

Layered double hydroxides and it's applications in polymers

Jiří Kalous

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Elaborate a literar study focused on the following two points:

1.Treatment and modification of double layered hydroxide

2.Using double layered hydroxide in polymer system

Elaborate a short summary of the advantages and disadvantages of polymer/double layered hydroxide composite system

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2. Haydn, H.M. Handbook of Clay Science (Development in Clay Science),Elsevier, c2006. ISBN-13 978-0-08-044183-2, ISBN-10 0-08-044183-1.
3. Wypych, G. Handbook of Fillers, Toronto, New York:ChemTec Publishing, c1999. ISBN 1884207693.
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Vedoucí bakalářské práce:

Ing. Lucie Kovářová, Ph.D.

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doc. Ing. Petr Hlaváček, CSc.
děkan



Ing. Roman Čermák, Ph.D.
ředitel ústavu

ABSTRAKT

Tato bakalářská práce, která je rešeršního charakteru, se zabývá hydrotalcity, jež jsou v posledních letech intenzivně zkoumány. Používají se nejen na přípravu nanokompozitů, ale i jako nosiče organických barviv nebo pomocné látky při katalytické polymeraci ethylenů. V první části je popsána příprava, zejména srážecí metoda. Zatímco druhá část se věnuje přípravě modifikovaných hydrotalcitů, které se získávají výměnnou vnitřní anionické vrstvy za širokou škálu anionů, např. anorganické a organické látky. Důvodem modifikace hydrotalcitů může být jak dosažení zvýšené kompatibility s polymerní matricí při přípravě nanokompozitů, tak interkalace sloučenin umožňující tvarově selektivní adsorpci nebo katalýzu. Poslední část je zaměřena na nanokompozity obsahující hydrotalcity za účelem zlepšení finálních vlastností.

Klíčová slova:

Hydrotalcity , nanokompozity

ABSTRACT

This bachelor thesis is a literal study of LDH's, which are intensively researched in recent years. They are used not only for nanocomposite preparation but also as aorganic-dye carriers and catalyst-support system for ethylene polymerization. In first part the coprecipitation method is described. Second part is devoted to preparation of modified LDH's, which are obtained by changing their anionic layer for wide variety of anions, organic or anorganic. The reasons why LDH's are being modified is to increase compatibility with polymer matrix, implement compound for shape-selective absorption or catalyst etc. Last part is devoted to nanocomposites containing LDH's to increase their final properties.

Keywords:

Layered double hydroxides, hydrotalcites, nanokomposites

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INTRODUCTION

Polymers are widely used materials in these days because of their wide range of properties. It is vital to find way how to improve their properties because polymer materials are used in great amount and cost reduction is main goal. One possibility of the improvement which emerged in recent years is preparation of nanocomposites from common commercial polymers. Nanocomposites are two-phased materials where one of these phases have a dimension in nanometer range (0,1-100 μm). Exfoliated structure is an ideal state of nanoparticle dispergation. It means that nanoparticles are completely separated into individual layers. Intercalated structure occurs when nanoparticles do not creates individual layers and LDH keeps its galery spacing and crystalography with a polymer between galleries.

When LDH is used to prepare nanocomposites, structure of obtained compopunds is influenced as by both weight percentage of LDH in nanocomposite and compatibly of LDH with matrix. Compatibly of LDH with polymer matrix depends on LDH modification. In the area of polymer-layered double hydroxides nanocomposites the main advantages of these materials stem from the improved thermal propetries, and reduced flammability. Moreover, the increased tensile properties are obtaned.

1 STRUCTURE AND PREPARATION OF LDH'S

The basic structure is formed by layers of $M(OH)_6$ with an anionic interlayer. This forms a hexagonal close packing of anions with total occupancy of octahedral holes by cations every two interlayers. The positive charge of the layers is balanced by anions located, together with water molecules, in the interlayer region. The universal formula of LDH's is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$. The nature of the layer cations can be changed in a wide range: main group cations ($M = Mg, Ca, Al, Ga$ or In) or transition metal cations ($M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y$) generally in the divalent or trivalent state. Also the molecular ratio of metal cations can be modified. The interlayer anions can be very different: halides, oxoanions, oxometalates, polyoxometalates, coordination compounds, and organic anions [1]

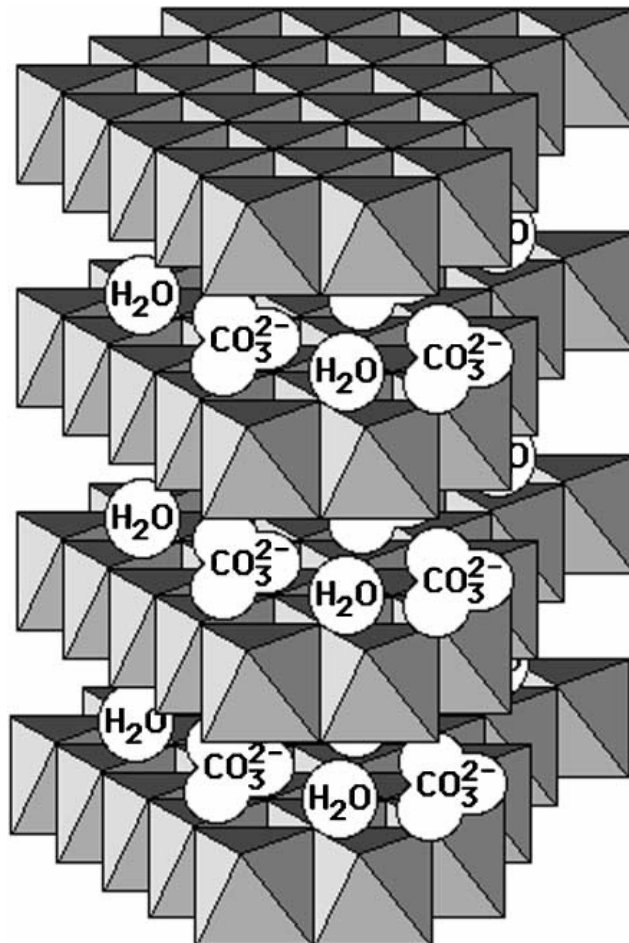


Fig. 1. Scheme of LDH's. (borrowed from [1])

1.1 Preparation of LDH's

Widely used method is co-precipitation. Most of the LDH's is prepared by using co-precipitation method. When preparing LDH by this method, they can be modified directly when they are prepared. This is why the preparation and modification are difficult to differ.

1.1.1 Co-precipitation method

Example of preparation of Mg/Al LDH by co-precipitation method

Aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dropwisely added to a basic solution of NaOH and Na_2CO_3 at a constant pH of 10. The system was stirred for 1 hour to reach and keep homogeneity of mixture. The precipitates formed were aged in their mother liquor for 16 h at room temperature and then filtered, washed with deionized water until Na^+ was not detected in the filtrate, and dried for 10 h at 120°C . A fraction of the hydrocarbonate precursor prepared by co-precipitation method was milled in an aqueous media. After milling, the sample was filtered, washed and dried [2].

Mg/Al LDH preparation as described by Jianxi Zhu et al [1]

Mixed solution of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0,25M) and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0,75M) both nitrates were provided by Sigmy Pty Ltd., Australia) and mixed solution of sodium hydroxide were placed in separated vessels and purged with N_2 for 20 minute. Both solutions were dissolved in decarbonated water. Cationic solution was added to anionic by a peristaltic pump at 40ml/min. Resulting precipitate was filtered and cleared by decarbonated water, then dried for few days in vacuum desiccator.

