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Flame retardant treatments of insulating agro-materials from flax short fibres

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ABSTRACT

Improving fire resistance of lignocellulosic agro-materials is essential to extend their application domain. In this study, flame retardant agents, among which aluminium tri-hydroxide (ATH), zinc borate (ZB), melamine phosphate (MMP) and melamine borate (MMB), were incorporated in insulating materials based on flax short fibres. All flame retardant fillers were fixed firmly and permanently on the flax fibres using a protein binder. The incorporation was also homogeneous and preserved materials open porosity and expanded structure.

Flame retardancy was characterized by Mass Loss cone calorimetry and UL 94 horizontal burning test. Materials morphology and thermal degradation were also investigated by scanning electron microscopy (SEM) and thermo-gravimetric analysis (TGA). Among all tested flame retardants, the best results were obtained with MMB. Immediate flame extinction was already achieved at 10 wt% loading rate, whereas the ignition time increased up to 6 times at 30 wt%, compared to the reference.

1. Introduction

Agro-materials from vegetal fibres represent an increasingly appropriate, environmentally friendly and economically viable alternative, particularly for building insulation [1–6]. Wools, nonwovens, mats, composites, rigid and semi-rigid panels, all these materials exploit and emphasize numerous intrinsic raw materials assets such as renewable origin, low toxicity, perspiration properties, mechanical resistance...Concerning the economic aspect, these materials are usually made of well available and low-cost by-products issued from local agricultures, as it is the case for flax (*Linum usitatissimum*) short fibres.

However, since they are rich in lignocellulosic fractions, agro-materials based on vegetal fibres intrinsically keep a pronounced hydrophilic character and are easily flammable. Thermal degradation, fire resistance, smoke emission and toxicity were evaluated for a variety of materials based on wood, flax, jute and sisal lignocellulosic fibres [7–9]. Improving flame retardancy of biobased insulating materials is therefore essential to enlarge their application domain.

The fire resistance of flax and hemp lignocellulosic particleboards can be greatly improved by the development of multi-layer structures, with expanded vermiculite as mineral filler and urea-formaldehyde (U-F) resin as a binder [10]. Sodium aluminate, zinc borate and aluminium trihydrate were also successfully incorporated as mineral flame retardants in U-F medium density fibreboards (MDF) [11]. Fire barrier nonwovens from flax short fibres were obtained with urea polyborates and polyphosphates flame retardants [12]. The flammability of polypropylene-flax composites was significantly reduced using various flame retardants such as aluminium hydroxide, magnesium hydroxide, expandable graphite or ammonium polyphosphate [13,14]. Also, ammonium polyphosphate was used in association with melamine to improve the fire behaviour of flax based composites [15]. The authors underlined the efficiency of a synergetic action between the charring of cellulosic materials and intumescent phenomena. Nitrogen phosphorus flame retardants were synthesized and successfully applied on wood particles as well, by the immersion of wood samples in flame retardant water solutions and by drying [16]. Diammonium phosphate and ammonium polyphosphate were also used as environmentally-friendly alternatives to improve the flame retardancy of biocomposites reinforced with natural fibres [17]. As previously, the pretreatments of lignocellulosic fibres with flame retardant additives were carried out in aqueous solution.

The main objective of this study was to improve the flame retardancy of insulating agro-materials made of flax short fibres, by using an innovative technique based on pea protein binder. Requiring no specific pretreatment of the lignocellulosic substrate, this approach allowed permanently fixation of the flame retardant agents directly onto the fibres during the materials' manufacturing

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process. Aluminium tri-hydroxide (ATH), zinc borate (ZB), melamine phosphate (MMP) and melamine borate (MMB) were incorporated as halogen-free flame retardants. Their efficiencies were compared at the same incorporation rate and the study was then exclusively carried on with the best additive at different incorporation ratios. The evolution of materials morphology and mechanical properties was also investigated.

