Applied Clay Science 101 (2014) 304–314

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Efficient immobilization of montmorillonite onto cotton textiles through their functionalization with organosilanes

A. Monteiro [a,b,1], B. Jarrais [b,*], I.M. Rocha [a], C. Pereira [a], M.F.R. Pereira [c], C. Freire [a,**]

[a] REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
[b] CeNTI, Centre for Nanotechnology and Smart Materials, Rua Fernando Mesquita 2785, 4760-034 Vila Nova de Famalicão, Portugal
[c] Laboratório de Catálise e Materiais — Laboratório Associado LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:
Received 21 April 2014
Received in revised form 8 August 2014
Accepted 12 August 2014
Available online 20 September 2014

Keywords:
K10 montmorillonite
Organosilylation
Cotton textiles
Dyeing-like process

ABSTRACT

The production of functional cotton textiles through their derivatization with montmorillonite (Mt) is reported. The K10 montmorillonite (K10) was functionalized with the organosilanes (3-bromopropyl)trimethoxysilane (BrPTMS), (pentafluorophenyl)trimethoxysilane (F_5PTMS) and (3-isocyanatopropyl)triethoxysilane (NCPTES) by a post-grafting methodology.

Subsequently, these materials were immobilized onto NaOH-activated cotton textile substrates through a dyeing-like process typically used in the industry. The silylated clay minerals were characterized by Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR), thermogravimetry (TGA), powder X-ray diffraction (XRD), scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM–EDX), which confirmed their successful functionalization. The Mt-functionalized cotton textiles were characterized by X-ray photoelectron spectroscopy (XPS), SEM–EDX and TGA before and after washing tests.

The previous activation of the cotton textile with NaOH promoted a more efficient immobilization of the clay minerals, whereas the addition of a common surfactant used in the dyeing industry did not exhibit any influence on the dispersion of the Mt materials in the textile substrates. The functional textiles submitted to ten washing cycles did not present significant Mt leaching, confirming the efficient immobilization of the mineral particles onto the textile substrates. The best results in terms of immobilization efficiency were obtained for the textile substrate functionalized with the BrPTMS-modified K10.

1. Introduction

Cotton is one of the most important natural textiles, being widely used in the clothing industry because of its excellent properties such as softness, compatibility with human skin, hygroscopic properties and environmental friendliness. However, cotton fabrics still present inherent disadvantages, such as wrinkling, photo-degradation and yellowing (Zohdy et al., 2009; Ugur et al., 2011). Moreover, cotton is more prone to house bacteria than synthetic fibers due to its large surface area and its highly hygroscopic nature, thereby providing a perfect environment for bacterial growth (Lim and Hudson, 2004; Bang et al., 2007; Yuan and Robin, 2008; Zhang et al., 2009).

Currently, global trends in the textile industry are oriented towards developing and manufacturing functional textile products with high added-value. The coating of textile substrates with nano- and microparticles constitutes a potential pathway to the production of highly active surfaces for protection against UV radiation (Daoud et al., 2005; Zhang et al., 2011), antimicrobial properties (Klemenčič et al., 2013), flame retardancy (Alongi et al., 2011), water repellency and self-cleaning (Daoud et al., 2005; Pagliaro and Ciriminna, 2005), while preserving the fabrics' appearance and comfort. Metal and metal oxide nanoparticles such as ZnO, titania and silver, carbon nanotubes and clay minerals are among the micro- and nanosized materials that have been investigated as additives to impart the aforementioned properties to fabrics (Nazari et al., 2009; Montazer and Morshedi, 2012). Moreover, it is important to establish incorporation methods that can be readily implemented by textile manufacturers, thus saving costs and manpower in an already competitive industry. The incorporation of multi-walled carbon nanotubes onto cotton and polyester substrates by a novel dyeing-like process has already been tested by our group (Gonçalves et al., 2012) for the fabrication of flame retardant and hydrophobic fabrics, using an adapted procedure from that traditionally used in textile dyeing industry. Bearing this concept in mind, in this work we describe the

* Correspondence to: B. Jarrais, REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.
** Corresponding author.
E-mail addresses: bruno.jarrais@fc.up.pt (B. Jarrais), acfreire@fc.up.pt (C. Freire).
[1] Current address: CeNTI, Centre for Nanotechnology and Smart Materials, Rua Fernando Mesquita 2785, 4760-034 Vila Nova de Famalicão, Portugal.

http://dx.doi.org/10.1016/j.clay.2014.08.019
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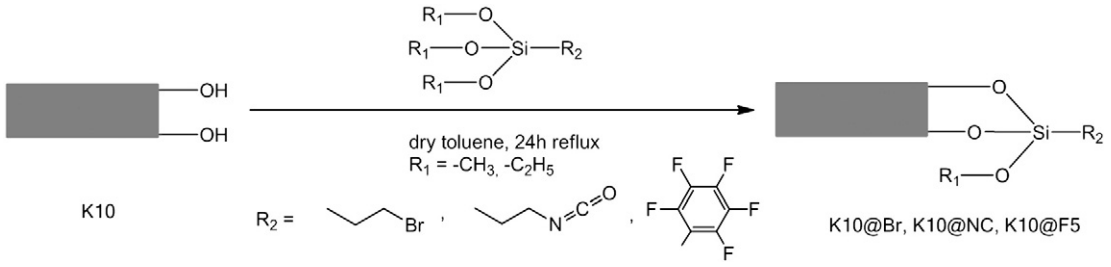

Fig. 1. Schematic illustration of K10 montmorillonite organosilylation by post-grafting methodology.

robust incorporation of organosilylated Mts onto cotton substrates by a dyeing-like process that can yield functional fabrics with potential properties such as controlled release and fire retardancy.

