



Enhancement of physical and reaction to fire properties of crude glycerol polyurethane foams filled with expanded graphite

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ABSTRACT

The reaction to fire of polyurethane foams (PUFs) has been a subject of increasing relevance, so in this study the reaction to fire performance of PUFs derived from crude glycerol (CG) has been improved using expanded graphite (EG). The influence of different loadings of EG on the physical-mechanical properties of composite foams has been assessed and the results obtained show that it has significant positive impact. Moreover, the reaction to fire of the PUF and EG/PUF composites has been investigated and the results obtained showed that the fire behavior of composite foams containing as little as 5 wt% of EG are significantly improved. Indeed a dramatic reduction of the rate of heat release, mass loss rate, effective heat of combustion and specific extinction area, has been observed even for a relative low amount of EG. Likewise, the use of Infrared Thermography as a function of time has proven that, when EG is used, the combustion stops suddenly and the temperature drops sharply compared with the behavior of the unfilled PUF sample, which suggests that EG acts like a flame extinguisher. The results obtained have proven the suitability of CG for the production of PUFs and that the addition of EG considerably improves the reaction to fire of composite foams.

1. Introduction

Polyurethane foams (PUFs), like other polymers, rely on fossil feedstock's, because the two main reactants (the polyol and the isocyanate) derive from petroleum feedstocks. However, the increasing concern over their environmental impact and scarcity of petroleum, has motivated the development of PUFs from bio and renewable raw materials [1]. In fact, extensive research has been concentrating on developing, bio-based polyols from renewable sources, such as biomass residues, vegetable oils or industrial by-products [2–8]. The resulting foams are mainly rigid due to the small chain length of the polyols, high crosslinking density associated with high functionality and, in some cases, the presence of rigid groups such as aromatic rings. Therefore, this type of materials is generally used as structural and thermal insulation materials for construction [9].

Rigid PUFs as well as most organic materials burn very easily. Despite of that, for many years the fire performances of PUFs were considered suitable, but nowadays materials have to meet ever more stringent requirements due to the greater attention paid to fire safety

and improved fire performances are thus required.

During combustion, PUFs generate highly toxic smoke, especially CO and hydrogen cyanide. The inhalation of these gases causes severe health problems or even death. Moreover, during a fire, there is a dramatic increase of temperature which leads to the decomposition of PUFs releasing small molecules into the gaseous phase. The mixture of these small molecules with air forms a flammable mixture. In other words, when the concentration of this mixture and temperature cross the flammability limit, the material starts to burn [10].

The behavior of a material towards fire, can be classified by: (i) resistance to fire and (ii) reaction to fire. The fire resistance provides information about how well a building element, such as a wall, floor, door, etc, can maintain its properties when exposed to a fire. It is only related to what happens after flashover. The reaction to fire is related with the instant after the beginning of a fire, its propensity to ignite or feed a fire. This behavior is assessed on the basis of standardized tests and described in a Euroclass classification.

As mentioned before, as a result of the increasing awareness of public opinion, the flammability properties of PUFs need be improved

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and this can be achieved by the incorporation of flame retardants [10]. The flame retardance mechanisms are physical and/or chemical thus, the use of different types of flame retardants can significantly change the flame retardance mechanisms.

Flame retardants can be used as additives or as reactives in order to interfere with combustion during different stages such as heating, decomposition, ignition, or flame spread. Halogenated paraffins and phosphorus containing compounds are the most common additive type flame retardants. The former may not be very compatible with PUFs and for that reason may jeopardize the mechanical properties of the materials besides releasing irritant acids. The latter, being reactive type flame retardants, can react with functional groups of PUFs. They act as char-forming agents, reducing the generation of flammable gases [10]. Reactive type flame retardants have the advantages of (i) increasing compatibility between polymer, (ii) not degrading the mechanical properties of the PU, (iii) having better compatibility as the flame retardant group is a part of the binder and (iv) using small amount or low concentration for the enhancement of fire-retardancy [10].

A very distinct type of flame retardants are inorganic fillers. These materials produce a stable organic–inorganic interface, which reduces the concentration of decomposition gases and increases the diffusion path barrier of the volatiles produced during the degradation process [10]. Nowadays EG is widely used as flame retardant in PUFs. Recently, A. Lorenzetti et al. [11] reported the effect of the volume expansion and of intercalants on the flame retardancy of EG in PUF and concluded that the expansion volume of EG does not seem to have a major influence on the flammability of this type of materials. Yet, the nature of EG intercalants does affect the fire retardancy properties of PUFs, being the sulfur based more efficient than the phosphorous based counterparts.

Polyols from renewable resources commonly used in the production of PUFs are obtained from different vegetable oils such as rapeseed oil, castor oil, palm oil or soybean oil (e.g., BASF castor oil-based Balance™, Cargill soybean-based BioH™, and Dow soybean-based Renuva™) [12]. Most of them are already used at industrial level but the production of these polyols is competing with the production of food. In that sense, crude glycerol (CG) which is a byproduct of the biodiesel production, has received considerable attention [6,13–15]. Aleksander Hejna et al. [16] reported the reaction to fire of PUFs derived from CG, however the CG was used as polymerization reactant, together with castor oil to produce a bio-based polyol and the synthesized bio-based polyol was used as partial substitute (0–70 wt%) of petrochemical polyol in the production of PUFs. Hence, to the best of our knowledge, this is the first report of PUFs derived from the direct use of unrefined CG evaluating its reaction to fire and improving it via the addition of EG.

