

## LAYERED DOUBLE HYDROXIDES INTERCALATED WITH ORGANIC ANIONS AND THEIR APPLICATION IN PREPARATION OF LDH/POLYMER NANOCOMPOSITES

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(Received October 2008, accepted February 2009)

### ABSTRACT

The intercalation of organic anions, namely acrylate, methacrylate, 2-acrylamido-2-methyl-1-propanesulfonate (AMPS), 4-vinylbenzoate, and 4,4'-azobis(4-cyanopentanoate) into Mg-Al and Zn-Al layered double hydroxides (LDHs) was studied. The coprecipitated Mg-Al-NO<sub>3</sub> and Zn-Al-NO<sub>3</sub> hydrotalcite-like compounds with M<sup>II</sup>/Al molar ratio of 2 were used as precursors. The anion exchange and rehydration of calcined LDH precursors were applied for the intercalation. The anion exchange appeared to be the most effective method; all examined organic anions were intercalated successfully by this way both in Mg-Al and Zn-Al host structures. The intercalated LDHs were used as comonomer and initiator for preparation of LDH/polymethacrylate nanocomposites: mixture of monomer and LDHs intercalated with organic anions were dispersed in aqueous phase and then the emulsion polymerization was performed in the presence of inorganic (nano)particles to obtain polybutylmethacrylate hybrid latexes. Nanostructured hybrid materials containing a low amount (1 – 3 wt%) of inorganic nanofiller were prepared. Particles with size of 60 – 100 nm were detected by dynamic light scattering and small-angle X-ray scattering methods. Furthermore, a hydrophobization of LDH nanofillers with dodecylsulfate (DS) was tested in order to facilitate their dispersion in the polymer matrix. A minor part of AMPS anions was incorporated into Mg-Al-DS LDH during anion exchange in the aqueous solution containing AMPS. Using Mg-Al-DS LDH modified with AMPS, the nanocomposites were obtained by emulsion polymerization and also by the solution polymerization in 1-methyl-2-pyrrolidone.

**KEYWORDS:** hydrotalcite, layered double hydroxides, intercalation, polymethacrylate, nanocomposite materials

### INTRODUCTION

Layered double hydroxides (LDHs), which are also known as hydrotalcite-like compounds or anionic clays, represent a class of layered materials with chemical composition expressed by the general formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}yH_2O]^{x-}$  where M<sup>II</sup> and M<sup>III</sup> are divalent and trivalent metal cations, A<sup>n-</sup> is an n-valent anion and x has usually values between 0.20 and 0.33. The ordering of hydroxide layers is similar to that of brucite, Mg(OH)<sub>2</sub>, where each Mg<sup>2+</sup> cation is octahedrally surrounded by six OH<sup>-</sup> anions and the different octahedra share edges to form infinite sheets. In the LDHs, the M<sup>II</sup>/M<sup>III</sup> isomorphous substitution in octahedral sites of the hydroxide sheets results in a net positive charge, which is neutralized by the interlayers composed of anions and water molecules. LDHs offer a great variety of applications, e.g., in heterogeneous catalysis, adsorption and decontamination processes, polymer processing and pharmacy (Cavani et al., 1991; Rives, 2001; Kovanda et al., 2006). LDHs represent also a host inorganic structure for preparation of hybrid materials with interesting physical and chemical properties.

In recent years, LDHs were applied also as nanofillers for synthesizing polymer-based nanocomposites, in which nanosized inorganic filler (at least one dimension) is dispersed in polymer matrix (e.g., Leroux and Besse, 2001; Leroux, 2006; Costa et al., 2008). The LDH/polymer nanocomposites represent a new class of materials alternative to conventional filled polymers. After dispersion at the nanoscale, inorganic nanoparticles added already in low concentration (0.1 – 10 wt%) in the polymer matrix can considerably improve its properties such as tensile strength, heat and chemical resistance, gas permeability, as well as fire retardation.

LDHs are usually prepared by coprecipitation, when a solution containing M<sup>II</sup> and M<sup>III</sup> metal cations in adequate proportions reacts with an alkaline solution. A weak bonding between interlayer anions and hydroxide sheets is characteristic for LDHs; thus, anions can be exchanged under suitable conditions. Another alternative procedure is rehydration of mixed oxides obtained after thermal decomposition of a LDH precursor containing volatile interlayer

anions (e.g.,  $\text{CO}_3^{2-}$  or  $\text{NO}_3^-$ ). Such mixed oxides prepared at moderate calcination temperatures (400 – 600 °C) can be rehydrated in aqueous solutions; the rehydration reaction results in the reconstruction of the layered LDH structure containing intercalated anions from the solution. This phenomenon known as reconstruction is often applied for the intercalation of various anions into the LDH hosts.

