



A new approach to sepiolite dispersion by treatment with ionic liquids



Juliana A. de Lima^a, Fernanda F. Camilo^b, Roselena Faez^c, Sandra A. Cruz^{a,*}

^a Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC, Avenida dos Estados, 5001, 09210-580 Santo André, SP, Brazil

^b Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo, Rua São Nicolau, 210, 09913-030 Diadema, SP, Brazil

^c Departamento de Ciências da Natureza, Matemática e Educação, Universidade Federal de São Carlos, Rodovia Anhanguera Km 174, 13600-970 Araras, SP, Brazil.

ARTICLE INFO

Keywords:

Sepiolite
Ionic liquid
Morphology
Thermal behavior
Dispersion
Imidazolium

ABSTRACT

The possibility of sepiolite disaggregation is a challenge to enhance significantly its performance and extend its application. In this direction, this work introduces the treatment of sepiolite (Sep) with three different ionic liquid (IL). The used ionic liquids were 1-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl) imide (BMImTf₂N), 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl) imide (OMImTf₂N) and 1-methyl-3-dodecylimidazolium bis(trifluoromethanesulfonyl) imide (DMImTf₂N). The influence on structural, thermal properties and morphology in Sep treated with IL were evaluated using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TG), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), N₂ sorption measurements, ²⁹Si nuclear magnetic resonance (²⁹Si NMR) and zeta potential. Sepiolite structure was preserved for all the samples treated with ionic liquids. FTIR and XRD results show that BMImTf₂N substitutes water molecules coordinated to Mg⁺² more efficiently. Thermogravimetric analysis indicated that the interaction between Sep and IL delayed the release of water. From these data, it was also possible to confirm the presence of 5 mass% of IL in all samples. FESEM and TEM images demonstrated more disaggregated Sep fibers with IL, especially the samples treated with BMImTf₂N. This fact is attributed to the immobilization of ionic liquid on Sep tunnels, which is coherent with ²⁹Si NMR analyses. The potential applications of these modified sepiolites are as reinforcing agent for polymers, template for nanostructured materials and support for catalysts.

1. Introduction

Sepiolite (Sep) is a hydrated magnesium silicate with a unit cell formula of Mg₈Si₁₂O₃₀(OH)₄(H₂O)₄·8H₂O (An et al., 2008). Its structure is constituted by a magnesium octahedral sheet between two layers of silica tetrahedrons, which extend as a continuous layer with an inversion of the apical ends every six units. This inversion produces a discontinuous octahedral sheet, allowing the formation of a rectangular section, tunnel-like, running parallel to the fiber axis (Tartaglione et al., 2008; Weir et al., 2002).

Sepiolite has attracted widespread attention due to its high specific surface area and microporous channels (0.30–1.06 nm) running parallel to the length. Because of these features, Sep has been used as adsorbent, drug and catalyst carriers, rheological modifier and inorganic fiber (Kuang et al., 2003; Tartaglione et al., 2008; Xu et al., 2013; Zheng et al., 2011). Therefore, thermally activated sepiolite was prepared and used as an adsorbent for efficient decoloration of crude palm oil. The results indicate that the thermal activation of sepiolite affects its structure and decoloration efficiency. Moreover, the thermal activation

improved the porous structure and surface activity of sepiolite by releasing different kinds of waters and creating new adsorptive sites (Tian et al., 2014).

Nanosized filler, as Sep, incorporated into a biodegradable polymer results in nano-biocomposite materials (Avérous and Pollet, 2012) with improved mechanical, thermal and barrier properties due the high interface area to develop strong nanofiller-polymer interactions, when a good dispersion is achieved (Olivato et al., 2017; Xie et al., 2013; Avérous and Pollet, 2012; Ray and Okamoto, 2003). However, Sep individual particles have a needle-like morphology usually lying in a highly aggregated state formed by bundles. Due to this characteristic, Sep is a non-swelling clay mineral and consequently does not allow the penetration of large molecules, in which the molecular size is the major limiting factor (García-Lopez et al., 2010; Liang et al., 2011; Weir et al., 2002; Yin et al., 2010). Therefore, Sep disaggregation can significantly enhance its performance and extend its application.

