



Research paper

Synthetic talc as a new platform for producing fluorescent clay polyurethane nanocomposites

Guilherme Dias^a, Manoela Prado^a, Rosane Ligabue^{a,b}, Mathilde Poirier^c, Christophe Le Roux^c, François Martin^c, Suzanne Fery-Forgues^{d,*}, Sandra Einloft^{a,b,**}

^a Programa de Pós-Graduação em Engenharia e Tecnologia de Materiais (PGETEMA), Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS), Porto Alegre, Brazil

^b Faculdade de Química (FAQUI), Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS), Porto Alegre, Brazil

^c ERT 1074 Géomatériaux, GET UMR 5563 CNRS, Université de Toulouse, Toulouse, France

^d SPCMIB, CNRS UMR5068, Université Toulouse III Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 9, France

ARTICLE INFO

Keywords:

Clay polymer nanocomposite (CPN)

Synthetic talc

Fluorescence properties

Mechanical properties

ABSTRACT

As a non-swelling clay, talc generally interacts very weakly with organic molecules. However, two new nanometric synthetic talcs that incorporate berberine chloride were successfully used as fluorescent fillers in clay polyurethane nanocomposites obtained by the blending method. A micrometric natural talc filler was also used for comparison. The clay polymer nanocomposites (CPN) were characterized by FTIR, molar mass analysis and XRD. All talc fillers were well dispersed into the polyurethane matrix even at high filler content of 5 wt%, as supported by TEM and SEM analyses. Morphological changes were confirmed by AFM. The optical properties of the fluorescent talcs, dye-doped polymer and CPN were compared. While the dye-doped polymer suffered from conventional fluorescence quenching due to dye aggregation, the emission quantum yield of the CPN was increased with increasing the filler content. The best emission efficiency was observed for the CPN that contains the smallest talc-berberine hybrid particles. The use of fluorescent synthetic talc resulted in materials with good thermal and mechanical properties, and can be considered as a new method to produce fluorescent CPN in view of multiple applications.

1. Introduction

Over the past fifteen years, the development of inorganic-filler polymer nanocomposites has stimulated extensive research in both industry and academia (Hussain et al., 2006; Paul and Robeson, 2008). The nature of nanofillers, their immobilization and the structuration of the polymer matrix around them lead to strong changes in the physical and chemical properties, and govern all possible applications. In this context, clay polymer nanocomposites (CPN) are of special practical and commercial significance, since their strength, fire retardation and chemical stability are markedly enhanced with respect to conventional polymers and polymer composites (Da Silva et al., 2013; Galimberti et al., 2013; Gürses, 2015; Shunmugasamy et al., 2015; Taheri and Sadeghi, 2015). They may also display additional specific properties, in particular fluorescence, after introduction of appropriate organic compounds (Aloisi et al., 2010; Esposito et al., 2010; Diaz et al., 2013; Hao et al., 2014; Zhong et al., 2017). A smart way to ensure good

dispersion of the photoactive agent into the CPN is to modify the clay filler by organic molecules before introduction into the polymer. To do so, two strategies can be considered. The most popular one requires synthesis efforts. It consists of covalently labeling the nanoclay with various dye molecules, as reported for montmorillonite linked to fluorescein, rhodamine and anthracene derivatives (Aloisi et al., 2010; Esposito et al., 2010; Diaz et al., 2013). Although it would be easier to implement, the non-covalent approach has seldom been used. For instance, the characteristic property of swelling clays, i.e. the replacement of interlayer inorganic cations by cationic organic molecules (Suzuki et al., 2011; Bujdák et al., 2011; Felbeck et al., 2013; Ley et al., 2015), has only recently been exploited to obtain a fluorescent CPN (Zhong et al., 2017). Besides, the non-covalent approach has not been extended to non-swelling clays, which do not contain inorganic charge-exchange cations, probably because they are known to interact very weakly with organic compounds.

The aim of the present work was to introduce fluorescence into CPN

* Corresponding author.

** Corresponding author at: Programa de Pós-Graduação em Engenharia e Tecnologia de Materiais (PGETEMA), Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS), Porto Alegre, Brazil.