All methods mentioned above, i.e., coprecipitation, anion exchange, and rehydration can be applied for intercalation of polymer molecules into LDH structure. The LDHs intercalated with water-soluble polymers can be prepared by direct coprecipitation (Oriakhi et al., 1996). An alternative way represents the intercalation of suitable monomers followed by in situ polymerization (Chen et al., 2004; Chen and Qu, 2005; Vaysse et al., 2004; Vieille et al., 2004). Most polymers are hydrophobic and their compatibility with hydrophilic LDH filler is improved by modifying inorganic layers with surfactants; such pretreatment results in a better dispersion of inorganic nanoparticles in polymer matrix. An intercalation of LDHs with bulky organic anions makes easier their exfoliation in some solvents or melts and improves generally the dispersion of hydroxide nanosheets in the resulting polymer nanocomposites (Hsueh and Chen, 2003a, 2003b; Costa et al., 2005; Costantino et al., 2005; Liu et al., 2008).

The increasing number of reports published in recent years shows that the synthesis and application of polymer nanocomposites have attracted considerable interest both from researchers and industry. The use of LDHs as nanofillers is advantageous due to their versatility in chemical composition and tunable charge density, allowing multiple interactions with the polymer. The polyacrylate-based nanocomposites are often obtained by in situ polymerization of monomer anions intercalated in LDH hosts (Aguzzi et al., 2007; Chen et al., 2004; Chen and Qu, 2005; Li et al., 2007; Vaysse et al., 2004). In the present work, the intercalation of acrylic acid and its derivatives into Mg-Al and Zn-Al LDH hosts and application of intercalated LDHs for preparation of LDH/poly-methacrylate nanocomposite latexes are studied. An application of LDH intercalated with hydrophobic anions (dodecylsulfate) and then modified with acrylate-derived ones (2-acrylamido-2-methyl-1-propanesulfonate) is also examined.

## EXPERIMENTAL

### SYNTHESIS OF LDH HOSTS

The Mg-Al and Zn-Al LDH hosts in nitrate form were prepared by coprecipitation. Carbonate-free distilled water was used for dissolution of chemicals and the preparation was carried out under nitrogen to avoid any contamination of the products by carbonate anions. An aqueous solution (450 ml) of

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with  $\text{M}^{\text{II}}/\text{Al}$  molar ratio of 2 and total metal ion concentration of  $1.0 \text{ mol l}^{-1}$  was added with a flow rate of  $7.5 \text{ ml min}^{-1}$  into a 1000 ml batch reactor containing 200 ml of distilled water. A flow rate of simultaneously added NaOH solution ( $3 \text{ mol l}^{-1}$ ) was controlled to maintain  $\text{pH} = 10.0 \pm 0.1$ . Coprecipitation was carried out under vigorous stirring at 75 °C. The resulting suspension was stirred for 1 h at 75 °C. The product was filtered off, washed thoroughly with distilled water and dried at 60 °C. The obtained LDHs were denoted as Mg-Al- $\text{NO}_3$  and Zn-Al- $\text{NO}_3$ .

### INTERCALATION OF ORGANIC ANIONS

The Mg-Al and Zn-Al LDH host structures were intercalated by anions derived from following acids: acrylic acid (AA), methacrylic acid (MAA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), 4-vinylbenzoic acid (VBA), 4,4'-azobis(4-cyanopentanoic acid) (ACPA), and dodecylsulfuric acid (DS). The samples were denoted by acronyms describing the composition of hydroxide layers and intercalated anions; for example Mg-Al-AA means the Mg-Al LDH intercalated with acrylate.

**Anion exchange:** The Mg-Al- $\text{NO}_3$  or Zn-Al- $\text{NO}_3$  sample was dispersed in 400 ml of carbonate-free aqueous solution of corresponding acid neutralized by NaOH solution; an excess of intercalated anion was used with respect to the LDH anion-exchange capacity (concentration of  $0.015$  and  $0.0043 \text{ mol l}^{-1}$ ,  $\text{pH} = 9$  and excess of 20 % were applied for intercalation of AMPS and ACPA, respectively; concentration of  $2.0 \text{ mol l}^{-1}$ ,  $\text{pH} = 7$  and excess of 280 % were applied for intercalation of AA and MAA). After mixing the components, the suspension was sealed in a 500 ml glass bottle under nitrogen and stirred for 6 days (AMPS and ACPA) or 2 days (AA and MAA) at room temperature. The intercalated products were filtered off, washed with carbonate-free distilled water and dried at 40 °C (AMPS and ACPA intercalates) or vacuum dried at room temperature (AA and MAA ones).

