Improvement of Thermal Stability and Flame Retardancy of Beech Wood Fibers Using Steam Explosion and Phosphorylation Reaction

Liangsong Cheng,[a,b,c] Tianyi Zhan,[b] Henri Vahabi,[d] Isabelle Ziegler-Devin,[c] Karina Antoun,[c] Zehui Ju,[b,c] Laurent Chrusciel,[c] Xiaoning Lu,[b] and Nicolas Brosse [c,*]

An environmentally friendly approach was studied for improving the fire retardancy of beech wood using a steam explosion process coupled with a phosphorylation reaction. Raw beech, steam-exploded, or bleached wood was subjected to phosphorylation employing etidronic acid (HEDP) and urea, and the resulting chemical composition and thermal behavior were analyzed using techniques such as elemental analysis, Fourier transform infrared spectroscopy, ionic chromatography, and pyrolysis combustion flow calorimetry. The thermal performance of beech wood underwent significant enhancements after the steam explosion treatment combined with soda impregnation. It resulted in a striking reduction in heat release rates (HRR), especially its peak (pHRR) and time-to-pHRR (T_{pHRR}) values (from 139.5 W/g and 365 °C to 40 W/g and 247 °C) and an increase in residue from 10.5% to 41.3%. The results demonstrate that the process created a self-extinguishing and non-flammable material that exhibited noteworthy flame retardancy improvement.

Contact information: a: College of Art and Design, Huainan Normal University, 232038, Anhui, Huainan, China; b: College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China; c: Laboratoire d'Etude et de Recherches sur le Matériau Bois–Green Process for Wood (LERMaB-GP4W), Faculté des Sciences et Technologies, Université de Lorraine, Vandœuvre-lès-Nancy, France; d: Université de Lorraine, CentraleSupélec, LMOPS, F-57000 Metz, France;
* Corresponding author: nicolas.brosse@univ-lorraine.fr

INTRODUCTION

One of the main disadvantages of wood and lignocellulosic materials is their low thermal stability and high flammability, which have a negative impact on their use, especially in construction and transportation sectors (Kim *et al*. 2018). To overcome these limitations, it is common to introduce various chemical reagents by surface modification (Mohanty *et al*. 2001; Khoathane *et al*. 2015). In recent decades, among all the flame retardants used for wood protection, cellulose phosphorylation reaction using a variety of phosphates or phosphoric acid reagents is being increasingly considered due to environmental and health concerns (Illy *et al*. 2015). Researchers have applied phosphorylation reagents in combination with nitrogenous molecules, and the synergic effect of nitrogen and phosphorous has been shown to improve the thermal properties of lignocellulosic fibers (Laoutid *et al*. 2009; Alongi *et al*. 2013). Urea is one of the most common sources of nitrogen. It acts not only as an expander agent but also as a catalyst in the process. It has been shown in several studies that phosphorylation of cellulose

decreased its thermal stability but improved carbonization and modified the composition of the released gases with formation of gases less rich in carbon (Inagaki *et al*. 1976; Suflet *et al*. 2006: Rol *et al*. 2020).

Steam explosion is considered an effective physico-chemical pretreatment method because of the short retention time of the cooking period (a few minutes) and its lower energy consumption compared to conventional processes (Ziegler-Devin *et al*. 2021). Steam explosion is a thermochemical pretreatment that breaks down the structural components of lignocellulose through a hydrolytic step with pressurized hot water and by mechanical breakage caused by shear forces due to water expansion (Jacquet *et al*. 2015). Steam explosion provides a strong alteration of the lignocellulose structure (*i.e.*, non-cellulosic polysaccharides hydrolysis, increase of porosity, degradation of the lignin seal) and a decrease of its recalcitrance. It was originally used for hardboard production at the industrial scale (Masonite process) (Boehm 1930) and was later experimented for the decomposition of wood fiber materials such as paper and paperboard pulp. It has been used in the pretreatment (prior to biotechnological transformations) of a wide range of lignocellulosic materials such as pineapple leaf (Cherian *et al*. 2010), kenaf bast (Jiang *et al.* 2017), wheat straw (Liu *et al*. 2017), corncob (Liu *et al*. 2020), oil palm (Marques *et al.* 2020), wood (Simangunsong *et al.* 2018), and hemp (Sauvageon *et al.* 2017), *etc*. The treatment reduced the content of non-cellular compounds that bind to the fibrous aggregates. Through steam explosion pretreatment, eco-friendly building blocks from oil palm mesocarp fiber were obtained (Marques *et al*. 2020). Furthermore, it was also used for homolytic and heterolytic cleavage of β-ether linkages in hardwood lignin (Obame *et al*. 2019) and the xylan recovery of beech wood (Simangunsong *et al*. 2018). According to reports by Martha *et al.* (2020), steam explosion might improve the flame retardancy of hemp fibers to some extent without adding flame retardants, but the effect was not significant. However, the effect of steam explosion treatment on the thermal behavior of wood has never been studied in detail, to the authors' knowledge.