K10 montmorillonite (K10) belongs to the family of smectite and presents a structure based on stacked layers made of two edge-sharing tetrahedral SiO_4 sheets fixed to an edge-shared octahedral sheet of alumina. The layer thickness is approximately 1 nm and the lateral dimensions may vary from 300 Å to several microns. The 2:1 adjacent layers are kept by electrostatic interactions through mono- and divalent exchangeable cations, which exist in the interlayer space. The composition of K10 varies greatly, with aluminum cations of the octahedral sheet being partially replaced by divalent cations. This is compensated by the presence of a high quantity of hydroxyl ions and different types of cations within the interlayer region, promoting a high cation-exchange capacity, which is reflected in an easier accommodation of organophilic cations and allows the intercalation of organosilanes (Porter et al., 2000; Wypych and Satyanarayanc, 2000; Ray and Okamoto, 2003; Silva et al., 2011; Huskić et al., 2013).

In this work, K10 was functionalized with three types of organosilanes – (pentafluorophenyl)trimethoxysilane (F_5PTMS), (3-bromopropyl)trimethoxysilane (BrPTMS) and (3-isocyanatopropyl) triethoxysilane (NCPTES) – by a post-grafting methodology. Subsequently, the exhaustion dyeing-like process, previously developed by us, was used in the immobilization of the resulting silylated Mts onto cotton textiles. The aim of this work was to fabricate robust functional fabrics with enhanced washing fastness and study the influence of the type of organosilane on the degree of Mt incorporation on the fabrics, binding stability and resistance to washing.

2. Experimental section

2.1. Materials, reagents and solvents

The commercial K10 supplied from Sigma-Aldrich was used as the starting material: according to the supplier, K10 has a surface area of 220–270 $m^2\ g^{-1}$. The following reagents were used in the K10 silylation reactions: dry toluene, purchased from Sigma-Aldrich, F_5PTMS (95.0%) purchased from ABCR, and BrPTMS (≥97.0%) and NCPTES (95%) obtained from Fluka. The cotton fabric was supplied by Arcotêxteis S.A. (Portugal): 100% cotton prepared for dyeing (warp: 3726 threads, weft: 52 threads), previously desized and bleached. To incorporate the Mts in the textile substrates the following reagents, all of analytical grade, were used: absolute ethanol and sodium hydroxide obtained from Merck, sodium chloride purchased from Panreac and Levegal RL purchased from Lanxess. The detergent used in the washing tests was SDC ECE Phosphate reference, purchased from SDC Enterprises Ltd.

2.2. Functionalization of K10 with organosilanes

The functionalization of K10 was performed by silylation, according to a methodology described elsewhere (García et al., 2010). Typically, the parent clay mineral was dried in an oven at 120 °C for 1 h, under vacuum. Afterwards, 0.500 g of K10 was dispersed in dry toluene (50 cm^3) and 2.5 mmol of organosilane (F_5PTMS, BrPTMS, NCPTES) was added. The final dispersion was refluxed for 24 h under argon atmosphere. The resulting material was filtered under reduced pressure, washed by reflux with dry toluene (2 × 50 cm^3) for 1 h and then dried in an oven at 120 °C under vacuum, for 3 h, Fig. 1. The resulting clays functionalized with F_5PTMS, BrPTMS and NCPTES will be referred to as K10@F5, K10@Br and K10@NC, respectively.

2.3. Incorporation of K10-based materials in cotton textiles

Prior to the chemical modification, 10 cm × 20 cm cotton fabric samples were sequentially washed with 100 cm^3 of toluene, 100 cm^3 of deionized water and 100 cm^3 of ethanol, by stirring at room temperature for 15 min with each solvent. Afterwards, the fabric samples were activated by immersing the fabrics in 30 cm^3 of a 5 M NaOH aqueous solution and stirring at 100 °C for 5 h. The cotton fabrics were then immersed in 30 cm^3 of deionized water in a round flask and refluxed for 1 h. Afterwards they were filtered while still hot in order to remove excess NaOH, and finally dried under vacuum at 120 °C for 15 h. Immediately before the dyeing-like experiments, the K10, K10@F5, K10@Br and K10@NC materials were dispersed in water for 1 h in an ultrasonic bath. Subsequently, the Mts were incorporated into cotton fabrics by the conventional exhaustion dyeing procedure, shown schematically in Fig. S1 in Supporting information, but replacing the dyes by Mt dispersions. Sodium carbonate and sodium hydroxide used in the traditional

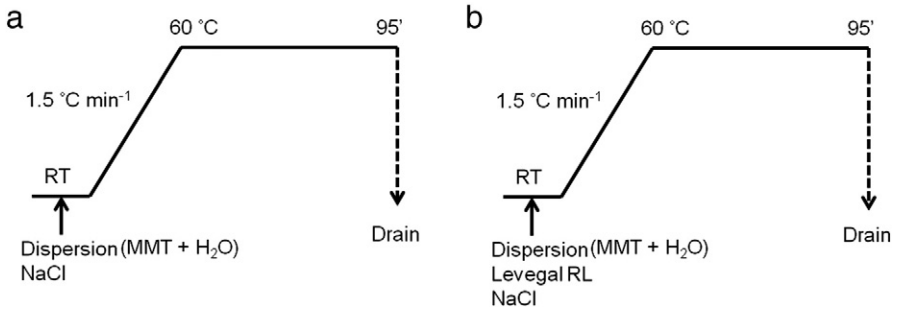

Fig. 2. Procedures used in the incorporation of the K10-based materials on the cotton textile substrate, according to (a) Method I and (b) Method II.