**Rehydration** was also used for preparation of Mg-Al LDH intercalated with AMPS and ACPA anions. The Mg-Al- $\text{NO}_3$  sample was heated for 4 h at 450 °C and then cooled to the room temperature. The obtained mixed oxide was dispersed in 400 ml of aqueous AMPS ( $0.015 \text{ mol l}^{-1}$ ) or ACPA solution ( $0.0043 \text{ mol l}^{-1}$ ) neutralized by NaOH ( $\text{pH} = 9$ ); the AMPS or ACPA were in excess of 20 % with respect to the formed LDH anion-exchange capacity. The suspension was stirred under nitrogen in the sealed 500 ml glass bottle at room temperature for 6 days. The rehydrated products were filtered off, washed with carbonate-free distilled water and dried at 40 °C.

**Direct coprecipitation** under nitrogen was applied for preparation of Mg-Al LDH intercalated with VBA and DS anions. During preparation of

Mg-Al-VBA sample, the aqueous solution (300 ml) of Mg and Al nitrates with Mg/Al molar ratio of 2 and total metal ion concentration of  $1.35 \text{ mol l}^{-1}$  was added with a flow rate of  $5 \text{ ml min}^{-1}$  into 200 ml of aqueous solution of 4-vinylbenzoic acid ( $1.0 \text{ mol l}^{-1}$ ) neutralized by NaOH solution ( $\text{pH} = 10$ ). A flow rate of simultaneously added NaOH solution ( $3 \text{ mol l}^{-1}$ ) was controlled to maintain  $\text{pH} = 10.0 \pm 0.1$ . The coprecipitation was carried out under vigorous stirring at  $25 \text{ }^\circ\text{C}$ . The resulting suspension was stirred for 3 h at  $25 \text{ }^\circ\text{C}$ . The product was filtered off, washed thoroughly with distilled water and vacuum dried at room temperature.

The Mg-Al-DS sample was prepared similarly. The aqueous solution (300 ml) of Mg and Al nitrates with Mg/Al molar ratio of 2 and total metal ion concentration of  $0.6 \text{ mol l}^{-1}$  was added with a flow rate of  $5 \text{ ml min}^{-1}$  into 200 ml of aqueous solution of sodium dodecylsulphate ( $0.6 \text{ mol l}^{-1}$ ). A flow rate of simultaneously added NaOH solution ( $3 \text{ mol l}^{-1}$ ) was controlled to maintain  $\text{pH} = 10.0 \pm 0.1$ . The coprecipitation was carried out under vigorous stirring at  $80 \text{ }^\circ\text{C}$ . The resulting suspension was stirred overnight at  $80 \text{ }^\circ\text{C}$ . The product was filtered off, washed thoroughly with distilled water and dried at  $60 \text{ }^\circ\text{C}$ .

#### PREPARATION OF LDH/POLYMETHACRYLATE NANOCOMPOSITES

Semi-continuous emulsion polymerization of hydrophobic vinyl monomer (butylmethacrylate) was performed under starved-feed conditions to obtain LDH/polybutylmethacrylate nanocomposite latexes. The polymerization was carried out in a stirred glass reactor under nitrogen at  $85 \text{ }^\circ\text{C}$ . Sodium dodecylsulphate (SDS) was used as surfactant and ammonium persulphate (APS) was used as initiator of radical polymerization. In a typical synthesis, the reactor was loaded with solution of deionized water (4.53 ml) and SDS (0.04 g). The initial charge was stirred at 500 rpm and heated up to  $85 \text{ }^\circ\text{C}$  under nitrogen for 10 min. The modified LDH was dispersed in monomer under vigorous stirring in amount of 1, 3 or 5 wt% related to monomer weight. Emulsion mixture containing 3.85 ml of water, 0.1 g SDS and the calculated amount of monomer and modified LDH mixture corresponding to 9.21 g of pure monomer was prepared in a separate flask and stirred for 30 min. Then 0.5 g of emulsion mixture was placed into the reactor and the solution of initiator, prepared by dissolving of 0.025 g of APS in 0.08 g of deionized water, was added. The charge was stirred for 10 min. Then, the reactor was fed with the remaining emulsion mixture under nitrogen and constant flow rate, slow enough to reach monomer starved conditions. The reactor was simultaneously fed with a solution of initiator (0.011 g of APS in 0.75 ml of water). The time period of feeding was 60 min; then the solution of 0.025 g APS in 0.15 ml of water was added and

the reaction mixture was stirred for another 30 min; afterwards, it was cooled to the room temperature. The final latex was obtained without any post preparative treatments. For latexes containing lower solid contents (corresponding to 37.5 or 25 wt%, respectively), the loading of monomer was lowered to 5.53 or 3.07 g.