E-mail address: Einloft@pucrs.br (S. Einloft).

<https://doi.org/10.1016/j.clay.2018.03.012>

Received 23 November 2017; Received in revised form 5 March 2018; Accepted 6 March 2018
0169-1317/ © 2018 Elsevier B.V. All rights reserved.

by using a non-swelling clay modified by a very simple and effective process. The clay is expected to confer both mechanical and spectroscopic properties to the polymer. Talc polyurethane nanocomposites were considered as the continuation of other works performed on this type of materials (Dias et al., 2015; Dos Santos et al., 2015; Prado et al., 2015). Polyurethanes (PU) are formed by hard and soft segment blocks that can be tailored by varying their chemical composition to enable a wide variety of applications such as coatings, foams, elastomers and biomaterials (Li et al., 2012; Amela-Cortes et al., 2015). The addition of talc particles decreases gas permeability, and improves corrosion resistance (Kantheti et al., 2015). However, in this system, the use of natural talc (NTlc) presents some disadvantages because talc particles cannot be ground homogeneously below one micron without losing their structure and becoming amorphous (Dumas et al., 2013, 2015; Youssi et al., 2013; Dos Santos et al., 2015). In contrast, synthetic talc (STlc), like the one developed in the team, has well-defined chemical composition, high purity, crystallinity, particle size and layer thickness control. Among numerous applications that have recently been reviewed (Claverie et al., 2018), STlc has been used successfully as nanofiller in CPN, in particular for the reinforcement of PU. The good compatibility of organic and inorganic phases has been attributed to hydrogen bonding interactions between the OH groups of the filler and the PU chain (Dumas et al., 2013, 2015; Dias et al., 2015; Dos Santos et al., 2015; Prado et al., 2015). Moreover, studies have shown that STlc has a remarkable capacity to adsorb colored and fluorescent organic molecules (Aymonier et al., 2017a,b). Berberine chloride (Fig. 1) was chosen as the fluorescent dye to be incorporated into the talc particles. This compound is emissive in organic phases (Díaz et al., 2009; Zhang et al., 2014), constrained media (Megyesi and Biczók, 2006; Gade and Sharma, 2014) and in the solid state (Soulié et al., 2016). Its fluorescence properties are closely dependent on the micro-environment and provide useful information in this regard. The incorporation into polymers has scarcely been investigated (Gade and Sharma, 2014). Besides, berberine is a natural alkaloid of wide therapeutic interest, and it can be used to mimic the behavior of drugs in systems designed for biomedical applications (Soulié et al., 2015; Duval and Duplais, 2017). Synthetic talc fillers were therefore synthesized, loaded with berberine, and introduced into PU matrices. A comparison was made with NTlc. Here, it is of significance to note that, for the sake of simplicity, all clay polymer composites have been called “nanocomposites” and abbreviated CPN, even if the inorganic filler is of micrometric size. At each stage, the compounds were characterized by various analytical methods. Special attention was brought to homogeneity because the simple dispersion of inorganic particles in a polymer matrix often leads to phase segregation, which is an obstacle in the preparation of CPN (Amela-Cortes et al., 2015). Present studies showed that modified STlc fillers can be used as original platforms to produce fluorescent CPN. This simple concept allows potential applications to be envisioned in various fields: materials for optics, light-emitting devices, and controlled released of drug molecules.

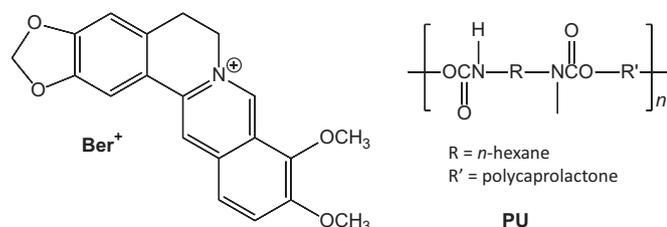


Fig. 1. Chemical formula of berberine chloride and the polyurethane used in this work.