1.1.2 Preparation of Ni/Ti LDH via urea method

Ni/Ti as described by W.H Zhang et al.[3]

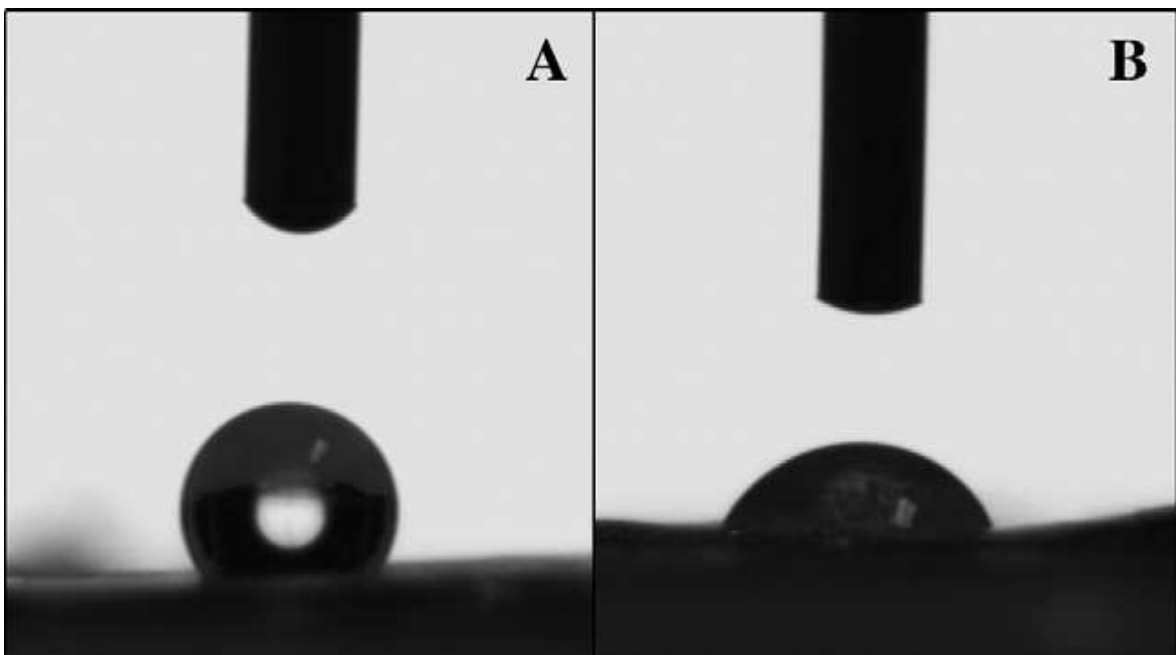
Solution of TiCl_4 in HCl at volume ratio 1:1, urea and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to deionized water under stirring. The obtained solutions was stirred for 6h at refluxing condition. Solution was filtered and filtration cake was washed by deionized water and anhydrous ethanol respectively. Washed filtration cake was dried for approx. 12h at 60°C [3].

1.1.3 Preparation of Zn/Al LDH in thin films

Zn/Al LDH in this films was prepared on the surface of anodic alumina oxide(AAO)membrane. The nanopores provide channels and nano-sized wall edges for supplying Al^{3+} . That means that LDH films can be grown very effectively on AAO membrane.

Zn/Al LDH film was prepared by direct precipitation method. 10ml of aqueous solution of $(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ and hexamethyltetramine were added into a sample vial with AAO membranes on the bottom. Vial was put to a preheated water bath for 1h and kept at 90°C .

The surface morphology of Zn/Al LDH film affects wettability. Unmodified film has low wettability. To increase it, LDH film is calcinated. Fig. 2[4]. shows shape of a water droplet on basic Zn/Al and on a calcinated one. Fig. 3[4] show diferences in surface morphology of basic Zn/Al LDH and calcinated LDH



*Fig. 2. Water droplet shape on basic Zn/Al LDH (A) and on a calcinated Zn/Al LDH (B)
(borrowed from[4])*

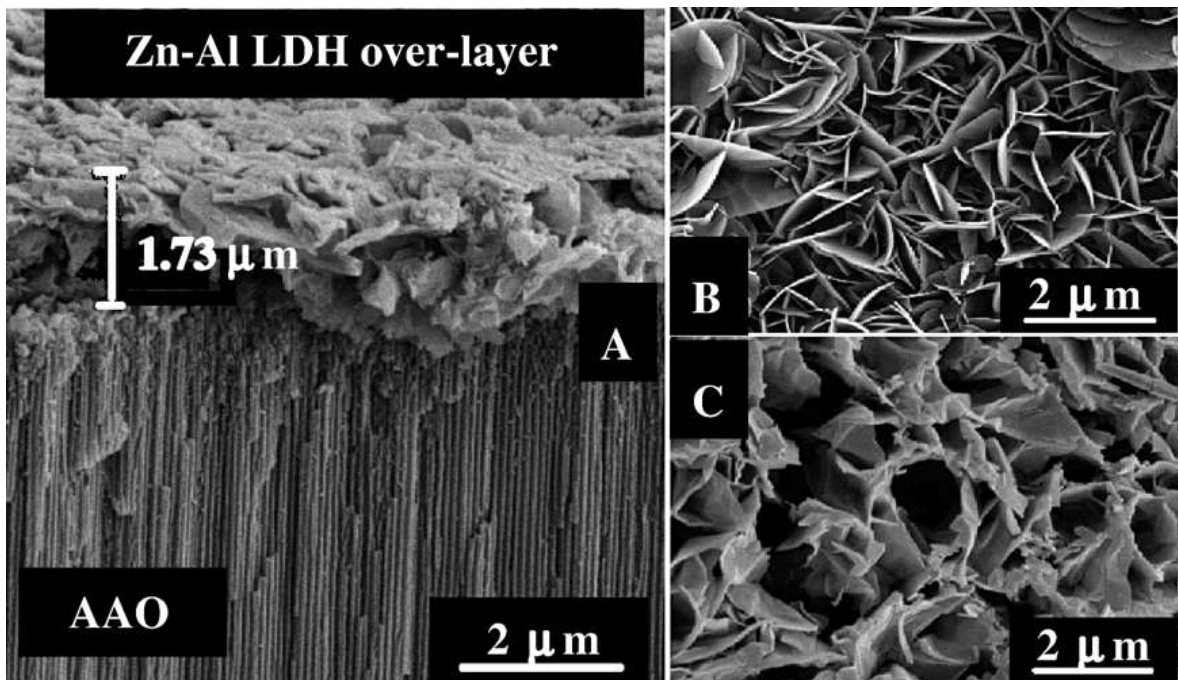


Fig. 3. (A) – Zn/Al layer on AAO membrane, (B) – surface morphology of basic Zn/Al LDH film, (C) – surface morphology of calcinated Zn/Al LDH film. (borrowed from [4])

2 OBJECTIVES OF THE BACHELORS THESIS

2.1 Modifications of LDH

Modifications of LDH are important when preparing polymer/LDH compounds due to increased compatibility of modified LDH with polymer matrix. The point is to describe most common methods of modification.

2.2 Using LDH in polymer system

LDH are used to prepare nanocomposites from common polymers. The goal is to compare properties of obtained compounds with unmodified common polymers.

3 MODIFICATIONS OF LDH'S

3.1 Tungstencobaltate(Co/W) anion-pillared Mg/Al LDH

Tungstencobaltate belongs to the group of polyoxometalates. Polyoxometalates are interesting group of compounds. They have definite size and shape. This makes them very useful for shape-selective adsorption and catalysis.

3.1.1 Synthesis of Co/W anion pillared Mg/Al LDH

Described by Xiaocui Wei et al. [5]

Starting components were MgAl(NO₃) LDH and K₅(CoW₁₂O₄₀)•20H₂O. Reaction was carried out in an aqueous slurry of MgAl(NO₃). The K₅(CoW₁₂O₄₀)•20H₂O was acidified in N₂ atmosphere to pH 6.5 and the mixture of these components was kept under N₂ atmosphere for 10 hours at a temperature of 95°C. Resulting solid was washed by boiling water and ethanol, then dried overnight at 70°C. The Fig. 4[5] shows mechanism of reaction.

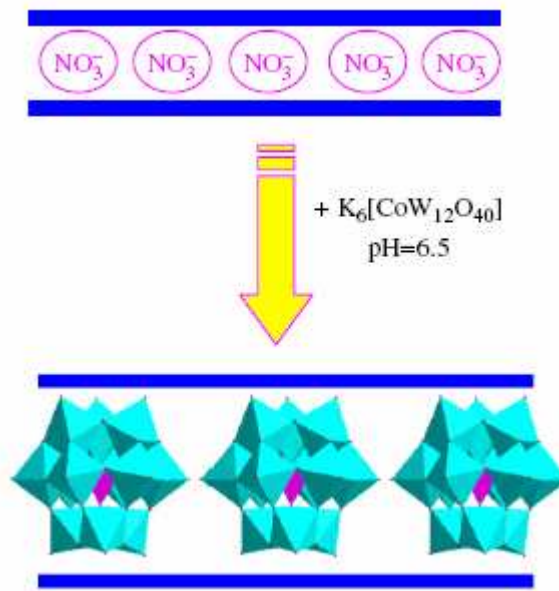


Fig. 4. Mechanism of anionic exchange (borrowed from [5])

Magnetic measurement showed weak antiferromagnetic interactions between magnetic center. This could lead to preparation of molecular magnets in a solid materials in a near future [5].

