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Research paper

Modification of anionic and cationic clays by zwitterionic imidazolium ionic liquid and their effect on the epoxy-based nanocomposites

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ABSTRACT

Zwitterionic imidazolium-based ionic liquid (ZIL) constituted by imidazolium cation and sulfonate anion was used to modify both cationic and anionic clay minerals, represented by montmorillonite (Na^+ -Mt) and calcined hydrotalcite (CHT). The organophilized clays were characterized using X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The ZIL was successfully intercalated into the interlayer space of Na^+ -Mt, and incorporated at the surface of the CHT, as indicated by XRD and FTIR analysis. Then, the unmodified and modified clays were mixed with epoxy prepolymer based on diglycidyl ether of bisphenol A (DGEBA). The modified clays resulted in epoxy networked materials with higher intercalation degree, and good transparency, as indicated by XRD, transmission electron microscopy (TEM) and Ultraviolet-visible (Uv-Vis) spectroscopy. The best intercalation was observed for the systems containing modified montmorillonite (ZIL-Mt). In addition, the clay-epoxy nanocomposites were also characterized by dynamic-mechanical analysis (DMA).

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1. Introduction

Layered clay minerals are nanofillers that have one dimension in nanometer range and have been extensively used for the development of polymer – based nanocomposites, especially epoxy nanocomposites, with outstanding physical and mechanical properties (Azeez et al. 2013; Bergaya et al. 2013). The lamellar structure of these fillers and their intrinsic thermal and mechanical characteristics endow composites with improved modulus, stiffness, barrier properties, thermal and flammability resistance by using small amount of filler. The unique characteristics of the corresponding nanocomposites are due to the large specific surface area and large aspect ratio of these fillers, contributing for an effective filler-polymer matrix interaction (Bergaya 2008). Clay dispersions are the first step to obtain clay polymer composite products with distinct size, shape, material composition and low cost. The stability and flow properties of clay dispersions are of great importance in the manufacturing of various products, as the final properties and formulation of the product, economic aspects of the process and storage stability of the product depend on these properties (Duman et al. 2012). Several polymers (Tunc et al. 2008, 2011), surfactant (Tunc et al. 2012) and salt

(Duman and Tunc 2009; Tunc and Duman 2009) solutions can be used to control the stability and viscosity of the clay dispersions.

Due to the hydrophilic character of the clay minerals and the hydrophobic nature of most polymer matrices, the separation of the stacked lamellae into nanoplatelets (exfoliation process) and a homogeneous distribution of the nano-objects within a polymer matrix are not easy to achieve without previous organophilization of the inorganic filler.

The most commonly used layered clay mineral for use in polymeric nanocomposites is montmorillonite (Mt), which belongs to the smectite family and contains exchangeable metal cations (e.g. Na^+ , Ca^{2+}) located in the interlayer space. To improve its compatibility with polymer matrices, Na^+ is usually exchanged by organic cations, such as, ammonium, imidazolium and phosphonium ions as organic modifiers (Ray and Okamoto 2003; Bergaya et al. 2013). This process, known as cation exchange, causes the expansion of the interlayer space, which associated with the organophilization favors the diffusion of the polymer, or its precursors in the case of thermosetting materials, into the interlayer space, resulting in an improvement of clay dispersion and exfoliation.

Other interesting and few studied clay minerals are those based on layered double hydroxide (LDH), where hydrotalcite (HT) is the most important example. They are constituted of layers positively charged and intercalated with anions and water molecules (Reichle 1986; Evans and Duan 2006; Ha and Xanthos 2010). In opposition to Mt, the LDH is an anion exchange clay, that is, their interlayer anions can be

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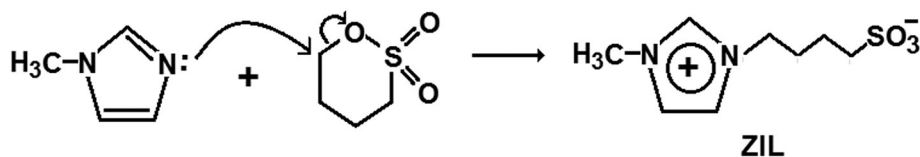


Fig. 1. Scheme of the synthesis of zwitterionic imidazolium-based IL (ZIL).

replaced by others as carboxylate, sulfate, sulfonate, which also promote an enlargement of the interlayer space (Costa et al. 2006; Kovanda et al. 2010).

Quaternary ammonium surfactants, widely used to intercalate the pristine Mt ($\text{Na}^+\text{-Mt}$), have low thermal stability. At high temperature, they can undergo degradation often by Hofmann degradation. Thus, thermally stable surfactants have been emerged to minimize these drawbacks. In this context, imidazolium-, phosphonium- and pyridinium-based ionic liquids (IL) have appeared as promising candidates for clay organophilization. IL are organic salts constituted by organic cation and organic or inorganic anion and display unique characteristics such as, low vapor pressure, low melting point (some of them are liquid at room temperature), good thermal stability, high ionic conductivity, etc. (Ueki and Watanabe 2008; Lu et al. 2009). Different IL have been used to modify both $\text{Na}^+\text{-Mt}$ (Kim et al. 2006; Livi et al. 2010, 2013, 2014; Ha and Xanthos, 2011; Reinert et al. 2012; Takahashi et al. 2012; Fontana et al. 2013; Wu et al. 2014a, 2014b; Totaro et al. 2015), whereas very few papers were devoted to the modification of LDH with IL (Ha and Xanthos 2010; Livi et al. 2012). The presence of both organic cation and anion in the IL structure affords the functionalization of both cationic and anionic clay minerals.

