

## SYNTHESIS AND CHARACTERIZATION OF HYBRIDS DERIVED FROM VERMICULITE CHLOROPROPYL AND ALIPHATIC DIAMINES

Ana Paula M. Alves, André Leonardo P. Silva, Oberto G. da Silva, Maria G. da Fonseca\*, Luiza N. H. Arakaki and J. G. P. Espínola

Departamento de Química, CCEN, Universidade Federal da Paraíba (UFPB), 58059-900 João Pessoa, Paraíba, Brazil

Silylation of vermiculite surface with organosilane  $(\text{H}_3\text{CO})_3\text{SiR}$ , being  $R$  is the corresponding organic moieties  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ , were carried out to yield organofunctionalized nanomaterial, named as VCl. The product reacted subsequently with three aliphatic diamines  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  ( $n=2, 4$  and  $6$ ). The new hybrids were characterized by elemental analysis, infrared spectroscopy, X-ray diffraction and thermogravimetry. The grafting chloro derivatives onto surface amounted to  $2.1 \text{ mmol g}^{-1}$ . The incorporation of alkyl amines was more effective for butyl>ethylene>hexyldiamines. The sequence is in agreement with thermogravimetry and elemental analysis data.

**Keywords:** clay, inorganic–organic hybrids, vermiculite

### Introduction

The most useful method of hybrid material preparations consisted in grafting a desired agent on the surface or by employing the sol–gel process under experimental control procedure by using catalyst or template molecules [1]. The grafting methodology takes into account a post-synthesis of a precursor support by attaching normally a molecule containing the functional moieties to the solid surface whose modification by incorporating organic groups is most commonly carried out by silylation. The majority of members of this class of hybrids available for immobilization with silylating agents, are inorganic polymeric natural or synthetic supports. There are large silanol group populations on their surfaces, which act as convenient points to anchor organic functionalization. In this context silica gel has been one of the most explored surfaces as shown by special investigations performed on analytical applications on preconcentration and retention of heavy cations from solutions [2–4], chemically bonded phases in chromatography [5] and adsorption of biological compounds [6]. However, other inorganic supports have been used as suitable supports for silylation by including metallic oxides, glasses, natural and phyllosilicates [7–14].

Framework layers of most natural clay minerals are generated by a combination of octahedral and tetrahedral sheets, normally classified in two hydrous phyllosilicates groups that have the inorganic structural arrangement in 1:1 or 2:1 layers. The first natural layered structure consists of single tetrahedral coordinated  $[\text{Si}_2\text{O}_5](\text{OH})_2$  layer, which is connected to an edge-shared octahedral  $\text{M}(\text{OH})_6$  sheet where  $M$  is nor-

mally  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$  [15]. The 2:1 layered material contains one octahedral sandwiched by two tetrahedral layers and in both cases the oxygen atoms are responsible for connecting the sheets. Isomorphous substitutions by cations of comparable radii are possible both in the tetrahedral and in the octahedral clay layers. These features illustrate the great versatility of the kind of compound, in particular this is explored in the present investigation: the synthesis and characterization of inorganic–organic hybrid resulting from reaction of chloropropyl trimethoxysilane of the general formula  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{R}$ , where  $R=\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  and its subsequent interactions with aliphatic diamines.

### Experimental

#### Materials

#### Chemicals

The silylating agent chloropropyl trimethoxysilane (Aldrich) was employed as received. All other reagents such as xylene (Merck) and ethanol (Merck) were used without previous purification. Ethylene, butyl and hexyldiamine (Aldrich) were used without treatment. The vermiculite sample was obtained from União Brasileira de Mineração, a Company from the municipality of Santa Rita (Paraíba, Brazil). Chemical analyses of the sample were performed by AAS using a PerkinElmer 5100 Model instrument with an air-acetylene flame. The samples were digested in a mixture of  $\text{HF}-\text{HCl}$ .