3.2 Organo-modified Zn/Al LDH

Organo-modified Zn/Al hydroxide was used as a support to a nickel- α diimine catalyst for ethylene polymerization. Comparison of PE prepared by supported and unsupported catalyst is described further(3.1)

3.2.1 Preparation of organo-modified Zn/Al LDH

For preparation was used co-precipitation method. At first, 0,03 mol of sodium benzoate was dispersed in 100ml of deionized water(solution 1).Then 0.03 mol $Zn(NO_3)_2 \cdot 6H_2O$ and 0.01 mol $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in another 100 ml deionized water.(solution 2). Solution 2 was added to solution 1 dropwisely. The pH was kept at value of 10 by adding 1mol/L NaOH. After complete addition of solution 2 to solution 1, the mixture was aged for three day at 70°C in N_2 atmosphere. The gained slurry was then filtered and washed by distilled water.White OZnAl-LDH solid was obtained by drying in a vacuum oven at 60°C[6].

3.2.2 Preparation of supported catalyst system for ethylene polymerization.

10.0g of organo-modified Zn/Al LDH was put in a glass vesel with a magnetic stirrer.Then 50ml of the hexane was added. After that, 10ml of $AlEt_3$ (400g in 1L of heptane) was added to mixture at 0°C at the system was stirred fo 20h. Threated Zn/Al LDH was decanted, washed with hexane and dried. To prepare the supported nickel α -diimine catalyst, 0.3 g $NiLBr_2$ was dissolved in 10 ml dichloromethane and then added to the suspension composed of threated Zn/Al LDH and 30 ml hexane. System was stirred at room temperature overnight. After decantation, the solid was washed up with hexane and then dried under vacuum. The supported catalyst was obtained as solid, yellow particles[6].

3.3 Dye-intercalated Zn/Al LDH

Organic dyes attracted much of attention in wide field of industry such a plastic, inks, paints and electronics devices. Their advantages are color strength, transparency and photosensitivity. But they are limited by instability under outdoor environment (temperature, oxygen, daylight etc.) For practical use they must be encapsulated in support like polymers or silicas. Zn/Al LDH can „carry“ dye anions intercalated in their layers. Result is a dye-LDH hybrid pigment. This pigments have increased thermal stability and higher mechanical strength. But they have also low dispersion ability, insufficient for industrial use. In order to improve its dispersion ability, the LDH was coated by colloidal nanosilica [7].

3.3.1 Preparation of dye-intercalated Zn/Al LDH

Described by Sung-Ho Hwang et al. [7]

LDH intercalation compounds were directly synthesized by hydrolysis of the mixed aqueous solution of aluminium nitrate, zinc nitrate and dyes. Four different types of dyes were used. (acid red 1 (AR)— $C_{18}H_{33}N_3Na_2O_8S_2$, acid yellow 3 (AY)— $C_{18}H_9NNa_2O_8S_2$, acid green 25 (AG)— $C_{28}H_2ON_2Na_2O_8S_2$, acid blue 45 (AB1)— $C_{14}H_8N_2Na_2O_{10}S_2$, AB 80 (AB2)— $C_{32}H_{20}N_2Na_2O_8S_2$). The pH was kept at value of 7-8 by dropwise addition of 0,1M NaOH. Whole system was under N_2 atmosphere. Dye/Zn/Al ratio was 5:3:1 in molar equivalent. After 12h of aging, products were separated, washed and dried.

In the silica-coating process, each LDH-dye hybrid was dispersed in silica sol solution and then the reaction mixtures were aged for 3 h. The products obtained were washed with ethanol and dried under vacuum.

Intercalation of organic dyes have impact on basal spacing of the LDH. Zn/Al LDH with intercalated CO_3^{2-} have basal spacing 7,8 Å, dye-intercalated LDH have basal spacing 22.5, 24.2, 20.6, 18.7, 24.3 Å for AR1, AY 3, AG 25, AB1 and AB2 respectively. As we can see on Fig. 6, LDH with intercalated CO_3^{2-} have different morphology then dye-intercalated LDH. Morphology can be modified by reaction conditions, shape of the dye and synthesis method[7]

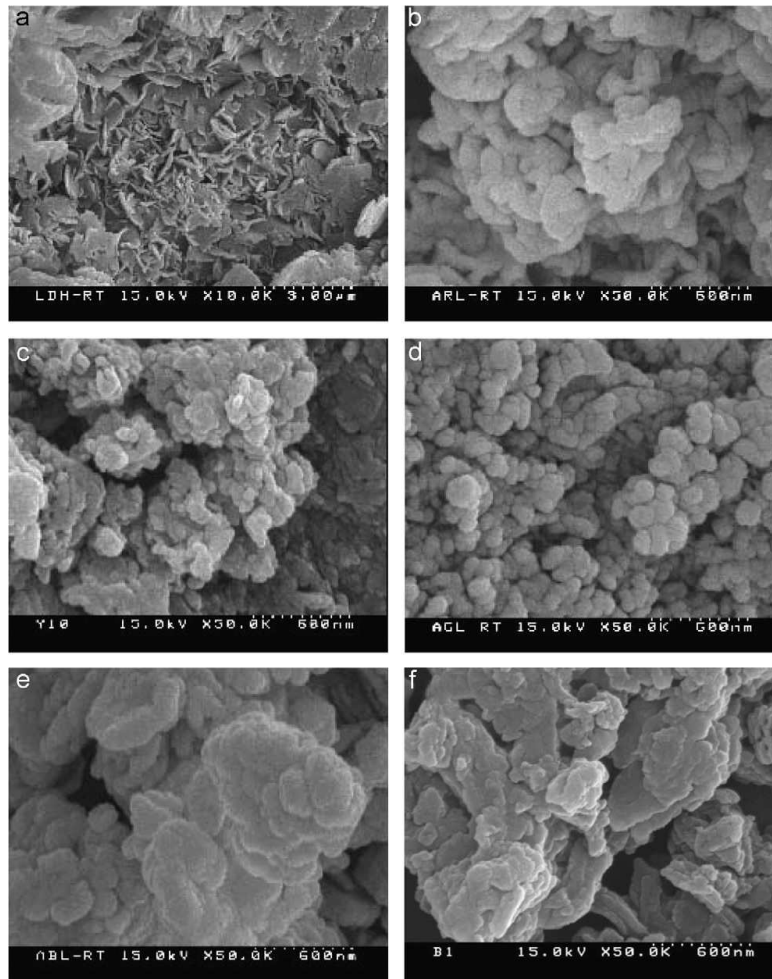


Fig. 5. Morphology of AR1, AY 3, AG 25, AB1 and AB2 dyes intercalated in LDH. (borrowed from [7])

3.4 Dodecyl sulfate modified Zn/Al LDH

Wei Chen, Baojun Qu [12] prepared dodecyl sulfate modified Zn/Al LDH (Zn/AIDS LDH). It was prepared by a spontaneous self-assembly method. A 100 ml of aqueous solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.03 mol), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.01 mol), and 3g of sodium dodecyl sulfate was prepared. pH of solution was maintained at value of 10. Obtained slurry was aged at 70°C for 12h. Precipitate was filtered and dried.

3.5 Surfactant/silane-modified Mg/Al LDH

Surfactant and surfactant/silane modified LDH are important for nanocomposite preparation. They can be also used to remove anionic organic pollutants in environmental technology. Both LDH's were prepared by co-precipitation method and were modified directly during preparation.

