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Lignin particle- and wood flour-reinforced phenolic foams: Friability, thermal stability and effect of hygrothermal aging on mechanical properties and morphology

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ABSTRACT

In the present work, the effect of lignin particles and wood flour weight fractions incorporated on friability and thermal stability of a phenolic foam was determined. In addition, the effect of hygrothermal aging on compressive mechanical properties and cell size of the materials was studied. The incorporation of lignin particles decreased friability of the phenolic foam; whereas, wood flour increased it. The influence of both reinforcements on thermal stability of the material was very low. Although the reduction in mechanical properties of reinforced foams was higher than for the unreinforced material after hygrothermal aging, modulus and strength of the reinforced foams were still superior to those of the unreinforced material. Hygrothermal aging did not influence cell size of the foams studied. The material which exhibits the best combination of features was 8.5 wt.% lignin particle-reinforced phenolic foam.

1. Introduction

Closed cell phenolic foams show excellent fire properties (high flame resistance, no dripping of molten plastic during combustion, low smoke density and smoke toxicity) and high thermal stability in a wide range of temperature, which have led to use them as insulators in applications where fire resistance is critical such as in buildings [1]. However, phenolic foams are extremely friable and show relatively low mechanical performance in relation to other commercial polymeric foams [2,3]. Thus, the use of these materials in some applications is limited and many efforts have been developed to strengthen them through the incorporation of several reinforcements [1–6].

In the last years, the use of reinforcements from natural resources such as lignocellulosic fibers and lignin in polymeric foams has attracted the attention of many researchers since these reinforcements, generally, are renewable and show low density and cost [7–12]. We studied the formulation of lignin particle- and wood flour-reinforced phenolic foams in previous works. The incorporation of these reinforcements resulted in increased mechanical properties of the phenolic foam. Moreover, the amount of blowing agent required for the formulation of the material was reduced due to the lignin particles and wood flour act as nucleating agents [4,5].

The determination of the friability and thermal stability of lignin particle- and wood flour-reinforced phenolic foams, as well as the knowledge of the behavior of these materials under moisture and temperature is essential to evaluate their suitability for structural and insulating applications. Friability of a material involves its capacity to be disintegrated easily in small particles. Materials which show high friability generate dust in the workplace causing a hazard for human health [2]. In addition, high friabilities in polymeric foams limit their application in sandwich panels, where a good adhesion of the materials is required [13]. The effect of temperature can degrade polymeric materials; therefore, it is crucial to know thermal stability of polymeric materials. Thermal stability is related to their initial step of pyrolysis [14], which is usually studied using thermogravimetry analysis. Aging tests are usually performed to study the effect of moisture, temperature, light, etc. on the properties of polymer composites, since these variables can have negative effect on material properties. For example, it has been widely reported that mechanical properties of polymeric materials decreased after moisture and temperature exposure [15,16].

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The characterization of reinforced phenolic foams through friability tests, thermogravimetry analysis and aging tests has been previously reported. For instance, Shen et al. [2] determined friability of aramid and glass fiber reinforced phenolic foams. Zhuang et al. [6] studied thermal stability of an atapulgita modified with hexadecyl trimethyl ammonium bromide phenolic foam composite. Desai et al. [17] studied the effect of hygrothermal aging on mechanical properties, mass loss and cell size of glass and aramid fibers phenolic foams. However, friability, thermal stability and hygrothermal aging studies of lignin particle- and wood flour-reinforced phenolic foams have not been reported yet.

In the present work, the influence of lignin particles and wood flour on friability and thermal stability of the phenolic foam (PF), as well as the effect of hygrothermal aging on compressive mechanical properties and cell size distributions of lignin particle-phenolic foams (LRPFs) and wood flour-reinforced phenolic foams (WRPFs) were studied. This research allowed determining the reinforced phenolic foam, which exhibited the best features for structural and insulating applications, that is, the foam with the lowest friability, the highest thermal stability and the greatest compressive mechanical properties after hygrothermal aging.

2. Experimental

2.1. Materials and synthesis of the foams

Momentive Specialty Chemicals provided the phenolic resol resin and hardener (ACE 1035) employed to prepare the materials. Phenolic foams were synthesized using Tween® 40 (Sigma Aldrich), phenol-4-sulfonic acid (Sigma Aldrich), and n-pentane (Panreac), as surfactant, catalyst and blowing agent, respectively. Materials were prepared with a density of 120 kg/m^3 as was described in previous works [4,5]. The lignin particles were calcium softwood lignosulfonate microparticles with an average diameter of 1.6 μm and was supplied by LignoTech Ibérica. Wood flour was obtained by milling and sieving *Pinus radiata* industrial chips provided by Instituto Nacional de Investigación y Technología Agraria y Alimentaria (CIFOR-INIA) to a size < 0.15 mm.

