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A New Wood Surface Flame-Retardant Based on Poly-m-Aramid Electrospun Nanofibers

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A New Wood Surface Flame-Retardant Based on Poly-*m*-Aramid Electrospun Nanofibers

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Abstract

Poly(*meta*-phenylene isophtalamide) (PMIA) was processed *via* electrospinning to provide nanofibrous membranes with randomly and aligned fibers. Mechanical performance of such membranes was evaluated, applying a normalization procedure that takes into account the peculiar morphology of such complex substrate where voids can sum up to almost 80% of the sample volume. Random and aligned fib~~b~~ers membranes are applied onto wood panels to test their fire resistance in cone calorimetry when coated in polyaramidic thin nanofiber ~~membranes~~mats. Tests highlighted that random fibers provide a better fire protection, increasing Time to Ignition and decreasing the Fire Performance Index. Another important parameter affecting the performance is the adhesive system used to apply the nanofibers onto wood that is able to significantly modify the fire performance of the polyaramidic-coated wood panels.

Presented at Time Of Polymers and Composites 2018

INTRODUCTION

Wood is an obvious green and sustainable material: it comes from renewable resources, is biodegradable and in the last years, the environmental concerns and the interesting properties possessed by this material led to a new interest in its application in a wider range of fields [1]. When wood is used on its own, it displays excellent strength/density ratio, thermal insulation, acoustic, and antiseismic properties, and it is thus widely used as a structural component for building purposes. Moreover, wood or some of its cellulosic derivatives can be applied to produce composite materials [2], where wood fibers or chips are dispersed in a polymeric matrix. Owing to its environmental friendliness, its attractiveness in many fields besides building structures is thus growing more and more. However, one of the most relevant limits to wood application, both in the structural and in the design/leisure field, either as bulk structural component or as composite reinforcement, is the flammability: in this context, fire retardancy is an essential element of safety, and one of the key challenges to increase wood use. Indeed, when exposed to moderately high temperatures (230–250°C) [3], the ligneous fraction, which is mainly composed of hemicellulose, cellulose, and lignin, decomposes producing heat, smoke, and soot [4]. When a fire ignites and propagates, most of the deaths are caused by inhalation of smoke and toxic combustion gases (mainly carbon monoxide), while the exposure to the heat, derived from fires, can cause serious injuries. The yearly effects of fire-related accidents are extremely high and, besides the humans casualties, which are obviously the most significant damage in such events, the overall global economic costs amount to tens of billions of dollars, that is, approximately 1% of global annual gross domestic product (GDP) [5, 6]. Thus, there are great economic, sociological, and legislative interests to produce materials with greatly reduced fire risk.

The issue with wood flammability dates back thousands of years, when the ancient Greek Historian Herodotus (484 BC – 425 BC) reported the even earlier attempt of the Egyptians to retard timber flammability by using potassium aluminium sulfate (alum); slightly later Romans tried to improve the process by adding vinegar to the mixture [7]. Since then the subject has been extensively investigated and much more is presently known in terms of fire safety and flame retardancy to help improving the wood fire performance [8]. The knowledge of the combustion process guides also the theoretical aspects of the flame retardant (FR) design, helping in identifying the best suitable methods to reach the highest efficiency in the wood/wood-composites FR modification. Since combustion is a gas phase reaction, which involves a fuel source and oxygen in a

multistep sequence composed of preheating, volatilization/decomposition, combustion, and propagation [9], FR can act on one or more of these steps to reduce the fire risk. FR systems are intended to inhibit or to stop the thermal decomposition and combustion process. Depending on their nature, they can interfere with the various processes involved in material combustion (heating, pyrolysis, ignition, and propagation of thermal degradation), acting both physically or chemically. The mode of action of FRs can follow different paths, such as the reduction of the flammable gas generated through the formation of a char layer (acting as physical barrier) or the separation of the comburent from the combustible. Moreover, additives can also limit the heat released during the degradation process in order to minimize fire propagation. One important parameter, that has to be taken into account when choosing a FR, is its chemical nature since it can display a non-negligible impact on the toxicity of the fumes released during material combustion [10]. FRs, when degraded, can release toxic agents (such as carbon monoxide) or even decompose to produce toxic products at high-T, increasing the total amount of dangerous gases released [11]. As an example, according to Registration, Evaluation, and Authorization of Chemicals (REACH) registry, only recorded FR that positively passed tests concerning emissions and possible end-of-life issues can be used [12]. The new regulations and the need to overcome health and environmental concerns lead to an increasing interest about the introduction of innovative, nontoxic and alternative FRs [13, 14].

The fire retardancy can be addressed with different approaches, such as: (1) the use of intrinsic flame-resistant materials, (2) the addition of FRs to the bulk of the materials, or (3) the application of coatings with a FR and/or intrinsic flame-resistant materials [15–17]. When dealing with bulk wood, however, only two approaches are available to deal with the flammability issues, since no bulk modification can be attained: wood impregnation with FR solutions or surface treatments of the final object with coatings. With the first approach, a complete and homogeneous distribution of FR within the wood mass is assured, but this technique also presents some downsides. Wood impregnation requires a solution, which implies dealing with solvent disposal at the end of the process; moreover, the treated product must undergo a drying step, to remove the solvent excess, prior its final application which, together with the long impregnation times, makes the overall procedure highly time consuming. Finally, the overall sustainability of the material can also be negatively affected by these procedures. Hence a surface coating, able to retard the flame development, appears a more efficient and eco-friendly approach for bulk wood.

