Construction and Building Materials 79 (2015) 34–39

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Thermal degradation and fire behaviour of thermal insulation materials based on food crop by-products

M. Palumbo [a], J. Formosa [b], A.M. Lacasta [a,*]

[a] Escola Politècnica Superior d'Edificació de Barcelona, Departament de Física Aplicada, Universitat Politècnica de Catalunya, Barcelona, Spain
[b] Departament de Ciència dels Materials i Enginyeria Metal·lúrgica, Universitat de Barcelona, Spain

HIGHLIGHTS

- Six bio-based insulation materials are evaluated in terms of their fire behaviour.
- Binders, even in small portions, greatly affect the fire behaviour of the composites.
- Materials including alginate perform more favourable than those containing starch.
- All the composites perform better than polystyrene or polyurethane.
- A smouldering process is observed that should be minimised in future work.

ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 30 December 2014
Accepted 4 January 2015
Available online 20 January 2015

Keywords:
Crop by-products
Natural thermal insulations
Fire behaviour
Flammability
Pyrolysis Combustion Flow Calorimetry

ABSTRACT

Natural thermal insulation materials developed from renewable crop by-products and natural binders are analysed in terms of their thermal degradation and fire behaviour. A Pyrolysis Combustion Flow Calorimetre (PCFC) is used to characterise some kinds of crop by-products, including rice husk, corn pith and barley straw. This technique is complemented with a TG analysis. Six thermal insulation materials, formulated with such crop by-products and two kind of natural binders, corn starch and sodium alginate, are developed and analysed. PCFC results show an improvement when sodium alginate is incorporated, especially in the corn pith composite. Fire reaction tests are also performed that yield results which are in qualitative agreement with the small-scale tests.

1. Introduction

The building sector is moving towards new approaches to energy efficient design, which includes not only the decrease of the thermal transmittance of the building envelope but also the improvement and use of natural and locally available building materials. The use of industrial crops and food crop by-products as raw materials for composites to be used in building applications is an interesting alternative to conventional products [1–4]. Although much of the research has been focused on the reinforcement in composites and the development of high and medium density boards, there is an increasing interest in their use in natural thermal insulations [5]. Together with the good hygrothermic properties of these natural materials, their availability from renewable resources is considered as one of their main advantages compared with other petroleum-derived insulations. In addition, the use of food crop by-products has a positive environmental impact because implies the revaluation of existing natural resources. All of these beneficial aspects encourage its use in building insulation, but it is necessary to analyse their potential response under real situations, in particular their behaviour in case of fire, before establish the feasibility of their use. The fire reaction of the vegetal compounds and the developed composites is a crucial aspect that should be well-known and improved. Several authors have analysed the thermal degradation and flammability of different natural fibres and composites that include such fibres [6]. Alvarez et al. [7] performed a thermal analysis of cellulose derivatives/starch blends with different sisal short fibre content, and found that the addition of the sisal fibres produced no significant effect on the thermal degradation of the composite materials in comparison with the matrix alone. Yao et al. [8] investigated the thermal decomposition processes of 10 types of natural fibres commonly used in the polymer composite industry. These fibres included wood, bamboo, agricultural residue, and bast fibres.

* Corresponding author at: UPC-EPSEB, Av Dr. Marañon 44-50, 08028 Barcelona, Spain. Tel.: +34 934016816; fax: +34 934017700.
E-mail address: ana.maria.lacasta@upc.edu (A.M. Lacasta).

http://dx.doi.org/10.1016/j.conbuildmat.2015.01.028
0950-0618/© 2015 Elsevier Ltd. All rights reserved.

Dorez et al. [9] considered cellulose, hemp, flax, sugar cane and bamboo as natural fibres, and polybutylene succinate (PBS) as a polymer matrix. The treatments of fibres prior to their use in composites have also been analysed in terms of possible changes in their thermal degradation properties. For example, Rana et al. [10] used a simple solvent and catalyst acetylation method on jute fibres and obtained that the thermal stability of acetylated jute was higher than the untreated jute. The addition of flame retardants in lignocellulosic materials has also been widely studied [9,11,12]. These kinds of retardants include phosphorus-based ones like diammonium phosphate (DAP) and sulfamic acid salts such as ammonium sulphamate [11].

The strategy commonly used to analyse thermal degradation and fire behaviour combines small-scale thermal analysis such as Thermogravimetric Analysis (TGA) and/or Differential Scanning Calorimetry (DSC) with fire reaction tests such as cone calorimetre and Limiting Oxygen Index (LOI). However, the use of a microcalorimetre known as Pyrolysis Combustion Flow Calorimetre (PCFC) is becoming also usual [13,14]. Microscale combustion calorimetry combines thermal analysis and oxygen consumption calorimetry thus enabling the determination of Heat Release (HR) and Heat Release Rate (HRR) of small samples. Data from the PCFC have been shown to correlate well with other established fire tests [15,16] and it has been approved as an ASTM International Standard for plastics and other solid materials [17].