Solution radical polymerization of polybutylmethacrylate nanocomposites with Mg-Al-DS LDH modified with AMPS was carried out in 1-methyl-2-pyrrolidone in sealed glass bottles at  $70 \text{ }^\circ\text{C}$  for 24 h. Concentration of monomer was 10 wt% and 2,2'-azobis(2-methylpropionitrile) (ABIN) was used as initiator. In a typical synthesis, the bottle was loaded with 5 g of butylmethacrylate, modified LDH, 45 ml 1-methyl-2-pyrrolidone and 0.02 g of ABIN. Reaction mixture was flushed with nitrogen for 20 min, sealed and kept in thermostat at  $70 \text{ }^\circ\text{C}$  for 24 hr. Then the polymer nanocomposite was isolated by pouring into an excess of ethanol. The precipitate was filtered off, repeatedly washed with ethanol and purified by repeated re-precipitation from chloroform solution to ethanol. The nanocomposite membranes prepared by casting from chloroform solution were then used for WAXS measurements.

#### CHARACTERIZATION OF SAMPLES

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D5005 instrument (Bruker AXS, Germany) with Cu  $K\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ , 40 kV, 30 mA, beam monochromator) in  $2\theta$  range  $2 - 80^\circ$ , step size  $0.02^\circ$ . The qualitative analysis was performed with a HighScore software package (PANalytical, The Netherlands, version 1.0d).

Size exclusion chromatography was used to determine the molecular weights and polydispersity indices of polybutylmethacrylate. The emulsion latex was de-emulsified by freezing following by filtration and thoroughly washed with deionized water.

The mean particle size and structure of the synthesized latexes were characterized by using of dynamic light scattering (DLS) and X-ray scattering (WAXS and SAXS) techniques. DLS measurements were carried out using a Coulter Nano-Sizer (Coulter, UK) in unimodal analysis, when a fraction of the latex was diluted with deionized water. The reported mean particle size values represent an average of four repeated measurements.

Small-angle X-ray scattering (SAXS) experiments were performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocussed X-ray beam generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental setups were used to cover the  $q$  range of  $0.005 - 1.1 \text{ } \text{Å}^{-1}$  ( $q = (4\pi/\lambda)\sin\Theta$ , where  $\lambda$  is the

wavelength and  $2\theta$  is the scattering angle). The mean diameter of the latex particles was determined by a least squares fitting of the scattering curves by a model of spherical particles with a Schultz-Zimm size distribution.

Wide-angle X-ray scattering (WAXS) patterns of the nanocomposites were obtained using powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Freiberg) with Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm, 40 kV, 45 mA, Ni-filter) in the  $2\theta$  range of  $4 - 60^\circ$ , step size  $0.25^\circ$ .

## RESULTS AND DISCUSSION

Chemical analysis (AAS) of the dried Mg-Al-NO<sub>3</sub> and Zn-Al-NO<sub>3</sub> LDH hosts showed that Mg/Al and Zn/Al molar ratios in the solid corresponded approximately to those in the nitrate solution used for coprecipitation. In the powder XRD patterns of these samples, only a well-crystalline hydroxide-like phase with  $d_{003}$  basal spacing of 0.88 (Mg-Al-NO<sub>3</sub> sample in Fig. 1) and 0.87 nm (Zn-Al-NO<sub>3</sub> sample) was detected. A marked increase in the  $d_{003}$  basal spacing of the obtained products (Table 1) indicated a successful intercalation of organic anions into the LDH interlayer space, when anion exchange was applied. On the other hand, a hydroxide form of the LDH (Mg-Al-OH) with  $d_{003}$  basal spacing of 0.77 – 0.78 nm was obtained during rehydration of the LDH-related Mg-Al mixed oxide in the aqueous solutions containing AMPS and ACPA (Fig. 1). Therefore, the rehydration procedure was not applied for intercalation of the other examined anions. The products with hydroxide-like structure were obtained also by direct coprecipitation in the presence of vinylbenzoate and dodecylsulphate anions; the increased  $d_{003}$  basal spacing confirmed an intercalation of organic anions in the LDH structure.