2. Materials and methods

2.1. Preparation

The PU synthesis was performed by reacting poly(caprolactone) diol (PCL, MM = 2000 g/mol, Sigma–Aldrich) and 1,6-hexamethylene diisocyanate (HDI, Merck) in a molar ratio of NCO/OH of 1:1. Dibutyl tin dilaurate (DBTDL, Miracema-Nuodex Ind.) was used as catalyst (0.1% w/w) and methyl ethyl ketone (MEK, P.A., Merck) as solvent (about 50 mL). Commercial natural talc was obtained from IMERYS (Talc de Luzenac). STlc was prepared as described elsewhere (Le Roux et al., 2013). Fluorescent talcs were prepared by mixing an aqueous solution of berberine (9,10-dimethoxy-2,3-methylenedioxy-5,6-dihydrodibenzo [a,g] quinolizinium) chloride hydrate (Sigma Aldrich, 1 mg/mL) with dry STlc or NTlc in a ratio of 0.6 mg berberine/1 g of talc. A volume of 100 mL of water was added. The dispersions were then sonicated and placed in an oven at 100 °C for 12 h.

To prepare dye-doped PU, berberine chloride (1.2×10^{-4} g, 3.6×10^{-4} g and 6.0×10^{-4} g) dissolved in 100 mL of MEK was mixed with 20 g of PU. To prepare the CPN, 20 g of PU were solubilized in 100 mL of MEK, and then various talc filler contents were added (1 wt %, 3 wt% and 5 wt% in relation to pure PU). All dispersions were stirred for 30 min. After solvent evaporation at room temperature, the films were prepared using a hydraulic press (1 Pa; 50 °C), resulting in a thickness of approximately 0.10 mm.

2.2. Characterizations

Fourier transform infrared (FTIR) spectroscopy was performed with a Perkin Elmer FTIR spectrometer model Spectrum100. The nitrogen adsorption–desorption isotherms were measured at 77 K using a volumetric method, with a Quantachrome Autosorb-1 apparatus. They were recorded in the 0.05–0.30 relative pressure range, and high purity N₂ was used. Samples were outgassed for 15 h at 120 °C under vacuum before analysis. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938). The XRD patterns were recorded on a Shimadzu XRD-7000 diffractometer using CuK α Bragg-Brentano geometry θ - θ radiations, operating between 5 and 80° with a step size of 0.02°, at 40 kV and 30 mA. For transmission electron microscopy (TEM), the samples were cryomicrotomed and analyzed in a Tecnai G2 T20 FEI apparatus operating at 200 kV. Size exclusion chromatography (SEC) was performed using a liquid chromatograph equipped with an isocratic pump 1515 (eluent: tetrahydrofuran (THF), flow: 1 mL/min) and a refractive index detector 2414 from Waters Instruments with styragel column set at 45 °C. Differential scanning calorimetry (DSC) was carried out using a TA Instruments model Q20 equipment. Analyses were performed in two heating cycles, under N₂ in a temperature range from –90 °C to 200 °C with a heating/cooling rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was made using a DSC-TGA coupled (SDT) equipment (TA Instruments Model Q600). Tests were carried out in a temperature range from 25 °C to 800 °C with a heating rate of 20 °C min⁻¹ under constant N₂ flow. The analyzed samples weighted between 15 and 20 mg. Tensile tests (stress/strain) were performed using a dynamic mechanical thermal analysis in the static mode (DMTA) equipment (TA Instruments Model Q800). Tests were carried out at 25 °C with rectangular shape films (thickness ~ 0.15 mm, length 12 mm, width ~7.0 mm) with a force-ramp rate of 1 N min⁻¹. The Young's moduli of the materials were determined according to the standard test methods ASTM D638. The field emission scanning electron microscopy (FESEM) analyses were performed using a FEI Inspect F50 equipment in secondary electron (SE) mode. The samples in the form of 200 μ m thick films were placed into a stub and covered with a thin gold layer. Atomic force microscopy (AFM) was performed in tapping mode using a Bruker Dimension Icon PT equipped with a TAP150A probe (Bruker, resonance frequency of 150 kHz and 5 Nm⁻¹ spring constant). The equipment was calibrated

Download English Version:

<https://daneshyari.com/en/article/8045951>

Download Persian Version:

<https://daneshyari.com/article/8045951>

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