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Research paper

Effect of the dispersive method in the preparation of the polyurethane/hydrotalcite nanocomposites by in situ polymerization

Danieli M. Carmo^a, Marcia G. Oliveira^{b,*}, Bluma G. Soares^c^a Instituto de Tecnologia (IT), Universidade Federal Rural do Rio de Janeiro (UFRRJ), Antiga Estrada Rio-São Paulo, Km 7, Seropédica, RJ, 23851-970, Brazil^b Divisão de Processamento e Caracterização de Materiais (DPCM), Instituto Nacional de Tecnologia (INT), Avenida Venezuela no. 82 sala 106, Saúde, Rio de Janeiro, RJ 20081-312, Brazil^c Macromolecular Institute (IMA), Federal University of Rio de Janeiro (UFRJ), Centro de Tecnologia, Bl. J, Ilha do Fundão, 21945-970 Rio de Janeiro, RJ, Brazil

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ABSTRACT

The dispersions were prepared in the proportion of 1 g LDH to every 100 ml of 1,6-hexamethylenediisocyanate employing four different methodologies. The FTIR results of the dispersions confirmed the presence of monomer in the clay interlayer space, for all methods studied. The XRD analysis showed that the presence of isocyanate contributed to a small structural disorder. Any significant differences between the experimental procedures adopted were observed in TGA results, whereas visual analysis showed that methodology combining ultraturrax and ultrasound bath (TBT) was more effective for dispersion and incorporation of the monomer remaining stable for about a month.

The dispersions studied were used in the synthesis of polyurethane nanocomposite. The in situ polymerization step had as objective favor the dispersion of nanofiller during the growth of the polymer chains. The polyurethane obtained was confirmed by the presence of characteristic bands of the urethane group in the FTIR spectrum. The diffraction patterns indicated that in situ polymerization contributed to the structural disorder of the nanocomposites. The strain sweep was carried out by rubber process analyzer (RPA), the lowest values of Payne effect ($G_0 - G_{\infty}$) were to TBT and T methodologies suggesting a lower filler-filler interaction.

The results of the dynamic mechanical thermal analysis (DMTA) showed significant differences that were associated with the dispersion method adopted and also a stoichiometry imbalance due to the interactions of the isocyanate with the hydroxyl groups of the hydrotalcite and/or water molecules within interlayer space and/or air moisture. SEM micrographs revealed better dispersion in the clay polyurethane nanocomposites, whose nanofiller was previously dispersed in the isocyanate monomer.

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1. Introduction

Hydrotalcite is a layered double hydroxides (LDH) belonging to the family of the clay mineral which have the octahedral layer structure represented generally by the formula $[M^{2+}_{(1-x)}M^{3+}_{(x)}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, situated in the center of the octahedral and A^{n-} is the anion, which together with water molecules, is located in the interlayer space (Ay et al., 2011; Cavani et al., 1991; Costa et al., 2012; Cunha et al., 2010; Kuang et al., 2010; Martínez and Carbajal, 2012; Pradhan et al., 2008).

The benefits of using LDH in the synthesis of hybrid nanocomposites are associated with the extensive possibility of combining divalent and trivalent cations and also with the facility in performing the anion exchange by the regeneration method, allowing to obtain materials with different properties and applications in various areas of science and technology (Acharya et al., 2007; Du et al., 2006; Huang et al., 2010; Rebelo et al., 2012; Saric et al., 2006).

The choice of a polyurethane matrix is because of its wide application, due to the combination of many monomers, which enable to obtain materials with elastomeric or thermoplastic character, depending on the monomers used in the synthesis (Kotal et al., 2012).

Concerning the properties of the clay polyurethane nanocomposites several studies in the literature indicate that, in general, exfoliated structures confer improved mechanical, thermal and electrical properties to these materials. Though, the degree of dispersion and the type of the structures formed, intercalated or exfoliated, significantly depend on the methodology used for nanofiller dispersion and may influence the final properties of the material (Botan et al., 2011; Esteves et al., 2004; Jeon and Baek, 2010; Rehab and Salahuddin, 2005; Woo et al., 2006).

The diffusion of monomers into the interlayer space, forming clay intercalated structures contributes to the formation of clay polyurethane nanocomposites with exfoliated structures during the stage of in situ polymerization. This procedure has been shown to be a promising alternative for the synthesis of these materials. However, the migration of monomer into the clay is not always easy to occur, because the basal spacing of LDH is small, about 0.76 nm. In this context, several

* Corresponding author.

authors are looking for routines to better disperse the nanofiller in the monomers before the in situ polymerization aimed of the synthesis of exfoliated nanocomposite (Guo et al., 2011; Lonkar et al., 2013; Salahuddin et al., 2010).

Considering the search for nanofiller exfoliation in the polymer matrix and the strong influence of the dispersive method in this process, this study aims to evaluate the effect of different methodologies of LDH dispersion in the monomer 1,6-hexamethylenediisocyanate, focusing on the achievement of an intercalated type material that further favors the formation of a wholly or at least partially exfoliated nanocomposite, during the in situ polymerization step.

2. Experimental

2.1. Materials

Synthetic hydrotalcite containing Mg–Al ratio of 3:1 and carbonate as interlayer anion (CO_3^{2-}), was purchased from Aldrich Chemical Company, Germany (CAS 11097-59-9). The monomer employed in the dispersions was 1,6-hexamethylenediisocyanate (HDI), purchased from Aldrich Chemical Company, Germany (CAS 822-06-0).

