Porous nanoclay polysulfone composites: A backbone with high pore accessibility for functional modifications

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ABSTRACT

Microporous, highly charged and cation exchangeable clays are interesting carriers not only for various functional molecules such as cationic dyes, surfactants, proteins, drugs and complexes, but also for water insoluble molecules. In water, swellable nanohectorite derivatives ("laponites") with dimensions of about 25 nm in diameter and 1 nm in height delaminate to form individual nanoparticles, which proved to be very useful for applications in aqueous dispersions, but less advantageous for the use in filter systems for water treatment, membrane technology, or as catalysts. To immobilize the particles in aqueous environments and still provide accessibility and high cation exchange rates on the clays, we used an inversion process to prepare porous nanoclay polysulfone composites with high clay contents up to 60%. Successful incorporation of the clays in the matrix required clay pre-modifications with reactive silanes such as octyltriethoxysilane or octadecyltriethoxysilane. Interestingly, unmodified laponite can also be used as a template to form a porous polysulfone network due to its leakage in the inversion process. The high accessibility and activity found in composites prepared with a mixture of unmodified and modified laponite particles pave the way for further modifications with functional molecules for various applications. In this study, we characterize the nanoclay polysulfone composites via scanning electron microscopy, nitrogen gas adsorption of the dried composite, and we determine the cation exchange capacity in the wetted state.

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1. Introduction

Nanoclays such as nanoscaled lithium magnesium silicates have proved to be useful additives in many commercial applications, for example, in coatings, lacquers and paints as film forming agents and rheological modifiers [1]. The unique properties of these nanoclays derive from the anisotropic sheet structure of clays, the complex charge distribution on their surface, and their ability to form electrostatically stabilized (see Fig. 1), clear aqueous dispersions [2]. We have been studying the nanoclay, laponite, as host matrix for various water insoluble dyes like Indigo, Nile Red, Coumarin 153 or Phthalocyanines [3—6], successfully solubilized them into aqueous environments and thus enabled the possibility for optical applications like sensors or as singlet oxygen generators.

However, here we investigate the incorporation of laponite into a suitable, stable polymer matrix (polysulfone) for further pursuit of novel application concepts, focusing on the following crucial aspects: a) The applicability of high filler (clay) contents, b) high accessibility of the filler in the matrix, c) the applicability in an aqueous environment (no leakage of the filler), and d) the cation exchangeability of the filler. Hence, our main interest lies on the adsorption ability of the microporous clay in the polymer matrix rather than its mechanical or thermal properties.

To obtain the desired properties we investigated laponite polysulfone (Laponite-PSU) composites with a high filler content, manufactured in an inversion process that is usually applied in membrane technologies [7]. Although clay polymer composites are exhaustively studied, most publications deal with low filler contents to improve the mechanical properties or the barrier
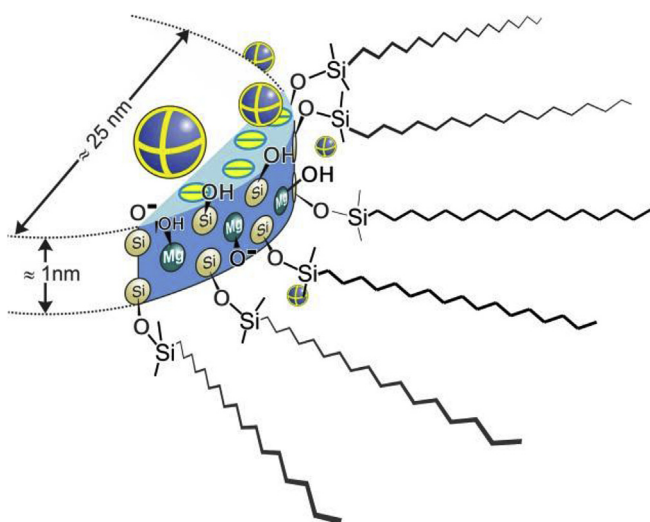
Fig. 1. Sketch of Laponite RD morphology and rim modifications employed in this work. Li^+ atoms partially replacing Mg^{2+} in the interior of the sheets give rise to negative surface charges on the faces of the platelets, which are in turn compensated by Na^+ ions that can hydrate and separate in aqueous media (blues spheres), while Si—OH and Mg—OH at the rims can be used for coupling to silane agents (e.g. octadecyldimethyl methoxisilane).

properties for gas separation techniques for an example [8—14]. For this, the clays were usually modified with organophilic quaternary amines via a cation exchange mechanism to grant a successful incorporation into the polymer [15,16]. Since it is our request that the cation exchange capacity (cec) of laponite in the composite should be maintained, we chose a modification with reactive organo-ethoxysilanes, octyltriethoxysilane (OTES) and octadecyltriethoxysilane (ODTES), that couple to the rim of the sheet particles [17,18]. This appears to be an appropriate method to increase the interaction forces of the laponite particles with the polysulfone (PSU) polymer and additionally retain the cec of the clay-filler.