In this frame, poly(*meta*-phenylene isophtalamide) - PMIA (NOMEX, DuPont) is a well-known fire resistant material [18, 19]: beyond being an inherently flame resistant and self-extinguishing polymer, PMIA fibers, in the form of fabric (155 g/m^2 each, four layers required), have been reported as flame shielding coating [17]. Furthermore in a recent study, the effect of PMIA nanofibrous mats as FR on carbon fiber reinforced polymer (CFRP) materials was reported [18]. Considering the promising results obtained, the potential flame-retardant effect of a micrometric thick superficial layer of PMIA nanofibers applied onto wood is thus been investigated in this article. It is worth noting that PMIA nanofibrous membranes, easily obtainable *via* electrospinning technique, offer a wide range of possible further modification: as already proved for other polymers, they could also act as nano-reinforcement [19] or could be tuned to provide additional structural and functional properties to the object onto which they are applied [20]. Hence, the present work reports an innovative approach to flame-shield bulk wood through the superficial application of a thin and lightweight PMIA electrospun nanofibrous sheet. Electrospun PMIA membranes with different thickness (about 12–15 and 24–26 g/m^2), and fibers orientation have been produced and superficially applied onto wood panels with different gluing systems. Furthermore, the difference in the fibers alignment could significantly modify the fire response of the final material, when used as outer coating: indeed, membranes based on randomly oriented fibers would guarantee a isotropic behavior to the coating layer, while the aligned ones are far better behaving in a single direction, while the cross-sectional behavior might suffer from the poor cohesion of the fibers. First the evaluation of the membrane intrinsic mechanical properties has been carried out, applying an innovative approach to the evaluation of the mechanical performance of the nanofibrous mats. Then, the fire behavior of such materials has been studied through cone-calorimeter tests in order to assess the effect of the thin PMIA layer on the flammability of the wood samples.

EXPERIMENTAL

Materials

Poly(*m*-phenylene isophtalamide) (PMIA) and lithium chloride (LiCl) (Sigma-Aldrich) were dried before use. They were treated in oven at 110°C for 3 and 24 h, respectively. *N*,*N*-dimethylacetamide (DMAc) (Sigma-Aldrich) was treated according to previously reported procedures [21]. The distillation was performed at 64°C and 18 mmHg under nitrogen flow. After distillation, the solvent was stored under nitrogen over molecular sieves (4 Å) before use. Vinyl glue (Vinavil) and a polyurethane paint (PPG Deltron D800/D841 2/1 vol.) were used in order to apply the PMIA membranes onto the wood surface. All other materials were used as received without further purification.

Nanofibrous Mats Production

Membranes were obtained accordingly to a published procedure [18]. Polymeric solutions were prepared dissolving LiCl in DMAc under magnetic stirring and mild warming (40°C) for at least 2 h, and then PMIA was added and the system stirred at 70°C until formation of homogeneous solutions.

PMIA nanofibrous mats were produced *via* electrospinning technique using a Spinbow® electrospinning machine equipped with four 5 mL syringes connected to needles (0.84 mm internal diameter) with Teflon tubing. Fibers were collected on a rotating drum covered with polyethylene (PE)-coated paper in a sheet with 30 × 40 cm lateral dimension for enough time to guarantee about 80 µm thickness and with the aim of achieving either completely randomly oriented fibers (PMIA-R) or highly aligned fibers (PMIA-A). In the first case, fibers were collected at a slow rotation of the drum (about 60 rpm), in the latter a speed of 2,500 rpm was applied to guarantee a prevailing alignment. Nanofibrous mats were finally washed with distilled water and dried at 70°C in order to remove LiCl salt residue, as previously reported [22, 23]; thickness of washed fibers membranes decreases down to about 50 µm.

Wood Samples Preparation for Fire Resistance Tests

Two kinds of samples were prepared covering wood panels with washed and dried electrospun PMIA mats with both randomly arranged (PMIA-R) and prevalently aligned (PMIA-A) fibers. In order to apply PMIA onto the wood surface, a polyurethane paint (PPG Deltron D800/D841 2/1 vol.) and common vinyl glue (Vinavil) were used. In all cases, for each batch three 100 × 100 × 2 mm specimens were produced, covered with the adhesive system and the nanofibers; upon membrane application, they were pressed with a roller in order to promote adhesion; finally, they were dried at 70°C for 20 min. With the first adhesive system, three batches of samples were prepared: reference wood panels covered on both sides with painting (WP), panels with painting where PMIA-R membranes were applied on top in order to completely cover the edges onto the surface of the wood (WG-PMIA-R), and analogue panels with the membrane based on aligned fibers (WP-PMIA-A). When using vinyl glue as adhesive system, two batches were produced: reference wood panels with vinyl glue on both sides (WG) and panels with vinyl glue and the random membranes (WG-PMIA-R), of which an example is displayed in Fig. 1.