In light of this, the search for more convenient, eco-friendly and efficient methods to separate the Sep agglomerated bundles is an object of interest. Ionic liquids (IL), which are compounds with excellent

* Corresponding author at: Departamento de Química, Universidade Federal de São Carlos, Brazil.
E-mail address: sandra.cruz@ufscar.br (S.A. Cruz).

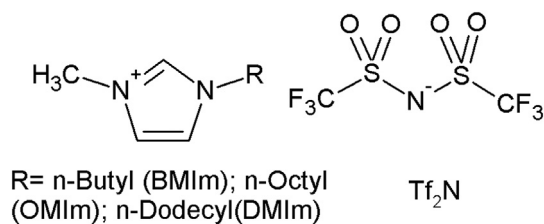


Fig. 1. Ionic liquids used in this work.

chemical and thermal stabilities, inflammable and nonvolatile, have emerged as interesting modifiers for clay minerals (Fredlake et al., 2004). To our knowledge, there is only one paper that shows the treatment of Sep with an ionic liquid named 1,1,3,3-tetramethylguanidine trifluoroacetic acid (Tao et al., 2009). According to the authors, this IL does not cause any expansion or collapse of the sepiolite framework.

In this context, this work reports the treatment of sepiolite, using sonication, with three types of ionic liquid: (a) 1-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl) imide (BMImTf₂N), (b) 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl) imide (OMImTf₂N) and (c) 1-methyl-3-dodecylimidazolium bis(trifluoromethanesulfonyl) imide (DMImTf₂N), Fig. 1, as an attempt to disaggregate its fibers in order to increase its applications. The motivation for using ionic liquids containing Tf₂N regards their good thermal and chemical stabilities and inferior viscosities when compared to non Tf₂N-based IL. Additionally, their cations have different alkyl side chains, which can influence the process.

2. Material and methods

2.1. Materials

Sepiolite was purchased from Tolsa S/A and used as received without any purification. The chemical composition (mass%) of sepiolite, detected by X-ray fluorescence (XRF), is SiO₂ 54.10, MgO 21.00, CaO 0.28, Al₂O₃ 1.56, Fe₂O₃ 0.70 and content mass loss-on ignition 21.60.

The ionic liquids 1-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (BMImTf₂N), 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide (OMImTf₂N) and 1-methyl-3-dodecylimidazolium bis(trifluoromethanesulfonyl) imide (DMImTf₂N) were prepared following procedure described in the literature (Bazito et al., 2007).

2.2. Preparation of the Sep/IL samples

Sepiolite (300 mg) was mixed with the ionic liquid (Sep/IL; 95/5 mass%) by sonication process for 1 h at room temperature. These samples were designated as: Sep/BMImTf₂N, Sep/OMImTf₂N and Sep/DMImTf₂N, according to the ionic liquid used.

2.3. Characterization

The infrared (IR) spectra in the range of 4000 to 400 cm⁻¹ using KBr pellets were recorded on a Perkin Elmer FTIR-Frontier model. X-ray diffraction (XRD) patterns of powdered samples were made on an Analytical Philips X'Pert diffractometer equipped with a back monochromator operating at 40 kV and using a Cu-Kα radiation with 1541 Å. The thermogravimetric analysis (TG) were made on a Q500 TA Instrument, in the temperature range of 30 °C to 700 °C, at constant heating rate of 20 °C min⁻¹ under argon atmosphere. Solid-state ²⁹Si cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR), at 5.0 kHz, was performed on a Bruker Avance III-400 instrument. The experimental conditions for the experiment were:

