UNIVERSITY OF FORESTRY – SOFIA
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UTILIZATION OF LIGNOCELLULOSIC AGRICULTURAL RESIDUES FOR OBTAINING MULTIFUNCTIONAL COMPOSITE MATERIALS

ABSTRACT OF A DISSERTATION

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Field of higher education: 5. Technical Sciences
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The dissertation has a total volume of 205 pages. The text uses 15 formulas, 16 tables and 67 figures. The list of references includes 285 sources. A total of 5 applied scientific contributions and 6 applied contributions were made. The work is structured in an introduction, 3 chapters and a conclusion. The numbering of the chapters in the abstract corresponds to those of the dissertation.

The dissertation defence will be held on 23.09.2025, at 08:30 in the Academic Hall "M. Dakov" at Building A of the University of Forestry, Sofia, 10 Kliment Ohridski Blvd. at an open meeting of a scientific jury approved by Order ЗПС-405/20.06.2025 of the Rector of the University of Forestry with the following members:

Chairman: Prof. Dr. Viktor Savov

Members: Prof. Dr. Petar Antov
Prof. Dr. Dimitar Angelski
Prof. Dr. Ivo Valchev
Prof. Dr. Sanchi Nenkova
Prof. Dr. Nencho Deliyski
Prof. Dr. Slavcho Sokolovski

This dissertation work was developed during part-time studies for the acquisition of the educational and scientific degree of "doctor" at the Department of "Mechanical Wood Technology", Faculty of "Forest Industry" at the University of Forestry, Sofia.

The research work was conducted in collaboration with the Lebanese University (Lebanon) and Université de Lorraine (France).

The materials for the defence are available to those interested on the website of the University of Forestry (http://www.ltu.bg/) and in the Dean's Office of the Faculty of Forestry, Room No. 221, University of Forestry, Sofia, 10 St. Kliment Ohridski Blvd.

INTRODUCTION

The increasing global population and consumption are putting immense pressure on the environment, leading to resource depletion, pollution, climate change and substantial amounts (billions of tons) of agricultural residues. These agricultural residues that are non-food waste biomass can be an excellent candidate for a safe and green future if used properly since their sustainability for long-term utilization is guaranteed. Using agricultural residues can contribute to slowing down climate change and reduce residue accumulation (Blasi et al., 2023; Haque et al., 2017). These residues, particularly lignocellulosic ones having low density, low cost, and good mechanical properties, can be used as reinforcing fillers in polymer matrices, reducing environmental impact while enhancing the mechanical properties of the resulting composites. These composites exhibit promising potential in various applications, including insulating materials and interior boards (Blasi et al., 2023).

To further enhance the sustainability and functionality of these bio-based composites, researchers are exploring the use of bio-based adhesives and treatments. Replacing existing synthetic adhesive systems with alternative products from renewable resources with zero toxic emissions, such as biobased polymers (Pizzi, 2016). Steam explosion technology, along with chemical structure modification by a phosphorus flame retardant like phytic can be employed as environmentally friendly processes to modify the properties of agricultural residues, unlocking their potential for a wide range of applications. The ultimate objective of this research is to develop fully bio-sourced multifunctional composites using agricultural residues and sustainable adhesives, potentially offering a valuable solution to mitigate environmental concerns and promote a more sustainable future. This research focuses on utilizing various agricultural residues and waste like *Miscanthus x giganteus*, olive waste, spent mushroom substrate, rice husks, and textile waste to develop fully bio-sourced, multifunctional composites.

CHAPTER I. STATE OF ART

As a result of the conducted literature review and analysis regarding on the utilisation of agricultural lignocellulosic residues and waste mainly *Miscanthus* × *giganteus*, olive waste, spent mushroom substrate, rice husks, textile waste and chitosan as an adhesive in composite production, as well as the pretreatment of lignocellulosic materials to improve their composition and fire behaviour, the following main conclusions can be drawn:

Researched and resolved problems

1. The wood-based composite materials industry relies on wood as the main source of particles and fibres in its different forms (strips, veneers, chips, strands, or fibres), causing a serious environmental issue.

2. Formaldehyde-based resins are the most used adhesives in woodworking. The worldwide consumption of urea-formaldehyde (UF) adhesives is estimated to be 11 million tons of resin solids yearly.

3. Formaldehyde exposure can cause severe human irritations (nose, throat and eyes) and complications (allergic contact dermatitis, menstrual disorders, pregnancy problems, asthma, and various types of cancer).

4. Chitosan, the second most abundant natural polysaccharide after cellulose, has been used as a biobased adhesive for environmentally friendly wood-based panels over the past decade, showing promising results.

5. Agricultural residues and waste are widely available and possess a composition comparable to that of wood. Their annual production exceeds 50 billion tons.

6. Agricultural residues and waste have become of great importance in the manufacture of wood-based composite materials as replacements to wood. Progress has been achieved regarding their use in the production of composites with favourable mechanical and ecological properties.

7. Among agricultural residues and waste, *Miscanthus* × *giganteus*, olive pomace, spent mushroom substrate, rice husks and textile waste are produced in huge quantities each year and their valorisation as possible substitutes for wood in composite production is recent.

8. Modifying *Miscanthus* × *giganteus* through steam explosion has been successfully done to obtain binderless high-density fiberboards.

9. Improving fire retardancy of lignocellulosic materials has gained more interest recently. Research now focuses on the use of phosphorus (non-halogenated) as an ecofriendly flame retardant for lignocellulosic materials.

10. A new solvent-free thermal grafting flame-retardant treatment of lignocellulosic materials has been developed using biobased phytic acid for flame-retardant lignocellulosic materials. This treatment has shown promising results in enhancing fire resistance of hemp fibres.

Unresolved problems

1. The use of chitosan as a biobased adhesive for composites made of olive waste, spent mushroom substrate, or for mixing of these lignocellulosic materials with textile waste, *Miscanthus* × *giganteus* or rice husks has not been investigated.

2. The potential use of *Miscanthus* × *giganteus* particles, textile waste, and rice husks to produce eco-friendly ultra-light insulating boards has not been studied. Their mechanical and thermal insulating properties have not been established.

3. The possible use of the olive pomace combined with the *Miscanthus* × *giganteus* particles, spent mushroom substrate, or textile waste for the conception of novel eco-friendly particleboards has not been studied. The mechanisms or interactions of these materials and their effect on mechanical strength and water resistance have not been clarified.

4. The effect of the novel flame-retardant treatment by phosphorus thermal grafting of phytic acid *Miscanthus* × *giganteus* particles to improve their fire retardancy has not been investigated yet.

5. The effect of steam explosion treatment on the composition of Miscanthus particles has not been explored.

6. There is currently no research available on the manufacture of Miscanthus-based binderless particleboards, making this an unexplored area of study.

7. The manufacture of binderless mixed boards, particularly the combination of steam exploded Miscanthus particles with olive pomace, has not been investigated yet.

AIM AND TASKS

Based on the conclusions drawn regarding the reviewed literature, solved and unresolved issues in the field of the researched problem, the aim of this dissertation is defined as follows:

Utilization of many agricultural lignocellulosic residues and waste (*Miscanthus × giganteus*, olive waste, spent mushroom substrate, rice husks and textile waste) in different formulations with and without chitosan adhesive to develop fully bio-sourced ultra-light insulating boards, particleboards, and fireproof binderless particleboards.

To achieve the goal thus defined, it is necessary to solve the following experimental tasks using a selected and described methodology:

1. Manufacture and characterization of ultra-light insulating boards using chitosan adhesive and *Miscanthus × giganteus*, rice husks and textile waste in different proportions.
2. Manufacture and characterization of particleboards using *Miscanthus × giganteus*, olive waste, spent mushroom substrate and textile waste in various formulations and chitosan as a binder.
3. Pretreatment of *Miscanthus × giganteus* by steam explosion and phosphorus grafting (phytic acid and urea mixture) to modify their surface and to improve their fire behaviour prior to incorporating them in binderless particleboard formulations with and without olive pomace.

CHAPTER II. MATERIALS AND METHODS

The experimental processes used for the preparation and the pretreatment of the lignocellulosic materials, the fireproofing process of the Miscanthus particles, the chitosan adhesive preparation and the approach followed for the design of the different composite panels are detailed.

II.1. Lignocellulosic materials preparation

First, it is important to specify that the textile waste, and the rice husks have not undergone any treatment before their use. However, the Miscanthus, spent mushroom substrate and olive waste required different pretreatment before use.