Montmorillonite, an aluminum magnesium silicate with dimensions of about 200 nm in diameter, was mainly used for the preparation of polysulfone and polyethersulfone clay composites [19—21]. Laponite, itself a lithium magnesium silicate with the empirical formula of $Na_{0.7}(H_2O)_n\{(Li_{0.3}Mg_{5.5})[Si_8O_{20}(OH)_4]\}$ and dimensions of about 25 nm in diameter, was only applied with sulfonated polysulfone up to 5 wt% after a He plasma treatment, followed by grafting of p-styrene sulfonic acid [22,23]. Besides that, various micro- and mesoporous materials like zeolites [24], MCM41 [25] and SiO_2 [26] have been investigated with polysulfone for gas separations. In contrast, our focus is set on the filler properties themselves, we decided to incorporate laponite in a PSU matrix with filler contents of up to 60 wt%, resembling in its goal the study of Thomas et al., who investigated laponite in form of a highly cation exchangeable hydrogel [27]. Although not at the very core of the present work, our eventual goal is the further modification of the laponite filler in PSU to introduce useful functional modifications such as optical moieties for sensing [28,29], as a host to antimicrobial species such as phthalocyanines [30] and peptides [31], or for catalysis [32,33], eventually.

2. Experimental

2.1. Synthesis of modified laponite particles

4 g of LAPONITE® RD $Na_{0.7}[Li_{0.3}Mg_{5.5}Si_8O_{20}(OH)_4]$ (Rockwood Additives, now marketed by BYK Additives & Instruments) were dispersed in 27 ml of ethanol (EMSURE® ACS, ISO, Reag. Ph Eur, Merck) and 3 ml of ammonia solution (for analysis 28—30%, Merck). After two hours of stirring 3.61 mmol of one triethoxysilane modifier was added and stirred for a further 16 h. Subsequently, the dispersion was centrifuged 3 times at 15,000 rpm for 20 min, washed and suspended with ethanol. The product was dried at 60 °C for 16 h. In the following, the nanoclay modification with n-Octyltriethoxysilane (97%, ABCR) is referred to as OTES-L, while the nanoclay modification with n-Octadecyltriethoxysilane (95%, ABCR) is referred to as ODTES-L. For unmodified LAPONITE® RD the term "laponite" is used (for modified laponite, see the sketch in Fig. 1).

2.2. Fabrication of nanoclay polysulfone membranes

Various amounts of modified laponite were added to a 10 wt% polysulfone (UDEL P-3500, Solvay) solution in N-Methyl-2-pyrrolidone (NMP). The clay content $(m(clay)*[m(clay)+m(PSU)]^{-1})$ was set to 0.30, 0.40, 0.50 and 0.60 with respect to the final laponite-PSU composite. For homogenization the mixtures were stirred for 16 h, resulting in slightly turbid dispersions. These dispersions were cast onto a glass plate and shaped with a doctor blade to a film with a thickness of 0.5 and 1.0 mm. Subsequently, the films were immersed in water to form the solidified membranes. The whole inversion process took 24 h with a repeated water exchange to remove the NMP solvent completely. Uniform samples, slices with a diameter of 1.5 cm were pierced out of the membranes and once again immersed in water for 16 h. The membrane samples with the OTES-L and ODTES-L material will be referred to as OTES-L-PSU and ODTES-L-PSU, respectively. One composite with 30% of laponite + 30% of ODTES-L is named Mixed-L-PSU.

2.3. N_2 adsorption/desorption

For N_2 adsorption and desorption measurements a Belsorp Max by Bel Japan Inc. was used. The samples were pretreated for 3 h under vacuum at 60 °C at 0.1 Pa using a turbo molecular pump. Measurement were taken at liquid nitrogen temperature (77 K). The relative pressure (p/p_0) in adsorption mode was set to 0.9, while p/p_0 was set to 0.3 in desorption mode. For every adjusted gas equilibrium, constant gas pressure was awaited (0.3% in a time range of 500 s). The specific surface area (α_s) was calculated with the software BELMaster™ using the BET equation.

2.4. Gravimetric analysis

To obtain information on the water content of the samples, they were desorbed at 60 °C for 180 min at a pressure of 0.1 Pa. The low temperature was chosen to prevent decomposition of the organic modifications and hinder sintering of the nanomaterial. Complete decomposition of the PSU matrix and the organic modifications was obtained in a furnace at 500 °C for 3 h and at 800 °C for 5 h. Taking sintering losses of laponite into account, we could thus calculate the composition of the modified powders and the membranes.

2.5. Calculation of the cation exchange capacity (cec)

Using a blue $[Cu(triethylenetetramine)]^{2+}$ $(Cu(TETA)^{2+})$ complex, we applied Meier's and Kahr's method to determine the cation exchange capacity (cec) [34]. A 0.01 mol L^{-1} stock solution was used to calculate the extinction coefficient at 578 nm between the absorbance of 0.10 and 0.45. 2 ml of the stock solution, and 2 ml of H_2O were added to membrane pieces or powder of about 0.2—0.3 g. After 2 h of being shaken at room temperature, the supernatant was