The formation of LDH/polymethacrylate nanocomposite latexes during in situ polymerization is schematically shown in Fig. 2. The interlayer anions of LDH can interact with monomer

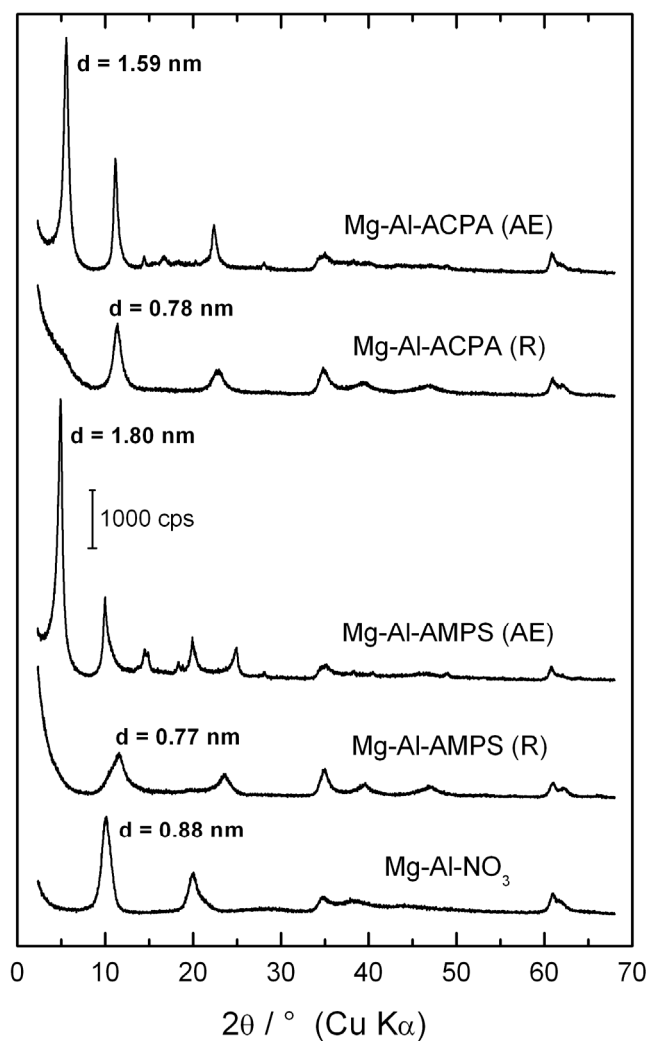
(butylmethacrylate) and subsequent formation of polymer chains results in a gradual disordering and exfoliation of the LDH structure. Finally, the inorganic nanoparticles (hydroxide nanosheets) are randomly dispersed in the polymer matrix. Organic anions containing vinyl group (AA, MAA, AMPS and VBA) can be used as comonomers in the polymerization reaction; ACPA is often used as polymerization initiator. The size exclusion chromatography of the parent polybutylmethacrylate latex showed the average molecular weight of  $2.5 \cdot 10^5$  and polydispersity index (PDI) of 2.48.

The WAXS patterns of the prepared LDH/polymethacrylate nanocomposite latexes are demonstrated in Fig. 3. It can be seen that the WAXS patterns of the latexes containing modified LDHs are very similar to that of the parent polybutylmethacrylate. The mean particle size of the synthesized latexes varied from about 60 to 100 nm (Table 2); the values determined by using of dynamic light scattering (DLS) were in good agreement with those determined by SAXS. The LDH/polymethacrylate nanocomposites were likely obtained after adding a low amount of the modified LDHs (1 – 3 wt% related to monomer weight). Better results were obtained with intercalated Zn-Al LDHs; the Mg-Al nanofillers added in reaction mixture often caused a precipitation of reaction mixture during emulsion polymerization.

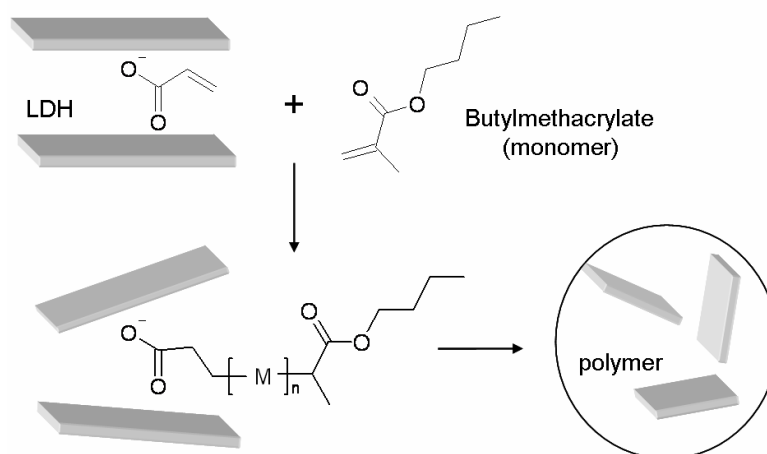
A delamination of Mg-Al LDH intercalated with dodecylsulphate in a polar acrylate monomer and subsequent polymerization giving polyacrylate nanocomposite was reported by O'Leary et al. (2002). A hydrophobization of LDH nanofillers can facilitate their dispersion in polymethacrylate matrix. The Mg-Al LDH intercalated with dodecylsulphate (Mg-Al-DS sample) was used as precursor for anion exchange in aqueous solution containing AMPS; the same conditions, i.e., AMPS concentration and excess, reaction pH, temperature and time were applied as in the anion exchange with Mg-Al-NO<sub>3</sub>