\* Author for correspondence: mgardennia@quimica.ufpb.br

### Silylation of vermiculite

Vermiculite (V) was initially activated by heating under vacuum for 48 h at 373 K. Immobilized silane was prepared by mixing. 5.0 g of activated inorganic matrix was stirred with 150 cm<sup>3</sup> of dry xylene under nitrogen atmosphere at 353 K. Then, 5.0 cm<sup>3</sup> of silane was added by using a syringe to this suspension and the reaction mixture was kept for two days under these conditions. Finally, the product was filtered, washed with ethanol and dried under vacuum at 323 K for a day. The new hybrid was named to VCI. The reproducibility of this reaction was checked by using an increased amount of silylant agent, to yield successfully the same products. The degree of functionalization on vermiculite was estimated by quantification of chlorite content by using Mohr method.

### Diamine incorporation

The solid VCI was submitted to reactions with three alkyl diamines. In a typical reaction 2.0 g of VCI was suspended in 100.0 cm<sup>3</sup> of xylene. Then, 5.0 cm<sup>3</sup> of each amine ethylene, butyl and hexyldiamine was added and reacted for 24 h. The products were separated by filtration. The new solids were designated as VCI-en, VCI-but and VCI-hex, respectively.

### Instrumentation

Elemental analyses were performed in triplicate using a PerkinElmer PE-2400 instrument.

X-ray diffraction (XRD) patterns were obtained on a Shimadzu XD3A model diffractometer equipped with monochromatic CuK<sub>α</sub> operating at 40 kV and 30 mA. The diffraction patterns were recorded from 1.4 to 70° at scan rate of 0.67° s<sup>-1</sup>.

Infrared spectra were recorded at room temperature by using a Bomem spectrometer MB series in the range of 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> and 30 scans for each run using KBr disks.

Thermogravimetric curves (TG) were recorded on a DuPont 1090 B model thermogravimetric apparatus coupled to a DuPont 951 thermobalance. The samples were heated up to 1273 K at a 0.17 K s<sup>-1</sup> heating rate in dry nitrogen atmosphere. The sample masses were between 3.0–15.0 mg.

## Results and discussion

The CHN contents increased with the increase of the size of the organic chain attached in the inorganic–organic hybrid formed as shown in Table 1. However, from the amount of nitrogen found in samples, the number of pendant moles of organic groups in the ma-

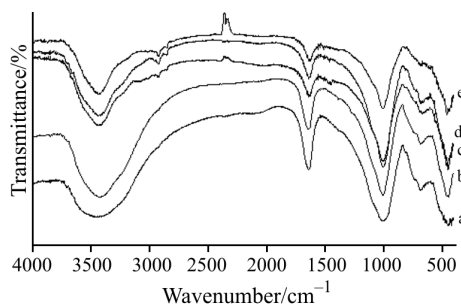
**Table 1** Carbon (C), hydrogen (H) and nitrogen (N) content, number of organic anchored groups (N<sub>f</sub>), and carbon/nitrogen molar ratio (in parenthesis the theoretical value) for the reaction of alkyldiamines in chloropropyl vermiculite

Hybrid	C/%	H/%	N/%	N <sub>f</sub> /mmol g <sup>-1</sup>	C:N
VCI-en	3.34	3.19	1.34	0.48	2.9 (2.5)
VCI-but	8.46	3.40	2.47	0.88	4.0 (3.5)
VCI-hex	7.68	2.98	1.72	0.61	5.2 (4.5)

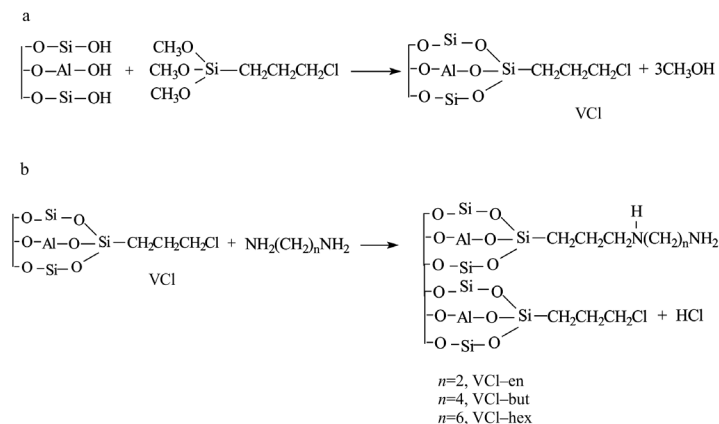
trices estimated were 0.46, 0.88 and 0.45 mmol g<sup>-1</sup> for VCI-en, VCI-but and VCI-hex, respectively.