2. Experimental

2.1. Materials

Scutched and cleaned dew-retted flax short fibres, containing between 5 and 8 wt% of shives, were provided by Albert Brille nv, Wavelgem, Belgium. Pea protein isolate Pisane® was provided by Cosucra Groupe Warcoing, Belgium. Flame retardant agents Melagard MP (MMP, melamine phosphate, d50 $<$ 4 μm) and Melagard MB (MMB, melamine borate, d50 $<$ 4 μm) were provided by Italmatch Chemicals, Genova, Italy. Firebrake ZB (ZB, zinc borate, d50 $<$ 9 μm) was provided by Borax, London, UK. Aluminium trihydroxide (ATH) was a commercial grade additive purchased from VWR, Louvain, Belgium.

2.2. Materials preparation

Insulating agro-materials from flax short fibres were manufactured by a wet process, which was exclusively based on mechanical and physico-chemical treatments. On the whole, it consists of 5 main steps: grinding, mixing, foaming, moulding and drying.

Short fibres were firstly ground at 6 mm, in order to facilitate the homogenization of fibres with the pea protein binder (7 wt% aqueous solution, 1200 mPa s). Flame retardant agents (ATH, ZB, MMP and MMB) were resuspended in water and than incorporated up to 30 wt% in the flax/protein aqueous mixture during the mixing step (5 min, 120 rpm). After the foaming step (2 min, 300 rpm), samples were moulded and dried at 140 °C to a constant mass. Each batch allowed preparation of a 30 × 20 × 2 cm^3 plate with mean density around 0.8 g/cm^3. At least 3 plates were manufactured for each formulation. Finally, these original plates were polished and cut into 100 × 100 × 10 mm^3, 80 × 20 × 20 mm^3 and 125 × 10 × 10 mm^3 specimens for morphological, mechanical and flammability characterizations. Samples were always selected in order to have as closest sets of densities as possible, for all formulations.

2.3. Morphology

Macroscopic pictures of agro-materials were made with a Canon PowerShot SX210 IS digital camera (Tokyo, Japan). More detailed morphology was analysed using a Leica MZ75 light binocular microscope (Wetzlar, Germany) connected to a JVC KY–F1030 color digital camera (Yokohama, Japan). Scanning electron microscopy (SEM) allowed the most accurate visualization of agro-materials morphology. The micrographs were generated with XL 20 Phillips scanning electron microscope (Eindhoven, The Netherlands). In order to facilitate observation, samples were coated with gold using a Leica EM SCD050 vacuum coater (Wetzlar, Germany). The thickness of the gold layer was ca. 5 nm.

2.4. Mechanical properties

Flexural resistance measurements were performed according to ISO 178 methods on a Tinius Olsen Hounsfield H10KT universal testing machine (Surrey, UK), at 2 mm/min speed and using 80 × 20 × 20 mm^3 samples. Materials were stored at 105 °C during 24 h before testing. All determinations were done in quintuple.

2.5. Thermo-gravimetric analysis

Materials thermal stability was determined by thermo-gravimetric analysis (TGA) using a TA Instruments Q500 equipment (Zellik, Belgium). Measurements were performed under inert nitrogen as well as under oxidative air atmosphere. Samples were heated from 30 to 600 °C at a heating rate of 10 °C/min. All analyses were performed in duplicate.

2.6. Mass Loss cone calorimetry

The fire behaviour was tested by FTT (Fire Testing Technology) Mass Loss Calorimeter (East Grinstead, UK). Heat release rate (HRR) of samples was measured according to the ASTM E 906 standard. A 100 × 100 × 10 mm^3 sheet was exposed to a radiant cone (35 kW/m^2) using a forced ignition. All materials were conditioned at 23 ± 2 °C and relative humidity of 50 ± 5% before testing. Results correspond to mean values obtained from at least 2 experiments for each formulation, for which a typical variation of 10% was observed.

2.7. Flammability

The flame behaviour of the reference and treated materials was estimated according to the UL 94 horizontal burning test (Underwriters Laboratories). Initially, materials were cut to 125 × 10 × 10 mm^3 test samples and stored at 50 °C during 48 h. The persistence of flames and combustion time were determined after 10 s application of the Bunsen burner, inclined at 45° and with a calibrated blue flame of 20 mm. All measurements were realized in triplicate.

Fig. 1. Rigid insulating panels from flax short fibres and protein binder.