Thus, as part of the authors' research program on the development of steam explosion, a steam explosion pretreatment process was used to degum bast fibers, such as ramie and hemp, and to produce fine fibers suitable for textile applications (Sauvageon *et al*. 2017; Segovia *et al*. 2021) and micro/nanofibrillated cellulose from *Eucalyptus globulus* barks (Nader *et al*. 2022a,b). In the present work, steam exploded and/or phosphorylated beech sawdust was produced and analyzed for chemical composition, thermal properties, and fire resistance.

EXPERIMENTAL

Materials and Methods
Materials

Beech wood sawdust (W) with a moisture content of 6% used in this study was obtained from Lorraine Forest (France) collected in 2019. Etidronic acid (60% aqueous solution), urea (solid crystalline 99.3%), sodium hydroxide (99.2%), sodium chloride (80%), and glacial acetic acid (99.8%) were acquired from Sigma-Aldrich.

Methods

Steam explosion pretreatment

The beechwood sawdust (W) was first mixed with 20 wt% sodium hydroxide solution for 15 h at 25 °C with a liquid/solid ratio of 1.5:1. Then, the impregnated biomass was sent to the steam explosion reactor and mixed with the steam at 200 °C and maintained for 8 min. With pressure release followed by filtration, the exploded beech sawdust fiber (ExW) was finally acquired by washing and drying the solid phase.

Bleaching process

The bleaching process was completed *via* an acid-chlorite delignification treatment at 80 °C for 2 h. The formula of the mixture used for bleaching was exactly as follows: each 1.5 g of dry fiber contains 1 g glacial acetic acid, 1 g sodium chloride, and 125 mL deionized water. With bleaching followed by cooling, the bleached exploded fibers (BExW) were recovered through fully removing the impurities by adequate flushing until neutral pH value.

Phosphorylation

A total of 10 g fibers (W, ExW, or BExW) were immersed in a mixed solution for 1 h. The composition of the solution was 100 mL deionized water, 30 g urea, and 13 g etidronic acid (HEDP) for every 10 g dry fiber. Vacuum suction filtration was used to remove the redundant solutions. After oven drying at 60 °C for 12 h, the grafted fibers were obtained as oven-dried under vacuum as a cooking step. Phosphorylated biomass, denoted as PW, PExW, and PBExW, respectively, was finally obtained by thoroughly washing with distilled water and vacuum filtration. All the fibers were naturally dried in a fume hood.

Characterizations

Chemical composition

The acid insoluble lignin and monosaccharide content were determined according to the standards TAPPI T222-om-11 (2011) and Sluiter *et al.* (2008). The procedure was as follows: Sulphuric acid (72%, 1.5 mL) was added to 0.175 g of sample, and the mixture was shaken in a water bath at 30 °C for 1 h. The sample was stirred every 15 min with a glass rod to fully mix the contents in sulphuric acid solution. Afterwards, 42 mL of deionized water was added, and the sample was hydrolyzed at 120 °C for 1 h. The sample was filtered under vacuum through a crucible and washed with ultrapure water until 100 mL of filtrate was obtained. The samples were autoclaved, filtered, and dried at 105 °C. The mass of the solid residue was recorded as the weight of lignin, and the dried residue was weighed to obtain the lignin content. The monosaccharide content of the filtrate was analyzed in the liquid fraction by high performance anion exchange chromatography with a pulsed amperometric detector HPAE-PAD (ICS-3000 Dionex) (Thermo Fisher Scientific, Waltham, MA, USA).

Phosphorus and nitrogen elemental contents

Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the amount of elemental phosphorus in the samples. In this experiment, 0.15 g of fiber was mixed with 5 mL of nitric acid solution in a glass tube. The prepared tubes were then placed in the mineralization apparatus (Ultra wave system) for 20 min to achieve a temperature of 230 °C and a pressure of 11 MPa. The samples were then left at this temperature and pressure for a further 10 min until fully mineralized. Thereafter, the

mineralized sample was diluted with 50 mL of deionized water and filtered prior to analysis.