In order to rationalize the obtained results, the amount of the organic chains anchored on silicate increases with the increase in size of the chain of the diamine employed, except for reaction with hexyldiamine. The values listed in Table 1 show some difference between the calculated and observed C:N relationships with high-calculated value in all cases. The observed disagreement can be interpreted as a partial substitution involving the chloropropyl groups on VCI by alkyldiamines causing an increase in carbon content. Thus, in the final product chloropropyl remains disposed on the surface. Based on CHN data a reaction scheme is suggested here. At first, the chloropropyl groups anchored on surface reacted subsequently with the diamines as illustrated in Scheme 1.

Infrared spectroscopy was useful tool to detect the success of immobilization process. This proposal can be clarified by comparing the precursor and the modified surfaces. Thus, the main characteristic feature in the spectrum of vermiculite (Fig. 1) is the complete absence of a very large band at 3500–3400 cm<sup>-1</sup> attributed to stretching of hydrogen-bonded silanol group modes and trapped water molecule presenting a well-known band at 3420 cm<sup>-1</sup>. The broad symmetric stretching modes assigned to Si–O–Si and Si–O–Al appeared at 1010 cm<sup>-1</sup>. Another band associated to Al–OH stretching is located at 814 cm<sup>-1</sup> [16, 17]. Absorption at 1640 cm<sup>-1</sup> was attributed to the characteristic bend deformation of the O–H group of water. For



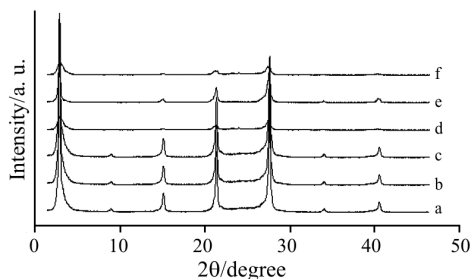
**Fig. 1** Infrared spectra of a – precursor vermiculite and their organofunctionalized forms: b – VCI, c – VCI-en, d – VCI-but and e – VCI-hex



**Scheme 1** Reaction scheme of immobilization of organic moieties on vermiculite a – silanization and b – subsequent immobilization of alkyl diamines

all modified hybrids the spectra can be characterized for the appearance of the new bands at 2950 and 2840  $\text{cm}^{-1}$  ascribed to asymmetric and symmetric stretching modes of  $\text{CH}_3$  groups [18], respectively. The band assigned to N–H group deformation can be overlapped by water angular deformation band at 1622  $\text{cm}^{-1}$ . A series of bands are also observed in the 3500–3000  $\text{cm}^{-1}$  range, but the presence of adsorbed water obscured them.

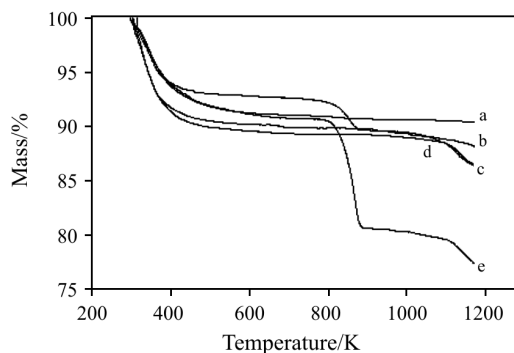
The diffraction patterns of precursor and the hybrid compounds are very similar as it is shown in Fig. 2, suggesting the maintenance of the original crystallinity of the inorganic matrix, when reactions take place. The same basal spacing values of 1422 pm were detected for all solids, reinforcing the hypothesis of immobilization of organic moieties on the external surface of vermiculite.



