an evaluation of the sedimentation of the tested material in the selected solvent. First, a small amount (10 – 15 mg) of a powder material was placed into a small glass vial with 5 ml of a selected solvent and put for 1 hour into an ultrasound bath (f = 37 kHz). Then the turbidity and sedimentation of the samples was evaluated by a visual observation immediately, after 1 hour and after 24 hours. After 24 hours the presence of Tyndall scattering was also assessed (see Figure 4). In a good solvent the sedimentation was slow and the light beam was clearly visible.

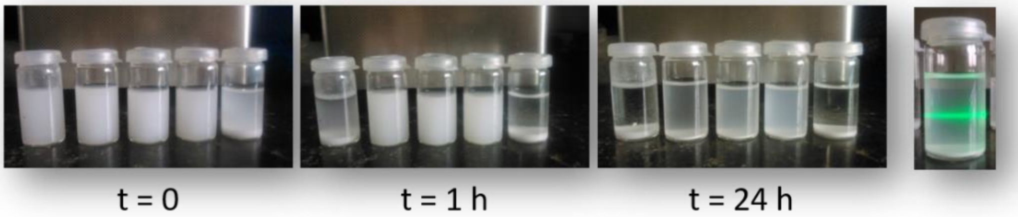

Figure 4 - Illustration of procedure of "vial test"

Exfoliation step includes a choice of suitable mechanical action, time, concentration of sample and eventually addition of a chemical agent.

Characterization of the obtained suspensions to evaluate if the exfoliation process was successful (it means that nanoplatelets are present) is done by atomic force microscopy, which is the only characterization technique which enables to measure thickness in the range of nanometers with sufficient accuracy. However, the AFM measurement is time consuming, thus it was necessary to introduce a selection step for the elimination of unsuccessful samples.

First, a suspension of possibly exfoliated particles is divided into three fractions by centrifugation at speeds of 3000, 6000 and 9000 rpm for 5 min. Then the presence of the Tyndall scattering in the supernatant is verified by a (green) laser beam. If the visible light trace in the sample centrifuged at speed 6000 rpm is weak and, in the sample centrifuged at speed of 9000 rpm, is not present at all, the exfoliation was not successful and the sample will not be subjected to a further evaluation.

Second, centrifuged fractions are measured by a dynamic light scattering. As the shape of the exfoliated particles is far away from an ideal sphere, the measured size is not relevant, however, for the evaluation of the sample quality, the most important is the trend of the obtained values. In the case of a system, which contains exfoliated particles, the distribution of the size fractions is similar for all three fractions. In the case of the sample, where the destruction processes prevailed and the sample contains mostly small fragments, the shift to smaller size values occurs with an increasing centrifugation speed.

Finally, the sample is measured by AFM. From the gained experience, the best suitable for the measurement is the fraction centrifuged at speed of 6000 rpm. This fraction contains not only full exfoliated lamellas but also particles, which are exfoliated partly. However, the height of the partly exfoliated particles is small enough so that these particles will not cover up the exfoliated ones.

3.2.2. Exfoliation results

As it is not possible to discuss all the results within the scope of this text, the obtained knowledge will be only briefly summarized. For the further details see the full text of the Doctoral dissertation.

The exfoliation of the prepared materials was performed either by a sonication in an ultrasound bath, where the normal forces are predominant, or by a treatment with homogenizer Ultraturrax® where high shear forces are present. To summarize the results, there is no universal method which would be suitable for all layered materials. The exfoliation conditions were studied for CaPhP. The ultrasound treatment is not preferable for this material. Although, it is possible to obtain some fully exfoliated sheets, the particles contain lots of defects. The most suitable technique for the CaPhP exfoliation is using high shear forces produced by Ultraturrax® but only for a short period of time (5 min). The obtained platelets were 1,6 nm high with lateral dimensions in hundreds of nanometers (Figure 5A). Longer time (1 h) leads to complete destruction of material (see Figure 5B). Optimal concentration of the exfoliated material in isopropyl alcohol was 5 g/l.

