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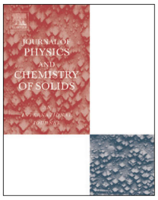

Intercalation of sulfonated melamine formaldehyde polycondensates into a hydrocalumite LDH structure

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ABSTRACT

A series of sulfonated melamine formaldehyde (SMF) polycondensates possessing different anionic charge amounts and molecular weights was synthesized and incorporated into a hydrocalumite type layered double hydroxide structure using the rehydration method. For this purpose, tricalcium aluminate was dispersed in water and hydrated in the presence of these polymers. Defined inorganic–organic hybrid materials were obtained as reaction products. All SMF polymers tested intercalated readily into the hydrocalumite structure, independent of their different molecular weights (chain lengths) and anionic charge amounts. X-ray diffraction revealed typical patterns for weakly ordered, highly polymer loaded LDH materials which was confirmed via elemental analysis and thermogravimetry. IR spectroscopy suggests that the SMF polymers are interleaved between the $[Ca_2Al(OH)_6]^+$ main sheets via electrostatic interaction, and that no chemical bond between the host matrix and the guest anion is formed. The SMF polymers well ensconced within the LDH structure exhibit significantly slower thermal degradation.

1. Introduction

Polyelectrolytes of various compositions are commonly employed in industrial colloidal systems such as ceramics preparations, coatings, pulp and paper manufacturing or to control the rheology of building materials. In the latter case, polycondensates of sulfonated melamine formaldehyde (SMF) type play an important role, e.g. as superplasticizers for cementitious systems [1–3]. The general structural composition of this polymer is presented in Fig. 1.

Many researchers have investigated the early stages of cement hydration in the presence of such polyelectrolytes and found strong adsorption and morphological changes of the hydration products [4–8]. Furthermore, some authors have reported that monomeric benzene sulfonates can be intercalated into a hydrocalumite host structure yielding stable LDH compounds, so called inorganic–organic (I/O) hybrid materials, which appear as hexagonal platelets [9]. However, it remained unresolved whether a large polyelectrolyte based on a similar building block, namely sulfonated methylol melamine, can undergo similar intercalation reaction. In order to clarify, a total of five sulfonated melamine formaldehyde (SMF) polycondensates possessing different molecular weights (M_W) and specific anionic charge amounts were synthesized and probed for their intercalation behavior. The resulting reaction products were characterized via X-ray diffraction, IR spectroscopy, thermogravimetry and scanning electron microscopy. A model for their composition is proposed.

2. Materials and methods

2.1. Polymer synthesis

A total of five sulfonated melamine formaldehyde polymers were synthesized according to the method of Aignesberger et al. [10]. There, melamine was reacted with formaldehyde and sodium bisulfite in a three stage process. The specific anionic charge amount of the polymers was varied by employing different amounts of sodium bisulfite during the synthesis of the precursor compound. The molar ratio of formaldehyde to melamine was kept constant at 3:1 for all polymers, while the sulfite content varied from 0.75 to 1.0. Firstly, melamine, formaldehyde and sodium bisulfite were reacted at pH = 11 (NaOH 20%) for 1 h at 75 °C. Next, condensation was carried out over 90 min at pH = 4 (H_2SO_4 10%) and 50 °C. Thereafter, the pH was adjusted to 8 (NaOH 20%) and the reaction mixture was heated to 80 °C for another 60 min. Finally, the polymer solutions were cooled to ambient and dialyzed prior to further investigation or use (SpectraPor dialysis

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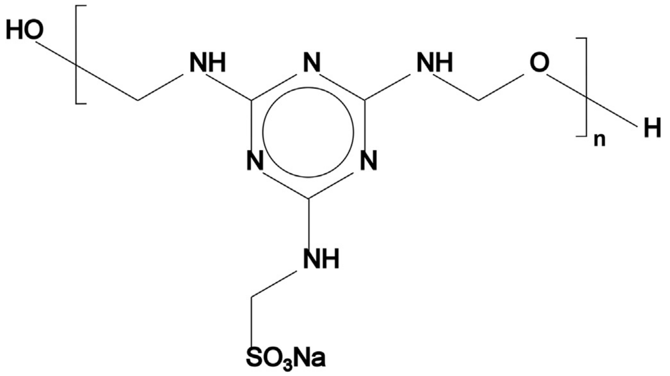

Fig. 1. : General structure of sulfonated melamine formaldehyde (SMF) polycondensate exhibiting the maximum degree of sulfonation of 1.0.

membrane, MWCO=6000 Da). All chemicals used were of analytical grade unless stated otherwise (Merck KGaA Darmstadt / Germany). Degassed ultrapure water (Millipore Synergy UV) was used throughout the experiments to avoid atmospheric contamination, especially from CO_2.