In this study, three different crop by-products have been used for the development of six natural thermal insulations, using corn starch and sodium alginate as binders. Both the composites and the raw materials are analysed in terms of their thermal stability and fire behaviour.

2. Experimental

2.1. Materials and formulations

Three types of crop by-products were analysed: rice husk, corn pith and barley straw. Table 1 summarises their chemical composition according to the values reported in the literature.

Natural thermal insulations were formulated with the above vegetal materials. Two polysaccharides, supplied by Cargill SA, were used as binders: corn starch and sodium alginate. The formulations, presented in Table 2, were optimised in a previous work [22] in order to obtain suitable composites, which appearance is shown in Fig. 1. Table 2 also shows the corresponding bulk densities. Since the thermal conductivity values are similar in all cases, the thickness required to achieve a given thermal resistance is the same in all cases. Therefore, insulations made with corn pith, which has the lowest density, will have the lowest mass per surface unit.

2.2. Pyrolysis Combustion Flow Calorimetre

Small-scale flammability tests were carried out on a Fire Testing Technology Pyrolysis Combustion Flow Calorimetre (PCFC). The heating rate at the pyrolyser was set to 60 °C/min up to a maximum temperature of 750 °C. Products from the anaerobic thermal degradation completed in a nitrogen atmosphere were mixed with a 20 cm^3/min stream of oxygen prior to entering the combustion furnace at 900 °C.

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed in an inert atmosphere using a TA Instruments SDT Q600. Measurements were taken out under a nitrogen atmosphere with a heating rate of 10 °C/min from 30 °C to 600 °C. For each experiment a mass of 5 mg ± 0.5 mg was used and the flow rate of gas was 50 ml/min.

Table 2
Formulations of natural thermal insulations and their corresponding densities.

Thermal insulation	Vegetal fibre (%)	Binder (%)	Density (kg/m^3)
Rice husk + starch	71.4	28.6	223
Corn pith + starch	90.9	9.1	89
Barley straw + starch	83.3	16.7	141
Rice husk + alginate	89.3	10.7	189
Corn pith + alginate	97.1	2.9	58
Barley straw + alginate	94.3	5.7	98

2.4. Ignition time and extinguishability

A radiator device described in the Spanish Standard UNE 23.725-90 was employed to measure the ignition time and the degree of extinguishability of combustion. Samples of surface 70 × 70 mm^2 and variable thickness were placed on a metallic grid 3 cm below a heat source of 500 W, which was removed and replaced after each ignition and extinction, respectively. The most important parameters determined were the number of ignitions and the average value of combustion extent during the 5 min of assay.

2.5. Limiting Oxygen Index (LOI)

The Limiting Oxygen Index was determined using the device described in UNE-EN ISO 4589-2. Samples of 70 × 2 × 0.5 mm were placed vertically in a test chimney. A gas mixture of nitrogen and oxygen was then blown through the chimney and the sample was ignited. This procedure was repeated a minimum of six times for each composite, the oxygen concentration of the gas mixture being changed every time in order to determine the concentration at which the sample burned.

3. Results and discussion

3.1. PCFC analysis of crop products and binders

Small samples of 10 mg (±0.5 mg) in mass were tested in the Pyrolysis Combustion Flow Calorimetre (PCFC). Each case was tested in triplicate. Fig. 2 shows an example of the results obtained for each type of crop by-product. The heat release rate (HRR) is represented as a function of temperature.

All the samples show a clear peak, mainly as a result of the thermal decomposition of cellulose. In some cases, a 'shoulder' is observed at lower temperatures (under 300 °C), which is commonly associated to the thermal decomposition of hemicellulose [8,23]. This shoulder is quite clear in rice husk and barley straw samples but is not present in corn pith. The high temperature tails that appear in all curves may be associated with lignin, the degradation temperature range of which is wide, from 200 °C to 500 °C [8]. Results qualitatively agree with the chemical composition shown in Table 1 despite the noticeable dispersion in values found in literature.

The heat release rate for the two binders used in the natural insulations conformation is presented in Fig. 3. The differences between these two binders are remarkable: whereas sodium alginate presents two peaks of a lower magnitude than peaks observed in the crop materials, starch has a sharp and much higher peak around 300 °C (the different scales may be observed in the figure).

The main parameters obtained from the Pyrolysis Combustion Flow Microcalorimetre that are associated with flammability and hazard in case of fire are:

Table 1
Main chemical composition of vegetable materials.

Crop type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Silica (%)	Ash (%)	Refs.
Rice husk	24.3	24.3	14.3	9–14*	15.3	[18,19]
Corn cob	43.2–50.5	31.0	14.6–15.0		2.2	[20,21]
Barley straw	31.0–45.0	24.0–29.0	14.0–15.0	3.6	3–7	[19,20]

* Data for rice straw.