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Preparation of hydrocalumite-based nanocomposites using polycarboxylate comb polymers possessing high grafting density as interlayer spacers

Johann Plank *, Bin Yu

Technische Universität München, 85747 Garching, Germany

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ABSTRACT

Fabrication of nanocomposites derived from layered double hydroxides is described. Synthesis was accomplished by rehydration of tricalcium aluminate ($Ca_3Al_2O_6$, abbreviation C_3A) in the presence of “comb like” polycarboxylate copolymers (PCs). The PCs possess low anionic charge density and high grafting density. Their side chains were made up of between 4.5 and 111 ethylene oxide units (EOUs). It was found that the length of the side chain in PC determines whether intercalation occurs or not. Polymers possessing short to medium size side chains intercalate well whereas PCs with long side chains interact with C_3A by surface adsorption only rather than chemical absorption. XRD, IR spectra, thermogravimetry (TG), elemental analysis and TEM images confirm that for polymers possessing side chains made of 4.5–45 EOUs, nanocomposites are formed with layered structure whereby the PCs are intercalated in between the inorganic $[Ca_2Al(OH)_6]^+$ host layers. Interlayer distance depends on the length of the side chains. The organic parts of the nanocomposites vary between 39 mass% and 62 mass%, resp. In contrast, PCs possessing long side chains (111 EOUs) do not show any significant intercalation. Their high grafting density coupled with large steric size of the side chain does not allow compression of the graft chains which is necessary for the molecule to fit in between the inorganic main layers. The results indicate that synthesis of inorganic–organic hybrid materials showing a controlled variation of the interlayer distance is possible by using the PCs studied here that possess high grafting density.

1. Introduction

Comb-shaped polycarboxylates are copolymers which consist of a trunk chain carrying carboxylate functionalities and side chains made from ethylene oxide units. They represent a new generation of superplasticizers which are applied to disperse inorganic binder systems such as e.g. concrete and mortar (Ramachandran et al., 1998). Depending on the grafting density (number of poly(ethylene oxide) (PEO) side chains attached to the polymer trunk), their molecular architecture is represented either by a decorated chain, a worm or a star-like shape (Gay and Raphael, 2001). Thus, the overall structure of the PCs can be fine-tuned easily which makes them useful compounds in the syntheses of nano-structured materials possessing defined interlayer distances. PCs are macrosurfactants which consist of a strongly hydrophilic and a hydrophobic part. At high pH values typical for cement suspensions, the backbone of the polymer is negatively charged because of the deprotonated carboxylate groups, whereas the PEO side chains do not possess any charge.

Layered double hydroxides (LDHs) are a group of anionic clays which possess high anionic exchange capacity (Bergaya et al., 2006). They consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. Their general composition can be expressed by the formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{II} and M^{III} represent metal cations and A^{n-} the interlayer anion. A typical example for LDH compounds is hydrotalcite, commonly abbreviated as Mg–Al–LDH. Its lamellar framework is displayed in Fig. 1.

Hydrocalumites, $[Ca_2Al(OH)_6]^+(A^{n-})_{1/n}\cdot mH_2O$, also belong to the family of layered double hydroxides. They may contain various inorganic or organic guest anions in between their cationic main layers. They differ from hydrotalcites in that their main layer is much more ordered, due to the large cationic radius of Ca^{2+} in comparison to Mg^{2+}. This cation completes its coordination sphere with one oxygen atom from an interlayered water molecule resulting in a coordination number of seven (Segni et al., 2006). Allmann and Brown et al. were the first to elucidate the structure of LDHs (Allmann, 1977; Brown and Gastuche, 1967).

