Preparation and characterization of new Ca–Al–polycarboxylate layered double hydroxides

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Abstract

The synthesis and characterization of composite materials based on calcium–aluminum layered double hydroxides (Ca–Al-LDHs), intercalated with organic polycarboxylate (PC) polymers, is described. The PC polymers, which exhibit a "comb-like" architecture, contain ethylene oxide side chains of different lengths. They are intercalated between the cationic Ca–Al–OH-layers when tricalcium aluminate is rehydrated in the presence of PC polymers. The intercalation compounds are characterized by X-ray diffraction (XRD), elemental analysis, IR spectroscopy and TEM. The basal spacings of the PC-LDH composite materials, determined by XRD, are dependent on the number of the ethylene oxide units (EOUs) in the side chain. Accordingly, first TEM micrographs reveal approximately similar layer distances. Elemental analysis as well as IR-spectroscopy proves the existence of the intercalated organic material.
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1. Introduction

Polycarboxylate-based superplasticizers are recognized as important admixtures for use in modern concrete technology [1]. They allow to produce a highly flowable concrete or to reduce the water/cement ratio of concrete, resulting in higher compressive strength. For this application, it is essential to profoundly understand the interaction between the PCs and LDH compounds formed during cement hydration. One such LDH compound is $[Ca_4Al_2(OH)_{12}](SO_4) \cdot 6H_2O$ (AF_m). It results from the hydration of the tricalcium aluminate phase with sulfate present in cement. It has been generally accepted that the high-range water-reduction and the high fluidity of concrete containing PC is attributed to the PCs adsorbing onto the surface of cement hydrate phases [2]. This way, a steric repulsive layer leading to the dispersion of the cement particle is formed [3–7]. Besides adsorption, intercalation (absorption) of the PCs into LDH layers is also possible. Up to date, only the intercalation of *beta*-naphthalene sulfonate formaldehyde condensate, a superplasticizer with very low molecular weight, has been studied [8]. In comparison, PC type superplasticizers are much larger molecules which makes their intercalation more demanding.

The incorporation of organic guest molecules into LDHs has received considerable attention in recent years [9–13]. Furthermore, the synthesis of LDH nanocomposites with polymeric guest molecules has been the focus of several studies [14–17]. Synthesis and characterization of polymer-intercalated layered double hydroxides recently have been reviewed by Leroux and Besse [18]. At present, different synthetic methods, including direct anion-exchange, coprecipitation and rehydration of calcined LDH in the presence of the polymer, are employed. Since the ion-exchange reaction process will be kinetically limited by the slow diffusion of the polymer, thus resulting in only partial intercalation, a co-organized assembly method is expected to produce monophasic nanocomposites incorporating polymers with high molecular weight. Several anionic polymers of medium molecular weight, such as poly(ethylene oxide) derivatives [19], poly(α, β-aspartate) [20], poly(acrylic acid) (PA), poly(vinyl sulfonate) (PVS) and poly(styrene sulfonate) (PSS) [21], have been intercalated into LDHs of different

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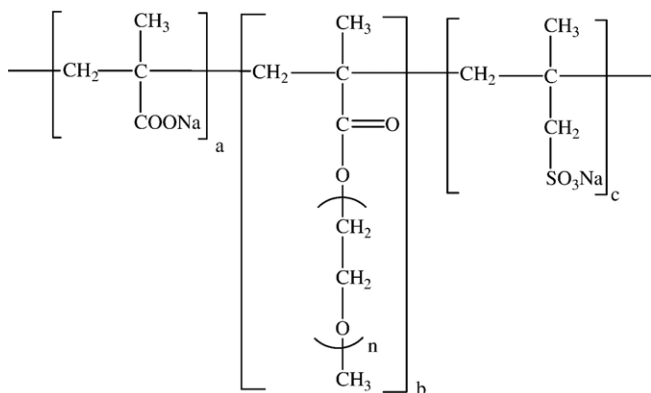*E-mail address:* johann.plank@bauchemie-tum.de (J. Plank).

Fig. 1. Schematic drawing of the studied polycarboxylates (a:b=6:1, n denotes the number of ethylene oxide units).

inorganic frameworks. However, considering the diversity of structures in polymer chemistry, these are relatively few examples. Particularly, there is no report on the intercalation of side chain functionalized "comb-like" polymers.

In this work, we have investigated several synthetic routes for the incorporation of four different polycarboxylate-based superplasticizers into calcium–aluminum layered double hydroxide. Only through the rehydration method that it was possible to successfully intercalate PCs, each of which contains ethylene oxide side chains of different lengths (Fig. 1), into the LDH interlayer space.