**Fig. 2** X-ray diffraction patterns of a – vermiculite, b – VCl, c – VCl-en, d – VCl-but and e – VCl-hex

Thermogravimetry data are summarized in Fig. 3. For precursor vermiculite the thermal decomposition occurred in a single stage with total mass loss of 9.68%, being attributed to the release of water present in the external surface and in the interlayer space. For modified vermiculites larger mass loss was detected depending on the length of organic moieties. Thus, for solids containing the largest groups, the highest mass loss values were observed. For chloro-

propyl vermiculite, this was 11.8% between 300 and 1200 K. For other hybrids, they were 13.6, 13.7 and 22.6%, respectively for materials derived from interactions of chloropropyl vermiculite with ethylene-, butyl- and hexyldiamine. These mass changes are associated to the water loss and the decomposition of the organic content.



**Fig. 3** Thermogravimetric data of a – precursor vermiculite, b – VCl, c – VCl-en, d – VCl-but and e – VCl-hex

## Conclusions

New organofunctionalized vermiculites were synthesized through silylating agent resulting in inorganic–organic hybrid with grafting of the external surface with chloro propyl chains. Suspended silanized vermiculite reacted with alkyl diamines. The results gave clear indication that the occurrence of subsequent reactions depends on the size of amine chain. The reactions are more effective for shorter chains.

## Acknowledgements

The authors are indebted to CNPq for financial support.

## References

- 1 N. M. Jose and L. A. S. A. Prado, *Quím. Nova*, 28 (2005) 281.
- 2 L. N. H. Arakaki, V. L. S. Augusta Filha, J. G. Espinola, S. F. Oliveira, T. Arakaki, M. G. Fonseca and C. Airoidi, *J. Environ. Monit.*, 5 (2002) 366.
- 3 A. Walcarius and C. Delacôte, *Anal. Chim. Acta*, 547 (2005) 3.
- 4 L. N. H. Arakaki, V. L. S. Augusta Filha, J. G. Espinola, S. F. Oliveira, T. Arakaki, M. G. Fonseca and C. Airoidi, *Thermochim. Acta*, 442 (2006) 176.
- 5 C. R. Silva, C. Airoidi, K. E. Collins and C. H. Collins, *J. Chromatogr. A*, 1114 (2006) 45.
- 6 D. Park, S. Haam, K. Jang, I.-S. Ahn and W.-S. Kim, *Proc. Biochem.*, 40 (2005) 53.
- 7 M. G. Fonseca and C. Airoidi, *J. Mater. Chem.*, 9 (1999) 1375.
- 8 M. G. Fonseca and C. Airoidi, *Mater. Res. Bull.*, 36 (2001) 277.
- 9 M. Erdemoğlu, S. Erdemoğlu, F. Sayılkan, M. Akarsu, Ş. Şener and H. Sayılkan, *Appl. Clay Sci.*, 27 (2004) 41.
- 10 K. W. Park, S. Y. Jeong and O. Y. Kwon, *Appl. Clay Sci.*, 27 (2004) 21.
- 11 P. A. Wheeler, J. Wang, J. Baker and L. J. Mathias, *Chem. Mater.*, 17 (2005) 3012.
- 12 H. He, J. Duchet, J. Galy and J. F. Gerard, *J. Colloid Interf. Sci.*, 288 (2005) 171.
- 13 S. Xue, M. Reinholdt and T. J. Pinnavaia, *Polymer*, 47 (2006) 3344.
- 14 A. M. Shanmugharaj, K. Y. Rhee and S. H. Ryu, *J. Colloid Interf. Sci.*, 298 (2006) 854.
- 15 M. M. Duane, C. Robert and Jr. Reynolds, *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, Oxford Press, London 1997.
- 16 V. C. Farmer and J. C. Russel, *Spectrochim. Acta*, 20 (1964) 1149.
- 17 P. J. Launer, *Am. Mineral.*, 51 (1967) 764.
- 18 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, John Wiley Sons, 2<sup>nd</sup> Ed., New York 1991.

---

DOI: 10.1007/s10973-006-7855-0