Composites Part B 89 (2016) 117–126

Contents lists available at ScienceDirect

Composites Part B

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

Hemp fabric/epoxy composites manufactured by infusion process: Improvement of fire properties promoted by ammonium polyphosphate

Luca Boccarusso*, Luigi Carrino, Massimo Durante, Antonio Formisano, Antonio Langella, Fabrizio Memola Capece Minutolo

Department of Chemical, Materials and Production Engineering (DICMaPI), University of Naples Federico II, Piazzale V. Tecchio 80, 80125 Naples, Italy

A R T I C L E I N F O

Article history:
Received 30 March 2015
Received in revised form
15 September 2015
Accepted 21 October 2015
Available online 28 November 2015

Keywords:
A. Polymer-matrix composites (PMCs)
Fire properties
D. Thermal analysis
E. Resin flow

A B S T R A C T

The interest for natural fibers as reinforcement in composites is growing for a large number of products also for aeronautic applications, where the flame retardant requirement is fundamental. In this research, ammonium polyphosphate was incorporated as flame retardant into hemp/epoxy biocomposites produced by infusion technology. Cone calorimeter, vertical burning, dynamic mechanical analysis and bending tests were performed in order to study fire and mechanical behavior of the produced biocomposites with different percentage of ammonium polyphosphate. The results showed a decisive improvement of the flame properties; no-effect on their mechanical properties and on the technological feasibility of the process were observed. Therefore, the addition of ammonium polyphosphate enhanced flame retardancy of hemp/epoxy-resin biocomposites without sacrificing their mechanical properties.

1. Introduction

The applications for natural fiber composites in automotive components, building materials and aerospace industry are increasing, due to ecological and economical advantages over conventional composites [1–3].

In this context, natural fibers are becoming alternative reinforcing fillers in various areas of polymer composites due to their advantages over synthetic fibers, e.g. low cost, less tool wear during processing, low density, environmental friendly, and biodegradability [4–8]. Recently, natural fiber reinforced polymer composites were commercially used in several fields such as automotive and interiors construction [8,9]. Among various kinds of natural fiber, hemp is one of the most interesting plants because it can easily be grown around the world, it has low cost, low density, high specific strength when compared to glass or aramid fibers and it is available as a renewable resource. Because of its good biodegradability together with the waste treatment requirements, it was used in the automotive industry mostly as interior components [10].

However, a chemical treatment of these fibers is necessary, in order to increase the adhesion with hydrophobic polymer matrix [11]. Normally, alkalization with sodium hydroxide (NaOH) solution is the most widely used process for the surface treatment of natural fibers due to its low cost, effectiveness, and convenience of use [12,13].

If the improvement of the fiber-matrix compatibility has generated many research papers, there are only few reports on the improvement of the thermal stability and the fire behavior.

As organic materials, the polymers and the natural fibers are very sensitive to flame; then, improvement of flame retardant requirement of the composite materials has become more and more important in order to comply with the safety requirements of the natural fiber/composite products.

The burning process is comprised of five fundamental steps, which are heating, decomposition, ignition, combustion and propagation. Flame retardancy can be achieved by the disruption of the burning process at any of these stages that can be lead to the termination of the process before actual ignition occurs. The most expeditious method used to acquire flame retardancy is the incorporation of additive that can interfere with the combustion during a particular stage of the burning process [3]. The most widely used additive types are inorganic compounds, halogenated compounds and phosphorous compounds [14,15]. In addition, boric acid, ammonium phosphates and borates, ammonium sulfate and

---

* Corresponding author. Tel.: +39 0817682370.
E-mail addresses: luca.boccarusso@unina.it (L. Boccarusso), luigi.carrino@unina.it (L. Carrino), mdurante@unina.it (M. Durante), aformisa@unina.it (A. Formisano), antgella@unina.it (A. Langella), capece@unina.it (F. Memola Capece Minutolo).

http://dx.doi.org/10.1016/j.compositesb.2015.10.045
1359-8368/

chlorides, zinc chloride and borate, antimony oxide, sodium borate and dicyanodiamide are also used [3].

The action mechanisms of flame retardants can happen both in the condensed phase, in which the degradation of the polymer occurs, and in the gas phase, in which the combustion of the volatile products occurs. In both cases, these mechanisms can be chemicals (blocking the radical process of combustion, dehydration process with char formation and intumescence resulting phenomenon, etc) or physical (cooling, dilution, coating, etc).

An example of a widely used inorganic flame retardant is the ammonium polyphosphate (APP) which, unlike the other phosphorus-based additives, is not harmful to health. The APP interferes with the process of initiation and development of the flame through different processes:

- release of water and gas, which dilutes the gases produced by the flame;
- cooling of the material surface;
- production of a resistant and non-flammable layer on the material surface, that acts as insulator both for the heat and the volatile fuels.

