Intumescent Biobased-Polylactide Films to Flame Retard Nonwovens

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ABSTRACT
The work focuses on the development of a new process to flame retard nonwovens, using films based on renewable resources. Films consist in intumescent formulations of polylactic acid (PLA), ammonium polyphosphate (APP) blended with lignin or starch and are coated on hemp or wool nonwovens. The objective of this study was to investigate the fire retardant and mechanical properties of textiles protected by FR PLA films for potential use in building applications. Horizontal and vertical flame spread tests as well as cone calorimetry tests show that flammability properties of nonwovens are significantly improved. Better mechanical properties are also obtained with coated nonwovens.

INTRODUCTION
Nonwovens play a significant role in roofing and construction applications to fulfill the demand for more energy efficient buildings [1] . However, fire safety is required in this application. The treatment method is a key issue to significantly improve the fire retardant properties of materials, and in particular in the field of textiles. In fact, Duquesne et al. [2] have evaluated the influence of the fire retardant method on the FR performance of an intumescent polypropylene nonwoven. The padding and back-coating methods have been compared to the blending of the fire retardant additives in the PP matrix during extrusion prior to make the fibers. In that study, they demonstrated that the performance of a system is closely linked with the fire treatment method used because the structure of the protective shield formed differs from one system to another.

To provide low flammability to nonwovens, different approaches can be used. In the field of nonwovens composed of inherently fire-resistant fibers, fibers such as aramids, melamine, or carbon fiber offering high thermal stability and good flame retardancy can be used. As an example Duflot Industrie has developed Isomex®, a 100% virgin aramid fibers nonwoven for the protection of firemen [3]. Another company, Technical Fibre Products, has elaborated a nonwoven which expands up to twenty times its original thickness when it comes into contact with fire. The product is an intumescent nonwoven and is based on a combination of expandable graphite and mineral fiber [4].

In the field of fire retardancy brought by incorporating flame retardant additives in commodity polymers before the processing of the fibers, Dong and Christine [5] have developed halogen free flame retardant melt blown nonwovens using phosphorus based additives blended with polyester or nylon resins prior to the extrusion process. Raponi et al. [6] patented a method describing the manufacture of fire resistant nonwoven fabrics containing polypropylene fibers and polyester fibers using the same blending approach.

Other approaches, widely used in the industry, concern the surface treatments such as the padding or back-coating of fire retardant formulations on textile structures during the finishing step. For example, Keep et al. [7] have used encapsulated flame retardants deposited or coated onto cotton fabrics to obtain durable flame-retardant properties. Several patents using the coating method have been applied [8]-[10]. According to Han and Park [11], different components (phosphorous-based and/or nitrogen-based additives with a rubber coating agent) of the fire retardant formulation are mixed and then diluted by water. The solution is coated on a nonwoven and then dried so that a functional textile is manufactured. A foamed non-flammable carbonizing layer is formed when the nonwoven comes in contact with a flame.

All these methods to fire retard nonwovens are interesting but they exhibit disadvantages. High performance fibers are expensive, the blending approach is limited by the use of nanoparticles and a solvent is often used for coating and if water is the solvent, only non-hydrosoluble compounds can be employed. In this article, an innovative method to flame retard any type of nonwoven using intumescent films is described. Upon heating, fire retarded (FR) intumescent materials form a foamed cellular charred layer which protects the underlying material from the action of heat flux and flame [12]. The proposed mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phase [13]. Generally, intumescent formulations contain an acid source, a polyhydric compound and a blowing agent. A previous study [14] demonstrated that compounds coming from renewable resources like lignin (LIG) or starch blended with ammonium polyphosphate (APP) can be used as intumescent systems for PLA to develop materials with enhanced fire retardant properties. Films are elaborated with the formulations PLA/APP/LIG and PLA/APP/starch and will be used as a potential flame retardant treatment on a nonwoven. The fire retardant properties of the materials will be evaluated through horizontal and vertical fire tests and also by cone calorimetry. This study will show that this new process improves the fire retardant properties as well as some mechanical properties of nonwovens and consequently potential uses for building applications (insulation panels) can be considered. First, the approach will be investigated with hemp nonwovens then validation of the method to wool nonwovens will be realized.

EXPERIMENTAL

Materials

The polylactic acid (PLA) is composed of 95.7 % L-lactide with a molecular weight of 74500 g/mol and is supplied by Cargill Dow (PLA 6200D NatureWorks). The melting temperature and the glass transition temperature are 165° and 60°C respectively.

The intumescent formulations were composed of ammonium polyphosphate (APP) ($(NH_4PO_3)_n$, n>1000 Exolit AP422 supplied by Clariant which acts as acid source and blowing agent) and carbon source (pentaerythritol supplied by Acros (PER), Kraft lignin (LIG) supplied by Westvaco (Indulinat) and maize starch (starch) supplied by Acros). Polyethylene glycol (PEG) with a molecular weight of 200 g/mol, used as plasticizer for starch [15], was purchased from Acros.

The experiments were realized on hemp nonwovens (hemp NW) and wool nonwovens (wool NW) with a surface density of 500 g/m^2 and 400 g/m^2 respectively and a thickness of 50 mm for each sample.

Preparation of samples

PLA, APP, PER, LIG and starch blended with PEG were dried under vacuum at 60°C for 24 h to eliminate moisture. The formulations used to make the films are described in *Table I.* The selection of the formulation components and of the different quantities has been discussed in a previous paper [14].

TABLE I. Composition of the different formulations

Formulations	**PLA** (Wt.-%)	**APP** (Wt.-%)	**PER** (Wt.-%)	**LIG** (Wt.-%)	**Starch** (Wt.-%)	**PEG** (Wt.-%)
1	100	0	0	0	0	0
2	60	30	10	0	0	0
3	60	30	0	10	0	0
4	60	30	0	0	6	4

The FR formulations were prepared with a counter-rotating twin screw extruder (L/D=7) (Brabender, Germany) at 180°C (from the feeding zone to the die) at a screw speed of 50 rpm. Compounded polymers samples were pelletized after air cooling.

Films were extruded from pellets using a Rheocord System 40 single screw melt extruder from Haake Buchler Product equipped with a film die with a width of 10 cm. The film was extruded horizontally downward and drawn by chilled rolls *(Figure 1)*. The thickness of the film was adjusted to 250 µm by controlling the takeup speed.

Films were applied on nonwovens using a Darragon molding press at 180°C at a pressure of 1 MPa for 5 min.

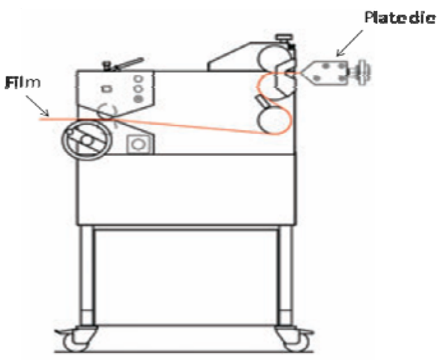

FIGURE 1. Sheet and ribbon haul-off system used for film extrusion

Fire testing

Horizontal flame spread test: Horizontal flame spread test was used to measure the flame spread rate of materials. It is a test developed in our laboratory similar to FMVSS 302 fire test (it does not correspond to any standard). A sample, 150 mm × 35 mm × 3 mm, is placed into the sample holder and was exposed to a burner flame for 10 s. The flame spread was then recorded.

Vertical flame spread test: A laboratory "hybrid" vertical test resulting from the combination of two normalized tests (IN ISO 11925-2 and NF G07-184) has been developed and used to measure the flame spread rate of materials *(Figure 2)*. A sample, 150 mm × 35 mm × 3 mm, is placed into the sample holder and is exposed to the burner flame with an angle of 45° for 10 s. The flame spread was then recorded.

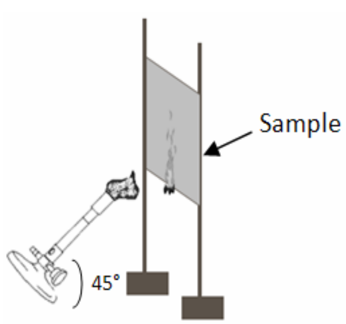

FIGURE 2. Vertical flame spread test

Mass loss calorimeter: FTT (Fire Testing Technology) Mass Loss Calorimeter was used to carry out measurements on samples following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain heat release rate (HRR) rather than employing the oxygen consumption principle. Our procedure involved exposing specimens measuring 100 mm x 100 mm x 3 mm in horizontal orientation. External heat flux of 35 kW/m² was used for running the experiments. This flux corresponds to common heat flux in mild fire scenario [16]. The mass loss calorimeter was used to determine the heat release rate (HRR). When measured at 35 kW/m², HRR is reproducible to within ±10%. The results presented later are averages from three experiments.

Mechanical properties

Tensile strength and elongation at break were obtained with a mechanical tensile tester (MTS 10/ME) according to French standard NF EN ISO 9073-3. The crosshead speed was 100 mm/min. The mechanical parameters were determined from an average of five tested specimens (100 mm × 50 mm in size).