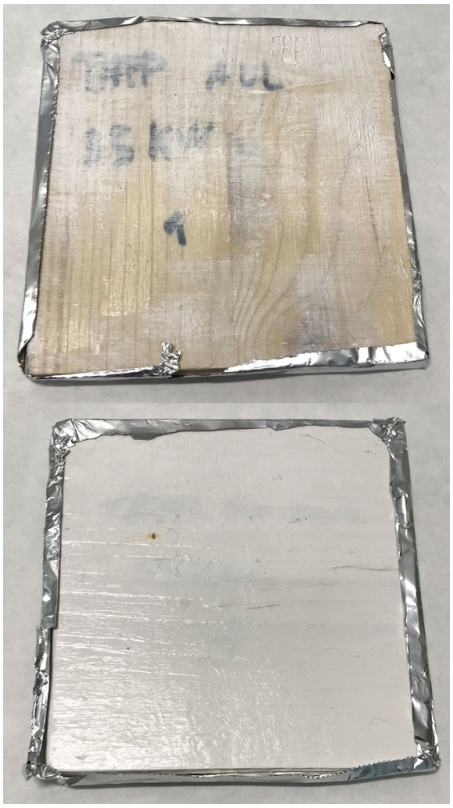

Figure 1 WG (up) and WG-PMIA-R (down) samples as prepared for the cone-calorimeter tests.

Characterization

In order to investigate the morphological aspects of the obtained nanofibers, micrographs were taken with a Scanning Electron Microscope (SEM) Phenom ProX. Energy dispersive X-rays analysis (EDX, Phenom ProX) was used to confirm the absence of chloride ions in nanofibrous membranes after the washing treatment. Stress-strain tests were performed using a Remet TC10 Instron-type dual column table frame machine framing the nanofibrous membranes with paper prior testing them. At least five different samples per ~~each~~ batch were measured to guarantee statistical significance of the recorded data. Flame behavior studies were performed using an oxygen consumption calorimeter (Fire Testing Technology Limited FFT Cone Calorimeter). The tests were performed at an incident Heat flux of 35 kW/m^2 in horizontal orientation using the cone shaped heater and specimens of 100 × 100 mm2. Three samples per formulation were tested. The cone calorimeter provides the following parameters: Heat Release Rate (HRR), calculated from the oxygen consumption, Time To Ignition (TTI), Time of Flame out (TOF), Average Heat Release Rate (HRR as a function of time), peak of Heat Release Rate (pHRR), Total Heat Release (THR), and Time to pHRR (TTP). Experimental data were reproducible within ±10%. The Average HRR is correlated to the heat released in a room where the flammable materials are not all ignited at the same time. Two other parameters were calculated from the measured cone-calorimeter data as they have been accepted as representative of the polymer combustion behavior in a real fire: Fire Performance Index (FPI), calculated as pHRR/TTI, and Fire Growth Rate Index (FIGRA) calculated as pHRR/TTP.

RESULTS AND DISCUSSION

Nanofibrous Membranes Production and Characterization

PMIA can be solubilized in the presence of inorganic salts (LiCl) and can be easily processed to produce nanofibrous membranes. The production of nanofibers *via* electrospinning starting from PMIA solution has been already approached and optimized [23], and nanofibers can be obtained with a significantly different extent of orientation both by playing on the processing and environmental parameters [18] or, as in the present case, by simply varying the rotation speed of the rotating drum used for accumulating and recovering the nanofibers. The difference in the fibers alignment could significantly modify the fire response of the final material, when used as outer coating: indeed, membranes based on randomly oriented fibers would guarantee a isotropic behavior to the coating layer, while the aligned ones are far better behaving in a single direction, while the cross-sectional behavior might suffer from the poor cohesion of the fibers. A first characterization of the obtained membranes (12–15 g/m^2), in order to assess their overall orientation, has been carried out *via* SEM microscopy: micrographs reported in Fig. 2 clearly highlight that it is possible to obtained randomly oriented fibers (PMIA-R) (Fig. 2a) or highly aligned fibers (PMIA-A) (Fig. 2b) just by varying the rotation speed of the recovering rotating drum, at least at the outer layer of the membrane, which is the one observed with this technique.

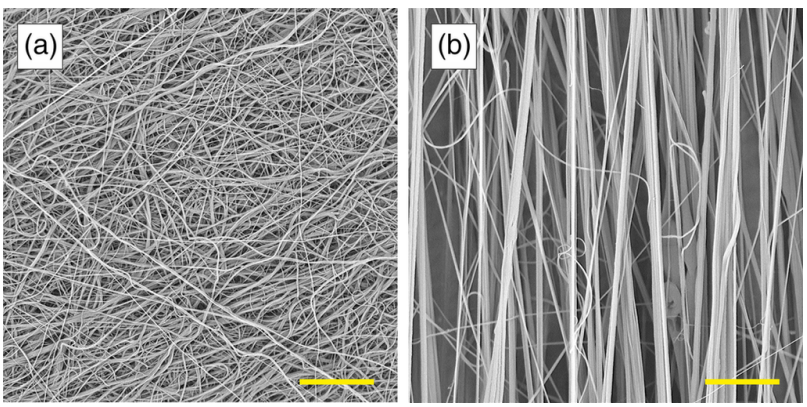

Figure 2 SEM images of washed PMIA nanofibrous mats: (a) random oriented, (b) aligned. Scale bar: 10 µm, 5,000×.

