

Inorganic-organic hybrids derived through grafting silane onto vermiculite leaching

F. A. R. Pereira^{(1)*}, A. P. M. Alves⁽¹⁾, M. G. da Fonseca⁽¹⁾, and M. A. Silva⁽²⁾

(1) DQ/PPGQ/UFPB, Universidade Federal da Paraíba, João Pessoa-PB, Brasil, e-mail: francisco_quimico@hotmail.com * Corresponding author.

(2) DQ/CCT/UEPB - Universidade Estadual da Paraíba, Campina Grande-PB, Brasil

Abstract-Four samples resulted from vermiculite leaching reacted with 3-aminopropyltrimethoxysilane to yield the solids named Vm-N. The precursor and modified matrixes were characterized by X-ray diffraction (XRD), CHN elemental analysis, FTIR and ²⁹Si and ²⁷Al NMR, specific surface area, and chemical analysis. The present study demonstrates that the intercalation of silane firstly happens during grafting reaction and the arrangement of the intercalated silane strongly depends on the properties of layered silicates.

Selective leaching of clay minerals with acid is a simple technique for porous silica preparation. The potential application of this material is very extensive, including immobilization of catalysts on its surface, metal retention/concentration, silylation/silanization onto surface, leading to organophilic properties, and chromatographic applications, among others [1]. This investigation deals with the grafting of active clay materials with a 3-aminopropyltriethoxysilane agent. The aim of this study is to elucidate the effect of silylation reaction inside interlayer microstructure of the grafting products of the clay materials, which is a proposed strategic step for application of final solids.

Nitric acid solutions at concentrations of 1.0, 2.0, 3.0 and 4.0 mol dm⁻³ were used as leaching agent. In a typical procedure, a sample of raw vermiculite (50 g) was suspended in 500.0 cm³ of acid solution for 4 h at 363 K. After, 100.0 cm³ of cold distilled water was added and the sample allowed cooling for 30 min. The suspension was filtered and dried at 383 K overnight. The samples were named Vm, where m = 1, 2, 3 and 4, corresponding to concentration of the aqueous acid solution. In silylation, samples of 3.0 g were previously heated at 373 K under vacuum for 24 h. The activated clay was suspended in 150 cm³ of dry toluene in a three-necked flask, in which 5.0 cm³ of silylating agent, 3-aminopropyltrimethoxysilane (γ -APS) was added, under dry nitrogen flux and the reaction was carried out under solvent reflux for 72 h. The obtained solid was separated by filtration and washed firstly with toluene, followed by ethanol and water. Possible remaining silane was removed by a 24 h Soxhlet ethanol extraction, to yield the solid named Vm-N.

The chemical analysis of the main components and specific surface area (S_{BET}) of the as-received and leached solids are listed in Table 1. The leached samples presented important alterations when compared to the precursor vermiculite, especially those derived from acid treatment at higher concentration. Table 1 - Chemical composition and specific surface area (S_{BET}) change of the raw and leached samples

Sample	S_{BET} (m ² g ⁻¹)	SiO ₂ (%)	MgO(%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)
V	16	44.62	9.18	5.46	20.64
V1	133	47.60	7.54	5.29	13.82
V2	339	55.80	5.01	4.04	6.94
V3	673	58.80	0.88	1.37	0.95
V4	575	61.30	0.62	0.79	0.92

The four new products synthesized from grafting silane onto leaching vermiculite were subjected to elemental analysis to evaluate the amount of carbon, hydrogen and nitrogen. The obtained percentage of each element is given as 2.29 ± 0.02, 3.19 ± 0.07, 4.96 ± 0.18, 7.95 ± 0.03 for carbon, and, 0.89 ± 0.02, 1.17 ± 0.05, 1.67 ± 0.13, 2.99 ± 0.05 for nitrogen for V-N, V1-N, V2-N and V3-N, respectively. Different degrees of lixiviated clays reflect in the XRD diffraction patterns, that could be summarized in two main points: i) the heterogeneity of the solids as shown XRD suggests that probably part of the original vermiculite remains inactivated, and ii) in the course of immobilization as the amount of the nitrogenated molecules are incorporated in the inorganic network, increased the way of possibility of these molecules to accommodate in the inorganic structure, due to the interaction of the basic groups with silanol groups of the lamella.

The present investigation demonstrates that the grafting reaction between the trifunctional silylating agent and the layered silicates is clearly influenced by acidic sample treatment. Consequently, it may lead to the different surface properties of the resultant products. It was also evidenced that the interlayer structure of the grafted products and the molecular environment of the grafted silane are strongly dependent on previously clay chemical laboratory operations. This obtained knowledge of handling such kind of inorganic material is of high importance for success in the synthetic procedure of polymer/layered silicate nanocomposites, in order to improve properties and to become useful extractable natural products.