Lignin particles and wood flour weight fractions incorporated in phenolic foams prepared for friability and thermal stability studies were 1.5, 5 and 8.5 wt.%. Lignin particles and wood flour thermal stability was also studied in order to gain a better understanding of thermal stability behavior of the reinforced materials. For the hygrothermal aging study, reinforcements weight fractions of lignin particles and wood flour incorporated in the material were 8.5 wt.% and 1.5 wt.%, respectively. These weight fractions were selected since they resulted in the greatest compressive modulus and strength of the material, as was reported in previous works [4,5].

2.2. Friability tests

Friability tests were performed according to ASTM C421 for block-type thermal insulation [18]. Samples were cut and polished to obtain cubic specimens of 25.4 mm of side. Twelve specimens were placed in an oak box of 190 × 190 × 197 mm with twenty four oak cubes of 19 mm of side. The box was motor driven at a constant speed of 60 ± 2 rpm/min. The specimens were weighted before and after test and friability was determined as the percent of mass loss during the test as follows:

$$Mass\ loss(\%) = \frac{m_o - m_f}{m_o} \cdot 100 \quad (1)$$

where m_o is the original mass and m_f is the final mass of the sample.

2.3. Thermogravimetry (TGA)

Thermal stability of the foams was studied by thermogravimetry analysis using a Mettler Toledo TGA/DSC1 TG apparatus. The mass of foams analyzed was 5 ± 0.5 mg, while in the case of lignin particles and wood flour was 10 ± 0.5 mg. Samples were placed in an alumina crucible of 70 μL and were subjected to thermal degradation at a heating rate of 10 °C/min in a temperature range of 30–900 °C. The tests were performed under nitrogen atmosphere at a flow of 20 mL/min. $T_{5\%}$ and $T_{25\%}$ were determined as the temperature at which the materials showed a 5% and 25% of mass loss at the step of thermal degradation, respectively. Ash content was determined as the remaining mass (%) at 900 °C. A minimum of three replicates of each sample was tested.

2.4. Hygrothermal aging

Hygrothermal aging was performed according to ASTM D2126 for rigid cellular plastics [19]. The samples were cut with a keyhole saw Bosh PST 900 PEL and polished with a Buehler MetaServ® 3000 to obtain specimens of 80 × 80 × 30 mm. Specimens were placed in an environmental chamber Vötsch VCL 4006 at 38 °C and 97% of relative humidity for two weeks.

2.4.1. Compression tests

Compression tests of unaged and aged samples were performed according to ASTM D1621 using a universal testing machine Zwick/Roell Z030 [20]. The samples were cut and polished to obtain cubic specimens of 25.4 mm of side. The specimens were placed between stainless steel plates and a load was applied uniformly with a crosshead rate of 2.5 mm/min in order to obtain strain–stress curves. Compressive modulus (E) was determined from the slope of the lineal step of the strain–stress curve. Compressive strength (σ_c) was obtained as the maximum strength of the strain–stress curve for strain ≤ 10%. A minimum of five replicates of each sample was tested.

2.4.2. Scanning electron microscopy (SEM)

Morphology of the specimens was observed via scanning electron microscopy (SEM) in order to determine the influence of hygrothermal aging on cell size of the materials. The samples were introduced in liquid nitrogen and then they were fractured. The fractured surfaces were subjected to a gold sputtering to make them conductive and analyzed using a scanning electron microscope Jeol JSM-6400 operating at 40 kV.

3. Results and discussion

3.1. Friability

The values of mass loss for the PF and LRPF and WRPF at several reinforcement weight fractions are shown in Fig. 1. In addition, PF, 8.5 wt.% LFPF and 8.5 wt.% WRPF before and after friability test are shown in Fig. 2. Friability of phenolic foams studied was ranged between 22.2 and 41.8 % of mass loss. Orpin [21] showed a mass loss value of 15–25% for insulating blocks of phenolic foam and Gardziella et al. [22] reported a value of mass loss lower than 30%. Friability of phenolic foams studied exhibited similar values to those reported.

8.5 wt.% LRPF specimen showed sharp angles unlike PF after friability test. Lignin particles decreased mass loss of the phenolic foam (Fig. 2). Mass loss of 8.5 wt.% LRPF was 22.2%; whereas, for PF was 32.2%. Therefore, when 8.5 wt.% of lignin particles was incorporated in the phenolic foam, friability of the material decreased up to 31% in relation to PF. This trend was due to