3.5.1 Preparation of anionic surfactant modified LDH.

Preparation as described by Jianxi Zhu et al. [1]

$\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100ml of deionized water (solution 1). NaOH and Na-dodecyl sulfate were dissolved in 100ml of deionized water (solution 2). Solution 1 was added to solution 2 by using peristaltic pump with stirring and refluxing. The obtained mixture was stirred for approximately 20 hours. Obtained product was washed with water and ethanol and then dried.

3.5.2 Preparation of anionic surfactants and silane modified LDH

$\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and phenyltrimethoxysilane were dissolved in 100ml of deionized water (solution 1). NaOH and Na-dodecyl sulfate were dissolved in 100ml of deionized water (solution 2). The rest of the procedure is same as 2.4.1[1]

As we can see on Fig. 6[1], each LDH have a different structure.

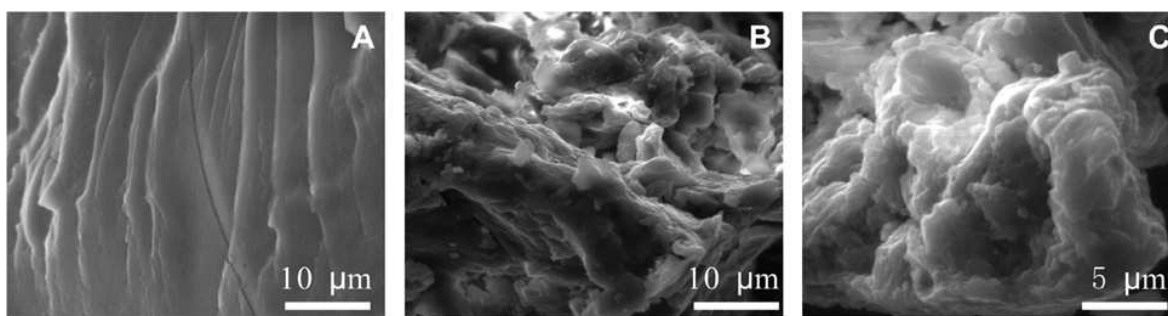


Fig. 6. Structure of Mg/Al LDH (A), anionic surfactant modified LDH (B) and anionic surfactant and silane modified LDH (C) (borrowed from [1])

4 LDH'S IN COMMON POLYMERS

LDH's can be used to prepare nanocomposites from common polymers (PE, PS, PET etc.) The result is improvement of properties, like thermal stability, particle morphology, increasing of decomposition temperature, strength modulus and many others.

4.1 Zn/Al LDH in PE

Zn/Al LDH was used as a support to a nickel *a*-diimine catalyst for ethylene polymerization. Properties of PE produced by only a nickel *a*-diimine catalyst and PE produced by a nickel *a*-diimine catalyst with a Zn/Al LDH were compared.

The polyethylene material with LDH showed good morphology, improved thermal stability, as well as enhanced storage modulus and complex viscosity.

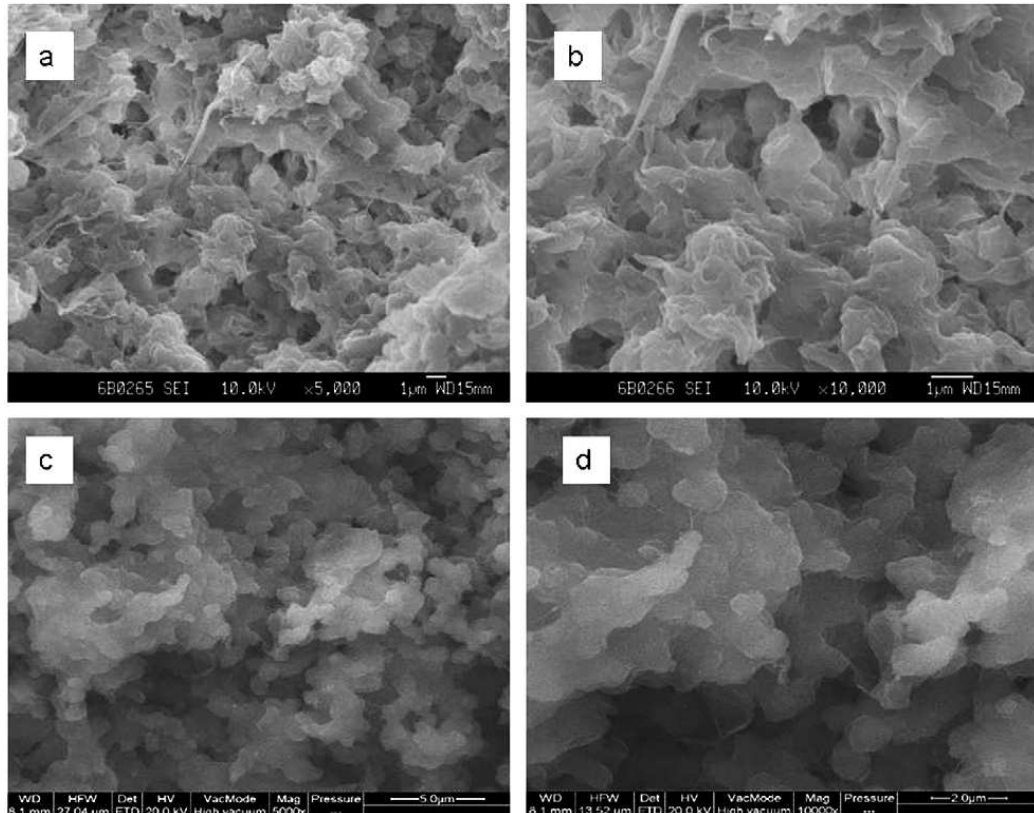
4.1.1 Preparation of PE by using supported catalyst system.

Described by Fu-An He and Li-Ming Zhang [6]

250 ml glass reactor, equipped with stirring, was filled by ethylene to pressure 0,1MPa. 50ml of heptane, cocatalyst (AlEt_2Cl) and required amount of supported catalyst system were added to a reactor. The polymerization was conducted and then terminated by addition of NaOH. Obtained products were filtered and washed with deionized water and ethanol, then dried in vacuum for 24h at 60°C. PE was also prepared by using unsupported catalyst system to compare properties, the preparation was conducted under same conditions.

4.1.2 Properties of Zn/Al LDH modified PE

As we can see on the Fig.7.[6], the structure of PE prepared in presence of the homogenous nickel *a*-diimine catalyst is porous and less homogenous (it seems to be „spongy-like“) then a structure of PE prepared by using nickel *a*-diimine catalyst supported on OZnAl-LDH, which is more smooth and regular. These results shows that the used OZnAl-LDH support has a great impact on the structural characteristics of the PE [6].



*Fig. 7. SEM images of the polyethylene prepared in the presence of the homogeneous nickel *a*-diimine catalyst and the nickel *a*-diimine catalyst supported on OZnAl-LDH [(a), (c) $\times 5000$; (b),(d) $\times 10,000$] (borrowed from [6])*

LDH in PE have also impact on thermal degradation. Homogenous PE starts to degrade at 350°C and has almost no residues above 560°C . PE prepared by supported catalyst degrades slower to 400°C and still has some residues at 560°C . At selected weight loss (30% wt), the temperature of homogenous PE was 402°C but PE prepared by supported catalyst has temperature 463°C .

PE prepared by using supported nickel *a*-diimine catalyst has a increased viscosity and elastic modulus when compared to homogenous PE. Increased viscosity in melt state can be consider as a disadvantage when procesing PE. The difference between the viscoelastic behaviours of two polyethylene products which was observed, it may be attributed to the fact that the intercalated or exfoliated ZnAl-LDH layers weakened the mobility of the polyethylene chains and then restrict their long-range relaxation [6].

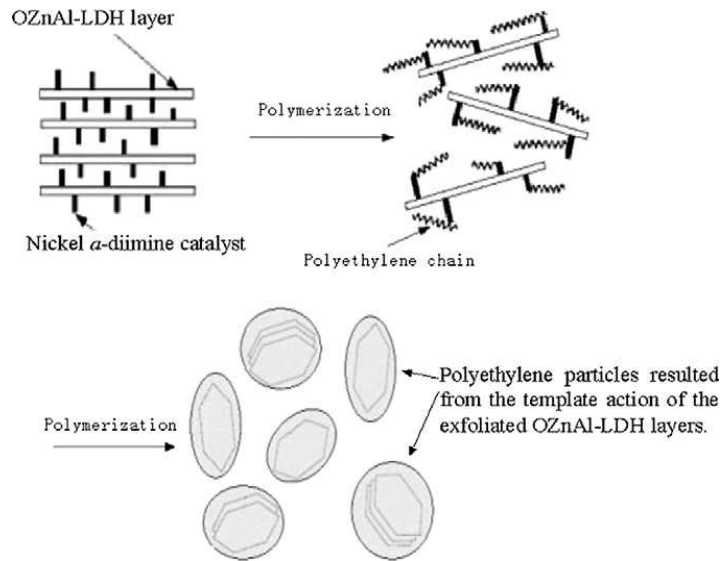


Fig. 8. Formation process of the PE with a granular morphology by the template action of the exfoliated OZnAl-LDH layers during the ethylene polymerization. (borrowed from [6])

4.2 Modified Mg/Al in PET

Three different PET nanocomposites were compared, each of them was prepared by using differently modified Mg/Al LDH (dodecylsulfate (Mg/AlDS), dodecylbenzenesulfonate (Mg/AlDBS) octylsulfate (Mg/AlOS) and basic LDH (Mg/AlCO₃)). Reason for using modified LDH's was to increase its compatibility with PET matrix.

4.2.1 Preparation of MgAl/PET nanocomposite.

Described by Wan Duk Lee et al.[8].

Nanocomposite was prepared by using direct melt compounding method. Twin co-rotating screw extruder was used. The compounding was carried out under a barrel temperature of 270 °C, roll speed of 200 rpm, and average residence time of 60 s. All materials were dried in vacuum oven at 75 °C for 24 h.

4.2.2 Properties of MgAl/PET nanocomposite.

As we can see from following pictures (Fig. 9[8]. and Fig. 10[8].), the Mg/AlDS shows highest increment of yield strength and modulus

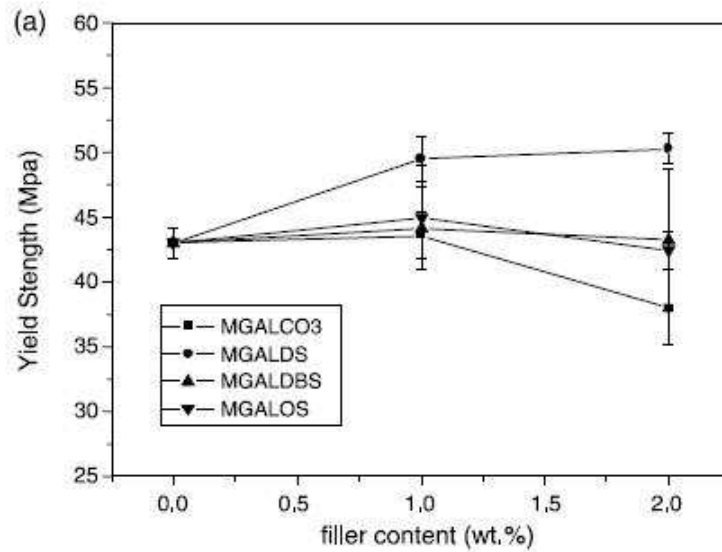


Fig. 9. Yield strength of PET nanocomposite depending on filler content. (borrowed from [8])

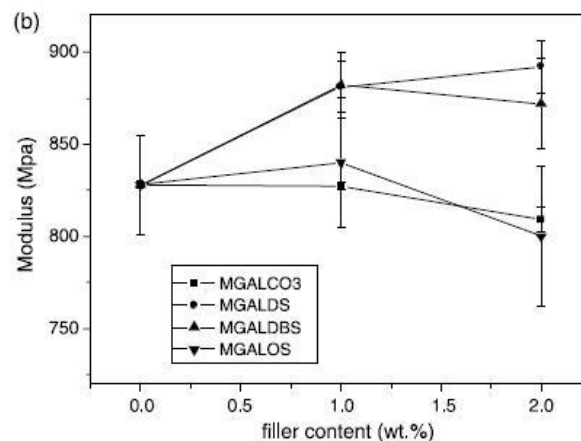


Fig. 10. Modulus of PET nanocomposite depending on filler content. (borrowed from [8])

Mg/AIDS LDH have the highest compatibility with PET matrix and therefore the increase of yield strength and modulus is best.

The properties of PET/LDH composites are highly impacted by weight percentage of LDH in the PET. If more than 2wt.% of LDH are used, the composite becomes very brittle. The reason why this happens is creation of LDH aggregates in PET matrix. Thermal properties of PET/LDH composites are nearly as same as the homogenous PET, the influence is minor [8].

4.3 Zn/Al LDH in PS

Homogenous PS and ZnAl LDH/PS nanocomposite were compared. Four samples with different weight percentage (1, 5, 10, 30,) of LDH were prepared. Weight percentage of LDH have impact on the morphological structure and thermal properties of the nanocomposite.

4.3.1 Preparation of ZnAl LDH/PS nanocomposite

Described by Peng Ding and Baojun Qu [9].

1.15g of N-lauroyl-glutamate(LG) and 1.00g of n-hexadecane were mixed in 12ml water at temperature of 40°C and stirred until a transparent solution was obtained (solution 1). Then the solution 2 was prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3$, at concentrations of 0.500 mol/L and 0.167 mol/L, respectively. Solution 3 is 15.3 ml of 1mol/L NaOH. Both solution 2 and solution 3 were added to solution 1 simultaneously, using peristaltic pump at discharge rate of 2ml/min. pH of the solution was kept at 9.5-10. Then the styrene at calculated amount was added. Finally, $\text{K}_2\text{S}_2\text{O}_8$ and Na_2SO_3 were added to initiate polymerization. The reaction was carried in oil bath at 80°C. Obtained ZnAl/PS samples were precipitated in methanol, filtered, and washed with alcohol and water respectively, then dried at 80°C

Pure PS was also prepared to compare properties.

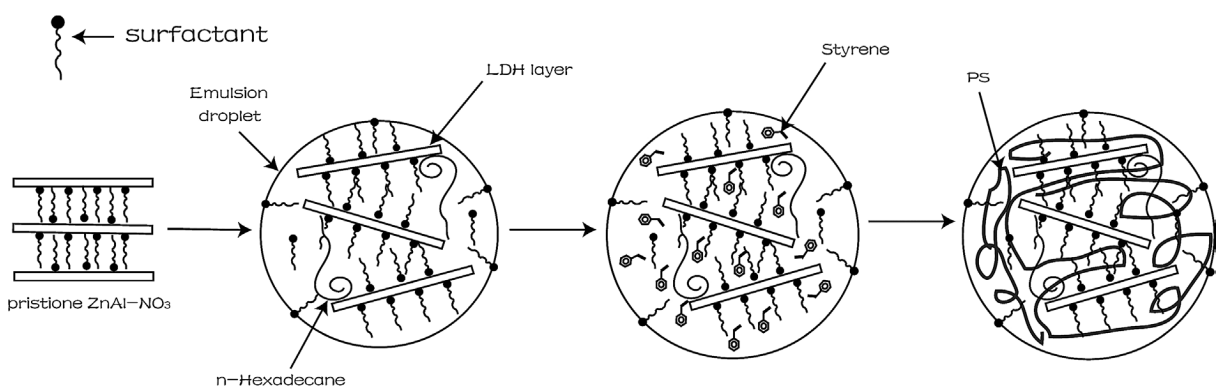


Fig. 11. Schematics diagrams of the formation process of the exfoliated PS/LDH nanocomposite.(borrowed from [9])

4.3.2 Properties of ZnAl LDH/PS nanocomposites

At 1 wt.% the structure is exfoliated(see Fig. 12.[9]), the LDH with surfactans is homogeneously disperzed in PS matrix.