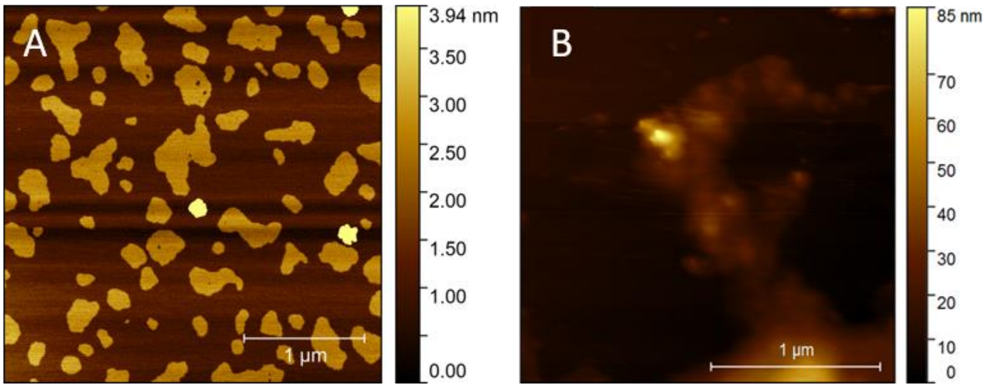

Figure 5 - Exfoliation of CaPhP using Ultraturrax; A) Exfoliated lamellas after optimization of time and concentration, B) Destructed material after too long time

The same procedure was not suitable for calcium phenylphosphonate-phosphites. The resulting material contained fragments resembling nanofibers. On the other hand, this method was suitable for calcium phenylphosphonate-phosphates and the obtained lamellas were even larger than the lamellas produced from CaPhP. To exfoliate 4-sulfophenylphosphonate, it was necessary to add an exfoliation agent [10] (the most suitable one was triethylamine), the mechanical action alone was not sufficient.

In the case of layered double hydroxides, it was possible to obtain exfoliated particles using Ultraturrax® and isopropyl alcohol as a solvent. The shape and thickness of the platelets differ with type of the charge compensating anion (see Figure 6 A, B, C). For ZnAl-DDS, the typical height of the lamellas is 0.7 – 1.1 nm, which corresponds to one layer but the shape of platelets is very heterogenous. For ZnAl-LAC there are large lamellas with height 3.5 nm, which corresponds to two layers, and in the case of ZnAl-CO_3, there are lamellas with height 1.6 nm which also corresponds to two layers and lateral dimensions are quite homogenous. Most of the studied materials was exfoliated in isopropyl alcohol, the only material which was successfully delaminated in distilled water was ZnAl-LAC using the ultrasound treatment.

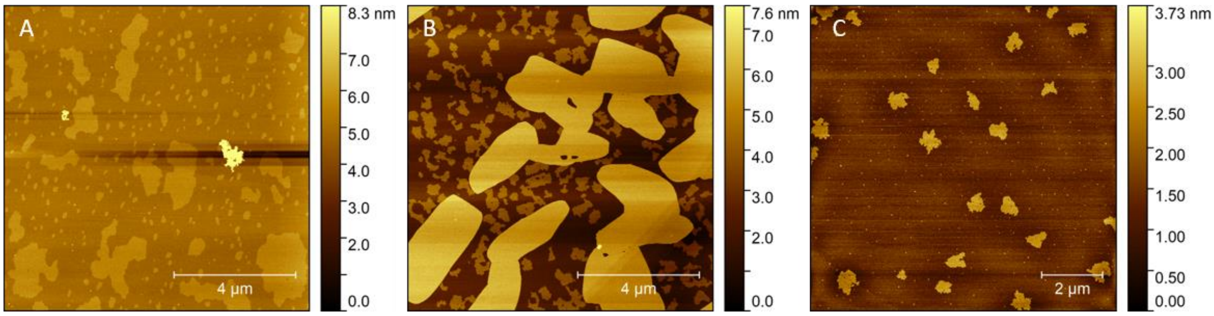

Figure 6 - LDH particles exfoliated in isopropyl alcohol using Ultraturrax®, A) ZnAl-DDS, B) ZnAl-LAC, C) ZnAl-CO_3

3.3. Polymer nanocomposites

Prepared layered materials, both in a pristine and in an exfoliated form, were tested as a filler in polymer systems.

In the case of CaPhP, the selected polymer matrix was high-solid epoxy resin CHS-520. It was found that this filler material is compatible with the selected resin [11]. For the dispersion of the particles in a pristine form it was beneficial to use a three-roll milling, in the case of the exfoliated filler, stirring with a shaft stirrer at low speed (350 rpm) was sufficient. The prepared mixtures were stable and no sedimentation or agglomeration was observed. there was a homogenous particle distribution within the composite. The influence on the mechanical properties was not significant, but the processing parameters were influenced. With the addition of CaPhP (either 1% of unexfoliated or 0.1 % of exfoliated form), addition of commercial leveling auxiliary agents could be omitted. Materials, which contain phosphor in their structure, are studied as a non-halogenated flame retardant [12]. The composite with CaPhP was tested according to the ISO 4589-2, to determine its Limiting oxygen index. In the case of the sample with 5 wt.% of unexfoliated CaPhP, the LOI increased from 19 (unfilled sample) to 21. This improvement does not meet criteria for flame retardancy, but may be useful in combination with other flame retardants.