2. Experimental

A typical synthesis of a PC$_n$-LDH (n denotes the number of EOUs in the side chain) is described as follows: polymer PC$_{n=4.5}$ (M_n=11,400 Da; M_w=44,000 Da) was dissolved in 100 ml of deionized water at a concentration of 2.5 wt.%. 1.5 g

of C$_3$A was added to the PC solution (pH ~ 12). The system was stirred under argon flow at 75 °C for 48 h. Subsequently, the precipitated composite was separated by centrifugation and washed with deionized water in order to remove residual polymer. The resulting solids were dried at 65 °C under high vacuum (10^{-2}–10^{-3} mbar) for 12 h. Similar routes were used to prepare the other three PC-LDHs, the number of EOU-lengths being 4.5, 8.5, 17 and 45. Ca–Al–NO$_3$-LDH was prepared by the pH-controlled coprecipitation technique of the corresponding metal nitrate salts [9].

The synthesis of the polycarboxylate copolymers was carried out via radical copolymerization in water, with methacrylic acid and methacrylic acid methoxy-poly(ethylene glycol) ester (with EOUs as 4.5, 8.5, 17 or 45) as the monomers (purchased from Sigma-Aldrich). Details of the synthesis and characterization (GPC, RI- and Light Scattering detectors) will be published elsewhere.

3. Results and discussion

3.1. X-ray patterns

X-ray diffraction patterns for Ca–Al–NO$_3$-LDH as well as for the series of intercalated PC-LDHs are shown in Fig. 2. The diffraction pattern for the inorganic Ca–Al–NO$_3$-LDH (Fig. 2a) shows a typical layered structure with a basal d-value of 0.87 nm, comparable with those previously reported in the literature [9,22]. For the organo-LDHs, it can be seen that the basal spacings differ according to the varying side chain lengths of the PCs. A series of broad new peaks appeared with d-values of 1.15 nm for PC$_{n=4.5}$-LDH (b), 2.95 nm for PC$_{n=8.5}$-LDH (c), 3.54 nm for PC$_{n=17}$-LDH (d) and 4.27 nm for PC$_{n=45}$-LDH (e).

Compared to the Ca–Al–NO$_3$-LDH, the crystallinity of the organo-LDHs appears to be lower, as shown by the broadening and the decrease in intensity of the X-ray diffraction signals. It should be
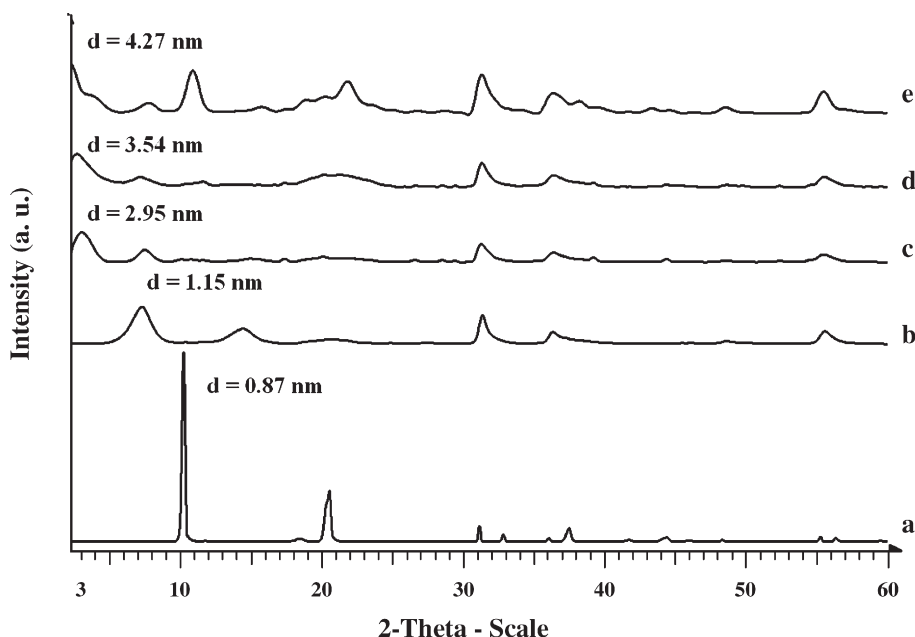

Fig. 2. X-ray diffraction patterns for Ca–Al–NO$_3$-LDH (a), PC$_{n=4.5}$-LDH (b), PC$_{n=8.5}$-LDH (c), PC$_{n=17}$-LDH (d) and PC$_{n=45}$-LDH (e).

Table 1
Chemical composition of Ca–Al–NO$_3$-LDH and PC-intercalated Ca–Al-LDHs

Composite		Ca wt.%	Al wt.%	C wt.%	H wt.%	N wt.%	Organic part wt.%	Formula
Ca–Al–NO$_3$-LDH	Found :	21.9	12.2	/	3.38	4.14		
	Calc. :	21.9	12.2	/	3.38	4.17	/	Ca$_2$Al(OH)$_6$(NO$_3$)·2.2H$_2$O, 0.63Al(OH)$_3$, 0.03Al(NO$_3$)$_3$
PC$_{(n=4,5)}$-LDH	Found :	20.9	6.9	17.09	4.95	/		
	Calc. :	21.1	7.0	16.84	5.35	/	29.3	Ca$_2$Al$_{0.98}$(OH)$_{6.10}$·[−PC$_{n=4.5}$−]$_{0.14}$·3.10H$_2$O
PC$_{(n=8.5)}$-LDH	Found :	14.8	4.9	24.75	5.87	/		
	Calc. :	14.6	4.8	25.11	6.43	/	44.2	Ca$_2$Al$_{0.97}$(OH)$_{5.41}$·[−PC$_{n=8.5}$−]$_{0.25}$·5.85H$_2$O
PC$_{(n=17)}$-LDH	Found :	12.0	3.9	28.39	6.87	/		
	Calc. :	12.0	3.9	28.20	7.01	/	50.4	Ca$_2$Al$_{0.96}$(OH)$_{5.38}$·[−PC$_{n=17}$−]$_{0.25}$·7.4H$_2$O
PC$_{(n=45)}$-LDH	Found :	13.3	5.4	29.80	6.44	/		
	Calc. :	13.7	5.6	29.39	6.52	/	53.0	Ca$_2$Al(OH)$_{6.28}$·[−PC$_{n=45}$−]$_{0.12}$·2.35H$_2$O, 0.21Al(OH)$_3$

Note: [−PC$_{n=x−}$] corresponds to one repeating polymer unit.

noticed that no peak with a *d*-value of 0.76 nm, corresponding to the frequently occurring carbonate form of LDH, is observed in the X-ray diffraction patterns for the PC-LDHs. Considering a thickness of 0.48 nm for the LDH sheets, the observed distances correspond to galleries with polymer layer dimensions along the *c* axis of 0.67 nm for PC$_{n=4.5}$-LDH, 2.47 nm for PC$_{n=8.5}$-LDH, 3.06 nm for PC$_{n=17}$-LDH and 3.79 nm for PC$_{n=45}$-LDH. Although details of the polycarboxylate conformation in between the layers cannot be determined from the XRD data, it should be remarked that with the increase of the side chain length from 4.5 to 45 EOU, the interlayer space of the Ca–Al–PC-LDH nanocomposites increased correspondingly.

3.2. Elemental analysis and thermogravimetry

In agreement with the XRD results, elemental analysis of the PC-LDH materials confirms the intercalation of the PC into the LDH (Table 1). C, H, N values were determined by conventional CHN-analysis. The Ca- and Al-contents were determined by analyzing diluted solutions of the synthesized compounds dissolved in concentrated HNO$_3$ utilizing ICP-AES. The formulae were developed using the following assumptions: a) the molar ratio of Ca to Al in the PC-LDH composites is 2:1. In case of a significant deviation from this ratio, the excess Al was attributed to Al(OH)$_3$ by-product — this phase has been detected by XRD (2θ=18.5°). For Ca–Al–NO$_3$-LDH, a small Al (NO$_3$)$_3$ impurity was considered, leading to a perfect match of the found elemental analysis data; b) all of the carbon content is attributed to the PCs. The absence of an XRD-reflex belonging to intercalated carbonate confirms this assumption. c) Hydroxide anions are present in order to achieve complete charge compensation with the positively charged Ca–Al-layer. The value of the organic part in the PC-LDHs, which was calculated based upon the carbon analysis, confirms the intercalation.

Furthermore, the thermal stabilities of Ca–Al–NO$_3$-LDH and the PC-LDH composites were investigated. For the Ca–Al–NO$_3$-LDH three major mass losses of 10% around 280 °C, 15% around 500 °C and 5% after 600 °C can be observed. These three weight losses correspond to the loss of physisorbed and interlayer water, dehydroxylation of the inorganic layers including a reduction of nitrates and a collapse of the layered structures, respectively [22]. For the PC-LDHs, a similar weight loss in the range of 110–310 °C was observed. A second major weight loss was observed between 310 and 500 °C with percentages of 20% for PC$_{n=4.5}$-LDH, 35% for PC$_{n=8.5}$-LDH and 45% for PC$_{n=17}$-LDH as well as for PC$_{n=45}$-LDH. The higher percentage of the second weight losses in the PC-LDHs, when compared to the Ca–Al–NO$_3$-LDH, is attributed to the decomposition of the PC molecules — a substantial amount of CO$_2$ is detected in the mass spectrometer. The darkening of the specimen after thermogravimetry
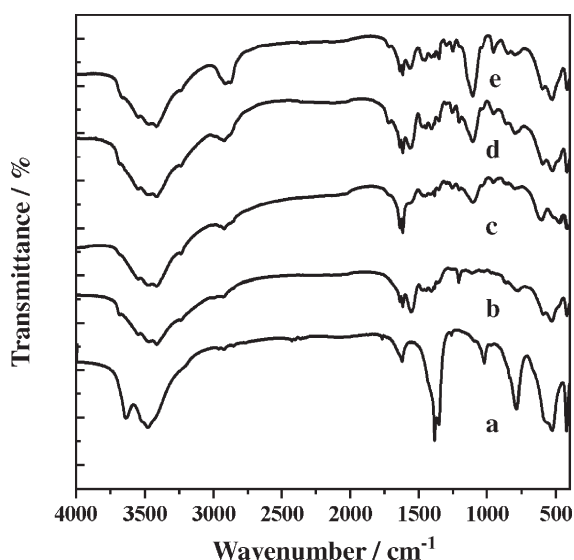

