

The effect of phosphorus containing polyol and layered double hydroxides on the properties of a castor oil based flexible polyurethane foam



Sandra Gómez-Fernández, Lorena Ugarte, Cristina Peña-Rodríguez, M. Ángeles Corcuera, Arantxa Eceiza*

Group 'Materials + Technologies', Department of Chemical and Environmental Engineering, Polytechnic School, University of the Basque Country (UPV/EHU), Plaza Europa 1, Donostia-San Sebastián, 20018, Spain

ARTICLE INFO

Article history:

Received 14 December 2015

Received in revised form

15 March 2016

Accepted 29 March 2016

Available online 1 April 2016

Keywords:

Layered double hydroxides

Anionic clay

Polyurethane

Polyurethane foam

Nanocomposite

Phosphorus polyol

ABSTRACT

In this work the effect of the addition of a phosphorus containing polyol (E560) and different type of layered double hydroxides (LDH) to flexible polyurethane foams synthesized with a castor oil based polyol (LB50) is reported. A carbonate intercalated commercial synthetic hydrotalcite (LDH-CO₃) and modified LDH with intercalated hydrogen phosphate and bis(2-ethylhexyl) hydrogen phosphate (LDH-HPO₄ and LDH-HDEHP, respectively) were used. The density and the compression force deflection values of the foams increased with the addition of E560, while the effect of the different LDH depended on their dispersion degree, which was analyzed by X-ray diffraction. It was found by thermogravimetric analysis that E560 catalyzed the first degradation stage whereas LDH, especially those modified with phosphorus, showed a barrier effect which delayed the thermal degradation with respect to unfilled foams containing E560. It was also observed by pyrolysis combustion flow calorimetry that the combination of E560 with LDH led to decrease the total heat release and heat release capacity comparing to foams fully synthesized with LB50. Both E560 and LDH resulted also to decrease the peak heat release rate separately in both stages of degradation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Flexible polyurethane foams (PUF) are widely used in several daily applications such as bedding, domestic and automotive seat cushioning, upholstered furniture and packaging, among others. They are synthesized by means of a simple molding process by mixing three main reactants (isocyanate, polyol and water) apart from other additives such as catalysts, surfactants and additional blowing agents that help the foaming process for producing tailor-made foams with the desired properties. Nevertheless, they present a major disadvantage, which is their vulnerability against fire as a consequence of their chemical composition and their cellular structure. Polyurethanes and particularly PUF, in addition to their high flammability, can also contribute to aggravate the fire scenario by the ignition of surrounding objects throughout burning droplets from the molten material [1]. Furthermore, they produce toxic

smokes composed by HCN and CO during their combustion, which can cause potential damage to health [2] due to smoke inhalation, the major cause of death during fires [3].

Therefore, the improvement of the fire behaviour of PUF would suppose a great progress for their further application, and can be achieved through the use of flame retardant (FR) compounds, which can be classified into additive or reactive FRs. Additive FRs are the most widely used due to their easy incorporation into the polymeric matrix by physical means. Their main drawbacks are that high additive loadings are needed to improve efficiently the fire behaviour and the migration of the particles to the surface over the time also must be taken into account, fact that can be detrimental to other physical properties of the material. Reactive FRs face these disadvantages since they are kept anchored to the polymeric matrix by chemical reaction, thus becoming a part of the network [4].

Halogenated flame retardants are the most effective compounds for improving the fire related properties, but they also produce toxic compounds of incomplete combustion because they act trapping radicals in the gas phase [5]. As a consequence of the

* Corresponding author.

E-mail address: arantxa.eceiza@ehu.es (A. Eceiza).

health hazards and the increasing concern of the potential damage for the environment of the use of halogenated FRs, efforts are nowadays focused on the development of not only effective halogen-free but also environmentally-friendly FRs. The popularity of phosphorus, boron, nitrogen and silicon containing compounds, together with the claim of nanosized silicate layered compounds and anionic clays (namely layered double hydroxides, LDH) is increasing nowadays. They are considered eco-friendly FRs due to the release of non-combustible and non-toxic compounds during their combustion, contributing to dilute the generated combustible compounds. In case of layered clays, they also act cooling locally the flaming material through their endothermic decomposition together with the release of water [6,7].

Layered double hydroxides are hydrotalcite-like compounds, a type of anionic clays that can be natural or synthetic. Their general formula is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-}_{x/n}) \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions with similar sizes, ranging x values from 0.20 to 0.33 forming a brucite ($Mg(OH)_2$)-like structure [8]. The presence of the trivalent cation causes an imbalance in the charge neutrality of the hydroxide layers leaving them positively charged. This surcharge is compensated by the presence of negative ions such as CO_3^{2-} , OH^- or NO_3^- among others. The main characteristic of LDH is that the interlayer anion can be exchanged for another one of greater interest, being able to select among a broad range of inorganic and organic compounds without compromising the brucite-like structure. There exist several approaches for this purpose, starting from an existing LDH and exchanging the anions by anion exchange or by the rehydration method, or synthesizing the LDH directly with the desired anion by the coprecipitation, urea hydrolysis or hydrothermal methods [9].