The particles of LDH were tested in three polymer systems: high-solid epoxy CHS-520, waterborne epoxy CHS-200 V and polyurethan-acrylate lacquer LV CC 220. It was possible to disperse LDH particles into a high-solid epoxy resin only in their exfoliated form because the shaft stirring was not sufficient to break up agglomerates and by using the three-roll milling the particles were broken to smaller fragments. In the case of the exfoliated form, the particle distribution within the polymer matrix was homogenous, with the exception of the sample filled with ZnAl-DDS, in which more particles were detected on the upper side of the prepared film (see SEM images in Figure 7).

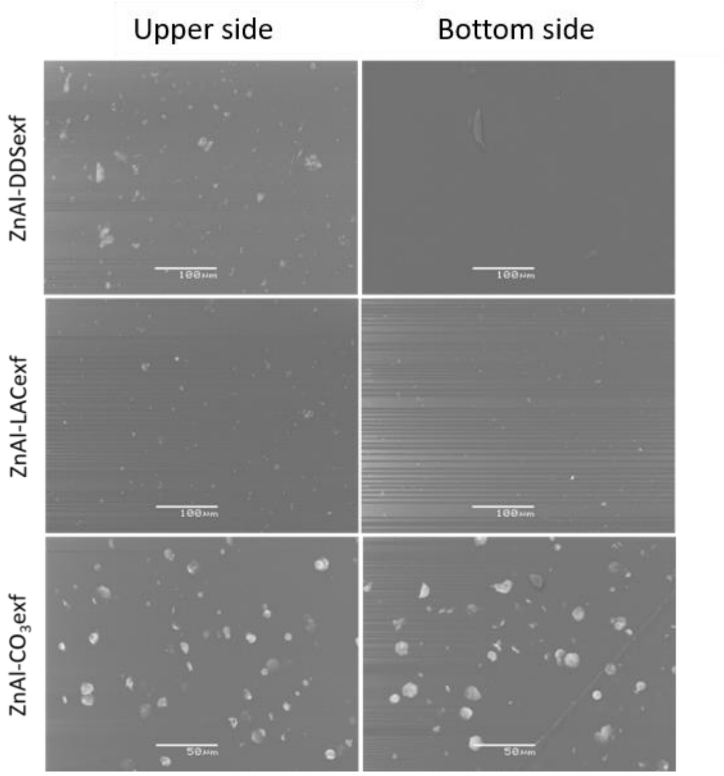

Figure 7 - SEM images of CHS-520 epoxy films prepared with exfoliated form of LDHs, comparison of upper and bottom side of the film. (Particles of the fillers are brighter than the polymer matrix.)

Compatibility of LDHs with waterborne system CHS-200 V varied for each form of LDH. All fillers were possible to disperse using a shaft stirrer at low speed (350 rpm) into the resin and their mixture was stable without a visible sedimentation. The sample with ZnAl-LAC contained large agglomerates, which were observed during the preparation of the free films with a gap applicator. On the contrary, no agglomerates were visible in mixture with ZnAl-CO_3. The SEM analysis of prepared films revealed, that during the curing of the samples, a massive sedimentation occurred and almost all particles of the fillers settled to the bottom side of the foil (this is most visible for ZnAl-CO_3, see Figure 8).

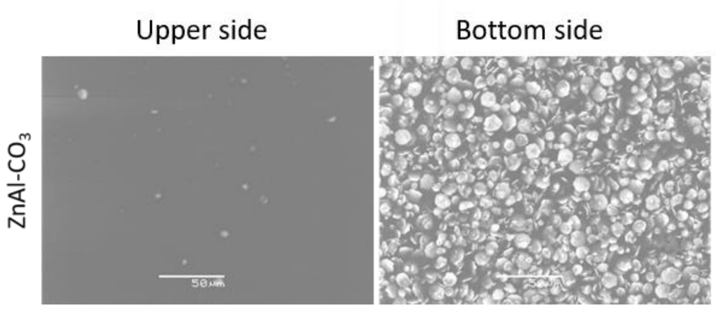

Figure 8 - Comparison of upper and bottom sides of the CHS-200 V foil filled with ZnAl-CO_3

Due to this inhomogeneity, no mechanical tests were performed, but barrier effect was evaluated by testing the chemical resistance of the film to the contact with acid (0.1M HCl) and base (0.1M NaOH). The standard unfilled foil was wrinkled at the point of contact with both solutions after 1 h, the same results were obtained for filled systems in contact with NaOH and also for foil with ZnAl-LAC in contact with HCl. In the cases of the foils in contact with HCl filled with ZnAl-DDS and ZnAl-CO_3, no visible changes were present even after 24 hours. The difference is documented in Figure 9.

