Colloids and Surfaces A: Physicochem. Eng. Aspects 506 (2016) 320–330

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Interlayer functionalization of magadiite with sulfur-containing organosilanes

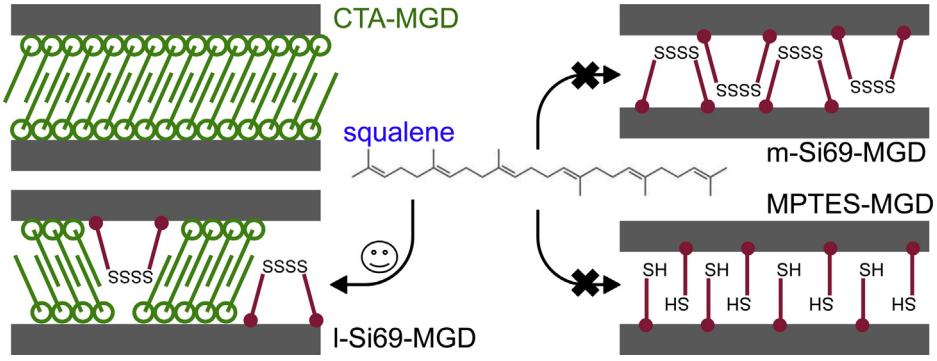
Shigeng Li, Yating Mao, Harry J. Ploehn*

Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, United States

HIGHLIGHTS

- Sulfur-containing silanes were grafted onto magadiite (MGD) interlayer surfaces.
- Silane grafting (Si69, MPTES) displaced CTA$^+$ cations from the interlayer surfaces.
- Reaction of squalene with silanized MGD probed accessibility of interlayer sulfur.
- High Si69 graft density decreases MGD layer spacing and precludes entry of squalene.
- Low Si69 graft density maintains layer spacing, permits interlayer squalene grafting.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form 22 June 2016
Accepted 23 June 2016
Available online 24 June 2016

Keywords:
Magadiite
Sulfur
Silane
Grafting
Squalene
Elastomer

ABSTRACT

Sodium magadiite (Na-MGD), a layered silicate, was synthesized, cation-exchanged with cetyltrimethylammonium (CTA$^+$), and functionalized with two sulfur-containing organosilanes, bis-(triethoxysilylpropyl) polysulfide (Si69) or 3-mercaptopropyltriethoxysilane (MPTES). ^{29}Si NMR and XRD showed that the silanes grafted uniformly on the MGD interlayer surfaces. TGA and elemental analysis (EA) results quantified the silane and CTA$^+$ content of the products and, with FTIR results, showed that silane grafting displaced CTA$^+$ from the MGD interlayer space. Moderate to high levels of Si69 or MPTES grafting led to nearly complete CTA$^+$ displacement and decreased interlayer spacing. This rendered the MGD interlayer inaccessible to squalene, a model compound for natural rubber prepolymer. A lower level of Si69 grafting displaced less CTA$^+$, resulting in a slight decrease in MGD interlayer spacing. For this product, XRD shows significant intercalation of squalene into the MGD interlayer space, possibly associated with sulfur-mediated crosslinking with the MGD-grafted silane. This work demonstrates the potential utility of sulfur-functionalized MGD as an active filler for elastomer composite formulations, as well as the use of squalene as a probe of interlayer accessibility of sulfur-functionalized layered clay minerals.