Since membranes with a significantly different orientation have been already observed to provide a significantly different mechanical behavior [18], with the aim of evaluating the actual mechanical performance both PMIA-R and PMIA-A nanofibrous mats have been mechanically characterized by means of tensile tests. Since these membranes are quite thin and might be difficult to handle during tensile testing operations, mat samples were fixed to a paper frame with glue to prevent the sliding of fibers and for a correct and safe fixing of the specimen on the machine grips [24]. Once the raw data have been recorded, the processing to evaluate the results raises some question about using the classic normalization approach commonly applied for bulk materials in order to determine the mechanical parameters typical of such membranes. Nanofibrous mats are, indeed, porous materials characterized by a high fraction of voids (up to 80% by volume). As a consequence, mat thickness evaluation is very tricky: the measure is strongly affected by the instrumentation used, since its value depends on the pressure applied to the specimen during measurement.

The classical approach used for stress calculation (σ, in MPa) requires the specimen thickness (t, in mm) for evaluating the cross-section area (A, in mm^2) normal to the force direction, as shown by the following *Eq.* (1):

$$\sigma = \frac{F}{A} = \frac{F}{wt} \tag{1}$$

where F is the force (in N) and w the specimen width (in mm). It is clear that any variation in the thickness value significantly affects σ, being F the force recorded by the load cell during tensile test. Moreover, even if

a correct and standardized evaluation of the actual thickness could be carried out, the nanofibrous mat would be wrongly considered as a bulk material and the calculation would still include some (a lot of) empty volume that does not effectively contributes to the mechanical response of the materials during stress application. The wrong assumption that the voids among nanofibers are filled by the polymeric material will finally lead to a significant underestimation of σ and of all the related properties (i.e., elastic modulus, σ at break, toughness).

Recently, the authors proposed a new way for σ evaluation [24], based on the measurement of simple and reliable parameters, as shown by the following *Eq*. (2):

$$\sigma = \rho \frac{F}{m} L \tag{2}$$

where ρ is the material density (in mg/mm^3, 1.38 mg/mm^3 for PMIA), m is the specimen mass (in mg), and L is the specimen initial length (in mm). The specimen mass is measurable after the execution of tensile tests without particular precautions, except that care has to be taken to recover all the specimen fragments. The mass evaluation is insensitive with respect to both the peculiar scale used, provided a sufficient sensitivity of the instrument (min. 0.1 mg, better 0.01 mg), and the operator, thus resulting in highly reliable values.

In Fig. 3, the elastic modulus of PMIA nanofibrous mats, evaluated upon raw data treatment according to *Eq*. (2), are represented. It is worth to point out that these values are obtained averaging the results of at least five different samples.

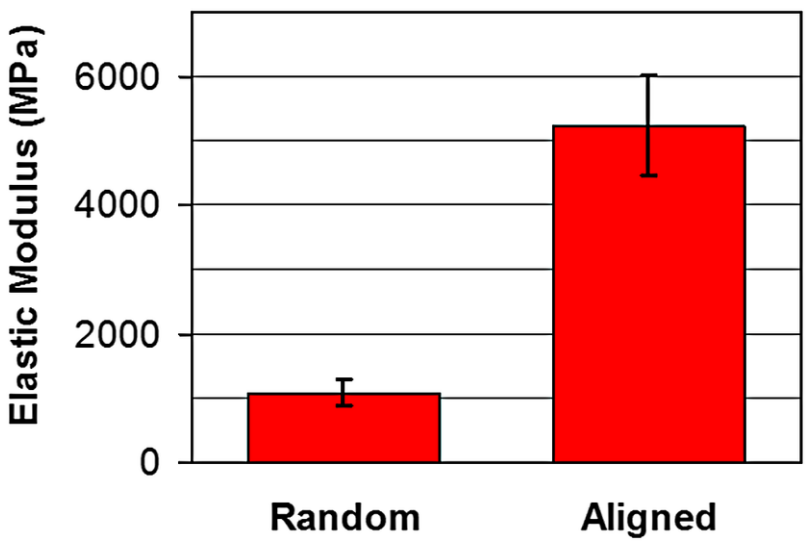

Figure 3 Elastic modulus of random and aligned PMIA nanofibrous mats derived from the σ calculation as per Eq. [2].

The elastic modulus of the aligned nanofibrous mat (measured along the preferentially oriented nanofiber direction) is significantly higher than the random one, about five times. This behavior is explained considering that in the aligned sample almost the entirety of the fibers are already oriented along the applied force direction, while in the random samples, only a fraction of fibers falls in this condition, thus in this case, the overall network of the fibers is responsible for the resulting mechanical properties. On the other side, it was not possible to carry out measurements on the oriented sample, when specimens were cut in the perpendicular direction with respect to fibers orientation: the handling of the sample was so poor, that not even the procedure of fixing the membrane onto the paper frame was possible. This behavior suggests an overall high extent of fibers alignment, that prevent a significant mechanical performance in the directions other that the main fiber axis.

Testing of Fire Behaviour

It is interesting to investigate how materials with the exact same composition and characteristics, but with different fiber morphology, might react in a fire event.