The spent mushroom substrate (SMS) undergoes a grinding step by a Moulinex coffee grinder followed by a sieving step using a Mateste electromagnetic sieving machine. SMS particles retained by the filter having a porosity of 850 µm are recovered and used in the manufacture of particleboards. Miscanthus particles (M) also undergo the same grinding step. Afterwards, a part of the obtained grinded Miscanthus undergo manual sieving to two different particle sizes: small size Ms of 0.2 – 0.5 cm and medium size Mm of 1 – 2 cm both used in the manufacture of ultra-light insulating boards. Another part of grinded M is sieved using a MATEST electromagnetic sieving machine. The Miscanthus particles retained by the filter having a porosity of 850 µm are collected and used in the manufacture of particleboards. Olive waste (OW) is milled using Moulinex coffee grinder then manually sieved using a 2 mm pore size sieve to separate the oily pomace (OP) from olive stones (OS). OS is mechanically crushed in a cement plant prior to sieving it. OS and OP are sieved separately using the MATEST electromagnetic sieving machine. OS and OP particles retained by the filter having a porosity of 1.18 mm are collected and used in the manufacture of particleboards and binderless particleboard. To obtain oil free pomace (OF), a portion of the 1.18 mm sieved OP is weighed properly, placed in a cellulose cartridge, and then washed first in toluene/ethanol mixture (2/1 v/v) then with ethanol alone using a Soxhlet extractor equipped with a cooler on the top. To eliminate the remaining oil, the solvent mixture was heated to reflux for 24 hours. Finally, OF was dumped onto a Teflon-coated metal plate and completely dried in the oven for 2 hours at 105°C prior to use in the manufacture of particleboards.

The chemical composition in terms of extractives, sugars and lignin of Miscanthus, oily pomace, olive stones, and spent mushroom substrate was estimated corresponding to three independent repetitions.

II.2. Steam explosion of Miscanthus particles

Miscanthus particles, as received, are used during the steam explosion treatment. The steam explosion pretreatment of Miscanthus particles involves three main steps: impregnation, stream explosion and drying. The steam explosion is done using a steam reactor. The particles were cooked using steam in a pressure resistant reactor. The explosion was caused by a sudden drop in pressure. The exploded particles were released into the discharge tank where they will be recovered. The obtained exploded Miscanthus samples are then washed by filtration through a 40-micrometer sieve, spread out and dried at room temperature. Finally, these particles are stored in bags at room temperature until use. Different impregnation solutions and steam explosion conditions are tested to study their impact on the resulting steam exploded Miscanthus particles. The different impregnation and steam explosion conditions are presented in Table 1.

Table 1. Impregnation and steam explosion conditions of Miscanthus particles

Sample name	Type of impregnation	Duration of impregnation (h)	Steam temperature (°C)	Pretreatment time (minutes)
Mse-B-1	NaOH 8%	15	190	4
Mse-A-1	$H_2S\ O_4$	15	190	4
Mse-N4-1	H_2O	15	190	4
Mse-N4-2	H_2O	15	190	8
Mse-N8-1	H_2O	15	210	4
Mse-N8-2	H_2O	15	210	8

The chemical composition in terms of extractives, sugars and lignin of the steam exploded Miscanthus particles obtained using different conditions, has been estimated corresponding to three independent repetitions. Length and width measurements were also carried out on different steam-exploded Miscanthus particles and raw Miscanthus particles as received. Particles of each type were scanned in 5 different batches on A4 paper using an office scanner. Then 100 measurements of length and width for each sample were taken using a ruler.

II.3. Fireproofing process of Miscanthus particles by phosphorylation

Mse-N8-2 steam exploded Miscanthus particles are treated with an aqueous solution of phytic acid and urea during the fireproofing process. The particles' name Mse-N8-2 will be simplified to Mse in all the fireproofing process analysis.

The phosphorylation process involves four steps. Firstly, Mse particles are sprayed with the aqueous solution of phytic acid and urea. Then, the sprayed Mse particles are dried in an oven at a temperature of 60°C for 15 hours. After drying, the grafting step follows, which involves cooking the dried Mse at a temperature of 150°C for a specific time (1 or 2 hours). At the end of the treatment, the grafted Mse referred to Mse-g particles, are washed 3 times abundantly with distilled water then vacuum filtered before being dried in an oven overnight at 60°C prior to use or analysis. To study the effect of phytic acid and urea ratios and the cooking duration on the grafting process, six batches of grafted steam exploded Miscanthus particles were prepared. Table 2 summarizes the different experimental conditions.

Table 2. Experimental conditions used to study the fireproofing process

Sample name	Phytic Acid (wt. %)	Urea (wt. %)	Cooking temperature (°C)	Cooking duration (h)	Washing 3 times
Mse-g1	5	10	150	1	+
Mse-g2	10	10	150	1	+
Mse-g3	20	10	150	1	+
Mse-g4	5	10	150	2	+
Mse-g5	10	10	150	2	+
Mse-g6	20	10	150	2	+

The phosphorus content in the steam-exploded Miscanthus particles before and after fireproofing treatment was quantified using X-ray fluorescence (XRF) analysis. Elementary analysis of nitrogen, carbon, oxygen, and hydrogen in steam-exploded Miscanthus particles before and after fireproofing was monitored using a "Thermo Finnigan Flash EA 112 Series". The fire resistance properties of grafted Miscanthus particle samples are studied using a pyrolysis combustion flow calorimeter (PCFC). Peak of heat release (pHRR), temperature at pHRR (TpHRR), total heat release (THR), heat of combustion (Δh) and final residue rate (%) are determined.

II.4. Chitosan adhesive solution preparation

Chitosan adhesive solution 4% (w/v) is prepared by dissolving 4.5 g of chitosan powder in 108 mL of 2% (w/v) glacial acetic acid solution at room temperature using mechanical stirring (1560 rpm) for 30 minutes until a homogeneous solution is obtained.

II.5. Ultra-light insulating boards manufacturing

Five formulations of insulating boards were manufactured with different components (small and medium size Miscanthus, textile waste and rice husks) as presented in Table 3.

Table 3. Designation of the insulating boards and their corresponding formulations

Board Name	Miscanthus particles (g)		Rice husk (g)	Textile waste (g)	Chitosan (g)	Acetic acid solution (ml)	Matrix wt. %
	M_s	M_m					
M_s	60	-	-	-	4.5	108	7
M_m	-	60	-	-	4.5	108	7
M_s60 T40	36	-	-	24	4.5	108	7
M_m60 T40	-	36	-	24	4.5	108	7
Rh60 T40	-	-	36	24	4.5	108	7

Firstly, a net amount of Miscanthus particles, textile waste, and rice husk are weighted according to each formulation. Particles and fibres are manually mixed for 10 minutes for combined boards to obtain good dispersion of the raw materials. Then, 108 ml of chitosan binder is poured into this mixture (Figure 37-b), followed by manual mixing. Then, the mixture is left to stand for 30 minutes to ensure the wetting of the reinforcements. After that, the mixture is filled in a stainless-steel mould of 200 x 50 x 70 mm^3 coated with a self-adhesive backing Teflon sheet and compacted at room temperature using a manual press and a backing mould until a thickness of 1.7 cm is reached. Compaction is maintained throughout the drying period. The compacted mixture is then placed in an oven at 60°C for 24 h. After that, the right and left edges of the mould were dismantled to speed up drying, which was kept for 19 hours. Finally, the board is removed from the mould and then left in the oven for 12 h to carry out complete drying.

The ultra-light insulating boards are extensively characterised. The apparent density of the ultra-light insulating boards is calculated as the ratio between the mass of the wood and its volume. The bulk density was measured on six samples from each formulation using the AccuPyc 133 Gas Pycnometer. The porosity rate (is calculated accordingly. The thermal conductivity (λ), effusivity (β) and diffusivity (α) of the ultra-light insulating boards are determined using FP2C-NeoTIM device at room temperature on six samples of each formulation. The thermal phase difference (ϕ, the heat capacity (Cp) and the thermal resistance (R) are then calculated accordingly. The mechanical properties of the ultra-light insulating boards are determined. The three-point bending test was conducted according to ASTM D790 at room temperature on four samples of each formulation. The modulus of elasticity (MOE) namely Young's modulus, maximum stress (MPa) and elongation at maximum stress (maximum elongation) (%), were calculated and provided by the testing machine. The compression tests were performed using the MTS Criterion press (model 45) testing machine. Measurements were taken on four samples of each formulation. The compressive Young's modulus (MPa), maximum stress (MPa) and densification strain at maximum stress (%) were calculated and recorded by the testing machine.