The flame retardants can be used either by direct incorporation into polymer matrix during the process or by impregnation or grafting onto natural fibers. Several authors demonstrated the interest to modify natural fiber surface using phosphorous compounds:

Dorez et al. [16] investigated the thermal degradation and fire behavior of different natural fibers/PBS biocomposites additivated with APP. This addition was beneficial to the formation of a strong char barrier and for a significant decrease of the peak of heat rate release (*PHRR*);

Shumao et al. [17] studied the influence of APP on the flame retardancy of a ramie fiber-reinforced poly(lactic acid). The authors obtained better flame retardancy with the incorporation of APP both in fibers and in matrix;

Nie et al. [18] used microencapsulated APP as flame retardant in poly(butylenes succinate)/bamboo composites. The results of cone calorimeter showed that *PHRR* and the total heat release (*THR*) decrease substantially with the addition of the flame retardant;

Schartel et al. [19] studied the incorporation of APP in flax/PP biocomposites. They delivered a comprehensive characterization of the fire response for forced flaming combustion.

Generally, in these researches single fibers were employed with a good distribution into the matrix but, nowadays, the fabrics represent the most widely used long fiber reinforcement that ensure good directionality with no filament winding technologies.

In this study, unidirectional fabric made from hemp fibers was used as reinforcement of an epoxy matrix. The epoxy resin is suitable for the realization of advanced composites for structural parts with high mechanical characteristics, but the properties of flame resistance are low. For this purpose, the resin was mixed with APP particles, in order to use this mixture in the infusion process and to study the technological feasibility of the process.

The additive was chosen for its properties of excellent inorganic flame retardant, environment-friendly and halogen-free characteristics and for its micrometric dimensions, which allowed a homogeneous dispersion within the material, particularly within the unidirectional fabric used in this study. The aim of this work was to study the influence, on the fire retardant properties and mechanical behavior, of APP content in unidirectional hemp/epoxy composites manufactured by resin infusion process, in order to fill this lack of knowledge highlighted by the scientific literature.

2. Experimental section

2.1. Materials and processing

An epoxy resin (I-SX10 by MATES [20]) and an unidirectional hemp fabric of 340 g/m^2 (by Fidia Srl [21]) with densities of 1.15 g/cm^3 and 1.5 g/cm^3 respectively, were used to produce composite laminates by resin infusion process, according to other works [22,23].

Fig. 1 shows, respectively, the fabric (Fig. 1a), a magnification of a single hemp yarn that composes it (Fig. 1b–c) and the infusion process for the realization of a laminate (Fig. 1d). From Fig. 1c, it is possible to observe that each yarn is formed by the winding of five filaments, with a twist angle equal to about 20°; in turn, each filament consists of several elementary fibers. Moreover, only 300 g/m^2 of hemp fibers are really available in the fabric direction, since about 10% of the content is related to the filaments that hold together the yarns of the fabric.

For each realized laminate, the ratio of fiber to resin was kept constant and equal to 35% in weight. For the treated samples, the resin and APP particles (by Tecnosintesi Spa [24]) were mixed on the ratio 100:5, 100:15 and 100:30.

Table 1 summarizes some of the characteristics of the flame retardant, extracted from the product data sheet, used in this work.

Table 2 reports the denomination of the different samples and their composition (the data start from a reference untreated sample of 100 g).

Before impregnation, the fabric was soaked in 2% NaOH solution at room temperature for 30 min. After treatment, fibers were copiously washed with water to remove any traces of alkali on the fibers surface and subsequently neutralized with 1% acetic acid solution. Then, the treated fibers were dried in an oven at 60 °C for 12 h.

The impregnation of the reinforcement, constituted by four fabric layers, with epoxy resin, along the fibers direction, was obtained by use of vacuum, generating also the reinforcement compaction, and by a close mold constituted by a glass plane and a flexible tool, a polymeric bag; no polymeric net (placed generally on the reinforcement layers) was employed as resin distributor because of the high values of permeability characterizing the fabric. Indeed, the wide mesh of this unidirectional fabric allows the resin to flow freely without filter action with respect to APP during the infusion process. The dimensions of the laminates were 550 mm × 350 mm, 2.5 mm thick; the time measured for different distances of impregnating flow is reported in Fig. 2.

From the data, it is clear that the presence of the additive in the epoxy increases the impregnation time compared to the untreated case; however, the feasibility of the technological process is not affected.

2.2. Experimental methods

In this section, a description of the carried out tests is reported.

A single laminate for each typology of biocomposites proved to be sufficient to extract all the specimens to conduct the experiments. From each laminate, three specimens were cut for every test type. A specimen for each experimental test is reported in Fig. 3.

2.2.1. Cone calorimeter analysis

Cone calorimetry provides much information on the combustion behavior and has good correlation with real fire disasters, so it is often used to evaluate the flame properties of materials. Several combustion parameters were determined: