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Research paper

Flexible polyurethane foam nanocomposites with modified layered double hydroxides

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ABSTRACT

A carbonate intercalated Mg/Al layered double hydroxide (LDH-CO_3) was subjected to a calcination–rehydration treatment in order to intercalate two different phosphorus containing anions (HPO_4^{-2} and bis(2-ethylhexyl) phosphate, $HDEHP^-$) into the hydroxide layers. The X-ray diffraction analysis showed that the anions were successfully intercalated presenting different crystallinity degree and crystallite size, being LDH-CO_3 the most crystalline, followed by LDH-HDEHP and LDH-HPO_4. The effect of the addition of unmodified and modified LDH in different quantities (1, 3 and 5 pphp) to a flexible polyurethane foam matrix containing a castor oil based polyether was studied. Depending on the crystallinity of the LDH, different dispersion degree was achieved in the nanocomposites affecting the properties differently. Density and firmness increased with the addition of LDH while lower resilience values were obtained in foams containing 3 pphp of LDH-CO_3 and LDH-HPO_4. In addition, thermal behaviour of nanocomposites was analysed by thermogravimetric analysis (TGA) and pyrolysis flow combustion calorimetry (PCFC) and was compared to the reference foam. A decrease in heat release rate was observed in the second stage of degradation, especially for LDH-HDEHP containing foam.

1. Introduction

Polyurethanes comprise a distinctive family inside of polymers due to their versatility and their capability for obtaining a broad range of materials with tailored properties depending on the nature of the selected precursors. Among them, flexible polyurethane foams (PUF) represent the most extended group and become from the reaction of three main constituents such as polyol, isocyanate and water, apart from additives (surfactant, catalysts, fillers, etc.), forming a segmented structure with separated polyether or polyester phase and hard urea domains (Gemeinhardt, 1965). PUF are widely used in daily life applications such as bedding, seat cushioning and automotive industry. Despite their excellent performance, PUF present two main drawbacks for their application. Firstly, their raw materials are conditioned by non-renewable sources, which depend on price fluctuations of the petroleum and its future depletion. On the other hand, they also present high flammability in presence of a heat source. This conduct needs to be improved for fitting the requirements of the current legislation depending on the final application of the material.

Nowadays, several studies are focused on the substitution of fossil based polyols for renewable-based ones (Cateto et al., 2008; Corcuera et al., 2010; Mosiewicki et al., 2013) which in addition to decrease the petroleum dependency, they contribute to reduce the greenhouse gas emissions and even to revalue industrial wastes (Cinelli et al., 2013). Vegetable oil based polyols, such as those based on castor oil, are good candidates for polyurethane synthesis due to their functionality and other properties in common with polyether and polyester polyols used for this purpose (Heinen et al., 2014; Ugarte et al., 2014; Zhang et al., 2014).

Regarding the flammability, the substitution of halogen-based flame retardants for eco-friendly ones such as mineral fillers like layered double hydroxides (Kiliaris and Papaspyrides, 2010; Kotal et al., 2010; Hull et al., 2011; Edenharter and Breu, 2015; Li et al., 2015), is currently of great interest for avoiding the release of corrosive and toxic volatile compounds from combustion (Shaw et al., 2011).

Layered double hydroxides (LDH) belong to the group of anionic clays, known as hydrotalcite-like compounds, existing as natural or synthetic. Their structure consists on $Mg(OH)_2$ (the so-called brucite) octahedra sharing their edges to form sheets stacked through hydrogen bonding. The stacking can follow hexagonal or rhombohedral symmetry, being the latter the stacking configuration of the natural

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hydrotalcite, which consists on a hydroxycarbonate of magnesium and aluminium. Its first formula, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ was given by Manasse (1915). The general formula of hydrotalcite-like compounds is $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}(A^{n-}{}_{x/n}) \cdot mH_2O$, which is constituted by the mixture of divalent (Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, etc.) and trivalent (Al^{3+}, Fe^{3+}, Ni^{3+}, etc.) metal ions with similar sizes, with values of x ranging $0.20 < x < 0.33$ (Evans and Slade, 2006). The trivalent cation is present in the structure as a partial substitution of the divalent one in the brucite-like structure, causing an imbalance on the charge neutrality of the clay, thus leaving the hydroxide sheets positively charged. This positive surcharge is compensated by the presence of anions in the interlayer space, usually CO_3^{2-}, OH^-, Cl^- or NO_3^-, being the carbonate the most common and the one with higher affinity among the clay sheets. These negative ions are exchangeable for a broad range of inorganic and organic anions, providing to these clays the flexibility of being used in several applications, such as catalyst or as catalyst support (Eshaq and ElMetwally, 2016), adsorbent in wastewater (Abou-El-Sherbini et al., 2015), drug carrier in medicine (Cunha et al., 2016), and even as flame retardant (Elbasuney, 2015) among other uses (Li and Duan, 2006).

LDH can have a flame retarding effect due to the coexistence along the interlayer space of anions, water of crystallization and OH^- from the sheets, acting as combustible compound diluters due to the generation of non-combustible gases (usually CO_2 and H_2O) (Cavani et al., 1991) and through the local cooling of the flaming material by the release of hydroxyl groups and interlayer water (Kiliaris and Papaspyrides, 2010). Hydrotalcite-like compounds can be synthesized from different paths such as co-precipitation, urea hydrolysis, hydrothermal treatment, ion exchange or calcination–rehydration process. After calcination, a mixture of the corresponding metal oxides is obtained allowing the regeneration of the brucite-like structure in contact with water due to their memory effect properties. If the desirable intercalating anion is diluted in this water under the adequate conditions of pH and temperature, the reconstruction can be performed together with the intercalation of the selected anion. Thus, the addition of phosphorus containing anions can contribute to the reduction of the flame spread through the catalytic effect of the phosphorus in the oxidation of polymeric chains, leading to the formation of a protective carbonaceous layer which can prevent the feeding of the flame (Lu and Hamerton, 2002; Ding et al., 2015).