2.2. LDH synthesis

The hydrocalumite type LDH compounds were prepared via rehydration of cubic tricalcium aluminate $(C_3A_c)_x$, which was prepared from $CaCO_3$ and Al_2O_3 via calcination at 1350 °C [11]. The resulting calcium aluminate was ground to a particle size (d_{50}-value) of 4.0 µm. Purity of the C_3A sample was confirmed via XRD measurement. Preparation of the Ca_2Al–SMF-LDHs was carried out as follows: Under vigorous stirring, 1 g of cubic C_3A was added to 100 mL of a 2 wt% aqueous SMF solution at room temperature. The polymer solution was flushed with nitrogen beforehand to exclude any carbon dioxide. A protective atmosphere was maintained throughout the entire reaction time of 24 h. The products were recovered by centrifugation and the wet precipitate was dried using a freeze drier ($p=0.01$ mbar, $T=-50$ °C, Christ Alpha 1-4 LDplus, Martin Christ Gefriertrocknungsanlagen GmbH, Osterode am Harz/Germany).

For comparison, a Zn_2Al–SMF-LDH sample was synthesized using the constant pH copreciptation method. There, a mixture of $ZnCl_2 \cdot 6H_2O$ (5 mmol) and $AlCl_3 \cdot 6H_2O$ (2.5 mmol) dissolved in 200 mL deionized H_2O and 1 N NaOH dissolved in 100 mL of freshly deionized H_2O were simultaneously added drop-wise to 200 mL of a SMF2 solution (10 mmol) at room temperature under nitrogen atmosphere. The amount of SMF present was 4 times the amount needed to counterbalance the Al^{3+} content. During synthesis, the pH of the reaction mixture was carefully maintained at 10.00 ± 0.01 by adding 0.1 N NaOH as required. The resulting suspension was aged for 24 h at room temperature. The precipitate was separated via centrifugation, washed three times with freshly deionized H_2O and dried overnight at 60 °C in an oven under N_2.

2.3. Characterization

The elemental composition of the samples was determined using conventional CHNS analysis (Hekatech Euro EA). Calcium and aluminum contents were obtained by atomic absorption spectroscopy (VARIAN AA 280 FS). The specific anionic charge amount of the polymers was assessed by streaming current potential determination via polyelectrolyte titration using a particle charge detector (PCD 03 pH, BTG Mütek GmbH). To capture the relative molecular weights of the SMF samples, micro-Ubbelohde viscosimetry was performed. The dialyzed polymers were measured at 25 °C (Lauda 015T Thermostat) using 0.1 M $NaNO_3$ solutions to compensate osmotic effects. From the intrinsic viscosity determined according to Huggins, M_W of the SMF polymers was calculated [12]. XRD patterns were recorded using Cu-Kα radiation with a Bruker AXS D8 diffractometer. Samples were dried (see 2.2.) prior to measurement and slight grinding was applied to the products. IR spectra were taken with a Bruker FT-IR spectrometer (Bruker Vertex 70 FT IR) using KBr pellets. TG measurements were performed in synthetic air on a Netzsch "STA409PC Luxx" TG system which was equipped with a mass spectrometer (Netzsch QMS403C Aeolos, Netzsch-Gerätebau GmbH). For SEM imaging, a FEI XL 30 FEG environmental scanning electron microscope was used.

3. Results and discussion

3.1. Characterization of SMF polymers

The synthesized and dialyzed polymers were characterized regarding their elemental composition, specific anionic charge amount and intrinsic viscosity. The results are shown in Table 1. There, the polymers are arranged in descending order regarding their intrinsic viscosity which is relative to their molecular weight. In previous literature, authors have shown that the molecular weight of water-soluble polyelectrolytes correlates with their intrinsic viscosity when measuring under a defined ionic strength [13,14]. Here, the absolute molecular weights were not determined, because UV activity of SMF prevented detection in size exclusion chromatography. For orientation, M_W of polymer sample SMF5 was determined in a so-called batch measurement (without separation on a chromatographic column) and was found at $\approx$ 100,000 g/mol. Accordingly, the molecular weights of the other SMF samples are higher, with sample SMF1 exhibiting by far the highest molecular weight. The specific anionic charge amounts of the polymers were captured via polyelectrolyte titration. According to this data, the high molecular weight SMF sample bears the lowest anionic charge amount. This correlates well with the data from elemental analysis, which show increasing sulfur content from SMF1 to SMF5.

Taking these elemental analysis results into account, approximate chemical formulas for the polymers were derived (see Table 2) whereby sodium was assumed to counterbalance the

Table 1
Elemental composition, specific anionic charge amounts and intrinsic viscosity (η) of the synthesized SMF polymers.

Polymer sample	Molar ratio M:F:S[a]	Elemental analysis				Anionic charge amount	Intrinsic viscosity [η]
		C/%	H/%	N /%	S / %	10^{-6} eq/g	mL/g
SMF1	1:3:0.75	24.5	4.2	30.7	8.0	2420	10.2
SMF2	1:3:0.85	23.1	4.0	29.0	9.3	2610	4.2
SMF3	1:3:0.90	23.5	4.0	29.4	9.6	2730	3.7
SMF4	1:3:0.95	22.0	3.9	28.9	10.2	3430	2.0
SMF5	1:3:1.00	22.6	3.7	25.1	11.8	4160	1.9

[a] M=melamine; F=formaldehyde; S=sulfite.