The gas chromatograph (Thermo Finnigan Flash EA 112 series, Thermo Finnigan, San Francisco, CA, USA) was used for the elemental analysis of nitrogen, carbon, oxygen, and hydrogen. The sample to be analyzed (1.5 mg) is burnt at high temperature (1000 °C) in the presence of tungstic anhydride under an oxidizing atmosphere for 15 s. This decomposition produces CO_2, H_2O, SO_2, and NO_x, which are reduced in the presence of copper in the nitrogen gas. These gaseous products were then analyzed by gas chromatography. The results were recorded and analyzed by the software "Eager 300" (Eager Systems, V1.0, San Jose, CA, USA), which directly calculates the percentage of each element in the compound.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

FTIR spectroscopy was performed using an attenuated total reflectance−Fourier transform infrared (ATR-FTIR) spectrometer Nicolet 6700 (Thermo Nicolet Corporation, Waltham, MA, USA). The various specimens were ground to a powder of 40 to 60 mesh prior to testing and oven-dried at 103 °C for 48 h to obtain a moisture content of less than 4% with a resolution of 2 cm^{-1} and a test range of 4000 to 400 cm^{-1}.

Thermogravimetric analysis (TGA)

The thermal stability of the fibers was evaluated in nitrogen from 30 to 800 °C with a heating rate of 10 °C/min using a STA 409 PC/PG (NETZSCH, Gerätebau, Germany) instrument. All the fibers were ground into powder before testing (0.4 to 0.5 mm, moisture content of 3%). The TG/derivative thermogravimetric (DTG) curves were obtained by recording the data as a function of weight loss with temperature. Temperature at maximum rate of weight loss (T_{max}), maximum rate of weight loss (R_{Tmax}), and the residue at 750 °C were obtained from the measurements.

Pyrolysis combustion flow calorimetry

The flammability of fibers was investigated by a pyrolysis combustion flow calorimeter (PCFC) according to the standard ASTM D7309 (2007) anaerobic pyrolysis – method A. In this case, heat rate release (HRR) as a function of the temperature was recorded to get the combustion curves of different biomass.

Preliminary flame test on fibers

A non-conventional flame test was conducted to evaluate the flame behavior of the fibers. The fibers were glued onto an aluminum box (around 2 cm length and 0.3 to 0.5 cm diameter) with one open face and held vertically before being ignited by a lighter. This strategy permits the fibers self-extinguishment (absence of flame spreading) to be assessed, such as flame propagation with or without stable residue, no flame propagation (self-extinguishing), and no flame take (non-flammable).

RESULTS AND DISCUSSION

Chemical Composition

According to a procedure previously published by Nader *et al*. (2022a), raw beech sawdust (W), exploded wood (ExW), and exploded and bleaching wood (BExW) were

obtained in turn. Phosphorylated wood (PW), phosphorylated exploded wood (PExW), and phosphorylated bleached exploded wood (PBExW) were generated from W, ExW, and BExW, respectively, using etidronic acid (HEDP) and urea, based on a reported method (Moussa *et al*. 2020). The chemical composition of each sample in terms of lignin, simple sugars (after hydrolysis), P%, and N% are given in Table 1.

As shown in Table 1, the composition of W in this study was similar to that of beech wood previously described (glucose ≈ 46%, lignin ≈ 23%, and xylose ≈ 14.5%) (He *et al*. 2020). The significant increase of the glucose content in ExW is explained by the hydrolysis and removal of non-cellulosic components. As expected, a sharp decrease of lignin was observed after bleaching in BExW from 12.5% to 2.18%.

The presence of N (1.15% to 2.71%) and P (2.07% to 4.66%) after thorough washings of PW, PExW, and PBExW revealed the efficient grafting of etidronic acid and urea on the fibers (see Table 1).

Table 1. Chemical Compositions Obtained from HPAEC PAD Analysis and N and P Contents from Elemental Analysis

Fibers	Lignin (%)	Glc (%)	Xyl (%)	Rha (%)	Ara (%)	Gal (%)	Man (%)	GalUA (%)	GlcUA (%)	N (%)	P (%)
W[a]	22.76	46.12	14.46	0.78	1.03	1.90	0.62	1.15	0.19	0	0
ExW[b]	12.50	75.28	10.75	0.05	0.36	0.20	0.33	0.10	0.08	0	0
BExW[c]	2.18	80.62	11.21	0.03	0.42	0.07	0.15	0.12	0.00	0	0
PW[d]	16.62	36.30	12.00	0.61	0.60	1.20	0.41	0.88	0.15	1.58	2.07
PExW[e]	10.01	54.12	7.13	0.00	0.08	0.07	0.21	0.10	0.11	2.71	4.66
PBExW[f]	0.90	72.57	9.70	0.00	0.00	0.00	0.20	0.21	0.17	1.15	3.32

a Raw wood (Beech wood);
b Exploded wood;
c Bleached exploded wood;
d Phosphorylated wood;
e Phosphorylated exploded wood;
f Phosphorylated bleached and exploded wood

FTIR analysis

Figure 1 gives FTIR spectra of all the samples studied. In accordance with the chemical compositions previously reported (Table 1), a decrease of the signals assigned to lignin (at 830 cm^{-1}, 1020 cm^{-1}, 1420 cm^{-1}, 1460 cm^{-1}, 1506 cm^{-1}, and 1735 cm^{-1}) and hemicelluloses (at 1231 cm^{-1} and 1367 cm^{-1}) was observed for ExW and BExW. Additional peaks at 830 cm^{-1} and 1655 cm^{-1} for PW, PExW, and PBExW, were assigned to the vibration absorption peak of P-O-C group (Ghanadpour *et al*. 2015) and the C=O group of urea (Fuensanta *et al*. 2020) respectively. This observation is consistent with the results of P% and N% analysis given in Table 1.

Thermal stability and flammability

Thermal degradation of non-grafted and grafted samples was analyzed at a microscale using thermogravimetric analysis TG and DTG (Table 2) and by PCFC analysis (Table 2 and Fig. 2).

As expected, a significantly different thermal behavior was observed between phosphorylated and non-phosphorylated samples. Indeed, the T_{max} (temperature at maximum weight loss rate) of phosphorylated samples (PW, PExW, and PBExW) was ≈ 80 °C lower than that of the corresponding non-phosphorylated samples and the R_{Tmax} (maximum weight loss rate) decreased 23.9%, 9.45%, and 7.1% respectively. They also

displayed lower heat release rates (HRR), especially its peak (pHRR) and time-to-pHRR (t_{pHRR}) values, as well as ΔH and higher residue percentage (Fig. 5) indicating that the flame retardancy was significantly improved after phosphorylation treatment. Additionally, in accordance with thermogravimetric analysis, T_{pHRR} of phosphorylated samples dropped from ~ 360 °C to ~ 250 °C. This is because of the well-known flame-retardant effect of phosphorylated fibers in the combustion process, which promotes the decarboxylation and dehydration reactions of the fibers, accelerating the charring process of the fibers (Nourry *et al.* 2016; Antoun *et al.* 2022).
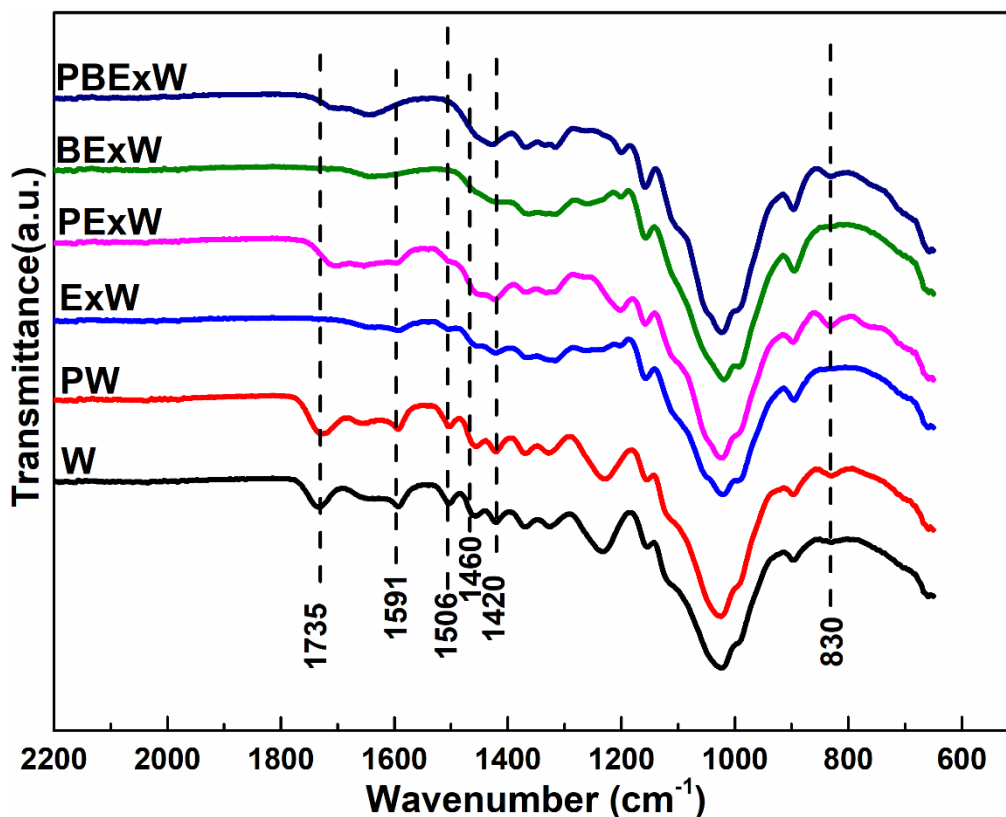

Fig. 1. ATR-FTIR spectra from 2200 cm^{-1} to 400 cm^{-1}

It is worth mentioning that a comparison of W with ExW showed that steam explosion dramatically increased the amount of final residue. A significant decrease of R_{Tmax} (R_{Tmax} = 9.47%/min and 1.32%/min for W and EW, respectively) and an increase of T_{max} (from 345 °C to 373 °C for W and ExW, respectively) was observed. The same trend was obtained for PExW compared to PW. As a result, PExW isolated after successive steam explosion and phosphorylation treatment displayed enhanced thermal stability and flame retardancy. These changes after steam explosion cannot be fully explained by the modifications in the chemical composition and decrease in lignin content as shown in Table 1, but confirmed previously published work by Moussa *et al.* (2020). Steam explosion could cause modifications in the lignin network like recondensation reactions (Obame *et al.* 2019), which then could impact its thermal stability and the ability of the fiber components to interact.
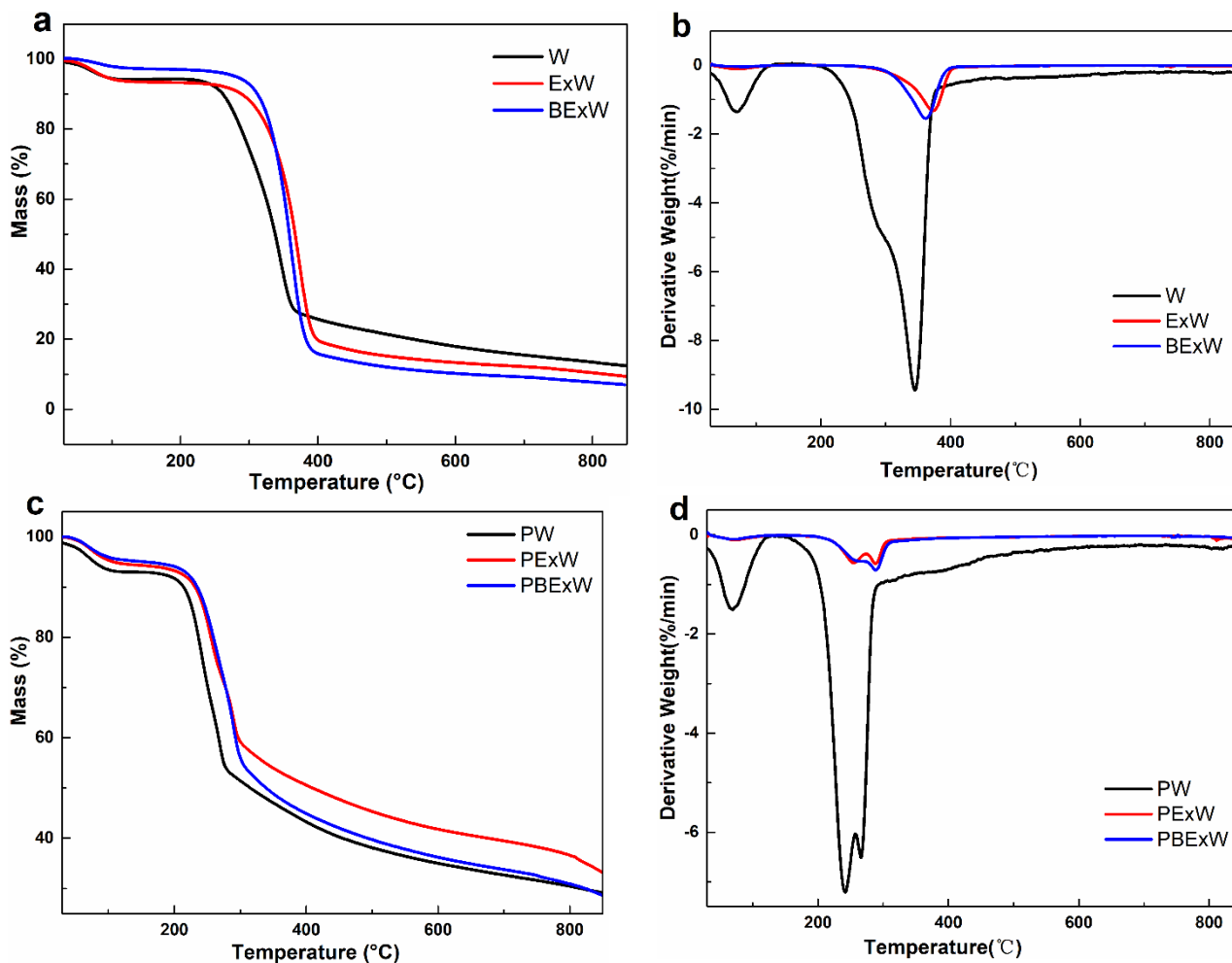
Fig. 2. TG/DTG graph for non-phosphorylated fibers(a), (b) and phosphorylated fibers(c), (d)

Table 2. Main Data from TG and PCFC Analysis

Fibers	T_{max} (°C)	R_{Tmax} (%/min)	Residue (%)	pHRR (W/g)	T_{pHRR} (°C)	THR (kJ/g)	Δh^1 (kJ/g)
W	345	9.47	14.54	139.5	365	11.9	13.3
ExW	373	1.32	11.47	182.5	365	11.1	12.3
BExW	361	1.55	8.52	201.5	355	12.1	12.9
PW	266	7.19	31.57	86.5	265	6.3	8.9
PExW	288	0.53	38.30	40	247	2.7	4.6
PBExW	288	0.71	34.21	52.5	263	3.0	5.0

[1]Calculated from THR and residue fraction (*f*) according to equation Δh = THR/ (1 - *f*)
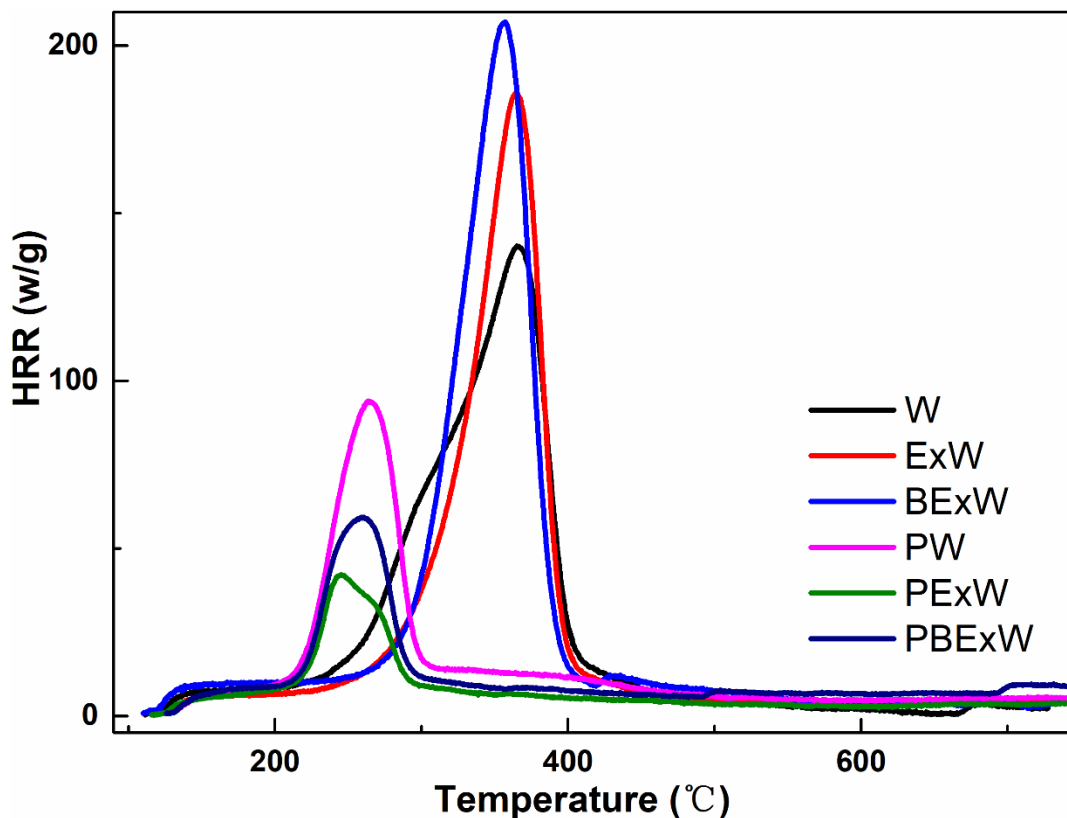
Fig. 3. Heat release rate curve for different fibers

To investigate the combustion behavior of fibers in different processes, they were subjected to flammability tests. In contrast to W, ExW, and BExW, the absence of flame propagation and self-extinguishing was observed for the phosphorylated samples.

CONCLUSIONS

1. It was shown that the steam explosion treatment resulted in a radical change in the thermal decomposition of beech wood with a large increase in T_{max} and a strong reduction in R_{Tmax}.

2. The thermal stability and fire-retardant properties of the exploded wood could be significantly improved by a phosphorylation reaction in the presence of urea. Because of its easy implementation, eco-friendly production, and low cost, it is hoped that this approach will open new opportunities in the field of advanced composites.

ACKNOWLEDGMENTS

of Huainan Normal University. LERMAB is supported by the French National Research Agency through the Laboratory of Excellence ARBRE (ANR-12- LABXARBRE-01).

Competing Interests

The authors have no relevant financial interests to disclose. All authors read and approved the final manuscript.

REFERENCES CITED

Alongi, J., Colleoni, C., Rosace, G., and Malucelli, G. (2013). "Phosphorus-and nitrogen-doped silica coatings for enhancing the flame retardancy of cotton: Synergisms or additive effects?," *Polymer Degradation and Stability* 98(2), 579-589. DOI: 10.1016/j.polymdegradstab.2012.11.017

Antoun, K., Ayadi, M., El Hage, R., Nakhl, M., Sonnier, R., Gardiennet, C., Le Moigne, N., Besserer, A., and Brosse, N. (2022). "Renewable phosphorous-based flame retardant for lignocellulosic fibers," *Industrial Crops and Products* 186, article ID 115265. DOI: 10.1016/j.indcrop.2022.115265

ASTM D7309 (2007). "Standard test method for determining flammability characteristics of plastics and other solid materials using microscale combustion calorimetry," ASTM International, West Conshohocken, PA, USA.

Boehm, R. M. (1930). "The Masonite process," *Industrial and Engineering Chemistry* 22(5), 493-497. DOI: 10.1021/ie50245a019

Cherian, B. M., Leão, A. L., de Souza, S. F., Thomas, S., Pothan, L. A., and Kottaisamy, M. (2010). "Isolation of nanocellulose from pineapple leaf fibres by steam explosion," *Carbohydrate Polymers* 81(3), 720-725. DOI: 10.1016/j.carbpol.2010.03.046

Fuensanta, M., Khoshnood, A., Rodríguez-Llansola, F., and Martín-Martínez, J. M. (2020). "New waterborne polyurethane-urea synthesized with ether-carbonate copolymer and amino-alcohol chain extenders with tailored pressure-sensitive adhesion properties," *Materials* 13(3), article 627. DOI: 10.3390/ma13030627

Ghanadpour, M., Carosio, F., Larsson, P. T., and Wågberg, L. (2015). "Phosphorylated cellulose nanofibrils: A renewable nanomaterial for the preparation of intrinsically flame-retardant materials," *Biomacromolecules* 16(10), 3399-3410. DOI: 10.1021/acs.biomac.5b01117

He, Q., Ziegler-Devin, I., Chrusciel, L., Obame, S. N., Hong, L., Lu, X., and Brosse, N. (2020). "Lignin-first integrated steam explosion process for green wood adhesive application," *ACS Sustainable Chemistry & Engineering* 8(13), 5380-5392. DOI: 10.1021/acssuschemeng.0c01065

Illy, N., Fache, M., Menard, R., Negrell, C., Caillol, S., and David, G. (2015). "Phosphorylation of bio-based compounds: the state of the art," *Polymer Chemistry* 6(35), 6257-6291. DOI: 10.1039/C5PY00812C

Inagaki, N., Nakamura, S., Asai, H., and Katsuura, K. (1976). "Phosphorylation of cellulose with phosphorous acid and thermal degradation of the product," *Journal of Applied Polymer Science* 20(10), 2829-2836. DOI: 10.1002/app.1976.070201017

Jacquet, N., Maniet, G., Vanderghem, C., Delvigne, F., and Richel, A. (2015). "Application of steam explosion as pretreatment on lignocellulosic material: A

review," *Industrial & Engineering Chemistry Research* 54(10), 2593-2598. DOI: 10.1021/ie503151g

Jiang, W., Han, G., Zhou, C., Gao, S., Zhang, Y., Li, M., Gong, Y., and Via, B. (2017). "The degradation of lignin, cellulose, and hemicellulose in kenaf bast under different pressures using steam explosion treatment," *Journal of Wood Chemistry and Technology* 37(5), 359-368. DOI: 10.1080/02773813.2017.1303514

Khoathane, M. C., Sadiku, E. R., and Agwuncha, C. S. (2015). "Surface modification of natural fiber composites and their potential applications," in: *Surface Modification of Biopolymers*, John Wiley & Sons, Inc., Hoboken, NJ, USA, pp. 370-400.

Kim, N., Dutta, S., and Bhattacharyya, D. (2018). "A review of flammability of natural fibre reinforced polymeric composites," *Composites Science and Technology* 162, 64-78. DOI: 10.1016/j.compscitech.2018.04.016

Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.-M., and Dubois, P. (2009). "New prospects in flame retardant polymer materials: From fundamentals to nanocomposites," *Materials Science and Engineering: R: Reports* 63(3), 100-125. DOI: 10.1016/j.mser.2008.09.002

Liu, B., Li, T., Wang, W., Sagis, L. M. C., Yuan, Q., Lei, X., Cohen Stuart, M. A., Li, D., Bao, C., Bai, J., *et al.* (2020). "Corncob cellulose nanosphere as an eco-friendly detergent," *Nature Sustainability* 3, 448-458. DOI: 10.1038/s41893-020-0501-1

Liu, Q., Lu, Y., Aguedo, M., Jacquet, N., Ouyang, C., He, W., Yan, C., Bai, W., Guo, R., and Goffin, D. e. (2017). "Isolation of high-purity cellulose nanofibers from wheat straw through the combined environmentally friendly methods of steam explosion, microwave-assisted hydrolysis, and microfluidization," *ACS Sustainable Chemistry & Engineering* 5(7), 6183-6191. DOI: 10.1021/acssuschemeng.7b01108

Marques, F. P., Silva, L. M. A., Lomonaco, D., Rosa, M. d. F., and Leitão, R. C. (2020). "Steam explosion pretreatment to obtain eco-friendly building blocks from oil palm mesocarp fiber," *Industrial Crops and Products* 143, article ID 111907. DOI: 10.1016/j.indcrop.2019.111907

Mohanty, A., Misra, M., and Drzal, L. T. (2001). "Surface modifications of natural fibers and performance of the resulting biocomposites: An overview," *Composite Interfaces* 8(5), 313-343. DOI: 10.1163/156855401753255422

Moussa, M., El Hage, R., Sonnier, R., Chrusciel, L., Ziegler-Devin, I., and Brosse, N. (2020). "Toward the cottonization of hemp fibers by steam explosion. Flame-retardant fibers," *Industrial Crops and Products* 151, article ID 112242. DOI: 10.1016/j.indcrop.2020.112242

Nader, S., Brosse, N., Daas, T., and Mauret, E. (2022). "Lignin containing micro and nano-fibrillated cellulose obtained by steam explosion: Comparative study between different processes," *Carbohydrate Polymers* 290, Article ID 119460. DOI: 10.1016/j.carbpol.2022.119460

Nader, S., Guzman, F., Becar, R., Segovia, C., Fuentealba, C., Peirera, M., Mauret, E., and Brosse, N. (2022). "Lignocellulosic micro and nanofibrillated cellulose produced by steam explosion for wood adhesive formulations," *Journal of Renewable Materials* 10(2), 263-271. DOI: 10.32604/jrm.2022.017923

Nourry, G., Belosinschi, D., Boutin, M. P., Brouillette, F., and Zerrouki, R. (2016). "Hydrophobization of phosphorylated cellulosic fibers," *Cellulose* 23, 3511-3520. DOI: 10.1007/s10570-016-1071-2

Obame, S. N., Ziegler-Devin, I., Safou-Tchima, R., and Brosse, N. (2019). "Homolytic and heterolytic cleavage of β-ether linkages in hardwood lignin by steam explosion," *Journal of Agricultural and Food Chemistry* 67(21), 5989-5996. DOI: 10.1021/acs.jafc.9b01744

Rol, F., Sillard, C., Bardet, M., Yarava, J. R., Emsley, L., Gablin, C., Léonard, D., Belgacem, N., and Bras, J. (2020). "Cellulose phosphorylation comparison and analysis of phosphorate position on cellulose fibers," *Carbohydrate Polymers* 229, article ID 115294. DOI: 10.1016/j.carbpol.2019.115294

Sauvageon, T., Lavoie, J.-M., Segovia, C., and Brosse, N. (2017). "Toward the cottonization of hemp fibers by steam explosion – Part 1: Defibration and morphological characterization," *Textile Research Journal* 88(9), 1047-1055. DOI: 10.1177/0040517517697644

Segovia, C., Hedri, M., Huot, H., Zigler-Devin, I., Liu, C., Tang, Y., Qiu, R., Morel, J. L., and Brosse, N. (2021). "Industrial ramie growing on reclaimed ion-adsorption rare earth elements mine tailings in Southern China: Defibration and fibers quality," *Waste and Biomass Valorization* 12, 1-6. DOI: 10.1007/s12649-021-01442-w

Simangunsong, E., Ziegler-Devin, I., Chrusciel, L., Girods, P., Wistara, N. J., and Brosse, N. (2018). "Steam explosion of beech wood: Effect of the particle size on the xylans recovery," *Waste and Biomass Valorization* 11, 625-633. DOI: 10.1007/s12649-018-0522-4

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL/TP 510-42618), National Renewable Energy Laboratory, Denver, CO, USA.

Suflet, D. M., Chitanu, G. C., and Popa, V. I. (2006). "Phosphorylation of polysaccharides: New results on synthesis and characterisation of phosphorylated cellulose," *Reactive and Functional Polymers* 66(11), 1240-1249. DOI: 10.1016/j.reactfunctpolym.2006.03.006

TAPPI T222 om-11 (2011). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA, USA.

Ziegler-Devin, I., Chrusciel, L., and Brosse, N. (2021). "Steam explosion pretreatment of lignocellulosic biomass: A mini-review of theorical and experimental approaches," *Frontiers in Chemistry* 9, article 705358. DOI: 10.3389/fchem.2021.705358