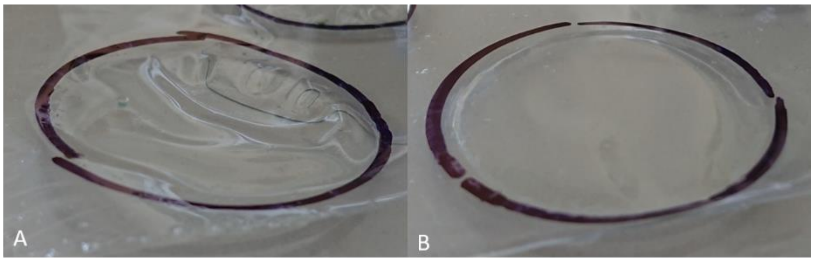

Figure 9 - Illustration of chemical resistance test. A) Wrapped unfilled foil after 1 h of contact with HCl, B) Foil filled with ZnAl-DDS after 24 hours in contact with HCl

Polyurethan-acrylate lacquer LV CC 220 was filled with the unexfoliated form of ZnAl-CO_3 and ZnAl-PBISA-1. For comparison, sample filled with pure 2-phenyl-5-benzimidazolsufonic acid was also prepared. In both cases of LDHs, no visible agglomerates occurred. Partial sedimentation was present after 24 hours but the sediment could be resuspended by mixing by hand. The SEM analysis revealed that lateral particle distribution in the prepared films was homogenous but a partial sedimentation occurred. However, the difference between the upper and bottom sides of the foil was not so significant as for the waterborne epoxy resin mentioned earlier. In the case of pure PBISA, the particle distribution is inhomogeneous. The intercalates with PBISA were prepared with intention to apply them as an UV protective agent in lacquers, so optical properties of the prepared foils were measured by UV/Vis spectroscopy. The transmittance of the samples differed significantly (see Figure 10). The standard and the film filled with the carbonate form of LDH showed the highest transmittance. The samples filled with ZnAl-PBISA and PBISA had low permeability typical for scattering on optically inhomogeneous parts, in our case the fillers. In the case of ZnAl-PBISA sample, there was a detectable indication of an absorption band in the region around 340 nm.

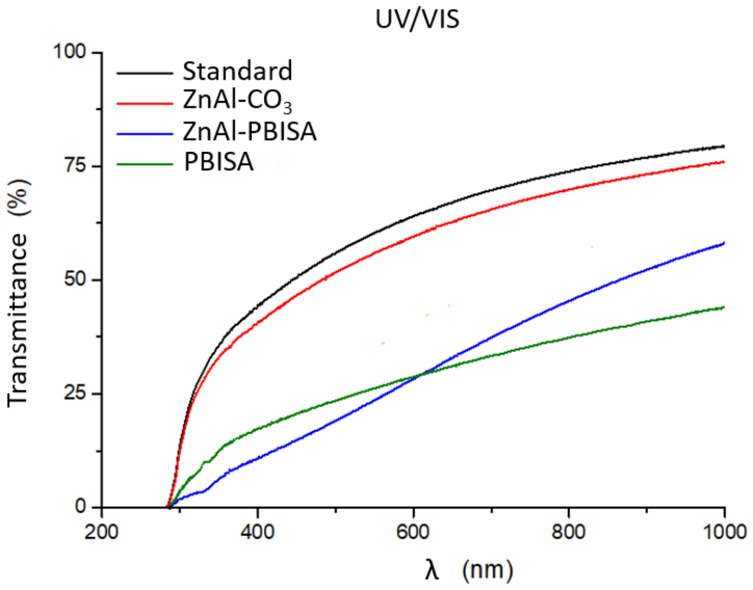

Figure 10 - UV/Vis measurement of filled foils from polyurethan-acrylate lacquer

If we compare transmittance of the samples at wavelength of 340 nm (Figure 11), the lowest transmittance is for the foil filled with ZnAl-PBISA. It is also worth noting the small deviations from the mean value, which means that the properties of the film are practically the same at all measured points, which is in line with the observed homogeneous distribution of the filler in the system. The developed UV absorber thus shows a higher absorption compared to the PBISA organic molecule alone and at the same time significantly improves its compatibility with the polyurethane-acrylate lacquer LV CC 220.