Possible differences in FR effect due to different nanofibers orientation were thus investigated using PMIA-R and PMIA-A samples. Initially, in order to apply the PMIA mats onto the wood surface, a polyurethane paint was used. Three different kind~~s~~ of samples, using polyurethane paint as adhesive system, were produced: reference wood panels with painting on both sides (WP), panels covered with painting and with the aligned fibers membrane (WP-PMIA-A) and panels covered with painting and with the randomly oriented fibers membrane (WP-PMIA-R). The flame behavior of the samples was assessed by cone-calorimeter, which is one of the most effective bench-scale methods for studying the flammability properties of materials [25]. In cone-calorimetric tests a sample of standard dimension is exposed to a heat source in the presence of a continuous sparkling source and the reaction to such an environment is studied. The most relevant and important data monitored during cone-calorimeter analysis are: HRR, reported in kilowatts per meter square, which defines the irradiated thermic power released by the sample per square meter; Total Heat Release (THR), reported in millijoule per square meter, which is the total heat released by the sample, from ignition to extinction; TTI, reported in seconds, it represents the time span between the start of the sample exposition to the heating source, in the presence of an ignition system, and the moment when the first flame is detected. Moreover, two additional parameters were calculated, derived from the measured values. First, the FPI, reported in kilowatts per meter square seconds and which provides an overall assessment of the fire safety of a material in the cone calorimeter test, has been calculated as the ratio between the maximum value of the Heat Release Rate (pHRR) and the TTI. According to the work of Petrella [26], such a parameter provides some indication for the ability of the investigated material to propagate the fire, in particular the predisposition of the material to flashover. The flashover is a possible consequence of a fire ignition, which requires specific conditions to occur, such as an intense and instantaneous amount of heat (high pHRR, short TTI) and is obviously an additional threat in the case of fire. The second is fire growth ~~RATE~~rate index (FIGRA), reported in kilowatts per meter square seconds, and is a helpful parameter in ranking the materials in terms of potential fire safety since it combines the most intense heat release (pHRR) and time needed to achieve it (Time To Peak, TTP). FIGRA is a good descriptor of the burning behavior of structural products.

Tests were carried out with a heat flow of 35 kW/m^2 (about 650°C) [3], which can be roughly compared to a small-scale fire, and at 50 kW/m^2, comparable to a big-scale fire (about 800°C). The instrument can work with a heat flow ranging between 5 and 100 kW/m^2: higher irradiation levels give better reproducibility, more clearly defined ignition, and shorter measurement times, but correspond to more fully developed fires. Often a smaller irradiation level better fits the fire protection goals, since it accounts for the material behavior in a condition close to the starting of a fire, showing its ability to ignite and propagate the flame. The main data monitored during the test at 35 kW/m^2 are reported in Table 1, and curve representative of the average behavior of the WP, WP-PMIA-R, and WP-PMIA-A samples is reported in Fig. 4a (HRR/time) and 3B (THR/time).

Table 1 Flame behavior of wood panels covered with paint, without or with aligning and random PMIA coatings as determined by cone-calorimeter measurements.

Sample	HRR[1] (kW/m²)	THR[2] (MJ/m²)	TTI[3] (s)	pHRR 1[4] (kW/m²)	TTP 1[5] (s)	pHRR 2[4] (kW/m²)	TTP 2[5] (s)	FPI[6] (kW/m²s)	FIGRA [7] (kW/m²)
Neat WP 35 kW	91 ± 2	50,4 ± 0,7	46 ± 6	154 ± 9	74 ± 2	203 ± 11	265 ± 5	3,4 ± 0,4	2,1 ± 0,1
WP-PMIA-A 35 kW	79 ± 9	42,9 ± 4	57 ± 8	159 ± 18	76 ± 8	180 ± 17	274 ± 17	2,9 ± 0,6	2,1 ± 0,4
WP-PMIA-R 35 kW	72 ± 1	39,0 ± 1	63 ± 9	153 ± 13	81 ± 5	160 ± 7	257 ± 5	2,5 ± 0,4	1,9 ± 0,2

[1]Heat Release Rate (HRR) is the irradiated thermic power released by the sample per square meter.

[2]Total Heat Release (THR) is the total heat released by the sample, from ignition to extinction.

[3]Time to ignition (TTI) is the time required for the first-flame detection, after the sample exposition to the heating source, in the presence of an ignition system.

[4]Peak Heat Release Rate (pHRR) is the most intense heat release.

[5]Time to Peak (TTP) time to achieve pHRR.

[6]Calculated as pHRR/TTI.

[7]Calculated as pHRR/~~t~~TTPpHRR.

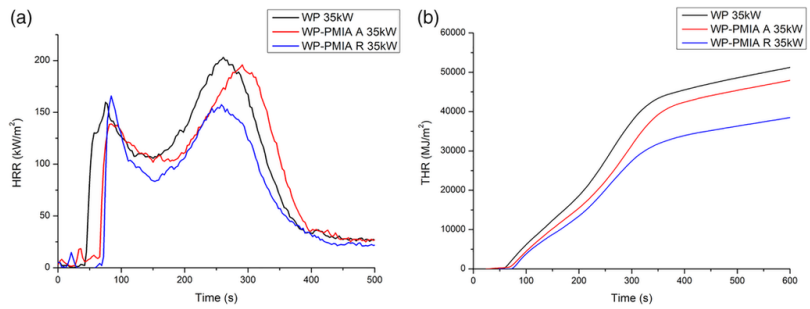

Figure 4 HRR (a) and THR (b) profiles measured by cone-calorimeter at 35 kW/m^2 of the investigated wood panels with the paint: WP (black), WP-PMIA-R (blue), and WP-PMIA-A (red). Curves displayed in the figure were selected to best fit the average values calculated for each batch of specimens.