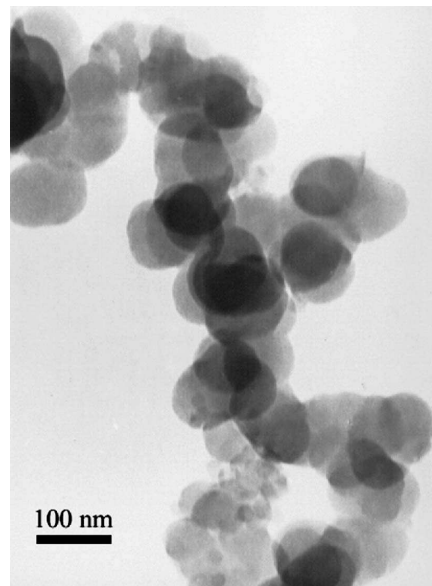


Fig. 12. Exfoliated LDH(dark parts) with LG surfactans(grey parts) in PS matrix (bright part), 1wt.% of LDH. (borrowed from [9])

At the 30 wt% of LDH the stucture become intercalated, as seen on Fig. 13[9].., but we cas still find some exfoliated structure (marked as „v“on the picture)

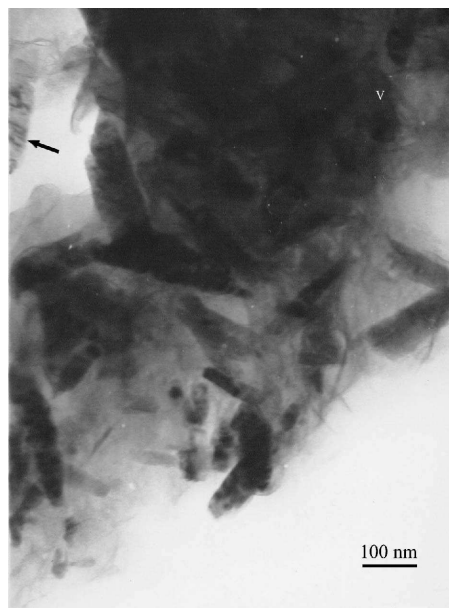


Fig. 13. Intercalated structure of LDH in PS with 30 wt% of LDH. (borrowed from [9])

ZnAl-LDH/PS composite with 10wt.% of Zn/Al LDH has all LDH completely exfoliated. When wt% increases over 10wt%, the structure changes from exfoliated to intercalated with some exfoliated parts.

Tab. 1 show influence of percentage of LDH to decomposition temperature. The 50% weight loss was set as a point of measure.

| wt.of LDH (%) | Decomposition temperature |
|---------------|---------------------------|
| 0 | 384 |
| 1 | 397 |
| 5 | 412 |
| 10 | 386 |
| 30 | 355 |

Tab. 1. Dependency of decomposition temperature at wt.% of Zn/Al LDH in PS

As seen of Fig. 14[9], ZnAl-LDH/PS nanocomposite starts to degrade earlier than pure PS. This is due to evaporation of physically absorbed water.

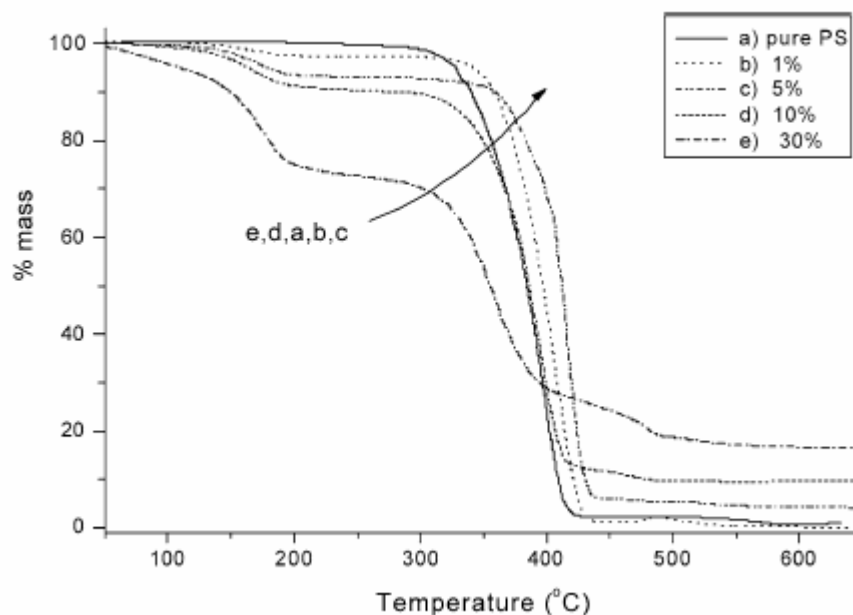


Fig. 14. TGA curves of ZnAl-LDH/PS nanocomposites . (borrowed from [9])

4.4 Mg/Al LDH in nylon-6

The nylon-6/MgAl LDH nanocomposite was prepared by melt intercalation of nylon-6 into the Mg/AlDS (dodecyl sulfate modified Mg/Al LDH). When compared to a common nylon-6, nylon nanocomposite have greatly changed thermal properties and combustion characterization.

4.4.1 Preparation of MgAl-LDH/Nylon-6 nanocomposite

MgAl-LDH/Nylon-6 nanocomposite samples were prepared by melt-mixing dodecyl sulfate modified Mg/Al LDH powders with a nylon-6 using a mixer with 64 rpm at 200°C [10].

4.4.2 Properties of MgAl-LDH/Nylon-6 nanocomposite

To compare properties of pure nylon-6 and MgAl-LDH/Nylon-6 nanocomposite, three different samples were prepared. NC-5 with 5wt.%, NC-10 with 10wt.% and NC-20 with 20wt%. MgAl-LDH/Nylon-6 nanocomposite have a lower mass loss rate (MLR) than a common nylon-6. Mass loss rate is lowering with increasing LDH loading. Fig. 15 [10] show comparison of pure nylon and MgAl-LDH/nylon-6 nanocomposites.

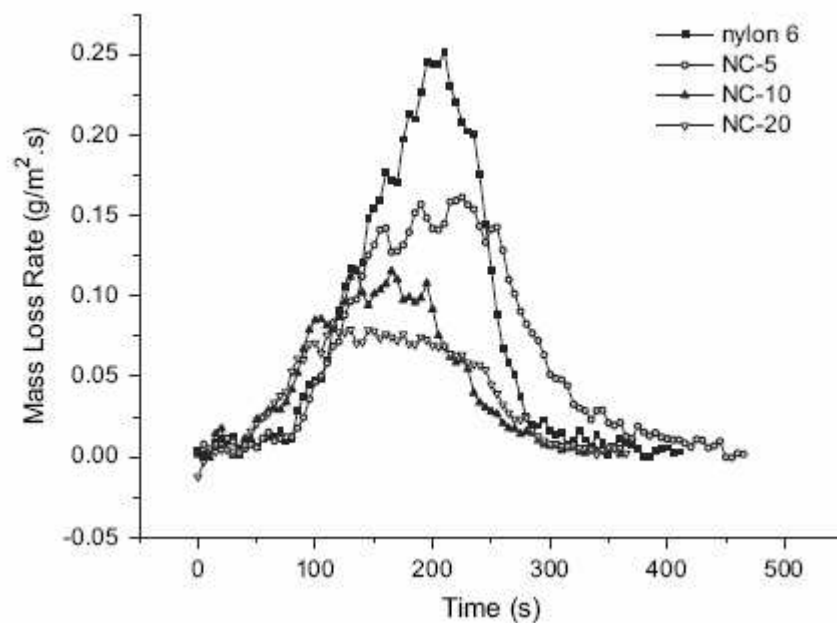


Fig. 15. Mass loss rate depending on time and weight % of LDH (borrowed from [10])

Next property that is affected by LDH is heat release rate(HRR). The dependency is similar like MLR, HRR is decreasing with increasing LDH weight percentage.