The aim of the present work was to discuss the ability of a zwitterionic imidazolium-based ionic liquid (ZIL) as a double ion (cation and anion) exchange agent for both Mt and LDH clay minerals ($\text{Na}^+\text{-Mt}$ and HT, respectively) and investigate these new modified clays on the development of epoxy-based nanocomposites. The synthesis of ZIL was well established and involved a nucleophilic attack of methyl-imidazole on 1,3-butane sultone, according to the scheme illustrated in Fig. 1 (Yoshizawa et al. 2001; Cole et al. 2002). The imidazolium cation and the sulfonate anion in the same molecule can act as ion exchange for both $\text{Na}^+\text{-Mt}$ and HT, respectively.

2. Experimental part

2.1. Materials

Epoxy prepolymer based on diglycidyl ether of bisphenol A (ER) (EPON 828) (epoxide equivalent = 185–192 g/eq; viscosity = 11–15 Pa.s) was purchased from Shell Chemicals do Brasil. The hardener used for curing the epoxy prepolymer was poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine D230) supplied by Hunstmann. Pristine Mt ($\text{Na}^+\text{-Mt}$) with cation exchange capacity of 0.92 meq/g (trade name: Cloisite- Na^{\circledR}) was supplied by Southern Clay Products Inc. Layered double hydroxide, known as hydrotalcite (HT), containing Mg–Al ratio of 3:1 and carbonate as interlayer anion (CO_3^{2-}), was purchased from Sigma-Aldrich. The hydrotalcite (HT) was calcined at 490 °C for 5 h before using on the modification reaction to remove the carbonate interlayer anion and stored under vacuum, as reported in the literature (Ha and Xanthos 2010). The calcined HT was designed as CHT. Methyl-imidazole and 1-butane sultone used for the preparation of ZIL were purchased from Sigma-Aldrich and used without purification.

2.2. Preparation of the zwitterionic imidazolium-based IL (ZIL)

ZIL, also named (1-(1-methyl-3-imidazole)butane-4-sulfonate), was synthesized according to the literature procedure (Fig. 1)

(Yoshizawa et al. 2001; Cole et al. 2002; Tamada et al. 2007). Typically 5 g (0.06 mol) of 1-methyl-imidazole was dissolved in 30 mL of toluene. Then, 8.29 g (0.06 mol) of 1,4-butanedisulfone was slowly added to the solution under stirring. The medium was stirred under nitrogen at 120 °C for 24 h, when a white powder was formed. The material was recovered, washed with hexane, filtered and dried under vacuum at 60 °C. The melting point of ZIL corresponded to 237 °C, obtained by differential scanning calorimetry (DSC). The structural characterization of the ZIL was performed by ^1H NMR ($\text{DMSO-}d_6$, 500 MHz): δ (TMS, ppm) = 1.77 (2H,t), 2.05 (2H,t), 2.83 (2H,t), 3.92 (3H,s), 4.25 (2H,s), 4.40 (1H,s), 7.54 (1H,s), 7.62 (1H,s).

2.3. Modification of clay minerals

The modification of the clay minerals was performed by ion-exchange reaction. 3.5 g of $\text{Na}^+\text{-Mt}$ or CHT were dispersed in 100 mL of a solution of ethanol containing 3.5 g (16 mmol) of ZIL at room temperature. The mixture was stirred using the high-speed mixer, ultra-turrax, at 13,500 rpm for 15 min, followed by sonication treatment with tip ultrasound working at 45 W for 10 min. After this treatment, the dispersion was kept under magnetic stirring for 24 h at room temperature. Then, the modified clay minerals were centrifuged, washed three times with ethanol, centrifuged and dried under vacuum at 80 °C for 24 h. The modified $\text{Na}^+\text{-Mt}$ and CHT clay minerals were designated as ZIL-Mt and ZIL-CHT, respectively.

2.4. Preparation of the epoxy-based composites

The pristine and the modified clay minerals were dispersed into ER with the assistance of acetone, as previously reported (Soares et al. 2013). 2.5 phr (phr = part per hundred part of resin) of clay was first swollen in around 20 phr of acetone and dispersed in the ER using a high-speed Ultra-turrax operating at 13,500 rpm for 20 min, followed by sonication using tip sonicator operating at 110 W, for 10 min. After these treatments, the acetone was removed at reduced pressure at 70 °C. Then, a stoichiometric amount of Jeffamine D230 (32 phr) was added. The mixture was gently mixed and heated under vacuum for 15 min at 60 °C for removal the bubbles and some residual acetone and poured into a silicon rubber molds. The samples were cured at room temperature for 24 h, followed by a post-curing process at 125 °C for 3 h.

2.5. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna I50S spectrometer in transmission mode (32 scans, resolution 4 cm^{-1}) using KBr pressed disk.

Thermogravimetric analysis (TGA) was carried out on a Q50 thermobalance from TA Instrument, Inc. Samples about 10 mg were heated from 30 to 700 °C at 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen flow.

X-ray diffraction (XRD) analysis was carried out on a Rigaku Ultima IV X-ray diffractometer operating with $\text{CuK}\alpha$ irradiation, 40 kV, 20 mA, in the range of $2\theta = 1\text{--}20^{\circ}$.

The rheology of the dispersions was carried out at room temperature on a Physica MRC302 rheometer from Anton Paar, equipped with disposable parallel plate geometry (25 mm) with a distance of 1.0 mm between the plates. The measurements were performed in oscillatory

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