The experimental data (Table 1 and Fig. 4) show an interesting effect of the PMIA mat presence concerning, in particular, the TTI value: the samples protected with PMIA nanofibers need longer time to ignite compared to the WP samples. This result is really promising since the delay was obtained using just a small amount of nanofibrous material (12–15 g/m^2). In a real fire scenario, the escape-time plays a fundamental role in the survival possibilities and therefore the longer the ignition time, the better the material. Moreover, there is also a clear decrease of HRR, THR, and pHRR, with a consequential reduction of the FPI, upon application of a thin nanofibrous polyaramidic outer layer. Even if wood is not renowned as an explosive material, FPI reduction is always a good index in terms of fire prevention. Comparing WP-PMIA-A and WP-PMIA-R samples, a clear difference in flame resistance of the specimens, due to the different fibers orientation, is observed. The samples containing randomly oriented fibers display a more consistent improvement in all the key factors previously reported in particular a reduction in pHRR, FPI, and FIGRA. Such a behavior can be explained by considering that, when a strong heat flux is applied to wood, decomposition of the wood panel can occur, and flammable gases are consequently generated. These gases accumulate below the nanofibrous mat and fibers start to detach from the wood surface to form bubbles rich in flammable gas, which, when broken, promote a burst in the fire due to the entrapped flammable gases. Such a heat burst can be a dangerous feature in terms of ability to propagate the fire to adjacent materials. During fire propagation, a poor adhesion of nanofibers can trigger a faster detachment of the membrane from the wood surface and the consequent formation of more flammable bubbles. This behavior is confirmed also by the visual appearance of blistering on the PMIA coating during the cone-calorimetric tests, which, upon bubbles explosion, leads to a flame boost. Thus, the better flame behavior obtained for WP-PMIA-R samples is probably due to a better failure behavior (higher ultimate stress) of the nanofibrous mats during the heating and bubble formation. In particular, aligned fibers display worse mechanical properties in perpendicular direction considering the fibers axis orientation. This lack in mechanical properties of aligned nanofibers can induce, when the samples are exposed to a heat, a lower resistance of the bubble gas retention, triggering the flame burst in shorter times.

The same kind of tests was performed heating the samples with analogue composition as those previously discussed, at a heat flow of 50 kW/m^2. Once again reference wood panels with paint (WP), panels with painting and the membrane with aligned fibers (WP-PMIA-A) and panels with painting and the membrane with randomly oriented fibers (WP-PMIA-R) were investigated. The main obtained data are reported in Table 2 and in Fig. 5a (HRR/time) and 5B (THR/time).

Table 2 Flame behavior of wood panels covered with paint, without or with aligning and random PMIA coatings as determined by cone-calorimeter measurements.

Sample	HRR[1] (kW/m^2)	THR[2] (MJ/m^2)	TTI[3] (s)	pHRR 1[4] (kW/m^2)	TTP 1[5] (s)	pHRR 2[4] (kW/m^2)	TTP 2[5] (s)	FPI[6] (kW/m^2s)	FIGRA[7] (kW/m^2)
Neat WP 50 kW	107 ± 2	51,9 ± 1	17 ± 6	209 ± 9	43 ± 2	260 ± 11	206 ± 5	12,5 ± 0,4	4,9 ± 0,1
WP-PMIA-A 50 kW	104 ± 9	50,0 ± 4	22 ± 8	223 ± 18	51 ± 8	234 ± 17	203 ± 16	10,5 ± 0,6	4,4 ± 0,4
WP-PMIA-R 50 kW	99 ± 1	47,1 ± 1	23 ± 9	201 ± 12	47 ± 5	223 ± 7	209 ± 5	8,9 ± 0,4	4,3 ± 0,2

[1]Heat Release Rate (HRR) is the irradiated thermic power released by the sample per square meter.

[2]Total Heat Release (THR) is the total heat released by the sample, from ignition to extinction.

[3]Time to ignition (TTI) is the time required for the first flame detection, after the sample exposition to the heating source, in the presence of an ignition system.

[4]Peak Heat Release Rate (pHRR) is the most intense heat release.

[5]Time to Peak (TTP) time to achieve pHRR.

[6]Calculated as pHRR/TTI.

[7]Calculated as pHRR/ tTTPpHRR.

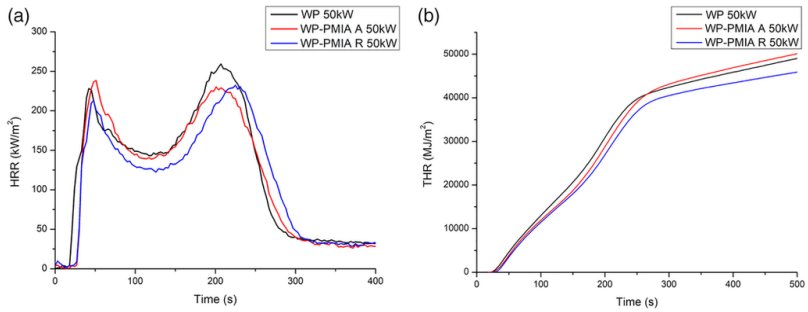

Figure 5 HRR (a) and THR (b) profiles measured by cone-calorimeter at 50KW of the investigated wood panels with the paint: WP (black), WP-PMIA-R (blue), and WP-PMIA-A (red). Curves displayed in the figure were selected to best fit the average values calculated for each batch of specimens.