RESULTS AND DISCUSSION

Horizontal and vertical flame spread test

The characteristic data obtained on the horizontal and vertical flame spread tests for virgin and coated hemp nonwovens are summarized in *Table II* and *Table III*. When the untreated nonwoven, without protective intumescent film was exposed to the flame, the sample ignites and tends to propagate flame upwards. In that case, the flame spread rate is 4 cm/min when the sample is in a horizontal position and increases to 30 cm/min for a vertical position of the sample. The addition of a 100% PLA film leads to a slight decrease of the flame spread rate but the sample is totally burnt at the end of the test. In presence of a flame, PLA/APP/PER, PLA/APP/LIG and PLA/APP/starch/PEG films lead to the formation of an intumescent structure which protects the nonwoven and stops the combustion of the sample. This effect is observed for the horizontal and vertical flame spread tests. Hemp NW + PLA FR films are all self-extinguishing.

TABLE II. Characteristic data obtained on the horizontal flame spread test with hemp nonwoven

Material	Char length (cm)	Burning time (s)	Flame spread rate (cm/min)	Observations
Hemp NW	13	195	4	Total burning, smoke
Hemp NW + PLA film	13	205	3,8	Total burning, smoke, melted
Hemp NW + PLA/APP/PER film	-	-	-	Charring, self-extinguishing
Hemp NW + PLA/APP/LIG film	-	-	-	Charring, self-extinguishing
Hemp NW + PLA/APP/starch/PEG film	-	-	-	Charring, self-extinguishing

TABLE III**.** Characteristic data obtained on the vertical flame spread test with hemp nonwoven

Material	Char length (cm)	Burn time (s)	Flame spread rate (cm/min)	Observations
Hemp NW	13	26	30	Total burn, smoke
Hemp NW + PLA film	13	39	20	Total burn, smoke, melted
Hemp NW + PLA/APP/PER film	-	-	-	Charring, self-extinguishing
Hemp NW + PLA/APP/LIG film	-	-	-	Charring, self-extinguishing
Hemp NW + PLA/APP/Starch/PEG film	-	-	-	Charring, self-extinguishing

Mass loss calorimeter

Cone calorimetry is a good technique to evaluate the fire retardant properties of materials in the stage of developing fire [17]. It provides characteristic data such as time to ignition (TTI), heat release rate (HRR) versus time curve and especially its peak value (PHRR).

In the cone calorimeter conditions i.e. at 35kW/m^2, the hemp nonwoven ignites at 15 s and burns for 110 s with a PHRR of 100 kW/m^2 *(Figure 3)*. The composite hemp nonwoven/100%PLA film exhibits a longer TTI than the virgin hemp nonwoven (32 s) but a higher PHRR (177 kW/m^2). During the experiments, some bubbles appear at the surface of the material which corresponds to the melting and then the combustion of the PLA film. The 100% PLA film is totally burnt and there are faded fibers left at the end of the experiment *(Figure 4a).*

When NW is covered with a film, the best result is obtained with the film containing PLA/APP/PER. The composite exhibits a time to ignition of 88 s and a PHRR of 73 kW/m^2. PLA/APP/LIG and PLA/APP/starch/PEG films increase by 50% TTI of the nonwoven and nonwovens treated with these coatings have a PHRR of around 100 kW/m^2.

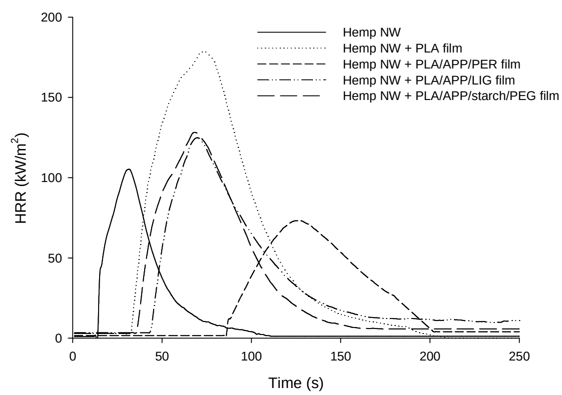

FIGURE 3. HRR as a function of time for samples with hemp nonwoven (external heat flux= 35 kW/m^2)

In the case of nonwovens coated with the PLA FR film, the beginning of the HRR curve can be assigned to the reaction of the intumescent additive which contains nitrogen and carbon [18]. Thermal degradation of ammonium polyphosphate leads to the release of ammonia and to the formation of polyphosphoric acid [19]. Ammonia acts as a blowing agent and the reaction of polyphosphoric acid with the carbon source leads to the development of a foamed charred layer which protects the underlying textile. At the end, the degradation of the structure leads to the formation of a carbonaceous residue *(Figure 4b*).