2. Experimental

2.1. Materials

The foams studied were produced from the reaction between CG with a polymeric isocyanate in the presence of a catalyst, a surfactant and a blowing agent. CG sample was kindly supplied by Bioportdiesel and had a water content of 1.6 ± 0.01 , an acid value (AV) of $23.1 \pm 0.2 \text{ mg}_{\text{KOH}}\cdot\text{g}^{-1}$ and an hydroxyl number (OH_{number}) of $399.0 \pm 4.7 \text{ mg}_{\text{KOH}}\cdot\text{g}^{-1}$. The polymeric isocyanate Voranate M229 MDI with a NCO content of 31.1% and a functionality of 2.7 was kindly supplied by Dow Chemicals. Tegostab B8404, a polyether-modified polysiloxane was used as silicone surfactant and was supplied by Evonik. Polycat 34, a tertiary amine was used as catalyst and was supplied by Air Products. As blowing agent, distilled water was used. EG (EG GHX PX 95) was supplied by LUH and had a thermal conductivity value of 0.290 mW/mK (at room temperature) and its density was 0.5436 g/cm^3 . A detailed characterization of the EG sample used has been provided in a previous report [3] including the evaluation of its reactivity towards the isocyanate using XPS analysis, Fourier transform Infrared (FTIR), FT-Raman spectroscopy, X-ray diffraction and

thermogravimetric analysis (TGA).

2.2. Characterization of CG

The acid value (AV), hydroxyl number (OH_{number}) and the water content of the CG were determined according to the procedures described in appendix.

2.3. Production of PUFs

The polyol component and the corresponding amounts of catalyst (3 parts per polyol (w/w)), surfactant (4 parts per polyol (w/w)) and blowing agent (6 parts per polyol (w/w)), were placed in a polypropylene cup and homogenized using a mechanical stirrer for ca. 10 s at 700 rpm. Note that the amounts of water present in the polyols were subtracted to the amounts of blowing agent added. Next, different amounts of EG (PUFs were filled with EG up to 20% (w/w)) were added and the mixture blended again. Even though EG should not be considered a nanomaterial, as all its dimensions tend to be larger than 100 nm, it is still a material of large surface area. Hence, in the present study, as the main objective was to achieve good reaction to fire performance, without jeopardizing the morphology of the ensuing PUF composites and subsequently the mechanical properties, the preparation of EG/PUF composite foams followed the same rational as that associated with the preparation of nanocomposites, e.g. explore the large surface area of EG in terms of reaction to fire, and minimize the amount of filler used in order to avoid altering the mixture rheology to such point that the foaming process could be compromised, as well as the extent of PU crosslinking. In view of this, and considering that loads between 5 and 10 w/w % relative to the matrix normally suffice to enhance the properties of nanocomposites, 5 w/w% was considered a good starting point to obtain a good reaction to fire. In turn, as it will be discussed later, as the percentage of EG was increased, the morphology of the ensuing composite foams was rather disrupted (see SEM image of PUF-EG20 Fig. 2 (e)) which indicated that the use of higher loads would compromise the composite foam's performance unless the formulation was changed which would limit direct comparison of results.

Finally, the appropriate amount of isocyanate to obtain a $R_{\text{NCO}/OH} = 1.10$ (ratio between NCO groups of isocyanate and OH groups) was added and the mixture homogenized again. The $R_{\text{NCO}/OH}$ used in the PUFs production was determined using Eq. (1).

$$R_{\text{NCO}/OH} = (m_{\text{ISO}} \times \%_{\text{NCO}}/M_{\text{NCO}})/(m_{\text{polyol}} \times (OH_{\text{number}} + AV)/M_{\text{KOH}} + (m_{\text{H}_2\text{O}} + m_{\text{BA}}) \times Eq_{\text{H}_2\text{O}}) \quad (1)$$

Where $R_{\text{NCO}/OH}$ is defined as the number of moles of NCO groups of the isocyanate per OH moles of each polyol and water, m_{iso} is the mass (g) of isocyanate, $\%_{\text{NCO}}$ is the quantity of NCO groups in the isocyanate (31.1%) and M_{NCO} is the molecular weight of NCO group. m_{polyol} is the mass (g) of each polyol, OH_{number} and AV are the hydroxyl number and the acid value of each polyol respectively ($\text{mg}_{\text{KOH}}\cdot\text{g}^{-1}$). M_{KOH} is the molecular weight of KOH. $m_{\text{H}_2\text{O}}$ is the mass of water present in each polyol, while m_{BA} is the mass of blowing agent (water) added. Finally, $Eq_{\text{H}_2\text{O}}$ is the equivalent of OH groups present in the water.

The foams were obtained by free expansion in the cup mold at room temperature and the formulations are listed in Table 1.

2.4. Characterization of PUFs

Fourier Transform Infrared Spectroscopy (FTIR), density, Scanning Electron Microscopy (SEM), mechanical essays, Dynamic Mechanical Analyses (DMA) using the material pocket accessory and Thermogravimetric Analysis (TGA) were determined according to procedures described in appendix.

The thermal conductivity measurements were performed using the Gustafsson Probe method (or Hot Disk) with the Thermal Constant

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