**Table 1** Basal spacing ( $d_{003}$ ) of the intercalated LDHs evaluated from powder XRD data.

LDH sample	$d_{003}$ basal spacing / nm
Mg-Al-NO <sub>3</sub>	0.88
Mg-Al-AA	1.33
Mg-Al-MAA	1.38
Mg-Al-AMPS	1.80
Mg-Al-ACPA	1.59
Zn-Al-NO <sub>3</sub>	0.87
Zn-Al-AA	1.29
Zn-Al-MAA	1.34
Zn-Al-AMPS	1.75
Zn-Al-ACPA	1.60
Mg-Al-VBA	1.82
Mg-Al-DS	2.75



**Fig. 1** Powder XRD patterns of Mg-Al LDHs intercalated with AMPS and ACPA anions.  
 AE – samples prepared by anion exchange,  
 R – samples prepared by rehydration



**Fig. 2** Schema of formation of LDH/polymethacrylate nanocomposite during in situ polymerization.

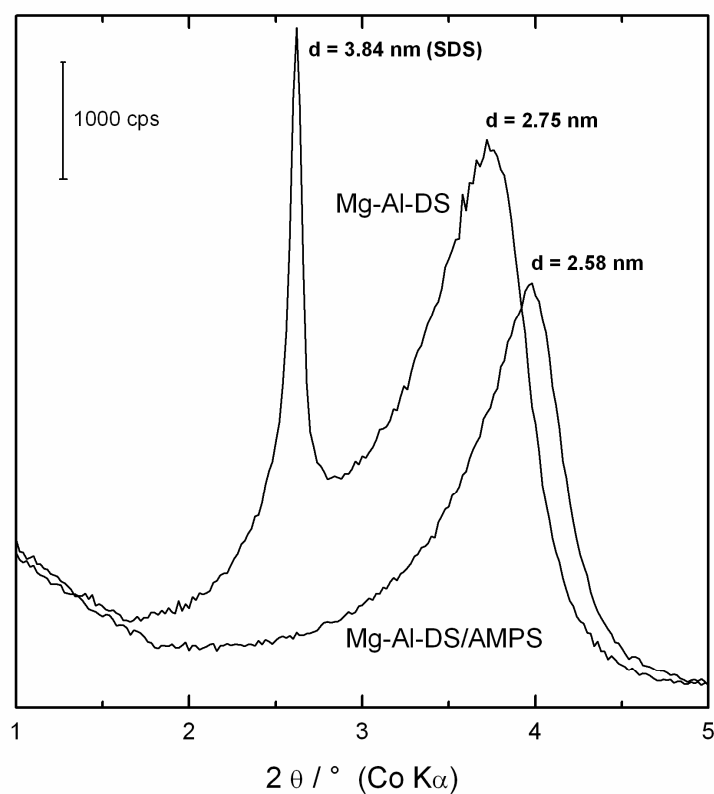
**Table 2** Mean particle size of prepared polybutylmethacrylate nanocomposite latexes containing LDH nanofillers in various concentrations.

LDH sample added in the nanocomposite latex	LDH content <sup>*)</sup> / wt%	Monomer content / wt%	Mean particle size /nm	
			DLS	SAXS
Zn-Al-AA	1	25	69	n.d.
Zn-Al-AA	1	37.5	90	93
Zn-Al-MAA	1	25	77	61
Zn-Al-MAA	1	37.5	102	84
Zn-Al-MAA	1	50	100	85
Zn-Al-MAA	3	25	76	62
Zn-Al-MAA	3	37.5	96	84
Zn-Al-MAA	3	50	99	91
Zn-Al-MAA	5	50	85	69
Zn-Al-AMPS	1	25	71	61
Zn-Al-ACPA	1	25	83	71