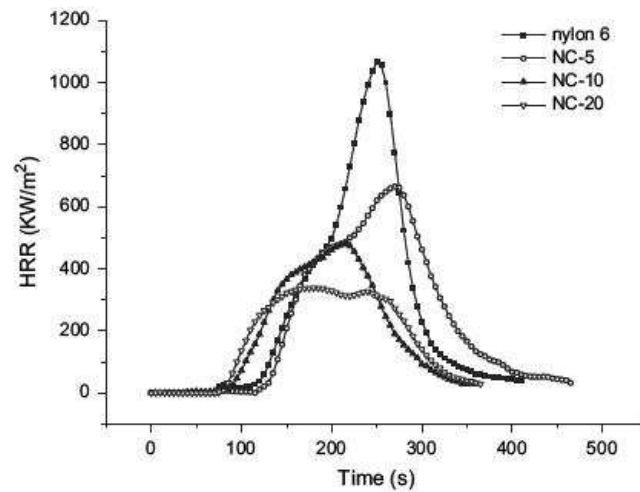


Fig. 16. Heat release rate depending on time and weight % of LDH. (borrowed from [10])

The disadvantage of nylon-6/MgAl LDH composite is thermal degradation at lower temperature. When 50% weight loss was set as a point of comparison, the decomposition temperatures were 447.8, 428.1, 413.1, and 420.7 °C for pure nylon 6, NC-5, NC-10, and NC-20 samples respectively.

NC-10 sample have a exfoliated structure. Fig.17 [10] show LDH as a dark layers, bright parts are nylon-6 matrix.

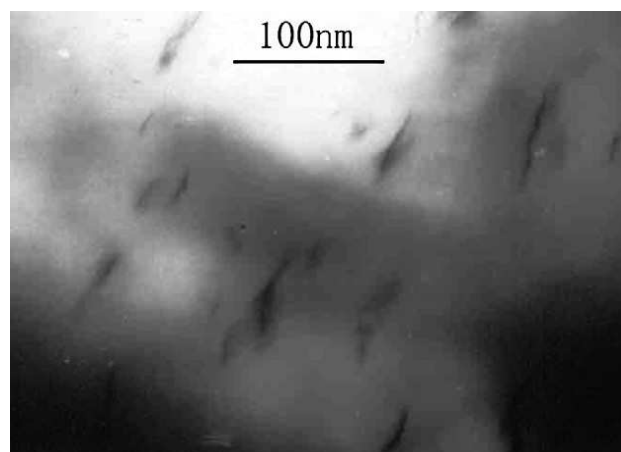


Fig. 17. TEM image of NC-10 sample. (borrowed from [10])

NC-20 sample have a intercalated structure. At Fig. 18[10] arrows shows intercalated LDH(dark parts). Bright part is nylon-6 matrix.

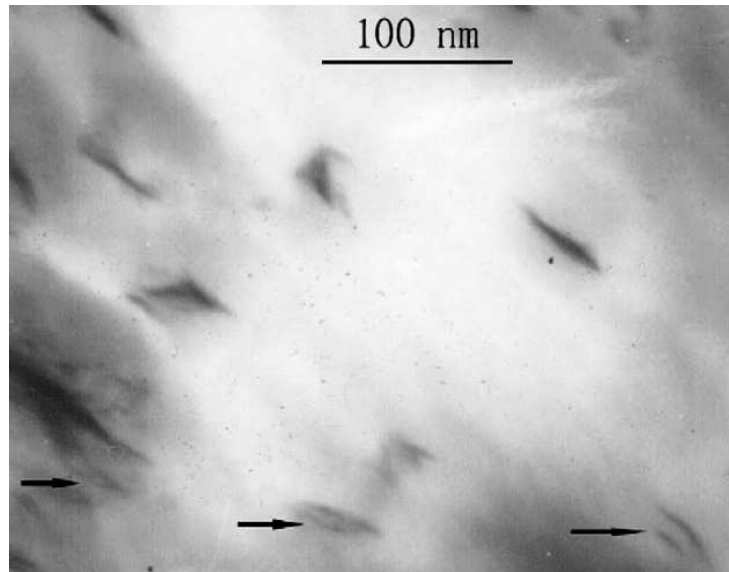


Fig. 18. TEM image of NC-20 sample. (borrowed from [10])

4.5 LDH/Epoxy nanocomposites

To prepare LDH/epoxy nanocomposite, organo-modified LDH was used by Huai-Bin Hsueh and Chuh-Yung Chen[11]. Modification of LDH is necessary to provide compatibility between LDH and epoxy

4.5.1 Preparation of LDH's – amino laurate (LDH's-Al)

LDH's-AL was prepared by co-precipitation method. 0.08g of NaOH was dissolved in 200ml of deionized water, then 4.3g of amino lauric acid was added to solved NaOH. Then 5.12g of magnesium nitrate and 3.75g of aluminium nitrate were dissolved in 50ml of deionized water. The nitrate solution was added dropwisely to the stirred amino lauric acid/NaOH solution at room temperature and the pH values was maintaned at value of 10 by adding of 1 M of NaOH solution. When all solution was added, mixture was kept at 80°C fo 16h. Then the slurry was filtered and washed by deoinzed water five times. Obtained LDH's-Al was dried at 70°C under N2 atmosphere[11].

To prepared exfoliated LDH/epoxy composite, LDH was added into the epoxy (Epon 828), obtained mixture was stried at 55°C for 3h. Then curring agent(Jeffamine D400)was added to mixture and further mixed for 2h at room temperature. After that, the mixture was put under vakuum and cured via thermal schedule (75 °C for 3 h and 135 °C for an additional 3 h). Mechanism of preparation is described by following Fig. 19[11].

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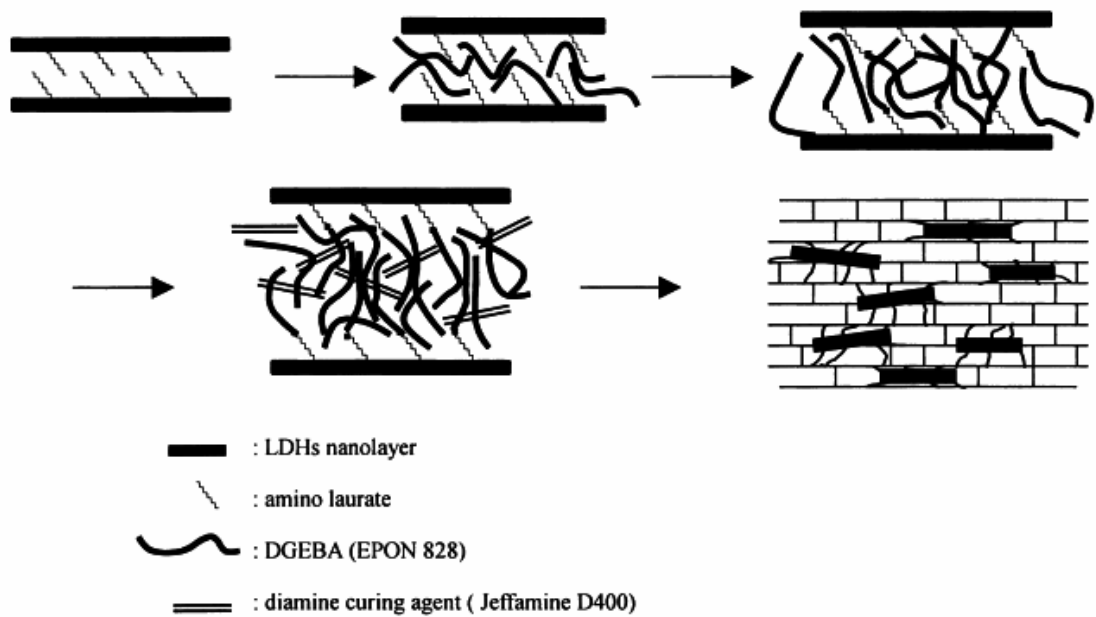


Fig. 19. Mechanism of epoxy/LDH nanocompositi preparation. (borrowed from [11])

4.5.2 Properties of Epoxy/LDH nanocomposite

Organo modified process increases gallery range between nanolayers and improves interfacial properties between anorganic and organic phases, which allows the epoxy molecules to diffuse into gallery to gain exfoliated LDH/epoxy nanocomposite. It also provides hydrophobic environment in LDH intergallery so the amino group of intercalated amino laurate can react with epoxy groups and generate adhesion between LDH's nanolayers and epoxy molecules. Compatible and exfoliated nanocomposite is obtained.

As a result of the compatibility of the nanocomposite, the tensile strength of the nanocomposites is superior to pristine epoxy. As we can see from Fig. 20, the tensile strength increases with increasing percentage of LDH in nanocomposite [11].

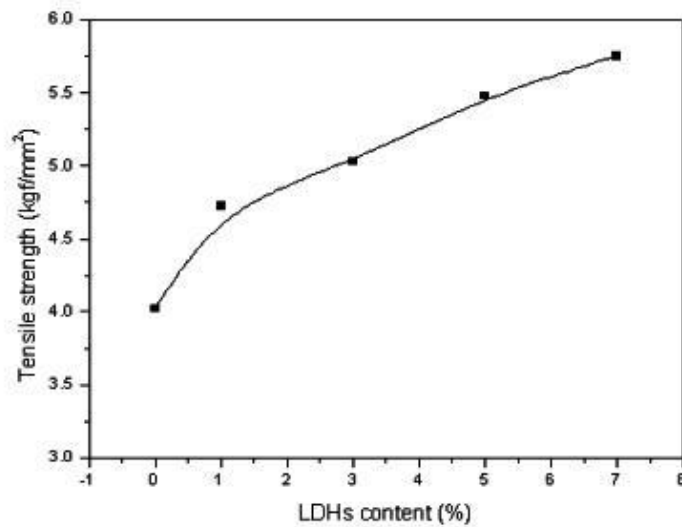


Fig. 20. Tensile strenght in dependacy at LDH kontent. (borrowed from [11])

The tensile strenght increment is the highest between pristine epoxy and 1% of LDH in LDH/Epoxy nanocomposite, further additon of LDH have approximately constant incre- ment of tensile strenght.

Thermal properties are improved when LDH/Epoxy nanocomposite is compared to pristine epoxy. Following Fig. 21 shows thermal stability of LDH/Epoxy nanocomposite.

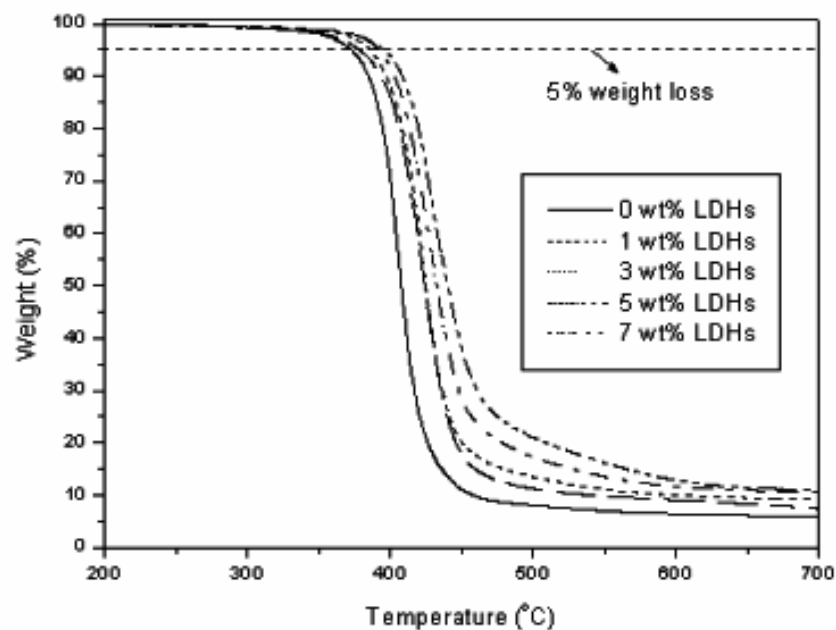


Fig. 21. Thermal stability of LDH's/Epoxy nanocomposites. (borrowed from [11])

At 5% weight loss set as comparison point, the nanocomposite with 7% of LDH degrades 23°C above pristine epoxy. Enhanced thermal stability is attributable to fact that LDH nanolayers restrict thermal movement of epoxy molecules. LDH nanolayers also works as gas barrier and prevent out-diffusion of volatile gas from decomposed products.

4.6 Poly(methyl acrylate)/ZnAl LDH nanocomposite

Wei Chen, Baojun Qu [12] prepared poly(methyl acrylate)(PMA)/ZnAl LDH nanocomposite by adding 60ml of methyl acrylate and 3.0g of dodecylsulfate modified Zn/Al LDH(ZnAlDS LDH) into three-necked round-bottle with a magnetic stirrer. The mixture was stirred under N₂ atmosphere for 1h at 70°C. Then 0.3g of AIBN(azobisisobutyronitrile) was added to start polymerization. When the solution became thick enough to prevent the deposition of LDH, the mixture was cooled quickly to room temperature and poured into a mould 5x5x2 cm The plate was placed in an oven at 50 °CC for 24 h, then at 100 °CC for 2 h, resulting in a homogenous opaque solid block of PMA/ZnAlDS LDH nanocomposite. For comparison, pure PMA was prepared by same method.

4.6.1 Properties of Poly(methyl acrylate)/ZnAl LDH nanocomposite

Structure of PMA/ZnAl LDH nanocomposite is intercalated with exfoliated parts, as seen on Fig. 22[12].The arrow shows exfoliated parts.

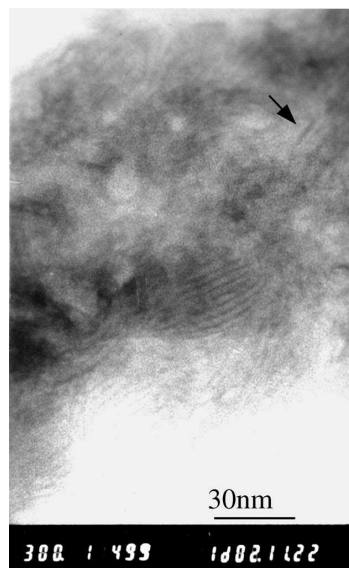


Fig. 22. TEM image of PMA/ZnAl LDH nanocomposite (borrowed from [12])

Due to the intercalation of PMA chains into the interlayers of ZnAIDS LDH, the particles of Zn/AIDS and PMA have strong interaction, which gives the PMA/ZnAIDS LDH nanocomposite enhanced mechanical properties[12]. As seen on Tab. 2 [12], the increase of tensile strength is significant.

| Sample | Tensile strength(MPa) |
|------------------------------|-----------------------|
| Pure PMA | 0,5 |
| PMA/ZnAIDS LDH nanocomposite | 3,8 |

Tab. 2. Tensile strength of pure PMA and PMA/ZnAIDS LDH nanocomposite(borrowed from [12])

Thermal properties are also enhanced. Measured at 10% weight loss by TGA method, the temperature of PMA/ZnAIDS LDH nanocomposite is 17°C higher than a temperature of pure PMA. In the temperature range from 150 to 350°C, PMA/ZnAIDS LDH nanocomposite has more residues than a pure PMS. Above 360°C the residues are nearly the same.

CONCLUSION

LDH are very perspective materials. There is a lot of options how to modify LDH. A huge variety of anions can be inserted between LDH layers. So, options how to use LDH are very rich. Using them as a molecular magnets in a solid materials is a demonstration of their capabilities. Other way how to use LDH is to prepare nanocomposites using common commercial polymers as a matrix and LDH as a nanofiller. Preparation of these nanocomposites is simple and improvement of properties is remarkable. Most of the nanocomposites show improvement in thermal stability and strength. Improved thermal stability means that LDH nanocomposites can be used as heat-resistant materials. Increased strength allows to use thinner walls when constructing products made of polymers/LDH nanocomposites and thus lower price of products. For example, tensile strength increase of LDH/Epoxy nanocomposite compared to pure epoxy is very significant (see Fig. 20.). Also the increase of tensile strength in PMA/ZnAl LDH nanocomposite is remarkable (see Tab. 2.). In other common polymers the increase of strength properties and thermal stability is not so significant and can be influenced by measurement error.

In field of LDH's/common polymer nanocomposites is still great area for research. That's the reason why is difficult to compare results of LDH's/polymers research from one scientist team to results of another research. To confirm results of compared polymers the further research is necessary

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LIST OF SYMBOLS AND ABBREVIATION

AAO...Anodic alumina oxide

AIBN...azobisisobutyronitrile

HRR...Heat release rate

LDH...Layered double hydroxide

MLR...Mass loss rate

PE...Polyethylene

PET...Polyethylene terephthalate

PMA...Poly(methyl acrylate)

PS...Polystyrene

TEM...Transmission electron microscopy

TGA...thermogravimetric analysis

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