In this work, PUF were synthesized combining a reactive type phosphorus-based FR (E560) and additive type FRs (three different types of LDH). E560 is a commercial liquid phosphorus polyol which can be used when low fogging is required, especially in seat cushioning applications [10]. Phosphorus acts in the solid phase during combustion by catalyzing the degradation of the polymer through its acid decomposition and increasing the release of nonflammable gases, thus reducing the concentration of combustible gases [11].

The impact on the properties of PUF of the addition of a commercially available synthetic hydrotalcite ($LDH-CO_3$) and phosphorus containing LDH ($LDH-HPO_4$ and $LDH-HDEHP$) obtained by the rehydration method, together with their combination with a phosphorus polyol was studied. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), compression force deflection (CFD), ball rebound or resilience, thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC) were used for this purpose.

2. Experimental procedure

2.1. Materials

The PUF nanocomposites were synthesized using toluene diisocyanate, TDI (Mondur T D-80, Bayer Material Science) as A-side formulation, which was selected due to its high reactivity, low price and its suitability for slabstock foam manufacture at industrial scale compared to other commodity isocyanates. The TDI was used without further purification. The B-side was constituted by Luprol Balance[®] 50 (LB50), a castor oil-based polyether polyol (BASF, OH-number = 50 mg KOH g^{-1} , functionality = 2.7 and viscosity = 725 mPa s) and blended with 5 and 10 parts per hundred of polyol (pphp) of Exolit[®] OP 560 (E560), a reactive type flame retardant oligomer phosphonate, (Clariant, OH-number = 489 mg KOH g^{-1} , functionality approx. 2, viscosity = 500 mPa s and content

in phosphorus of approx. 12 wt%). The general structural unit of a phosphonate polyol is shown in Fig. 1. Prior to their use, both polyols were dried in a rotary evaporator at 70 °C for 6 h. The OH-number of both polyols was calculated following the ASTM D 4274-05 Test A standard. The additives, amine type catalyst (Tegoamin[®] B 75) used for balancing the blowing and gelling reaction, organometallic co-catalyst (Kosmos[®] 29) for balancing the gelling reaction and silicone surfactant (Tegostab[®] B 4900) for stabilizing the mixture and the structure of the foam during reaction were provided by Evonik and were used as received. Deionised water was used as blowing agent. Synthetic hydrotalcite, ($Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$) and intercalation agents for the modification of LDH, potassium phosphate monobasic (KH_2PO_4 , $\geq 99\%$) and bis(2-ethylhexyl) hydrogen phosphate (HDEHP, $\geq 97\%$) were purchased from Sigma Aldrich. Ammonia (NH_3 , 30% v/v) and sodium hydroxide (NaOH, 1 M), used for adjusting the pH of the rehydration media, were also from Sigma Aldrich.

2.2. Preparation of the modified LDH

The modification of the synthetic hydrotalcite ($LDH-CO_3$) was carried out following the calcination-rehydration process [12] in basic media for both organic ($LDH-HDEHP$) and inorganic phosphate ($LDH-HPO_4$) based intercalation agents, following the procedure reported before [13]. Prior to their use in nanocomposite synthesis, pristine and modified layered double hydroxides were dried in an oven at 110 °C overnight for moisture removal.

2.3. Synthesis of polyurethane foam nanocomposites

The preparation of the polyurethane nanocomposite foams containing 3 pphp LDH (1.89 wt% of the total foam weight) was carried out by *in situ* polymerization process. The different LDH were incorporated into the LB50 or LB50-E560 mixture and dispersed in a rotor-stator mixer (Polytron[®] PT 2500 E from Kinetika) during few minutes and then sonicated with a Bioblock Scientific ultrasonic probe (VibraCell[®] 75043). Once the dispersion was prepared, the additives (water, catalysts and surfactants) were added and homogenized during few minutes with vigorous mechanical stirring. Then, the isocyanate was incorporated to the B-side formulation and after stirring during few seconds, the liquid mixture was poured into an open mould with dimensions $150 \times 135 \times 90 \text{ mm}^3$, polymerizing under free rise conditions at room temperature for 48 h. The PUF samples were synthesized following a formulation reported previously [14] with an isocyanate index of 120. Fig. 2 shows the followed synthesis procedure, being the reaction mechanisms of the amine-based and the organometallic catalyst adapted from Refs. [15] and [16], respectively.

A reference sample with LB50 as the unique polyol, denoted as PUF-REF, and foams with 5 and 10 pphp E560 (PUF-5E and PUF-10E respectively) were synthesized. The series of nanocomposites with 3 pphp of different type of LDH were denoted as follows. The foams synthesized with 100 pphp LB50 were named PUF-LCO₃, PUF-LHPO₄ and PUF-LHDEHP; the foams containing 5 pphp E560 were

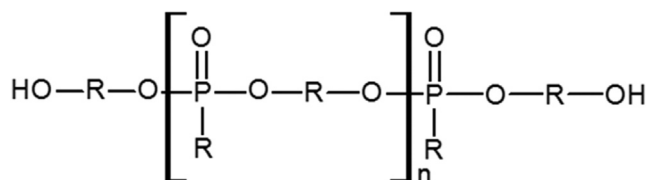


Fig. 1. Structural unit of an oligomeric phosphonate diol.

Download English Version:

<https://daneshyari.com/en/article/5200998>

Download Persian Version:

<https://daneshyari.com/article/5200998>

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