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Yasmina Khalaf, Peter El Hage, Julia Dimitrova Mihajlova, Anne Bergeret, Patrick Lacroix, et al.. Influence of agricultural fibers size on mechanical and insulating properties of innovative chitosan-based insulators. Construction and Building Materials, 2021, 287, pp.123071. 10.1016/j.conbuildmat.2021.123071 . hal-03182666

HAL Id: hal-03182666

https://imt-mines-ales.hal.science/hal-03182666

Submitted on 25 May 2021

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Influence of agricultural fibers size on mechanical and insulating properties of innovative chitosan-based insulators

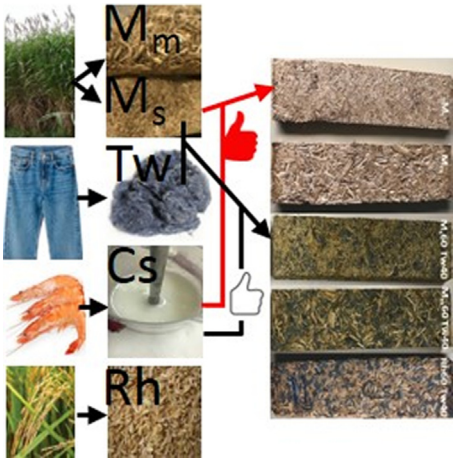
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HIGHLIGHTS

- Thermal chitosan based insulating panels made of miscanthus fibres, rice husks and recycled textile wastes were developed.
- Better insulating properties were obtained for medium sized fibres panels.
- Linear relationship is found for thermal conductivity and effusivity compared to particles size.
- Better mechanical performance for short miscanthus fibers (Ms < 1 mm) alone or mixed with textile waste.

GRAPHICAL ABSTRACT



ABSTRACT

This work is dealing with the use of miscanthus, recycled textile and rice husks as reinforcement for chitosan matrix to elaborate new insulating composites for building application. Insulating composites having thermal conductivity of 0.07–0.09 $W.m^{-1}.K^{-1}$ and density of 350–400 $Kg.m^{-3}$ were manufactured by thermocompression. Different granulometry of miscanthus (0.2–0.5 cm and 1–2 cm) and rice husks (1–2 cm) have been used with and without textile to evaluate the effect of reinforcements particle size and nature on composites thermal and mechanical properties. Thermal conductivity and effusivity shows a linear behavior related to their increasing by raising up the reinforcement's particle size. The highest mechanical properties in bending (modulus: 69–65 MPa; stress: 0.48–0.45 MPa) and compression (modulus: 36–26 MPa; stress: 0.65–0.56 MPa) were found for the formulations with small size miscanthus. Thus, the incorporation of small miscanthus particle size <1 mm leads to satisfying and promising results in terms of composites competing with the conventional insulating materials used nowadays.

Keywords:
Natural fibers
Composites
Mechanical properties
Porosity
Thermal properties
Building insulation

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1. Introduction

Environment is always the greatest victim of all development made by human beings. Earth wealth from raw materials to energy sources were consummated without being limited to any consequences. That is why it becomes urgent to save the remaining resources and replace them with energy saving materials especially in the construction sector which is their main consumer. Insulators with low thermal conductivity values are key products used to decrease heating and cooling energy costs inside buildings and to achieve the highest possible thermal resistance. Not only energy saving is the criteria of environmental consciousness, the pollution and wastes production reduction are also important.

Hence, bio-based insulating materials made from agricultural and industrial by-products seem to be an interesting alternative to traditional insulators based on fossil fuels [1]. Since the last decade, due to their important advantages, natural fibres have been incorporated into composites in order to obtain renewable, eco-friendly materials with low density and good thermal properties [2].

Among natural origin-based byproducts, rice husk (Rh) is widely available. Rh contains nearly 20% silica which make it naturally non-flammable biomass. The interest in these discards of rice processing is not recent. In 1998, Ajiwe et al. [3] show promising results using glued Rh to make ceiling boards. These wastes present also good thermal insulation capacity. Buratti et al. [4] found thermal conductivity values of glued Rh composite panels having a density of 170 $kg.m^{-3}$ about 0.07 $W.m^{-1}.K^{-1}$. Muthuraj et al. [5] elaborated rice husks biocomposites which are considered as insulators (thermal conductivity of 0.08 $W.m^{-1}.K^{-1}$ for a density of 378 $kg.m^{-3}$) using biodegradable Ecovio adhesive. None of the studies carried out so far on Rh have studied the use of chitosan as a binder for this type of composites.

Such as rice husk, Miscanthus (Miscanthus × Giganteus) named M in this paper is an abundant perennial grass. According to its high productivity (about 25 tonnes of dry matter per year), its rapid growth (up to 3 m tall each year) and its ability to adapt to several climates [6,7], it is advantageous to use this non-food lignocellulosic biomass in the composite industry. M has recently attracted many researchers to investigate about its use as reinforcement in a biodegradable matrix. It has been incorporated in Mater-Bi matrix, PBAT and poly(butylene succinate) bioplastic [8–10]. Eschenhagen et al. [11] has recently successfully developed insulating composites using M particles with three different bio-based binders (starch, casein and gelatine) with a density range between 130 and 230 $Kg.m^{-3}$ and thermal conductivity between 0.057 and 0.067 $W.m^{-1}.K^{-1}$.

