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Effects of LDH synthesis and modification on the exfoliation and introduction of a robust anion-exchange procedure

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HIGHLIGHTS

- Layered double hydroxide (LDH) was synthesized under different conditions.
- Some of the influencing factors during the modification of LDH were explored.
- An effective anion-exchange intercalation procedure was introduced.
- The effect of filler preparation on dispersion in the matrix polymer was investigated.

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ABSTRACT

Layered double hydroxides (LDHs) were synthesized and modified with different methods and also with different functional molecules. An easy and successful one-pot anion-exchange intercalation procedure was introduced and the influencing parameters of the modification were investigated in comparison to other modification methods. LDH based polymer nanocomposites were prepared with a microcompounder using melt-mixing method. The exfoliation behavior of organomodified LDHs was investigated with two different rheological models and visualized with electron microscopy techniques. Some of the relations between modification of LDH and the extent of exfoliation were identified. Highly exfoliated nanocomposites were successfully prepared after intercalation even with a small molecule like hexanesulfonic acid by performing the introduced anion exchange method.

1. Introduction

Layered double hydroxides (LDHs) have attained immense importance with their nanocomposite applications in the last years [1–4]. LDHs consist of positively charged layers and this positive charge is electrostatic balanced with interlayer anions. Thus, in this group of clays ion exchange reactions with a variety of different anionic molecules can be employed unlike in cationic clays, which is usually modified by organic ammonium ions [5]. These anionic modifications of LDH are a prerequisite of the nanocomposite preparation in order to reduce the attractive coulomb forces between the adjacent layers and to reach higher exfoliation degrees. The well-dispersed and exfoliated clays in the matrix polymer lead to several advances in the final material properties such as better strength or modulus without any loss from toughness [6,7]. Moreover, rheological and microscopical methods are often used to investigate these filler–matrix interactions and to understand the state of dispersion [8,9].

The modification of LDH is conducted based on exchanging the interlayer ion with the selected species. LDH, however, exists in the nature in its carbonate form, which shows quite low affinity for the exchange reactions compared to monovalent ions [10,11]. Homogeneous precipitation of LDH during urea or hexamethylenetetramine (HMT) hydrolysis, on the other hand, is a very common method to synthetically produce LDH. This leads to homogeneous, well-crystallized LDH platelets [12,13]. Drawback of the urea method regarding the following modification step is again the generated carbonate ions in the LDH galleries due to hydrolysis of ammonia releasing reagents.

The memory effect of LDHs can be used for the decarbonation of LDH and subsequent regeneration of the layers with the desired anionic species [10,14]. LDH is exposed to high temperatures for long times and the reaction after decarbonation is needed to be carried out in a carbonate-free environment, which makes the procedure complicated and energy costly.

Another approach for the modification of LDH is the co-precipitation method. This method can be used to directly modify LDH

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with the desired anion during the synthesis. Alternatively, LDH can be synthesized with an anion with a higher capability for the exchange reactions [10,15]. The main drawbacks of this method are the necessity of the thermal treatment afterwards for better crystal structure and the rather complexity of the procedure (i.e. constant pH).

LDH–CO_3 can be also initially decarbonated with solutions like HCl–NaCl, ammonium salt alcohol, or acetate buffer/NaCl. The obtained LDH–Cl or LDH–CH_3COO show higher affinity for exchange reactions and can be used for further modification by exchanging its monovalent interlayer ions (Cl^-/CH_3COO^-) with the selected one [16–19]. These procedures, however, are rather complex and reported quantities are in mg range, which makes it difficult to use in polymer nanocomposite preparation, especially with conventional melt-mixing techniques. Hence, there is a need of a simple procedure for the modification of CO_3^{2-} containing LDH, which exists naturally and is present in the industrial production. In the presented work, a new and easy procedure for the modification of LDH was developed. LDH–CO_3 was converted to LDH–NO_3 form and subsequently NO_3^- ion was exchanged with different surfactants in one pot and in short reaction times. LDHs were synthesized and modified with different conditions and methods. The influencing parameters for a successful modification were investigated. The prepared nanofillers were further melt-mixed and the nanocomposites were characterized rheologically using rather a new evaluation method and microscopically. Some of the relations between the synthesis and modification conditions of the LDH and the extent of exfoliation were explored.

2. Experimental

2.1. Materials

The chemicals used for the synthesis and organomodification of LDH were purchased from Sigma–Aldrich. Commercial LDH products, MG 63 HT and MG 70 HT, were delivered by Sasol GmbH, Germany. Polybond 3109, maleic anhydride grafted polyethylene, was supplied by Crompton Corporation, USA.