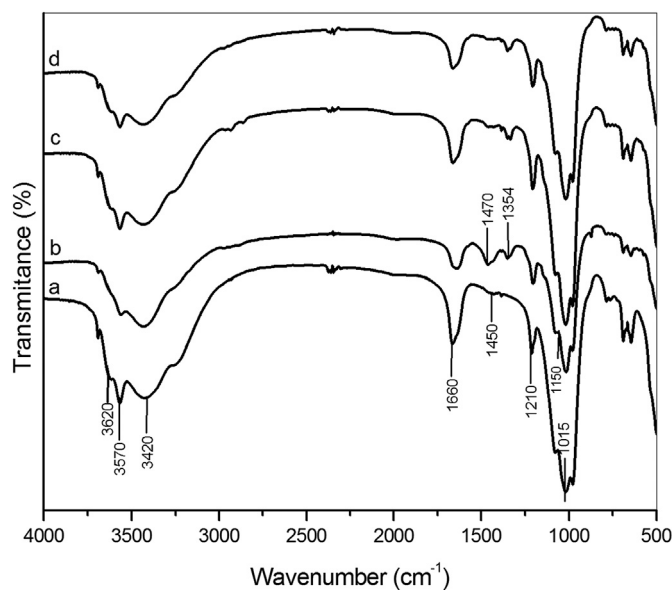


Fig. 2. IR spectra of: (a) sepiolite, (b) Sep/BMImTf₂N, (c) Sep/OMImTf₂N and (d) Sep/DMImTf₂N.

repetition delay of 2 s, acquisition time of 34 ms and scan number of 2048. Morphological studies were carried out using field emission scanning electron microscope (FESEM JMS-6701F JEOL) at an acceleration rate of 20 kV and c Philips CM-120) operating at an acceleration voltage of 100 kV. The nitrogen adsorption/desorption isotherms were obtained at liquid nitrogen temperature (77 K) by using a Quantachrome Nova 2200 automatic system. Before measurements, the samples were degassed for 2 h at 110 °C under 2 mmHg vacuum. Specific surface areas were determined using multi-point BET analyses and the pore sizes were measured by the BJH method of adsorption. The Zeta potential of sepiolite dispersions was measured using a Zetasizer NanoZS (Malvern®). A sepiolite sample of 0.02 g in 50 mL distilled water containing the desired ionic liquid was added to an orbital shaker incubator and rinsed for 10 min at 25 ± 1 °C. The samples were allowed to stand for 1 min to let larger particles settle. An aliquot taken from the supernatant was used to measure the zeta potential. All measurements were made in triplicate.

3. Results and discussion

Fig. 2 represents the FTIR spectra of neat Sep and Sep/IL samples.

Sepiolite contains four different types of water molecules: (1) adsorbed water, (2) zeolitic water inserted into the channels, (3) water molecules coordinated to the octahedral cations and (4) structural water (Dogan et al., 2008).

All FTIR spectra show a broad band in the 4000–3000 cm⁻¹ range, which is attributed to different O–H stretching vibrations, Fig. 2 (Ahlich et al., 1975; Liang et al., 2011). The bands at 3620 cm⁻¹ and 3570 cm⁻¹ are attributed to the stretching vibration of O–H associated with Mg⁺² cations in octahedral coordination (Gionis et al., 2006; Xu et al., 2013). The broad band centered at 3420 cm⁻¹ is attributed to the hydrogen bonded O–H stretching, mainly from the zeolitic water molecules (Dogan et al., 2008). The band at 1660 is due to the hydroxyl bending vibrations of zeolitic water molecules (Dogan et al., 2008; Rives, 2001). Antisymmetric and symmetric stretching modes showed at 1450 cm⁻¹ is attributed to the (CO₃)⁻², which confirms the presence of carbonate impurity (Franco et al., 2014; Suárez et al., 2016). The bands at 1210 cm⁻¹ and 1015 cm⁻¹ correspond to the Si–O in the Si–O–Si groups of the tetrahedral sheets (Dogan et al., 2008; Xu et al., 2013).

Analyzing comparatively the spectra of the Sep/IL samples

Download English Version:

<https://daneshyari.com/en/article/5468918>

Download Persian Version:

<https://daneshyari.com/article/5468918>

[Daneshyari.com](https://daneshyari.com)