1. Introduction

Magadiite (MGD, $Na_2Si_{14}O_{29}{\cdot}9H_2O$) is a layered silicate hydrate [1] found in nature [2] or readily synthesized under hydrothermal conditions [1,3–7]. The crystallinity of MGD and its unit cell dimensions are known via XRD [1,8,9], although the detailed crystalline

* Corresponding author.
E-mail address: ploehn@mailbox.sc.edu (H.J. Ploehn).

http://dx.doi.org/10.1016/j.colsurfa.2016.06.043
0927-7757/

structure has not been conclusively established. Nonetheless, XRD shows that sodium MGD (Na-MGD) has a layered structure with a basal spacing value (d_{001}) of 1.56 nm. Acid treatment of Na-MGD [1,10] produces the protonic form (H-MGD) with 1.32 nm basal spacing. Both Na-MGD and H-MGD readily undergo cation exchange with a variety of organic cations, expanding the MGD interlamellar space and facilitating access to silanol groups on the interlamellar surfaces [1,4,10–16]. The reactivity of MGD silanol groups with organosilanes is well established [1,17–29], sharing this characteristic with precipitated silica used as an active filler in tire manufacturing. The possibility of using expanded, sulfur-functional MGD as an active filler in elastomer composites motivates this study of MGD functionalization with sulfur-containing silanes.

Interlamellar functionalization of MGD must be preceded by expansion of the interlayer space by bulky organic cations [19–29]. Lagaly et al. [4] carried out an early, comprehensive study of Na-MGD intercalation by a wide variety of alkylammonium and alkylpyridinium cations. In all cases, cation exchange increased MGD basal spacing from 1.56 nm to between 3 and 6 nm, depending on cation type, head group type, and alkyl chain length. Elemental analysis indicated complete exchange of straight chain *n*-alkylammonium cations for Na^+ (2.0 mol per mole of MGD unit cells), accompanied by additional intercalation of neutral *n*-alkylamine molecules. This implies that intercalated *n*-alkylammonium molecules (plus guest *n*-alkylamines) pack efficiently in the MGD interlayer space.

In contrast, quaternary *n*-alkyltrimethylammonium (C_nTMA^+) cations exhibited incomplete exchange with Na^+ but were equally effective in expanding MGD's interlayer space. For example, C_{16}TMA-MGD was reported [4] to have a basal spacing of 3.72 nm (2.92 nm air-dried), but only 0.59 mol of $C_{16}TMA^+$ intercalated per mole of MGD unit cells. This suggests that the interlayer packing of organic cations with bulkier head groups may leave considerable room for water clusters [4] or intercalation of other guest molecules. More recent studies [12,13,15] of Na-MGD intercalation by $C_{16}TMA^+$ report smaller d_{001} values (3.10–3.19 nm) and higher $C_{16}TMA^+$:MGD ratios (up to 1.66:1), but the qualitative implications are the same.

Almost all subsequent studies of organosilane interlamellar grafting in MGD employed Na-MGD pretreated with either $C_{12}TMA^+$ [19–24,26,28] or $C_{16}TMA^+$ [25,27]. In general, the silane:MGD ratio in solution controls the grafted silanes' surface areal density, with grafting accompanied by C_nTMA^+ de-intercalation [20–25]. Unlike Na-MGD, MGD functionalized with octyltrichlorosilane [21,24,25] can adsorb *n*-alcohols, resulting in considerable additional interlayer expansion (up to 4.87 nm for n-C_{16}OH); the amount of alcohol uptake varies with silane graft density and alcohol chain length.

Several studies [30–33] explored organic cation-exchanged MGD as a route to polymer nanocomposites, but only one (to our knowledge) investigated organo-silanized MGD for this purpose. Isoda et al. [23] used C_{12}TMA-MGD (d_{001} = 2.87 nm) as the intermediate for interlamellar grafting of γ-methacryloxypropyltrimethoxysilane (γ-MPS). Displacement of C_{12}TMA by grafted γ-MPS decreased the basal spacing to 2.15 nm for the γ-MPS-MGD product. γ-MPS-MGD was dispersed in a toluene solution of methyl methacrylate (MMA), followed by solution polymerization. The increased MGD basal spacing in the final product (2.66 nm) and ^{13}C CP/MAS NMR results demonstrate that at least some MMA entered the MGD interlayer space and reacted with C=C groups in the grafted γ-MPS.