II.6. Particleboards manufacturing

Nine formulations of particleboards were manufactured with different components (Miscanthus of 850 µm (M), SMS, Textile waste and olive waste (OP, OS or OF) as presented in Table 4.

Firstly, 24 g of OP, OS or OF according to each formulation are weighted and added to the pre-prepared chitosan binder solution then stirred for 5 minutes to ensure a good dispersion of these particles in the solution. Then, this mixture is poured over 36 g of M, T or SMS followed by manual mixing. The whole mixture is left to stand for 30 minutes to ensure the good wettability of the reinforcements. After that, the mixture is preheated at 105°C for 60 minutes to achieve a 30 wt% relative humidity. Afterward comes the moulding step during which the pre-heated mixture is filled in a 180 x 50 x 70 mm^3 stainless steel mould coated with a self-adhesive backing Teflon sheet. The moulded mixture is then compacted at room temperature to reach a thickness of 1 cm using a backing mould and a hydraulic press. The compacted mixture is then placed in an oven at 105°C overnight (15 h) until totally drying while maintaining the compaction. Finally, the resulting particleboard is removed from the mould and conditioned for 2 days in a climate-controlled room with a relative humidity of 50% and a temperature of 23°C before testing.

Table 4. Designation of the particleboards and their corresponding formulations

Name of the formulation	Types of waste (36 g /24 g)	Dry Chitosan (g)	Acetic Acid 2% (mL)	Waste mass (g)	Ratio waste/ binder (%/% m/m)
MOP	Miscanthus / oily pomace	4.5	108	60	93/7
MOS	Miscanthus / olive stones	4.5	108	60	93/7
MOF	Miscanthus/ oil free pomace	4.5	108	60	93/7
SMSOP	Spent mushroom substrate /oily pomace	4.5	108	60	93/7
SMSOS	Spent mushroom substrate / olive stones	4.5	108	60	93/7
SMSOF	Spent mushroom substrate /oil free pomace	4.5	108	60	93/7
TOP	Textile waste/ oily pomace	4.5	108	60	93/7
TOS	Textile waste/ olive stones	4.5	108	60	93/7
TOF	Textile waste/ oil free pomace	4.5	108	60	93/7

The particleboards are extensively characterised. The apparent density of the particleboards is calculated as the ratio between the mass of the wood and its volume. The bulk density is measured on small cubes from each formulation using a density kit by measuring the mass (m) of a small cube in air and then in ethanol. The porosity rate (is calculated accordingly. The thermal conductivity (λ) is determined using FP2C FP2C-NeoTIM device at room temperature on three samples of each formulation. Surface and lateral observations of particleboards are evaluated using a Ladybird

MZ1240 Trinocular stereomicroscope before and after the water immersion test. The wettability of particleboard's surfaces is evaluated using a contact angle goniometer. The water absorption capacity and thickness swelling of the particleboards are measured by recording the changes in the samples from each formulation after soaking them in cold water. At different immersion times, the mass and thickness of each particleboard are taken, and the water absorption and thickness swelling are then calculated. Immersion was stopped until reaching the saturation of all the particleboards. The mechanical properties of the particleboards are determined. The three-point bending test was performed according to EN 310 and achieved on at least three panels of each formulation. The bending strength (MOR) and modulus of elasticity (MOE) are calculated. The internal bonding (IB) strength was performed according to the EN 319, using at least three samples from each formulation to determine the perpendicular tensile strength. The compression test was performed in the contrary direction of the panel's compacting pressure during manufacturing to measure the compressive strength of each particleboard, both before and after water immersion test.

II.7. Binderless particleboards manufacturing

Four formulations of binderless particleboards were manufactured with different components (Steam exploded Miscanthus particles so-called Mse, steam exploded grafted fireproof Miscanthus particles so-called Mseg, and oily pomace (OP) as presented in Table 5.

Table 5. Designation of the binderless particleboards and their corresponding formulations

Name of the formulation	Components composition	Oily pomace ratio (wt %)
Mse	Steam exploded Miscanthus	0
MseOP	Steam exploded Miscanthus/ oily pomace	40
Mseg	Phosphorus grafted steam exploded Miscanthus	0
MsegOP	Phosphorus grafted steam exploded Miscanthus/ oily pomace	40

Firstly, Miscanthus particles undergo a steam explosion step using the conditions of Mse-N8-2 (see Table 3) to recover the exploded Miscanthus particles (Mse). Some of the Mse particles undergo then a fireproofing step using the method of part II.2.3 to obtain Mseg. 150 g of particles are weighted (150g of Mse or Mseg or 90 g of Mse or Mseg mixed with 60 g of OP manually together) and then put into a mould of 20 cm x 20 cm. The binderless particleboard is then prepared using a hot-press by pressing the mixture of particles at 220°C. Pressing is carried out by applying a load of 12 MPa for 5 minutes followed by a one-minute discharge (breathing) at 0 MPa and a second load of 12 MPa for 2 minutes. After pressing, the particleboards obtained are left to cool to room temperature before their characterization.

The binderless particleboards are extensively characterised. The density is calculated as the ratio between the mass of the wood and its volume. The bending test was performed to determine bending modulus of rupture and modulus of elasticity according to EN 310 standard. The internal bond (IB) is evaluated according to EN 311 standard. The water absorption capacity and thickness swelling are determined following the EN 317 standard. The mass and the dimensions (length, width, and thickness) of the binderless particleboards are measured with a calliper before and after impregnation in water at both 60 minutes and 24 hours. The fire behaviour of the binderless particleboards is preliminary evaluated using a non-standardized flammability test by applying a flame at the top of each sample for 30 seconds. The cone calorimeter was also used to test the fire behaviour of these boards. The peak heat rate (pHRR), time to ignition (TTI), total heat released (THR), effective heat of combustion (EHC) and final residue rate are determined.

CHAPTER III. RESULTS AND DISCUSSION

III.1. Chemical composition of the lignocellulosic raw materials

The composition of the main components of the Miscanthus, oily pomace, olive stones, and spent mushroom substrate is presented in Table 6. All these raw materials contain cellulose, hemicellulose, lignin, and extractives in varying proportions. In all cases, the lignin content is approximately the same, around 26%. M particles have the highest cellulose

(40 wt %) and lowest extractives (0.95 wt %) content. SMS has the lowest hemicellulose content (≈10 wt %). OP has the highest extractives content (26 wt %), which is expected given that olive pomace contains residual phenolic compounds and fatty acids (Medouni-Haroune et al., 2018).

Table 6. Chemical composition of the tested lignocellulosic raw materials

Raw material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
OP	22.55 ± 1.59	21.6 ± 0.97	28.37 ± 0.26	26.28 ± 0.13
SMS	20.91 ± 0.21	9.99 ± 0.35	25.08 ± 0.96	5.06 ± 0.49
OS	22.92 ± 2.50	24.75 ± 2.06	26.03 ± 0.52	6.16 ± 0.13
M	40.07 ± 2.54	21.20 ± 1.40	26.72 ± 0.37	0.95 ± 0.01

III.2. Steam explosion effect on Miscanthus particles

The chemical composition of the various obtained steam exploded Miscanthus particles is presented in Table 7.

Table 7. Chemical composition of Miscanthus after SE pretreatment

Sample name	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Mse-B-1	62.11 ± 9.73	3.09 ± 0.75	5.29 ± 0.31	2.69 ± 0.21
Mse-A-1	53.27 ± 2.41	3.75 ± 1.15	30.5 ± 1.63	13.13 ± 0.18
Mse-N4-1	44.72 ± 1.06	21.19 ± 1.54	20 ± 0.67	6.9 ± 0.34
Mse-N4-2	46.1 ± 2.17	11.5 ± 0.79	22.09 ± 0.33	0.49 ± 0.02
Mse-N8-1	45.06 ± 2.25	15.29 ± 1.65	27.32 ± 0.46	1.75 ± 0.1
Mse-N8-2	47.43 ± 2.75	8.55 ± 1.3	36.19 ± 1.77	5.36 ± 0.42

It was found that the impregnation of M particles in NaOH prior to SE treatment allows recovery of the highest cellulose content, and the lowest content of lignin for Mse-B-1. Contrariwise, the acidic impregnation of M particles resulted in an increase in the lignin content with an increase in cellulose content and a decrease in hemicellulose content. These results are consistent with the literature where the authors studied the influence of steam explosion treatment combined with sulfuric acid pre-impregnation on Miscanthus, poplar and wheat straw (Auxenfans et al., 2017). Regarding the water impregnation of M particles, all the experimental conditions tested resulted in an increase of cellulose content and a decrease of hemicellulose content. When the pretreatment temperature increases from 190 to 210°C, the lignin and cellulose contents increase while hemicellulose content decreases. When the pretreatment residence time increases from 4 minutes to 8 minutes, the cellulose content remains nearly the same, while the hemicelluloses content decreases. Meanwhile, the lignin content increases and reaches 36% for Mse-N8-2. The increase in cellulose and lignin contents after the treatment can be explained based on literature as previous studies stated that hemicellulose fraction is easily hydrolysed during the steam explosion treatment while cellulose degradation is limited and requires high treatment severity. A depolymerisation of lignin may be also induced due to the high reactivity of its hydroxyl groups or repolymerisation by a C-C bond formation (Jacket et al., 2010; Moussa et al., 2020; Ziegler-Devin et al., 2021; Moukani et al., 2022).

The size of Miscanthus particles obtained after SE treatment combined with water pre-impregnation are evaluated in terms of length and width of particles. Figure 1 shows the box plots of the particle's length (Figure 1-A) and width (Figure 1-B).

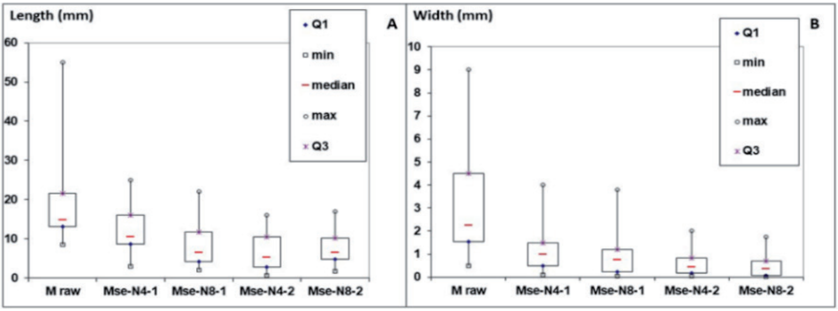

Fig. 1. Box plots representing the sizes of raw M and the different M exploded particles: A- Length of particles (mm); B-Width of particles (mm)

The results showed a reduction of length and width of M particles after SE treatment in comparison with those of untreated M particles. The median value of particle's length decreases from about 15 mm for raw M to 7 mm for Mse-N8-2 and the median value of particles width decreases from about 2 mm for raw M to about 0.4 mm for Mse-N8-2. It was clear from this statistical study that Mse-N8-2 has the best homogeneous particle size.

Based on the literature, a higher lignin content is recommended for the preparation of binderless particleboards (Hashim et al., 2011). Mse-N8-2, which is the result of a water impregnation of M particles followed by a SE treatment at 210°C for 8 minutes, presents the highest content of lignin, and the best homogeneous particle size. For that, this sample was selected to be used in the fireproofing process and in the conception of binderless particleboards.

III.3. Fireproofing of Miscanthus by phytic acid and urea

The effect of phytic acid and urea ratio and the cooking duration on the grafting process is investigated. The PCFC data, the nitrogen and phosphorus contents grafted onto the exploded Miscanthus particles are shown in Table 8.

Table 8. PCFC data, phosphorus and nitrogen contents grafted onto exploded Miscanthus particles

Sample name	Elementary composition		PCFC				
	N (wt%)	P (wt%)	pHRR ($W.g^{-1}$)	TpHRR (°C)	THR ($kJ.g^{-1}$)	Residue (%)	ΔH ($kJ.g^{-1}$)
Mse	0	0.01	178	381	12.4	7.4	13.3
Mse-g1	1.05	0.49	136	295	7.6	25.8	10.2
Mse-g2	1.07	0.66	110	290	6.3	25.6	8.4
Mse-g3	1.03	0.76	125	292	6.7	26.0	9.0
Mse-g4	1.23	0.64	112	290	6.0	26.3	8.0
Mse-g5	1.39	0.96	108	287	6.1	27.8	8.5
Mse-g6	1.25	0.99	107	288	6.0	28.0	8.4

The results obtained show that phytic acid is the source of grafted phosphorus and that the phosphorus content (grafted P) on the Mse particles increases proportionally with the levels of phytic acid used in the impregnation solution. Likewise, urea is the source of nitrogen. It was also clear that increasing the cooking duration results in increasing of the phosphorus and the nitrogen grafted contents.

Figure 2 shows the HRR curves for the seven batches of particles tested in PCFC.

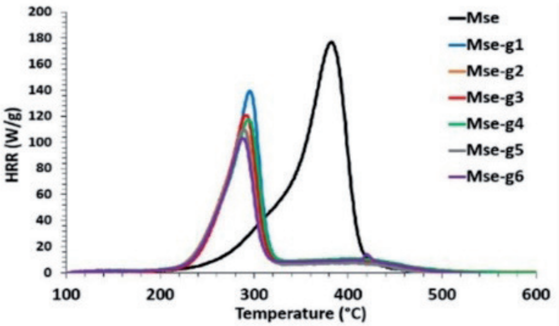

Fig. 2. Evolution of the heat release rate (HRR) as a function of temperature for the exploded Miscanthus particles with and without grafting

HRR curves as a function of temperature show that the pHRR intensity decreases sharply with increasing phosphorus content from 178 $W.g^{-1}$ for Mse (non-grafted) to 107 $W.g^{-1}$ for Mse-g6 with 1 wt% phosphorus. The pHRR temperature also decreases from 381 to 288°C. The same trend is seen for THR which decreases by 49% upon reaching the threshold of 6.1 $kJ.g^{-1}$ for Mse-g6 grafted with 1 wt% of phosphorus compared to 12.4 $kJ.g^{-1}$ for untreated Mse. Conversely, as the percentage of phosphorus grafted onto the Miscanthus particles increases, the residue percentage increases, reaching 28 wt% for Mse-g6 grafted with 1 wt% phosphorus. The increase in pHRR and THR values observed can be explained by the increase in char formation promoted by the grafted phosphorus compounds. The phosphorus acids formed during thermal decomposition of the cellulose catalyse their dehydration by removing water and promoting the formation of carbon-carbon bonds. This process is followed by a dehydrogenation (release of hydrogen), and an increase of the degree of unsaturation promoting thus the formation of aromatic structures. The unsaturated aromatic structures obtained undergo cross-linking reactions to form a stable char layer (Horrocks et al., 2000; Horrocks et al., 2001). Grafting of urea/PA (phosphorylation) leads to a reduction in thermal stability, pHRR, THR, and ΔH and to an increase in char content.

III.4. Ultra-light insulating boards

Ultra-light insulating boards were produced using agricultural and industrial by-products (Miscanthus, textile waste and rice husks) with chitosan as a bio-based adhesive. The physical, mechanical, and thermal insulating of the boards are presented. The impact of particle size of Miscanthus and components content on the properties of these boards is highlighted.

The density and porosity values of the prepared ultra-light insulating boards are presented in Table 9.

Table 9. Density and porosity values of the ultra-light insulating boards prepared

	Density ($Kg.m^{-3}$)	Porosity (%)
M_s	367.9 ± 1	60.0
M_m	354.0 ± 6	59.6
M_s60 T40	356.7 ± 8	72.1
M_m60 T40	334.4 ± 8	71.8
Rh60 T40	405.0 ± 6	73.0

The different properties of the prepared ultra-light insulating boards are gathered in Table 10.

Table 10. Thermal properties of the ultra-light insulating boards

	λ ($W.m^{-1}.K^{-1}$)	α (10^{-07} m^2s^{-1})	B ($W.s^{1/2}m^{-2}K^{-1}$)	ϕ (h)	Cp ($Jkg^{-1}K^{-1}$)	R ($m^2.KW^{-1}$)
M_s	0.084 ± 0.004	3.6 ± 0.7	171 ± 2	4.6	946	1.43
M_m	0.080 ± 0.004	3.8 ± 0.1	179 ± 2	4.5	1132	1.50
M_s60 T40	0.081 ± 0.004	4.6 ± 0.7	166 ± 14	4.1	965	1.50
M_m60 T40	0.079 ± 0.002	4.2 ± 0.3	176 ± 6	4.3	1167	1.52
Rh60 T40	0.076 ± 0.005	4.4 ± 0.6	176 ± 2	4.2	1006	1.58

Figure 3 represents the different bending properties: A) MOE, B) Maximum stress and C) maximum elongation respectively.

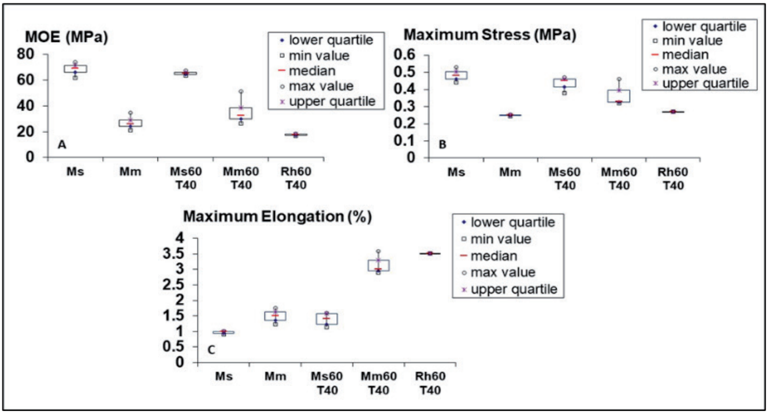

Fig. 3. Bending results of ultra-light insulating boards: A) MOE (MPa), B) maximum stress (MPa) and C) Maximum elongation (%)

Figure 4 represents the different compression properties: A) Young's modulus, B) maximum stress, and C) densification strain at maximum stress (deformation).

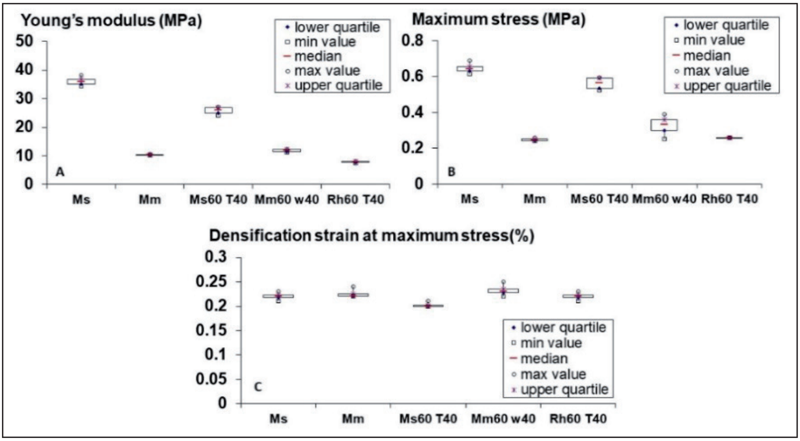

Fig. 4. Compression results of the ultra-light insulating boards: A) Young's modulus (MPa), B) Maximum stress (MPa) and C) Densification at maximum stress (%)

All the produced boards possess low densities that range from 334 $Kg.m^{-3}$ for M_m60T40 to 405 $Kg.m^{-3}$ for Rh60T40 and show a high porosity rate. The prepared boards have thermal conductivities values ranging from 0.076 to 0.084 $W.m^{-1}.K^{-1}$; subsequently, they are considered insulating boards as their thermal conductivities are less than 1 $W.m^{-1}.K^{-1}$ (Jelle, 2011). Higher porosity leads to lower conductivity, while higher density leads to higher conductivity. Additionally, larger particle sizes tend to decrease conductivity, possibly due to compaction and alignment of the particles that increases density of the insulating board. This, in turn, results in higher thermal conductivity, thereby reducing the effectiveness of the insulation board (Stacy et al., 2014).

In bending, the highest median MOE value (69 MPa) corresponds to M_s boards which contain small Miscanthus particles. The MOE significantly decreased when medium size Miscanthus particles (M_m) were used likely due to particle size limiting wettability and impacting the particle/matrix interface. However, the rigidity value was not severely impacted by replacing 40 wt% of Ms particles with textile waste (T). A significant increase in MOE was observed when 40 wt% of M_m were replaced by T (M_m60T40), possibly due to improved wettability. This observation is attributed to the hydrophobic nature of rice husks (Rh), which leads to poor adhesion and reduced rigidity (Park et al., 2003). The addition of textile waste improved stress values only in the presence of M_m.

Young's modulus and maximum stress in compression followed the same trend as bending tests. The modulus values in compression were approximately half of those obtained in bending. The highest modulus and maximum stress values were found for M_s boards (36 MPa and 0.64 MPa respectively). The increased rigidity of M_m60T40 compared to M_m in compression further confirms that adding 40 wt% of textile waste (T) with higher wettability enhances the boards' rigidity.

Finally, all the prepared ultra-light insulating boards meet the requirements of the European standard EN 13171 which often requires a compressive stress ranging from 0.20 to 0.50 MPa for the most wood-based insulation materials used in buildings (EN 13171). Insulating boards which contain small size Miscanthus particles (M_s and M_s60T40 insulating boards) exhibit a notably high compressive stress of approximately 0.6 MPa, surpassing the range specified by EN 13171 for wood-based insulating materials. Due to their exceptional mechanical robustness, these insulating boards are well-suited for applications requiring enhanced load-bearing capabilities.

III.5. Particleboards

Particleboards were produced from agricultural and industrial by-products using the different parts of olive waste (oily pomace, olive stones and oil free pomace) combined with Miscanthus, spent mushroom substrate or textile waste with chitosan as a bio-based adhesive. The effect of lignocellulosic material nature on the different properties on the particleboards are presented.

The bulk density, apparent density and porosity values of the prepared particleboards are summarized in Table 11.

Table 11. Density and porosity values obtained for the particleboards

Particleboard name	ρ_{bulk} (kg.m^{-3})	Average $\rho_{apparent}$ (kg.m^{-3})	Porosity (%)
MOP	824	665 ± 80	16.2
MOS	821	685 ± 9	19.4
MOF	993	710 ± 42	11.4
SMSOP	994	899 ± 47	10
SMSOS	1029	806 ± 14	15.8
SMSOF	1022	907 ± 28	3.4
TOP	945	695 ± 14	21.6
TOS	974	695 ± 14	15.5
TOF	945	774 ± 20	10.5

Figure 5-a and 5-b respectively show the surface and cross-sectional observations of the different panels.

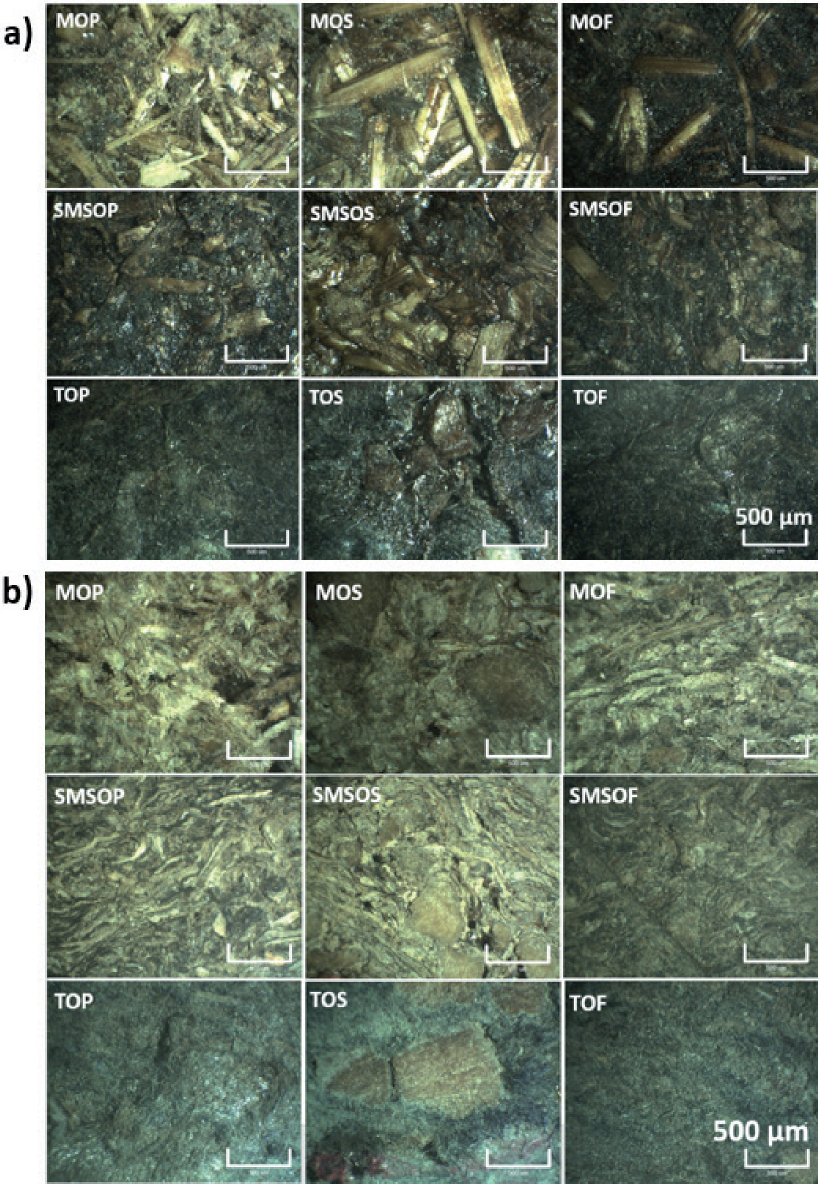

Fig. 5. a) surface and b) cross section microscopic observations of the different particleboards

Figure 6 presents the contact angle θ values of the particleboards.

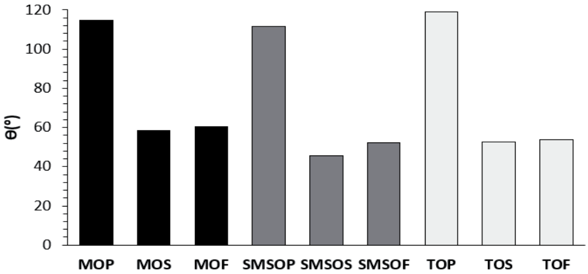

Fig. 6. Contact angles of the particleboards

Figure 7 shows the water absorption capacity (Δm) variation of the particleboards during the first 30 minutes of immersion (Figure 7A), Δm variation during the 5 days (Figure 7A) and the thickness swelling (TS) during the 5 days (Figure 7C).

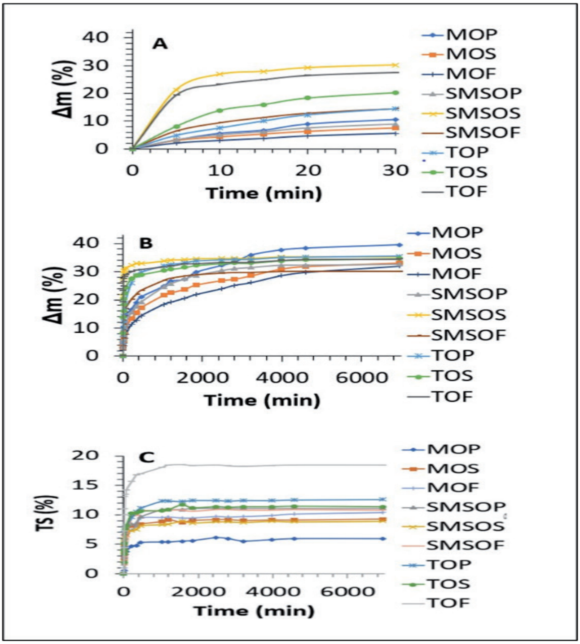

Fig. 7. Water immersion test results for the different particleboards: A) water absorption capacity for 30 minutes; B) Water absorption capacity for 6000 minutes (5 days); C) thickness swelling for 5 days

The modulus of elasticity (MOE) and Bending strength (MOR) of the produced particleboards are presented in Figure 8-A and Figure 8-B respectively.

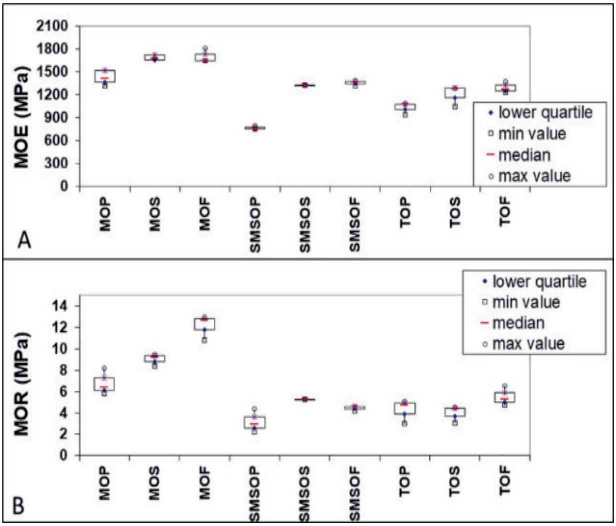

Fig. 8. Bending properties of different particleboards: A) Modulus of elasticity (MPa); B) Bending strength (MPa)

Figure 9 presents the average IB strength values of the particleboards.

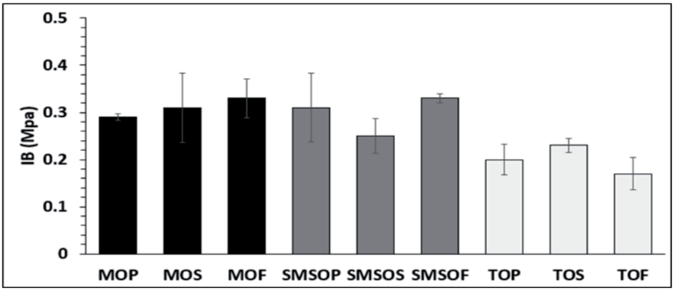

Fig. 9. IB strength values of particleboards

Figure 10-A shows the compressive strength of the various particleboards before and after immersion and drying, while Figure 10-B presents the surface microscopic observations of the particleboards after immersion and drying.

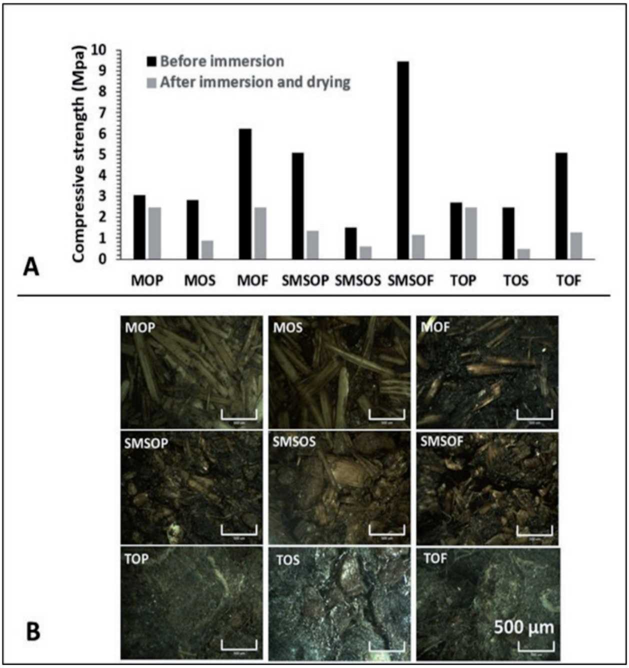

Fig. 10. A) Compressive strength values (MPa) of the medium density particleboards before and after the immersion test; B) Microscopic observations of the surface of the different particleboards after immersion and drying

The bulk density of particleboards ranges from 665 ± 80 to 907 ± 28 kg.m^{-3}, with SMS-based boards exhibiting higher densities due to volume shrinkage caused by microtube collapse and mycelium adhesion (Khoo et al., 2020). Porosity values, varying between 3.4% and 21.6%, decrease as bulk density increases. The particles display a glossy layer of chitosan adhesive, ensuring they are well wetted, with M, SMS, and T particles being evenly distributed and aligned parallel to the surface. OF-based particleboards exhibit large pores due to the absence of extractives, unlike OP-based panels where extractives reduce visible porosity, while voids between OS and other particles suggest interface issues. OP-based particleboards exhibit hydrophobic properties with high θ values, likely due to fatty acids “e.g. oleic acid” in olive pomace (Medouni-haroune et al., 2018). In contrast, OS- and OF-derived particleboards show hydrophilic behaviour, with contact angles ranging from 45.33° to 60.55°.

The absorption capacity of all particleboards is partially dependent on the nature of the olive waste and the other particles used. For short immersion times, SMSOP and M-based particleboards show low absorption capacities ($\Delta m < 10$ wt%), while SMSOS and TOF particleboards exhibit the highest absorption ($\Delta m = 27 – 30$ wt%). For a long immersion time (5 days), MOP particleboards reach the highest mass gain at 40 wt%, while SMSOF particleboards show the lowest at around 30 wt%, likely due to the absence of oil in OF and the mycelial enhancement in SMS. TOF particleboards exhibit the highest thickness swelling (19%) due to the absence of oil in OF and the hydrophilic nature of textile waste, while MOP particleboards show the lowest TS (6%), likely due to the chitosan adhesive's effect on particle wettability and the presence of extractives in OP.

MOS particleboards exhibit the highest rigidity, outperforming other OS-based panels. Miscanthus-based boards display superior rigidity especially OF-based ones, due to improved compaction and interface, with MOF achieving an MOR of 12.7 MPa, meeting EN 312 standards for general-purpose use. Compared to values reported in the literature, the MOE and MOR values obtained in this study are similar to those of rice straw and peanut hull particleboards, but lower than sugarcane bagasse and sunflower stalks particleboards. All M-based and SMS-based particleboards meet the requirement of EN 312 standard for general-purpose use of particleboards in dry conditions, with M-based and SMS-based boards combined with OF showing the highest IB values (0.33 MPa). MOS exhibits superior IB strength among OS-based boards (0.31 MPa). These results confirm that the use of chitosan as a bio-sourced adhesive enhances IB strength, making it competitive with other natural and formaldehyde-based adhesives. SMSOF particleboards have the highest compressive strength (9.5 MPa) due to the mycelium presence which acts as an additional intrinsic adhesive. Extended water immersion (5 days) degrades mechanical properties for all particleboards, with OP-based ones retaining better compressive strength despite chitosan adhesive dissolution and increased porosity.

III.6. Binderless particleboards

The binderless particleboards with dimensions of 200 mm x 200 mm x 5 mm were produced by thermo-pressing Miscanthus particles previously exploded with steam, alone or with oily pomace. The mechanical, water absorption and fire-resistance properties of these particleboards are presented. The impact of using fireproof Miscanthus exploded particles and olive pomace addition on the different properties is highlighted.

The density results and the different mechanical properties of the prepared binderless particleboards are summarized in Table 12.

Table 12. The density and the different mechanical properties of the binderless particleboards

	Density ($Kg.m^{-3}$)	IB strength (MPa)	MOE (MPa)	MOR (MPa)
Mse	699 ± 33	0.07 ± 0.013	2628.09 ± 168.24	7.52 ± 0.86
MseOP	697 ± 43	0.04 ± 0.003	1271.00 ± 2.55	2.66 ± 0.61
Mseg	702 ± 53	0.07 ± 0.004	1164.97 ± 110.48	2.58 ± 0.05
MsegOP	717 ± 30	0.04 ± 0.007	1284.54 ± 93.00	0.98 ± 0.25

The water absorption and thickness swelling values after 1 hour and 24 hours of soaking in water are presented in Table 13.

Table 13. The water absorption and thickness swelling values of binderless particleboards after 1 hour and 24 hours of soaking in water

	Δm (%)	TS (%)	Δm (%)	TS (%)
	after 1 h		**after 24 h**	
Mse	19.28 ± 2.74	16.01 ± 3.52	53.91 ± 1.51	23.96 ± 3.67
MseOP	28.22 ± 6.17	14.22 ± 0.64	48.33 ± 4.44	30.96 ± 3.27
Mseg	10.18 ± 1.01	4.08 ± 0.88	29.52 ± 2.26	12.87 ± 0.46
MsegOP	25.65 ± 1.67	5.82 ± 0.52	46.57 ± 5.97	14.87 ± 0.11

Figure 11 shows the particleboards before and after flame exposure (Figure 11-A and Figure 11-B respectively).

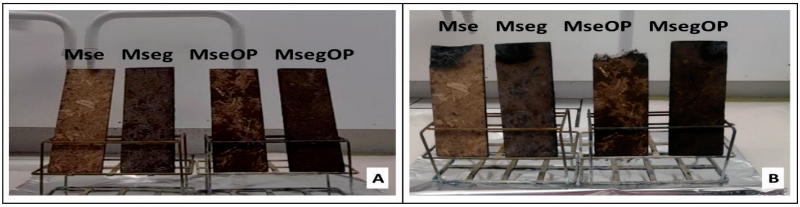

Fig. 11. Binderless particleboards: A) before the flammability test; and B) after the flammability test

The main data obtained using a cone calorimeter, including the peak heat release rate (pHRR), time to ignition (TTI), total heat release (THR), effective heat of combustion (EHC) and final residue rate, are presented in Table 14.

Table 14. Main data measured by cone calorimeter for the binderless particleboards

	Mse	MseOP	Mseg	MsegOP
TTI (s)	76	32.5	192	38.5
pHRR1 (kW.m^{-2})	162	183	56	144.5
pHRR2 (kW.m^{-2})	231.5	279	-	245
THR (MJ.m^{-2})	46.75	50.3	5.8	33.4
THR (KJ.g^{-1})	12.6	13.7	0.7	8.6
EHC (kJ.g^{-1})	14.1	16	1.3	12.8
Residue (%)	10.5	14	44.7	33.2

Figure 12 shows the evolution of the HRR curves for different particleboards at an irradiance (heat flux) of 35 kW.m^{-2}.

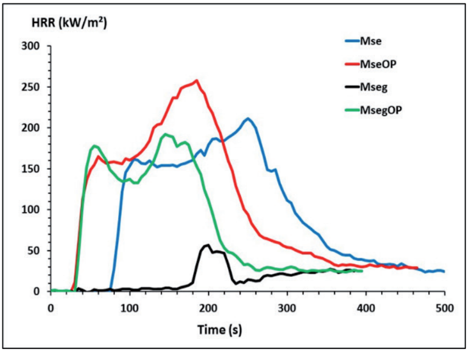

Fig. 12. HRR curves obtained by cone calorimeter at an irradiance of 35 kW/m2 for binderless particleboards

The photographs of the different particleboards after the cone calorimeter test are shown in Figure 13.

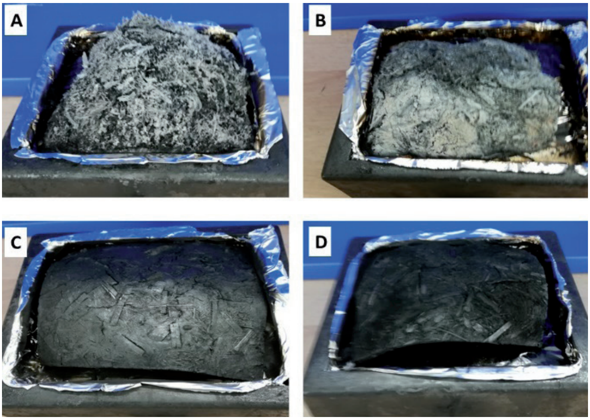

Fig. 13. Photographs of the particleboards after the cone calorimeter test (A: Mse; B: MseOP; C: Mseg; and D: MsegOP)

The particleboards exhibited consistent density across all variations, ranging between 697 and 717 kg/m³ (Table 12). IB strength values are low (0.04 – 0.07 MPa). However, the presence of OP significantly reduced IB strength by 43% (from 0.07 MPa to 0.04 MPa) attributed to its presence in large amount (40 wt %) and to the reduced binding by surface lignin (Quintana et al., 2009). Phosphorus grafting, on the other hand, did not affect IB strength. Untreated Miscanthus (Mse) particleboards displayed superior mechanical properties, boasting the highest Modulus of Elasticity (MOE, 2628 MPa) and Modulus of Rupture (MOR, 7.52 MPa). Both OP and phosphorus grafting led to significant reductions in MOE (by 52% and 55%, respectively) and MOR (by 65% and 66%, respectively) due to poor bonding and weakened grafted particles (Antoun et al., 2022).

AS shown in Table 13, water absorption Δm after 1-hour ranges from 10% to 28%. After 24 hours, Δm reaches 30 – 54%, the thickness swelling (TS) follows similar trends andTS ranges from 13% to 31%. The addition of OP significantly increased water absorption (Δm) and thickness swelling (TS) due to its high hemicellulose content (Tupciauskas et al., 2021). Conversely, replacing Mse with Mseg (phosphorus grafted) dramatically reduced both Δm and TS, due to the reduced water retention capacity caused by the phosphorylation of cellulose (Nasir et al., 2019; Zhang et al., 2011).

During flame exposure (Figure 11), the binderless particleboards exhibit three distinct fire performance behaviors. Mse and MseOP boards, containing untreated Miscanthus (non-grafted with phosphorus), are easily flammable and lose significant mass during the test. MsegOP particleboards, combining phosphorus-grafted Miscanthus and oily pomace (OP), are self-extinguishing, igniting briefly but extinguishing rapidly. Meanwhile, Mseg particleboards made entirely from phosphorus-grafted Miscanthus particles demonstrated exceptional fireproof properties, showing no ignition or flame propagation, and can be considered fireproof.

Further investigation using a cone calorimeter revealed the following findings (Table 14, Figure 12, and Figure 13). Mseg boards exhibited a significantly higher time to ignition (TTI) than Mse (192 vs 76 seconds), indicating a delay in ignition due to phosphorus grafting (Hernandez et al., 2018). OP, however, accelerates ignition resulting in TTI values of 32.5 seconds for MseOP and 38.5 seconds for MsegOP particleboards, with an 18.5% increase due to the grafted phosphorus.

Regarding heat release rate (HRR), Mse and MsegOP particleboards display double-peaked HRR curves, corresponding to ignition and subsequent thermal decomposition. Whereas Mseg boards exhibited a single pHRR, suggesting less flammable gas release and superior fire resistance. Consequently, the effective heat of combustion (EHC) drops significantly from 14.1 $kJ.g^{-1}$ for Mse to 1.3 $kJ.g^{-1}$ for Mseg, linked to phosphorus enhancing fire resistance (Hajj et al., 2018; Sonnier et al., 2015). MseOP particleboards show increases in pHRR1 (183 $kW.m^{-2}$), pHRR2 (279 $kW.m^{-2}$), and total heat release (THR: 13.7 $kJ.g^{-1}$) suggesting that the incorporation of OP leads to more intense combustion attributed to OP's flammable extractives (Guizani et al., 2016).

After cone calorimeter tests, Mse particleboards yielded 10.5 wt% residue, while MseOP showed a slight increase to 14 wt%. In contrast, Mseg and MsegOP retained their structure, forming significantly more char 44.7% and 33.2%, respectively, effectively acting as a fire barrier which slow decomposition (Horrocks et al., 2001; Antoun et al., 2022). This char formation is attributed to the grafted phosphorus and its ability to promote the dehydrogenation of carbohydrates and crosslinking.

CONCLUSIONS AND CONTRIBUTIONS

This dissertation explored the development of fully bio-sourced composite materials using agricultural lignocellulosic residues and waste. It investigated the use of *Miscanthus* × *giganteus*, olive waste, spent mushroom substrate, rice husks, and textile waste in different formulations with and without chitosan adhesive for the conception of ultra-light insulating boards, particleboards, and fireproof binderless particleboards. As a result of the implementation of the tasks set in this dissertation, various findings have emerged.

Firstly, chemical analysis revealed distinct compositions among the raw materials, highlighting the high cellulose content of Miscanthus (40%) and the high lignin (28%) and extractive (26%) content of olive waste.

The steam explosion pretreatment of Miscanthus particles, specifically at 210°C for 8 minutes, effectively reduced hemicellulose content and altered particle length and width, resulting in particles richer in lignin (36%) and more homogeneous in size (7 mm length and 0.4 mm width). In addition, the green fireproofing process applied by grafting phytic acid and urea successfully modified the thermal decomposition behavior of steam exploded Miscanthus particles, demonstrating that a two-hour cooking time is essential for increased phosphorus and nitrogen grafting on the particles. Impregnation with a 20 wt% phytic acid and 10 wt% urea solution resulted in fireproof particles with minimal phosphorus and nitrogen contents (1 wt% P and 1.5 wt% N).

Moreover, ultra-light insulating boards were successfully produced using *Miscanthus x giganteus*, rice husks and textile waste as reinforcements with chitosan adhesive. These boards exhibited high porosity (60 – 75%) a density of (350 – 400 $Kg.m^{-3}$) and demonstrated good thermal insulation and mechanical properties. The boards displayed thermal conductivities between 0.076 and 0.0874 $W.m^{-1}.K^{-1}$, considered moderate insulation with slightly higher than typical thermal conductivity of that of wood-based insulation materials according to EN 13171. In contrast, these boards showed compressive stress higher than 0.2 MPa, meeting the requirements of the same standard. The mechanical analysis showed that boards made of small size Miscanthus particles (Ms) exhibited the highest rigidity and stress.

Eco-friendly particleboards with densities ranging between 685 and 907 $kg.m^{-3}$ were also successfully produced using *Miscanthus* × *giganteus*, olive waste, spent mushroom substrate, and textile waste with chitosan adhesive. Particleboards based on oil free pomace and Miscanthus (MOF) or spent mushroom substrate (SMSOF) exhibited promising overall performance. The MOF board meets the EN 312 standard requirements in term of both bending MOR and IB strength while the SMSOF board shows better compressive performance and meets the EN 312 standard requirements for IB strength making them suitable for general use in dry condition.

Lastly, the study successfully developed binderless particleboards with densities around 700 $kg.m^{-3}$ using steam exploded Miscanthus particles, with and without fireproofing treatment and oily pomace. The IB strength of the particleboards was influenced by oily pomace presence but not by the fireproofing treatment of Miscanthus particles. Boards made of untreated Miscanthus particles (Mse) showed the best bending properties. The resistance to humidity was enhanced using fireproof Miscanthus particles but decreased with the inclusion of oily pomace. Binderless particleboards prepared from grafted Miscanthus particles (Mse), displaying significant fire resistance, are considered fireproof and hold potential for use in fire-sensitive applications.

Overall, this research demonstrates the potential of agricultural lignocellulosic residues and waste as sustainable alternatives to traditional materials, paving the way for a circular economy and promoting the development of high-performance composite materials.

As a result of the conducted experimental studies on the utilization of many agricultural lignocellulosic residues and waste (*Miscanthus* × *giganteus*, olive waste, spent mushroom substrate, rice husks and textile waste) with and without chitosan adhesive for the conception of fully bio-sourced ultra-light insulating boards, particleboards and fireproof binderless particleboards, the following applied scientific and purely applied main contributions were obtained from the development of the dissertation.

Applied scientific contributions

1. It has been proven that steam explosion treatment at 210°C for 8 minutes after water impregnation is necessary to obtain Miscanthus particles with a high lignin content (36%) and uniform dimensions (7 mm in length and 0.4 mm in width), making them ideal for binderless particleboard production.

2. The feasibility of eco-friendly fireproofing *Miscanthus* × *giganteus* particles using a combination of phytic acid (20 wt %) and urea

(10 wt %) was demonstrated. Optimal fireproofing was achieved with a 2-hour cooking time.

3. The production of ultra-light insulating boards of moderate insulation and densities between 350 and 400 $Kg.m^{-3}$ using *Miscanthus* × *giganteus*, rice husks, and textile waste in various formulations with chitosan as a biobased adhesive has been successfully achieved.

4. Ecofriendly particleboards with densities between 685 and 907 $Kg.m^{-3}$ have been successfully manufactured using *Miscanthus* × *giganteus*, olive waste, spent mushroom substrate and textile waste in different formulations and chitosan adhesive.

5. Binderless particleboards with densities around 700 $Kg.m^{-3}$ have been successfully manufactured using steam exploded Miscanthus particles either treated with phytic acid and urea solution or untreated, with or without olive pomace.

Applied contributions

1. It has been found that increasing the phytic acid levels and the duration of cooking during the fireproofing process leads to an increase in the phosphorus and nitrogen grafted on Miscanthus particles.

2. It has been proven that the use of chitosan as a biobased adhesive in the production of composites improves their internal bonding making it competitive with other adhesives.

3. It has been proven that the ultra-light insulating boards meet the mechanical compressive requirements of the relevant European standard EN 13171.

4. It has been found that due to their exceptional mechanical strength, insulating boards that contain small size miscanthus particles (Ms and Ms60T40 boards) are very suitable for applications requiring improved load-bearing capacities.

5. It has been found that the eco-friendly chitosan-based particleboards manufactured using Miscanthus and oil free pomace, as well as those produced with spent mushroom substrate and oil free pomace, meet the requirements of the European standard EN 312 and are suitable for general purposes in dry conditions.

6. Fireproof binderless particleboards displaying significant fire and humidity resistance and that retain their structure when burned have been successfully developed using phosphorus grafted Miscanthus particles.

PUBLICATIONS AND COMMUNICATION ON THE TOPIC OF THE DISSERTATION

Publications:

Khalaf, Y., Sonnier, R., Brosse, N. and El Hage, R., 2025. An extensive study of an eco-friendly fireproofing process oflignocellulosic Miscanthus x Giganteus particles and their application in flame retardant panels. *Polymers, 17(2),* pp. 241. https://doi.org/10.3390/polym17020241. Impact Factor: 5.0 (2025). Cite Score: 8.0; Quartile: Q1 (Chemistry) and Q1 (Polymers and Plastics). Cited: 1 time

Khalaf, Y., El Hage, P., Mansour, S., Brosse, N., Mihajlova, J.D., Bergeret, A., Lacroix, P. and El Hage, R., 2024. Eco-Friendly Chitosan Composites: Transforming Miscanthus, Mushroom, Textile and Olive Waste into Sustainable Materials. *AppliedChem, 4*, pp.302-319. https://doi.org/10.3390/appliedchem4030019. ISSN 2673-9623. Indexed in Scopus. Cited: 4 times

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