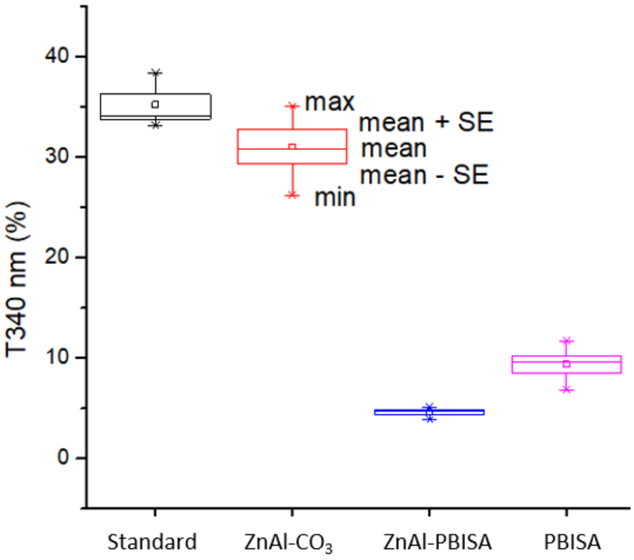

Figure 11 - Comparison of transmittance of foils at 340 nm

4. Conclusion

The presented dissertation was focused on the study of exfoliation of layered materials from the group of layered metal phosphonates and double layered hydroxides and the possibility of their use in polymer composites. First part of the work was the synthesis of studied materials. New layered materials based on calcium phenylphosphonate in which part of the phenyl groups was replaced by phosphite hydrogen or phosphate hydroxyl group with the general formula $Ca(C_6H_5PO_3)_x(HPO_3)_{1-x}{\cdot}nH_2O$ and $Ca(C_6H_5PO_3)_x(HPO_4)_{1-x}{\cdot}nH_2O$ were prepared and characterized. These materials are formed when a mixture of phenylphosphonic and phosphorous or phosphoric acids, respectively, is used in the preparation. The ratio of reacting acids must be in favor for phenylphosphonic acid, otherwise more phases occur or apatite is formed. Besides, zinc-aluminum double layered hydroxides were prepared and characterized, in which the positive charge of the layers was compensated by carbonate (ZnAl-CO_3), dodecyl sulfate (ZnAl-DDS), lactate (ZnAl-LAC) and 2-phenyl-5-benzimidazole sulfonate (ZnAl -PBISA).

The main part of the work was the research of the process of exfoliation of layered materials for the preparation of lamellas with a thickness in the order of nanometers. Mainly, a simple methodology for selecting a suitable solvent and a systematic way to evaluate the success of the exfoliation process based on characterization of exfoliated materials by observing the Tyndall effect and measuring particle size distribution by DLS,and finally characterization by AFM, which is the only characterization technique that provides evidence of the presence of layers with a nanometer thickness. Ultrasonic exfoliation and shear exfoliation were studied. It has been shown that for some materials it is more efficient and appropriate to use ultrasound, while for others good results are obtained only by shear forces. The evaluation for each material is given in the relevant section of the results. An important finding is that the appropriate method cannot be selected only on the basis of the similarity of the basic structure of the material, but the functional groups also play a role.

Exfoliated materials could be prepared in sufficient quantities to prepare polymer composites. Compatibility of fillers and techniques for their incorporation into high-solid epoxide CHS-520, waterborne system CHS-200 V and polyurethane-acrylate varnish LV CC 220 was verified. Calcium phenylphosphonates positively influenced leveling of high-solid epoxy resin and, thanks to the phosphorus content in the structure, it slightly reduces flammability, thus could be used as a non-halogenated synergistic additive in coating systems or composites. In the case of double layered hydroxides, the application properties of the high solids epoxide were not positively affected, however, the presence of ZnAl-DDS has a positive effect on increasing resistance to acids of the waterborn system CHS-200 V. To increase UV stability, the ZnAl-PBISA filler was developed, which enabled homogeneous distribution of the photoabsorbent molecule in the polyurethane-acrylate lacquer LV CC 220. For double layered hydroxides, it is necessary to emphasize that the developed exfoliation process is crucial for incorporation of filler into the polymer matrix. Conventional dispersion techniques such as three-roll milling cause destruction of particles into smaller fragments and their platelet-like shape is lost.

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