From the results obtained from the samples tested at 50 kW/m^2 only a slight delay in TTI, compared to the reference WP specimens is now observed. WP-PMIA-A and WP-PMIA-R both display just a small decrease in HHR, THR, pHRR, and FPI. Furthermore, comparing WP-PMIA-A and WP-PMIA-R data, only minor modifications are detected between the two samples: their flame behavior at 50 kW/m^2 condition are very similar and comparable effects are obtained. This lack in fire resistance of the samples can be due to the harsh condition used for the test. Probably PMIA nanofibrous mats are not thick enough to provide a consistent shield action to withstand developed fire condition as proved by the very fast formation of bubble on the wood surface, detected in all samples by visual inspection during the experiment execution.

The previously obtained results seem to suggest the hypothesis that paint does not produce well adhered coating between the nanofibrous PMIA mat and the wood panel. The paint used to apply the membrane to the wood surface penetrates the wood porosity and does not stay onto the surface. Indeed, when measured, it was observed that the overall thickness of the panel is not affected at all by paint application, and this ends up leading to a poor adhesion of the PMIA membrane. If the membrane is not able to fully adhere to wood ist will not be able to shield the surface, prevent the flammable gas blisters production and keep all the evolved gases entrapped within the PMIA mat. For this reason, instead of polyurethane paint, vinyl glue (Vinavil) was thus applied as adhesive. In this case, the adhesive layer does not penetrates in the wood porosity allowing to the nanofibers to soak in the adhesive layer creating a complete composite structure.

Since from the previous study the best results were obtained for the samples WP-PMIA R, for this kind of test only random PMIA mats of increased thickness (24–26 g/m^2) were used. The prepared samples were named WG, as reference, and WG-PMIA-R. A heat flow of 35 kW/m^2 was used to carry out cone-calorimeter tests, since the previous analysis at 50 kW/m^2 did not highlighted remarkable differences between the different samples tested, and nevertheless the applied conditions would be far from the safety and protective effect that is the purpose of the present work. Data obtained in the WG and WG-PMIA-R cone-calorimetric measurements are reported in Table 3 and Fig. 6.

Table 3 Flame behavior of wood panels covered with paint, without or with aligning and random PMIA coatings as determined by cone-calorimeter measurements.

Sample	HRR[1] (kW/m^2)	THR[2] (MJ/m^2)	TTI[3] (s)	pHRR[4] (kW/m^2)	TTP[5] (s)	FPI[6] (kW/m^2s)	FIGRA[7] (kW/m^2)
Neat WG	68 ± 1	34 ± 0.1	77 ± 8	297 ± 20	160 ± 14	3,9 ± 0,7	1,9 ± 0,3
WG-PMIA-R 35KW	92 ± 1	42 ± 1	133 ± 6	369 ± 21	203 ± 11	2,8 ± 0,3	1,8 ± 0,1

[1]Heat Release Rate (HRR) is the irradiated thermic power released by the sample per square meter.

[2]Total Heat Release (THR) is the total heat released by the sample, from ignition to extinction.

[3]Time to ignition (TTI) is the time required for the first flame detection, after the sample exposition to the heating source, in the presence of an ignition system.

[4]Peak Heat Release Rate (pHRR) is the most intense heat release.

[5]Time to Peak (TTP) time to achieve pHRR.

[6]Calculated as pHRR/TTI.

[7]Calculated as pHRR/tTTPpHRR.

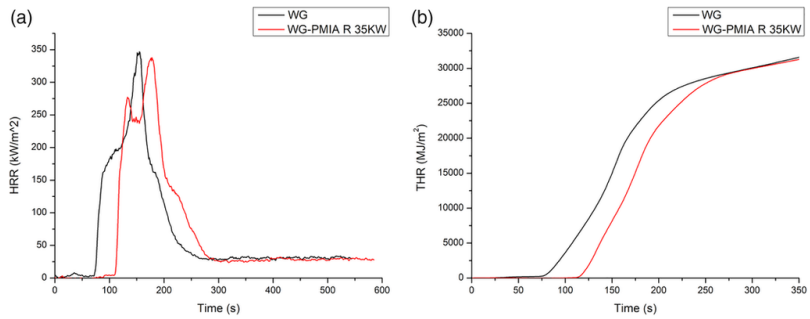

Figure 6 HRR (a) and THR (b) profiles measured by cone-calorimeter at 35 kW of the investigated wood panels with the vinyl glue: WG (black) and WG-PMIA-R (red). Curves displayed in the figure were selected to best fit the average values calculated for each batch of specimens.