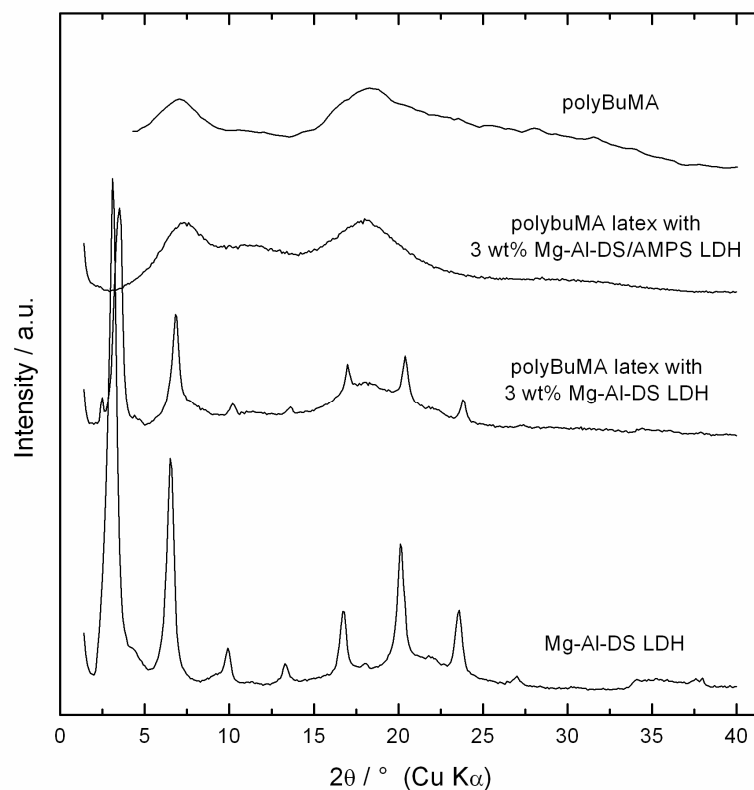
<sup>\*)</sup> LDH content related to monomer weight

DLS – dynamic light scattering, SAXS – small-angle X-ray scattering,

n.d. – not determined



**Fig. 4** Low-angle part of powder XRD patterns of the samples Mg-Al-DS and Mg-Al-DS/AMPS obtained after anion exchange in the AMPS solution.



**Fig. 5** WAXS patterns of polybutylmethacrylate latexes containing Mg-Al-DS and Mg-Al-DS/AMPS LDHs prepared by emulsion polymerization (monomer content of 25 wt% and 3 wt% LDH related to monomer weight were applied, polyBuMA – polybutylmethacrylate membrane).

precursor. In the powder XRD pattern of the obtained Mg-Al-DS/AMPS sample, only a slight shift of the  $d_{003}$  basal spacing from 2.75 to 2.58 nm was detected (Fig. 4). Therefore, a low incorporation of AMPS anions into Mg-Al-DS LDH can be expected. A slight amount of residual sodium dodecylsulphate remained in the coprecipitated Mg-Al-DS sample after washing (the sharp SDS diffraction peak with  $d = 3.84$  nm); it was evidently dissolved during anion exchange reaction and the diffraction peaks corresponding to the SDS disappeared in the powder XRD pattern of the Mg-Al-DS/AMPS sample.

The Mg-Al-DS and Mg-Al-DS/AMPS samples were tested as nanofillers in polybutylmethacrylate latex prepared by in situ emulsion polymerization. The regular diffraction lines in the WAXS pattern of the polybutylmethacrylate latex with added Mg-Al-DS LDH (3 wt%) correspond to the LDH filler (Fig. 5). This periodicity was not detected in the WAXS pattern of the latex containing Mg-Al-DS/AMPS LDH (partially exchanged with AMPS); it indicates a formation of the LDH/polybutylmethacrylate nanocomposite. The polybutylmethacrylate obtained by solution polymerization in 1-methyl-2-pyrrolidone exhibited the same results (not shown here).

## CONCLUSIONS

The Mg-Al and Zn-Al LDH hosts were intercalated with anions of acrylic acid, its derivatives (MA, AMPS) and other organic anions (ACPA, VBA, DS) by anion exchange reaction or direct coprecipitation. A successful intercalation of the examined anions was confirmed by increasing in  $d_{003}$  basal spacing of the obtained products in comparison with Mg-Al-NO<sub>3</sub> and Zn-Al-NO<sub>3</sub> LDH precursors. Rehydration of calcined Mg-Al-NO<sub>3</sub> LDH in the aqueous solutions containing AMPS and ACPA anions resulted in formation of hydroxide form of Mg-Al LDH and intercalation of organic anions into the LDH structure was not observed.

The Mg-Al and Zn-Al LDHs intercalated with examined organic anions were used as nanofillers in LDH/polybutylmethacrylate latexes prepared by in situ emulsion polymerization. The nanocomposite latexes were formed after adding low amounts of the intercalated LDHs (1 – 3 wt% related to the monomer weight); better results were obtained with Zn-Al LDHs. The LDH/polybutylmethacrylate nanocomposite was not formed with Mg-Al LDH intercalated with dodecylsulphate but a partial exchange of Mg-Al-DS sample with AMPS anions resulted in obtaining LDH-based nanofiller material

suitable for preparation of LDH/polymethacrylate nanocomposites.

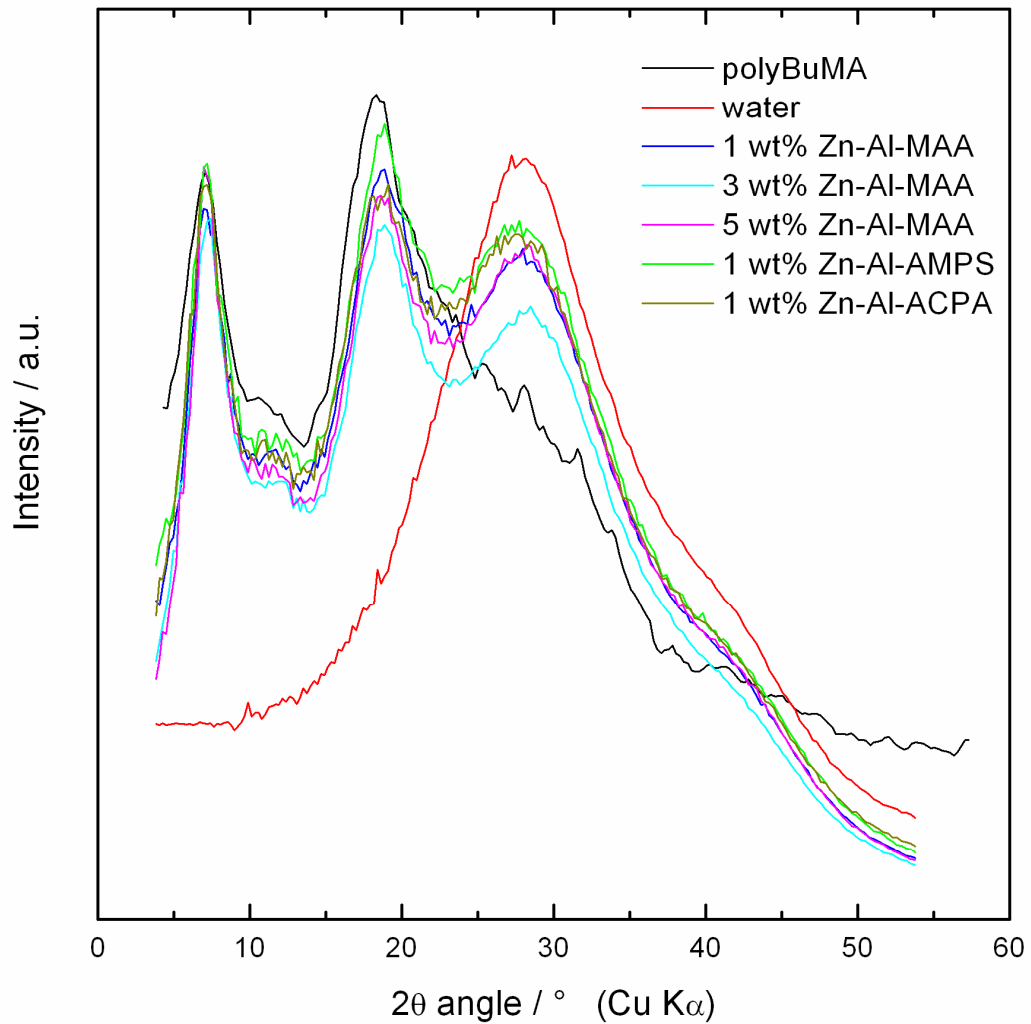
#### ACKNOWLEDGEMENTS

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (project No. KAN 100500651) and by the Ministry of Education, Youth and Sports of the Czech Republic (project No. MSM 6046137302).

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**Fig. 3** WAXS patterns of prepared polybutylmethacrylate latexes containing modified LDHs; monomer content of 25 wt% was applied (polyBuMA – polybutylmethacrylate membrane)