2.2. Experimental procedure

2.2.1. Preparation of the dispersions

The dispersions were prepared in glass flasks with lid by four different methodologies employing the ultraturrax (T), ultrasound bath (B) and sonicator (S), and adopting the proportion of 1 g of LDH to every 100 ml of HDI. The procedures are described below:

- *Methodology TBT*: 30 min in ultraturrax, 2 h ultrasound bath and again 5 min in ultraturrax, without interruption;
- *Methodology TST*: 30 min in ultraturrax, 1 min in the sonicator and again 5 min in ultraturrax, without interruption;
- *Methodology T*: 30 min in ultraturrax; and
- *Methodology B*: 2 h ultrasound bath.

2.2.2. Preparation of the nanocomposites

For the synthesis of hydrotalcite polyurethane nanocomposites, prepolymer was first obtained by the reaction of polypropylene glycol (PPG) (MW 2700) with HDI in excess, in a 2:1 molar ratio (isocyanate/polyol). This isocyanate consisted of clay/monomer dispersion prepared in the previous step. Subsequently, the chain extender 1,4-butanediol (BDO) was added in the molar ratio of 1:0.5 (isocyanate/BDO) and dibutyltin dilaurate (DBDL) as catalyst. The amounts of PPG and BDO, in grams, used in the reactions were calculated according to the molar ratio adopted and based on the initial amount, in grams, HDI used to make the LDH dispersions.

The total reaction time was approximately 3 h and twenty minutes, at 85 °C. The nanocomposites obtained were poured into a Teflon mold and dried under vacuum for 2 h.

The nomenclature of the nanocomposites follows the order: name of the polymer followed by name of the clay and the dispersive methodology of the nanofiller (e.g. PU/LDH_T for polyurethane containing LDH that was previously dispersed in isocyanate employing ultraturrax).

As a comparison a nanocomposite was synthesized with hydrotalcite without any previous dispersion in the monomer, which was called PU/LDH. The sample of the polyurethane without clay was called pure PU.

2.2.3. Characterization techniques

The dispersions obtained by the methodologies described previously were under ambient conditions stored and observed for a period of about one month in order to enable a macroscopic evaluation of dispersion stability over the time.

These dispersions were centrifuged and the collected precipitate was dried in oven at 80 °C for 24 h for carrying out the analysis of FTIR, XRD and TGA. Whereas the nanocomposites were pressed with Teflon film, obtaining a thickness of approximately 0.5 mm for the same characterizations above.

Fourier transform infrared (FTIR) spectra were obtained with the help of a Thermo Nicolet model 470 Nerus, transmittance mode, using the KBr disks technique for dilutions and film methods for clay polymer nanocomposites, in the wavenumber range between 4000 and 400 cm^{-1} and average of 32 scans.

X-ray diffraction (XRD) was performed on a Rigaku diffractometer, Model Miniflex, at 25 °C using $\text{CuK}\alpha$ radiation ($\lambda = 1,5418 \text{ \AA}$), 40 kV voltage, 30 mA current, goniometer speed of 2°/min, step of 0.02° and 2 θ scanning from 2° to 70°.

Thermogravimetric analysis was obtained by using an equipment of TA Instruments, model TGA Q50. The heating rate was 20 °C/min, the temperature range was from 25 to 700 °C and nitrogen gas as inert atmosphere.

Dynamic mechanical analyzer (Q-800, TA Scientific) was employed for measuring storage modulus and tan delta of nanocomposites, at a fixed frequency of 1 Hz and heating rate of 3 °C/min. It was employed flexural mode with samples of 25 mm \times 10 mm.

The Payne effect was evaluated by strain sweep tests conducted in the Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 100 °C, 0.5 Hz as fixed frequency and strain range from 0.28% to 1255%. The sample amount was approximately 5 g.

The nanocomposites were coated with carbon in an Emitech K550X metallizer, adopting 20 mA for 4 min. The morphological evaluation of nanocomposites was made using a SEM with field emission gun (FEG-SEM).

3. Results and discussion

3.1. Macroscopic observation of the stability of the dispersions stored for a month

The photographs presented in Fig. 1 show the stability of LDH/HDI dispersions submitted to different methodologies. In the visual analysis the dispersion method using a combination of ultraturrax with ultrasound bath (TBT) was more effective with respect to dispersion stability.

In this method the start of suspended clay decantation happened only after one month storage, whereas for other dispersion procedures the sedimentation started in a few hours or even minutes after the dispersion. However, the methodology using only the ultraturrax (methodology T) also showed promising results because it proved to be more favorable for swelling clay, while the TST and B methodologies showed the worst result among those studied.

3.2. Effect of different methods of dispersion in the incorporation of isocyanate monomer in LDH

FTIR analyzes are shown in Fig. 2-A, the absorption bands at the 775, 547 and 447 cm^{-1} were observed and are related to the vibration of the metal–oxygen (M–O) of network layered double hydroxide. A broad band in the region above 3000 cm^{-1} corresponds to the stretching vibration of the OH group, which may be attributed both to the hydration water as the interlayer layer structure (hydroxide) of LDH. Water also manifests at 1566 cm^{-1} (OH bending) (Lonkar et al., 2013).

For hydrotalcite without the presence of monomer, the free anion carbonate (CO_3^{2-}) showed characteristic bands at 1376 cm^{-1} (asymmetric stretching) and 665 cm^{-1} (bending angle). Furthermore, the interaction of the carbonate with the hydration water molecules resulted in the appearance of the band at 3050 cm^{-1} , which are ascribed to hydrogen bonding. These values are in agreement with those reported in the literature, 1365 cm^{-1} (asymmetric stretching), 665 cm^{-1}

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