The data reported in Table 3 show a remarkable effect of the nanofibrous PMIA mat presence concerning, in particular, the TTI value: samples covered with PMIA nanofibers need longer time to ignite compared to the neat WG samples. The ignition delay observed for the samples covered with nanofibers was approximately 60 s if compared with the samples ~~Neat~~ WG, thus TTI is almost doubled. Concerning HRR, THR, and pHRR values, a slight increase is registered in the coated samples and this effect can be due to the presence of the different gluing systems (a flammable material), that when ignited, might further contribute to the amount of material able to burn. FIGRA index of the covered samples shows a small decrease compared to the neat samples accounting for an overall sign that the coated composite is definitely less prone to propagating a fire. As explained before, correlation of THR, which in the present case is almost unaffected, and FPI leads to a good assessment of the material predisposition to propagate a fire. Analyzing FPI parameter of WG-PMIA-R, it shows a decrease of the 30% compare to Neat WG, due to the presence of PMIA superficial nanofibers. Hence, it is demonstrated that the simple addition of the micrometric outer membrane is able to reduce the fire propagating tendency of wood and accounts for a higher safety of final material. The increase in the time required to ignite the sample can be due to the better adhesion of the nanofibrous mat to the wood using of glue instead of paint. All the glue-coated samples display a good PMIA skin adhesion, with no blistering during the cone-calorimetric tests and this might be responsible for the good TTI performance. It has indeed been reported that the coating permeability strongly affect the fire performance, and the good adhesion to the substrate might promote a sealing action of the porous wood surface, which is more efficient, then the results obtained in the case of polyurethane paint. In order to better point out substantial differences between WP/WG and the respectively PMIA coated samples (WP-PMIA-R and WG-PMIA-R samples), in Fig. 7 some of the most relevant cone calorimeter data are reported as percent variation of the PMIA covered sample compared to the relative neat one (taken as 100% reference value, irrespective of the absolute values scored).

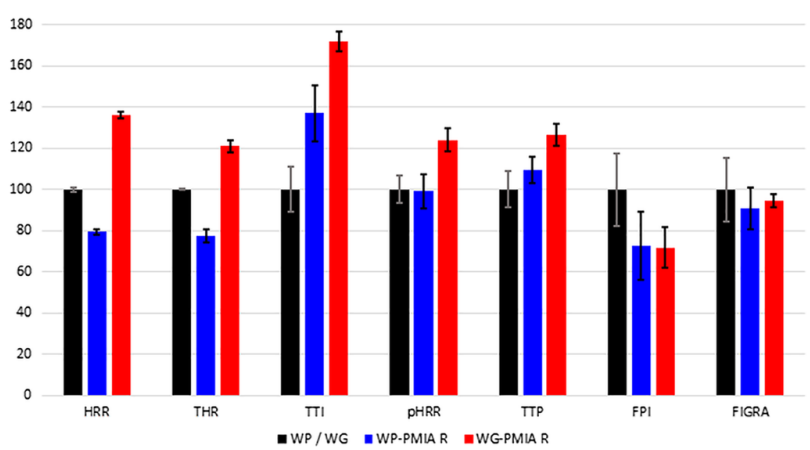

Figure 7 Fire behavior significant data, HRR, THR, TTI, pHRR, FPI, and FIGRA, relative to WP/WG (black), WP-PMIA-R (blue), and WG-PMIA-R (red), expressed as % variation with respect to the covered wood (WP or WG), with the relative standard deviation. (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The more interesting result obtained, as reported above, concerns the TTI, which almost doubles for WG-PMIA-R. but is also substantially modified in the case of WP-PMIA-R. Similar improvement in TTI was also attained on polyurethane foams [26], coated with four PMIA fabric layers (155 g/m^2 each). The final object thickness is, however, undesirably affected since commercial PMIA fabrics with micrometric fiber diameter were used while PMIA nanofibrous mat achieved the same TTI enhancement using less than a twentieth of FR material weight (a maximum of 24–26 g/m^2 instead of 620 g/m^2).

All the discussed results confirm the possibility to use polyaramidic nanofibrous coatings as a smart way to modify the flame behaviour, even for objects which are already finished and are characterized by peculiar shape a geometry. PMIA membrane, given their lightness and thinness (24–26 g/m^2), are able to achieved exceptional flame behaviour without significantly modifying the object dimensions. The easy pliability, convenient when covering complex surfaces, and the fire-retardant behaviour, obtained with the simple approach described before, lead the way to a new approach in the fire retardancy field. The present work demonstrated how the flame behaviour is dependent to some of main factors influencing the performance such as the fire response in different heat flux conditions, the type of polymeric matrix effect of the paint, the membrane alignment (random or highly aligned) and thickness of the mats used, giving a more complete frame of the full potential of PMIA nanofibers.

CONCLUSIONS

Poly(*meta*-aramidic) nanofibers were produced and their mechanical behaviour was assessed applying a new approach to evaluate the mechanical performance of the nanofibrous mat: this new method takes into account the peculiar morphology and the voids typical of nanofibrous aggregates when normalizing the Force to provide the stress value and allows better and finer data calculation. This procedure highlighted some significant difference in the performance of aligned and randomly oriented fibers.

Such difference was also observed to affect the flame behaviour of such membranes when applied onto wood: the randomly oriented ones are better performing due to their isotropic behaviour able to entrap flammable gases. Moreover, the importance of the gluing system was also highlighted: a glue that has a better adhesive effect helps delaying the ignition, while the scarce adhesion of the membrane prevents the coating from fully exert its flame-retardant action.

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