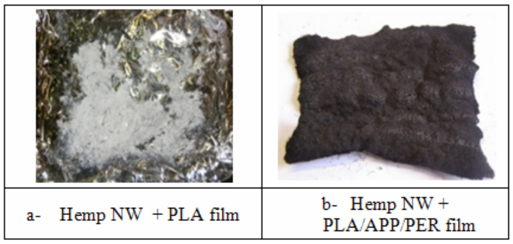

FIGURE 4. Residues of hemp NW + PLA film and hemp NW + PLA FR film after a test carried out with the cone calorimeter (35 kW/m^2)

Mechanical properties

Tensile strength and elongation at break of the initial hemp nonwoven and the coated hemp nonwovens are shown respectively in *Figure 5* and in *Figure 6*. The untreated nonwoven is a flexible material with poor mechanical strength. There is very little cohesion between the fibers forming the nonwoven so the material easily tears. The untreated nonwoven has a tensile strength at break value of 34 N. The coating with the pure PLA film leads to an increase in the tensile strength value to 390 N against about 170 N for PLA FR films. This difference may be explained by the presence of “defaults” in the film due to the poor adhesion between the fillers (starch, APP) and PLA [20]. Moreover, the virgin nonwoven shows an elongation at break of 50% because of the destruction of the nonwoven mechanical structure during the test. The decrease of the elongation at break value of coated nonwovens is caused by the rigidity of the PLA FR films and proves that films enhance mechanical reinforcement. PLA FR films significantly improve the tensile strength of the nonwovens which is interesting for building applications.

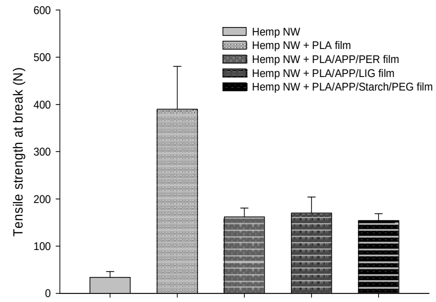

FIGURE 5. Tensile strength at break of hemp nonwoven and coated hemp nonwoven

Validation of the method to other materials

Such PLA FR films have also been tested on another nonwoven. *Table IV* shows the characteristic data obtained with the vertical flame spread test for wool nonwovens. The same phenomenon is observed with wool nonwovens as for hemp nonwovens. The combustion of wool nonwoven is total with a flamespread value of 39 cm/min. The coating of the virgin nonwoven with 100%PLA film leads to a decrease in the flamespread to 26 cm/min still with a full combustion but the appearance of ignited drops. It is necessary to coat the wool nonwoven with PLA FR films to improve the fire retardant properties and this way to obtain a self-extinguishing material.

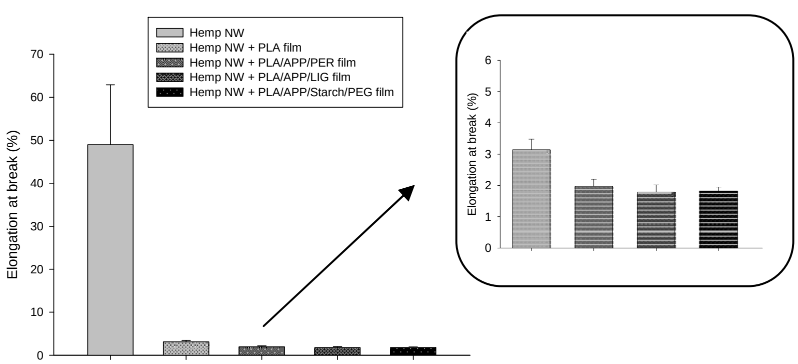

FIGURE 6. Elongation at break of hemp nonwoven and coated hemp nonwoven

TABLE IV. Characteristic data obtained on the vertical flame spread test with wool nonwoven

Material	Burn length (cm)	Burn time (s)	Flame spread rate (cm/min)	Observations
Wool nonwoven	13	20	39	Total burning, smoke, melted
Wool NW + PLA film	13	30	26	Total burning, smoke, melted, ignited drops
Wool NW + PLA/APP/PER film	-	-	-	Charring, self-extinguishing
Wool NW + PLA/APP/LIG film	-	-	-	Charring, self-extinguishing
Wool NW + PLA/APP/starch/PEG film	-	-	-	Charring, self-extinguishing

CONCLUSIONS

This work has shown that intumescent films based on renewable resources can be used to bring flame retardancy to nonwovens composed of hemp or wool. FR properties of hemp nonwovens coated with PLA FR films have been evaluated. Horizontal and vertical flame spread measurements have shown no combustion when PLA FR films are coated on nonwovens. Self-extinguishable materials were obtained. The cone calorimetry analysis shows that the presence of a PLA FR film leads to the formation of a protective layer at the surface of the sample and improves the reaction to fire of nonwovens. Moreover, PLA FR films improve the tensile strength of nonwoven. The main advantage is that this process is very flexible, easy and quick. It can be applied to all types of textile material (whatever the thickness or the composition of the nonwoven) to improve their fire retardant properties and also, different intumescent formulations based on thermoplastic materials can be used.

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