Tricalcium aluminate (C_3A) is an important constituent in cement. At ordinary temperature, its hydration in the absence of sulphate initially produces layered calcium aluminium hydroxides belonging to the family of hydrocalumites, namely $4CaO\cdot Al_2O_3\cdot 19H_2O$ (C_4AH_{19}) or $2CaO\cdot Al_2O_3\cdot 8H_2O$ (C_2AH_8). Their structures show $[Ca_2Al(OH)_6]^+$ main layers with OH^- anions and H_2O molecules in the interlayer region. Also, some solid solutions of these metastable phases with variable contents of calcium (ranging from 2.0 to 2.4) and water (ranging from 8.0 to 10.2) and amorphous, gel-like $Al_2O_3\cdot 3H_2O$ are formed. The metastable phases quickly convert to the stable cubic phase $3CaO\cdot Al_2O_3\cdot 6H_2O$ (katoite, C_3AH_6). In the presence of an appropriate amount of sulphate ions, C_3A

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* Corresponding author. Tel.: +49 89 2891 3150; fax: +49 89 2891 3152.
E-mail address: johann.plank@bauchemie.ch.tum.de (J. Plank).

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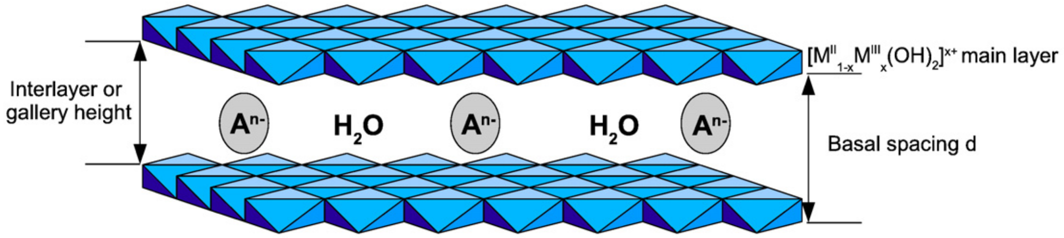

Fig. 1. Schematic illustration of the lamellar LDH structure (A^{n-} = anion).

forms another layered compound called monosulfoaluminate, $3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$ (Taylor, 1990). There, sulphate is the guest anion which is intercalated into the host structure. Additionally, it has been described that under certain conditions, organic anions or polyelectrolytes which are used as admixtures to improve the quality of concrete may also intercalate into C_3A hydrate phases. An example is the group of superplasticizers based on β-naphthalene sulfonate formaldehyde (BNS) polycondensates (Fernon et al., 1997; Raki et al., 2004) which are commonly added to concrete to enhance its flow properties. Also, in situ polymerization of styrene-4-sulfonate in the interlayer space of Ca–Al–LDH has been reported (Vieille et al., 2003).

It has been shown that PCs can interact with cement hydrate phases by physical adsorption onto the surfaces of positively charged cement minerals such as ettringite or monosulfoaluminate (Plank and Hirsch, 2003). Competing with this physical process of adsorption is chemical absorption (also called intercalation), whereby the anionic PCs are intercalated into the lamellar structure of cement hydrate phases. This way, they no longer become available for the desired dispersing effect. Previously, we have proven that PCs made of methacrylic acid (MA) and ω-methoxy polyethylene glycol (MPEG) methacrylate ester in a molar ratio of 6:1 can intercalate into the interlayer region of calcium aluminium layered double hydroxides (Ca–Al–LDHs) during rehydration of C_3A at 75 °C over 2 days. There, the basal spacing (interlayer distance) of the nanomaterials roughly increased with the increasing side chain length of the PCs (Plank et al., 2006a). This way, the PCs act as spacers which determine the interlayer distance in the inorganic host structure. Additionally, we have shown that at an elevated temperature, another type of comb-shaped PC composed of maleic anhydride-*co*-α-allyl-ω-methoxy poly(ethylene glycol) ether also intercalates well into the Ca–Al–LDH-like host structure (Plank et al., 2006b).

The PCs studied so far possess an exceptionally high anionic charge. Their intercalates were prepared under conditions of long reaction time and elevated temperature to obtain a sufficient yield, particularly of highly crystalline material which can be detected by XRD. In the present work, we have investigated the intercalation tendency of PCs possessing lower anionic charge density and high grafting density at room temperature and 2 h reaction time only. This type of PC is very common to achieve high fluidity in ready-mix concrete because it adsorbs less and provides a plasticizing effect which lasts over 2 h. For this study, C_3A was rehydrated in the presence of PCs prepared from MA and ω-methoxy polyethylene glycol-methacrylate (MPEG-MA) ester in a molar ratio of only 1.5:1. The resulting reaction products were then characterized by XRD, IR, TG, elemental analysis, and TEM. Intercalation tendency of these PCs possessing lower anionic charge will be compared with those previously reported. Also, their usefulness as spacers in the synthesis of nanocomposites possessing well-defined interlayer distances will be discussed.

2. Experimental

2.1. Sample preparation

Details of the synthesis and characterization of the comb polymers designated *n*PC1.5 (*n* denotes the number of EOUs in the PC side chain, whilst 1.5 stands for the molar ratio between MA and MPEG-MA) have been published before (Plank et al., 2008). The chemical composition of the PCs is shown in Fig. 2. Note that a small amount of methallyl sulfonic acid which was used as chain transfer agent in the synthesis is incorporated into the PC. The characteristic properties of the *n*PC1.5 are shown in Table 1. Number average molecular weight (M_n), weight average molecular weight (M_w), polydispersity index (PDI) and hydrodynamic radius (R_h) of the PCs were obtained from GPC measurements using 0.1 mol/L $NaNO_3$ at pH 12 (adjusted with NaOH) as eluent and Waters 2695 Separation Module equipped with light scattering and refractive index detection. Based on M_n, the main chain length (MCL) of the copolymers can be calculated following a method described before (Plank et al., 2006b). Additionally, the side chain lengths (SCLs) of the *n*PC1.5 polymers were determined in analogy to previous work (Ohta et al., 2000). A schematic representation to the scale of the molecular architectures of the synthesized copolymers is shown in Fig. 3. Obviously, the PCs possessing SCLs of 4.5, 8.5, 17 and 45 EOUs, resp. are brush or worm polymers whereas the PC polymer with 111 EOUs in the side chain shows a star-like architecture. Thus, the synthesized PCs can be categorized into two distinctly different classes.

The following is an example of a typical synthesis used to prepare the nanocomposites: Comb polymer 4.5PC1.5 was dissolved in deionised water at a concentration of 2.5 mass%. Next, 1.5 g C_3A was added to 100 mL of this PC solution to allow rehydration. The suspension (pH ~ 11.7) was stirred under nitrogen flow at room temperature for 2 h. Subsequently, the precipitated reaction product was separated by centrifugation. When PC intercalation had occurred, the precipitate showed a whitish gel phase at the top (1/5–1/3 of total volume of precipitate) containing the nanocomposite whereas the bottom phase consisted of a compact solid containing the essentially PC-free hydrates of C_3A (C_4AH_{19} and C_2AH_8). The gel phase was totally absent when no intercalation had occurred. For characterization of the nanocomposites, only the gel phase was used. The gel phase was rinsed with deionised water once in order to remove residual PC polymer and dried at ambient temperature in a desiccator under

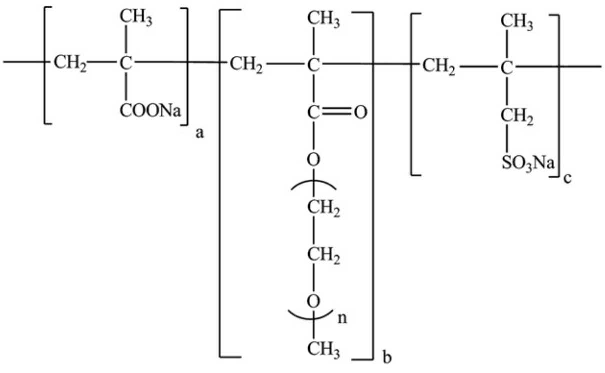

Fig. 2. Chemical structure of the studied polycarboxylates (a:b:c = 1.5:1:0.2, *n* denotes the number of the ethylene oxide units; sodium methallyl sulfonate is chain transfer agent).