The ability to functionalize MGD's interlamellar surfaces with sulfur-containing organosilanes might lead to a new class of active fillers for elastomer composites. Previously, Ide and Ogawa [28] reported interlamellar silylation of MGD using a sulfur-containing organosilane, 3-mercaptopropyltrimethoxysilane (3-MPTMS), via the C_{12}TMA-MGD intermediate. Upon grafting, d_{001} decreased from 2.8 to 2.1 nm, consistent with C_{12}TMA de-intercalation. This study did not investigate the accessibility of the 3-MPTMS-MGD interlayer space to guest molecules. However, Ide et al. [34,35] investigated interlayer grafting of 3-MPTMS using another layered silicate (octosilicate) and found good accessibility of grafted thiol groups for subsequent reactions.

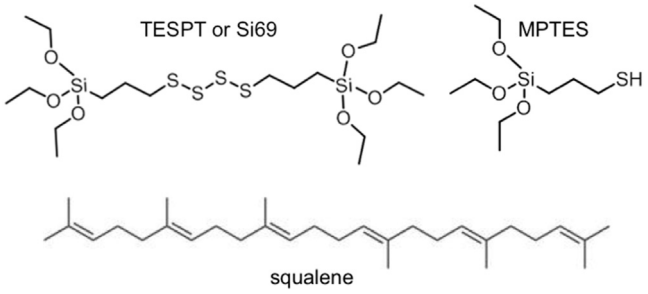


Fig. 1. Chemical structures of TESPT (also known as Si69), MPTES, and squalene.

This work reports the interlamellar silylation of C_{16}TMA-MGD using two sulfur-functional silanes (Fig. 1), bis-triethoxysilylpropyltetrasulfide, (TESPT, known in the rubber industry as Si69) and 3-mercaptopropyltriethoxysilane (MPTES). ^{29}Si NMR, FTIR and XRD measurements confirm grafting on MGD interlayer surfaces accompanied by de-intercalation of C_{16}TMA. Elemental analysis and TGA quantify the silane grafted amounts and areal grafting densities.

Finally, this work employs squalene (SQ, Fig. 1), a model compound for natural rubber [36–45], to probe the accessibility and reactivity of silane-tethered sulfur atoms in the MGD interlayer space. Sulfur-functional MGD was dispersed in pure liquid SQ and "cured" using additives and conditions that mimic rubber vulcanization. Quantifying the change in MGD basal spacing and SQ grafted amount may be useful for predicting the ability of monomers or pre-polymers (used to prepare elastomers) to access the interlayer spaces in sulfur-functional MGD.

2. Materials and methods

2.1. Synthesis of Na-magadiite and CTA-magadiite

The preparation of Na-MGD in this study followed published recipes [5,14,46]. Beginning with a 300 mL solution of 1.11 M NaOH (0.333 mol, Fisher), 165 mL of colloidal silica (1 mol, Alfa Aesar) was added slowly with mechanical stirring. The silica/NaOH slurry was put into a Teflon-lined Parr reactor (700 mL capacity), heated to 150 °C, and stirred for 50 h. After cooling, the suspension was diluted with water and centrifuged at 3700 rpm for 30 min. This product was washed and centrifuged twice to remove the excess NaOH, filtered, and dried. The cleaned Na-MGD was ball-milled (10 wt% slurry in water, overnight) to break up agglomerates and decrease the MGD particle size. The product was removed from water by centrifugation and then dried overnight at 60 °C.

Na-MGD was cation-exchanged with cetyltrimethylammonium (denoted below as CTA^+, purchased as the bromide CTAB from Sigma Aldrich and used as received) to prepare CTA-MGD. CTAB (8.46 g) was added to 500 mL of deionized water and heated to 50–60 °C with stirring to ensure CTAB dissolution. Na-MGD (20.0 g) was added to the CTAB solution and stirred for 5 days; these amounts yield a 1.16 mmol/g CTA:MGD ratio. The suspension was filtered using a small Buchner funnel, rinsed with deionized water to remove excess CTA^+, and then dried at 100 °C overnight prior to use.