Fig. 3. IR spectra for Ca–Al–NO$_3$-LDH (a), PC$_{n=4.5}$-LDH (b), PC$_{n=8.5}$-LDH (c), PC$_{n=17}$-LDH (d) and PC$_{n=45}$-LDH (e).
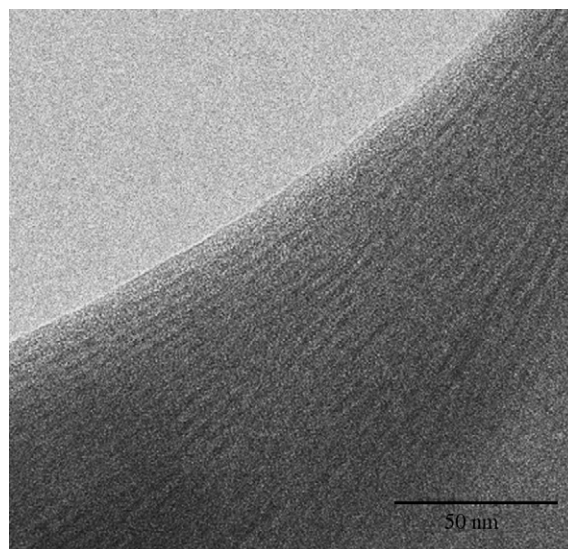

Fig. 4. TEM picture of the PC$_{n=45}$-LDH.

further indicates decomposition. The third weight losses beyond 600 °C were similar to the ones observed in the Ca–Al–NO$_3$-LDH.

3.3. IR-spectroscopy

The IR spectra are provided in Fig. 3. In all samples, the peak around 3600 cm^{-1} represents the vibration of –OH groups of the inorganic layers and the interlayer water.

For the compound Ca–Al–NO$_3$-LDH, the adsorption centered at 1385 cm^{-1} is assigned to the presence of nitrate anions within the structure. In the spectra of the organo-LDHs, strong vibration bands related to the stretching of carboxylate groups appear around 1560 and 1455 cm^{-1}. The vibrations of C–O–C around 2790 and 1100 cm^{-1} are also characteristic for intercalated PC-LDHs. The typical vibrations of M–O and M–OH (M = Ca, Al) in the LDHs appear around 421, 530 and 790 cm^{-1}. They are observed in both the Ca–Al–NO$_3$-LDH and the PC-LDHs, which illustrates that the layered structure was maintained with the intercalation of PC.

3.4. TEM studies

The layered structure of the composite materials also was confirmed by TEM. The stacking of the layers for PC$_{n=45}$–Ca–Al-LDH is shown in Fig. 4. It can be seen that the stacks of Ca–Al–OH double layers are expanded by the PC organic molecules because of intercalation into the layer space. The dark areas represent the skeletons made of calcium aluminate hydrate with a thickness of approx. 1 nm, while the light areas correspond to the sections of homogeneously constituted organic polymers with four times the thickness of the inorganic layers. Although there are morphological changes due to the large increase of the interlayer space (we will discuss this in the following paper), the layered structure is preserved perfectly. The parallel stacking of the layers have an average basal spacing of approx. 4.5 nm, which is in good accordance to the basal spacing of 4.27 nm obtained from XRD analysis.

In this report, we have described the synthesis and characterization of a series of composite layered double hydroxides based on the intercalation of PCs containing ethylene oxide side chains of different lengths. The rehydration method was used to overcome the large steric hindrance of the branched polymers and led to monophasic materials. The nanostructure consists of LDH sheets separated by distances between 0.67 and 3.79 nm, respectively, which is consistent with the increase in side chain length. This is the first report on the intercalation of such branched "comb-like" polymers, providing useful insight into the mechanism of the interaction between superplasticizers and cement.

Further investigation, e.g. on the polymer conformation within the LDHs and the ratio between intercalation and surface adsorption, is in progress and will be reported in the future.

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