In this work, a commercial carbonate intercalated Mg/Al LDH with a 3R rhombohedral stacking, was calcined for subsequent rehydration and reconstruction of the LDH structure with organic and inorganic phosphorus containing anions in order to determine their effect when incorporated into flexible polyurethane foams. The dispersion of different amount of unmodified and modified LDH was performed into a vegetal oil based polyether polyol, prior to the synthesis of different flexible polyurethane foam systems. The effect of the addition of LDH on the properties of the PUF matrix was analysed by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), density and average cell size measurements, compression and ball rebound tests, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The impact on thermal behaviour was studied by thermogravimetric analysis (TGA) and pyrolysis flow combustion calorimetry (PCFC).

2. Experimental procedure

2.1. Materials

Synthetic hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$), namely LDH-$CO_3$, and potassium phosphate monobasic ($KH_2PO_4 \geq 99\%$) and bis(2-ethylhexyl) hydrogen phosphate (HDEHP ≥ 97%) as intercalation agents, were purchased from Sigma Aldrich. Ammonia (NH_3, 30% v/v) and sodium hydroxide (NaOH, 1 M) (Sigma Aldrich), were used in order to adjust the pH of the rehydration media for the intercalation of KH_2PO_4 and HDEHP respectively.

The flexible polyurethane foam samples with different LDH contents were synthesized using as A-side formulation toluene diisocyanate, TDI (Mondur TD-80, Bayer Material Science). The B-side formulation was constituted by a castor oil-based polyether-polyol (Lupranol Balance® 50 from BASF, OH-number = 50 mg KOH g^{-1}, functionality = 2.7 and viscosity = 725 mPa s) and a series of additives kindly provided by Evonik, such as a mixture of triethylene diamine and bis(2-dimethylaminoethyl) ether (Tegoamin® B 75) as amine catalyst for the blowing and the gelling reaction, an organometallic co-catalyst constituted by stannous octoate (Kosmos® 29) and a silicone surfactant (Tegostab® B 4900) which contributes to the nucleation of the blowing agent bubbles and stabilizing the cell structure, obtaining a foam with high air permeability.

2.2. Preparation of the modified LDH

The modification of LDH-CO_3 was accomplished following the rehydration process (Miyata, 1980), in basic media for both organic and inorganic phosphate-based intercalation agents, LDH-HDEHP and LDH-HPO_4 respectively. The procedure was performed as follows: first, the LDH-CO_3 was calcined in a muffle furnace (Selecta) at 500 °C for 5 h in order to remove the water, hydroxyl groups and carbonate anions accommodated between the hydrotalcite layers. In this calcination process, the layered structure is destroyed achieving a mixture of aluminium and magnesium oxides (cLDH-CO_3) which in contact with water restores the original brucite-like layer arrangement due to its structural memory effect (He et al., 2006). The rehydration media were prepared dissolving the intercalation agents in deionized water to obtain a 250 mL solution for each one, considering their purity and adding an excess of 50% for the ionic reconstruction regarding the synthetic hydrotalcite formula, for ensuring the presence of an intercalated monovalent anion for each aluminium atom. The pH of the corresponding solutions was adjusted to 9 with ammonia in case of LDH-HPO_4 in order to favour the dissociation of phosphorus as a divalent anion, HPO_4^{-2} (O'Neil, 2001), and to 10 in case of LDH-HDEHP with NaOH, forming a sodium salt in presence of the HDEHP monovalent anion (Wang et al., 2009). The solutions were decarbonated with nitrogen during 20 min for minimizing the contamination with atmospheric CO_2 before adding the calcined LDH to the mixtures. The time for the regeneration process was selected depending on the size of the intercalating anion. LDH-HPO_4 was obtained refluxing cLDH-CO_3 for 24 h at 80 °C under nitrogen with vigorous stirring (600 rpm) and in case of LDH-HDEHP, the cLDH-CO_3 was refluxed in the same conditions but during 48 h, allowing the bigger organic molecules more time to accommodate between the interlayer galleries. Fig. 1 shows a brief scheme of the regeneration procedure. In both cases, the slurry was then centrifuged at 4500 rpm during 5 min and washed with deionized water. This procedure was repeated four times to remove the excess of intercalation agent. Finally, the filtrate was dried under vacuum at 60 °C during 48 h and the resulting powder was ground in a mortar, sieved with a 0.5 mm mesh and stored in a desiccator into polyethylene containers.

2.3. Synthesis of polyurethane foam nanocomposites

The preparation of the polyurethane foam nanocomposites was carried out by in situ polymerization process, drying firstly pristine and modified layered double hydroxides in an oven at 110 °C overnight for moisture removal and then dispersing them in the polyol. Different quantities of LDH (1, 3 and 5 parts per hundred parts polyol, pphp) were incorporated into the polyol and were mixed at 12,000 rpm in a rotor-stator mixer (Polytron® PT 2500 E from Kinematika) during 2 min. Thereafter the mixture was sonicated with a Bioblock Scientific ultrasonic probe (VibraCell® 75043) in pulses of 4 s during 15 min at 20 kHz and amplitude of 20%.

The polyurethane foam nanocomposites were synthesized following a formulation reported previously by Ugarte et al. (2014) with an