2.2. Synthesis of the LDH

Synthesis of LDH was conducted using urea hydrolysis method as described elsewhere [12]. LDH was synthesized with different urea proportions (k), where $k = [\text{urea}]/([\text{Mg}] + [\text{Al}])$ and at different reaction times. LDH used for the modifications was synthesized for $k = 3.5$ and reaction time was 3 days unless it was not specified differently. Besides self-produced LDH the modifications of LDHs were also performed with commercially available products (see Table 1).

Table 1
The compositions of the used LDHs during the experiments.

Sample name	Description	[Mg]/[Al] ratio
LDH1	Self-produced LDH	2:1
LDH2	Commercial product	2:1
LDH3	Commercial product	3:1

2.3. Modification of the LDH

2.3.1. Regeneration method

MgAl–CO_3 was calcined at 490 °C for 3 h and resultant calcined LDH was dispersed in the solutions of the salts of the desired anionic species in stoichiometric ratio. The reactions were carried out under nitrogen environment to avoid the CO_2 contamination. The mixtures were stirred for the following 24 h and the product was filtered and washed. For the surfactants, which are not soluble in the room temperature, the reactions were carried out at 60 °C.

2.3.2. Co-precipitation method

Magnesium and aluminium were co-precipitated from their chloride salts as described in the literature [15]. The Mg:Al ratio was kept to be 2:1 and pH was maintained at 10 ± 0.2. The solutions of selected anions were prepared prior to precipitation reaction and co-precipitation of magnesium and aluminium hydroxide layers took place in the presence of these anions resulting modified LDHs.

2.3.3. Extended homogeneous precipitation method

The experiments were carried out based on the work of Iyi et al. [20]. Urea was selected as ammonia releasing reagent and Mg:Al ratio was 2:1. The surfactants were introduced prior to precipitation reaction and LDH was precipitated in the presence of anions similar to co-precipitation method.

2.3.4. One-pot anion-exchange intercalation method

In a typical reaction, 0.048 mol nitric acid was mixed with 200 ml water at 65 °C in a round-bottom flask with reflux condenser. 0.024 mol MgAl–CO_3 was then added in one portion and stirred for the following 1 h. Excess nitric acid maintains better decarbonation conditions. The sodium salt of the selected surfactant was then separately dissolved in water and added to the mixture in stoichiometric ratio. After surfactant addition the reaction was continued for another 2 h and the reaction was ended.

Besides the methods also several different surfactants were used during the experiments. In order to avoid repetition the surfactants were classified due to their carbon atom number on the backbone and their functional group. i.e. hexanesulfonic acid was presented as 6Cs, where "s" represents sulfonic acid and tetradecanoic acid was demonstrated as 14C, where absence of "s" represents carboxylic acid. For the modified LDHs, these notations were also used. For instance, 14Cs-LDH1 represents tetradecanesulfonic acid modified self-produced magnesium aluminium LDH with Mg:Al ratio of 2:1.

2.4. Nanocomposite preparation

Nanocomposites were prepared on a two-step basis using conventional melt-mixing method with help of a 15 cm^3-microcompounder (DSM Xplore 15, Geleen, The Netherlands). The masterbatch was prepared with a PE-g-MA/filler weight ratio of 2:1. Then in the second step the masterbatch was diluted again with PE-g-MA. The processing of polymers was carried out at 190 °C with a 100 rpm stirring speed and 10 min mixing time. The inorganic content (metal hydroxide part of the organomodified LDH) was set to 5 wt.% for all prepared nanocomposites. The organic content of the filler was varied based on the molecular weights of the intercalated organic species.

2.5. Techniques

X-ray diffractograms were recorded using a 2-circle diffractometer (XRD 3003 θ/θ, Seifert-FPM Freiberg/Sa., now: GE Sensing & Inspection Technologies GmbH). Fourier transform infra-red (FTIR) investigation was carried out with a VERTEX 80V (Bruker) spectrometer. Thermogravimetrical analysis (TGA) was performed with a heating rate of 10 °C/min using TGA Q 5000 of TA instruments under nitrogen environment. Scanning electron microscopy (SEM) images were taken with Ultra Plus and transmission electron microscopy (TEM) images were taken with a Libra 200MS. Energy-dispersive X-ray spectroscopy (EDX) was carried out using