Cotton fibres is one of the most used fibres in clothes in the world especially in Jeans fabrication. The no longer used clothes produce tonnes of wastes every year. These wastes could not be valorised excluding incineration [12] until their recycling. The recycled textile wastes (Tw) have found an interesting use in thermal and acoustical materials and most recently in bio-binders like PBAT/PLA, sodium alginate and chitosan [5,13–15].

All bio-based adhesives reduce the harmful formaldehyde and volatile organic compound emission from wood-based panels and insure more sustainable composite production [16,17]. Different natural binders from animal and vegetable resources have been used in the manufacturing of insulating materials such as alginate, casein, starch, gelatine and chitosan [11,14,15,18].

Chitosan (Cs) is a water soluble in acidic media semi-crystalline polymer [19]. This second most abundant natural polysaccharide after cellulose is composed of the random distribution of D-glucosamine linked in ß- (1–4) and N-acetyl-D-glucosamine [20]. It is produced from the chitin which is a structural element found in the exoskeleton of crustaceans such as shrimps, lobsters and crabs [21]. Being degradable and nontoxic, Cs has recently received wide attention as a good binding adhesive in the bio-sourced composites [14,18,22].

The mechanical and thermal properties are the main factors characterizing the quality of the insulating composites. One of the most important parameters influencing these factors is the size of the fibres. Many researchers have studied the effect of changing the size of natural fibre particles in the thermoplastic matrix like polyester, polylactic acid, polyvinyl chloride, polypropylene polyethylene and others [23–31]. They have obtained different results which sometimes lead to contradictory conclusions. Some of them have found that the smaller size, the better properties and others have found the opposite. These results are probably due to other parameters mainly such as the filler content, the geometry of the particles, the processing method and the nature of the matrix. Other researchers, in their turn tried to predict, by theoretical and numerical models, the fibre size effect on the thermal conductivity properties of many fibrous medias [32,33]. They have found that heat flux and the thermal conductivity can be reduced by using fine and small fibres and by optimizing the fibre diameter. To our knowledge, so far, no study has been carried out in order to understand the effect of the particle size of the charge in the chitosan matrix, hence the novelty of our study.

In previous paper [34], we reported the preparation of chitosan based composites reinforced with big size miscanthus particles (2–6 cm), textile waste fibres or a combination of both of them. The results showed promising results in term of thermal insulation and fire behavior despite their relatively high density (≥250 $Kg.m^{-3}$).

The purpose of this work is to prepare chitosan-based composites reinforced with two different size of miscanthus particles alone or combined with textile wastes (Tw). Rice husks are also used as reinforcements in some formulations alone or combined with Tw. A deep comparison analysis of the physical, thermal and mechanical properties of the prepared composites is carried out taking into account also the results obtained for other innovative insulating materials in order to judge the particle size effect on their performances.

2. Materials and experiment

2.1. Materials

Miscanthus × Giganteus (M) were provided by EARL Ar Gorzenn (France). Dried M were milled using Moulinex coffee grinder and then sieved to two different particle sizes: small size M_s of 0.2–0.5 cm and medium size M_m of 1–2 cm.

Rice Husk (Rh) were supplied by Silo de Tourtoulen (France). It is a co-product from husking rice by simple abrasion without any chemical transformation. They were used as received.

Textile wastes (Tw) namely METISSE with an average length/diameter of 6 ± 3 mm/15 ± 3 µm were provided by Le Relais Co. (France). These T from recycled jeans were used as received.

A photography of the different reinforcements shape is shown in Fig. 1.

A commercial chitosan powder having an average molecular weight of 250 000 $g.mol^{-1}$, a deacetylation degree above 90% and a viscosity of 30–100 cps was purchased from Glentham Life Sciences (UK) and was used as an adhesive binder. Glacial acetic acid (purity ≥ 99.7%) purchased from VWR International (France), was used as received for chitosan dissolution.



Fig. 1. Selected fibers for the composite processing.

Table 1
Designation of the bio-composite samples and their corresponding formulations.

Name	Miscanthus particles (g)		Rice husk (g)	Recycled textile fibres (g)	Chitosan (g)	Acetic acid solution (2%v/v) (ml)	Matrix wt. %
	M_s	M_m					
M_s	60	–	–	–	4.5	108	**7**
M_m	–	60	–	–	4.5	108	7
M_s60 Tw40	36	–	–	24	4.5	108	7
M_m60 Tw40	–	36	–	24	4.5	108	7
Rh60 Tw40	–	–	36	24	4.5	108	7

2.2. Composites manufacturing

The five bio-composites were manufactured with different components as presented in Table 1.

To prepare the chitosan binder, 45 g of chitosan powder are dissolved in 100 ml of glacial acetic acid solution 2% (w/v) at room temperature using mechanical stirrer (1560 rpm) for 60 min until a homogeneous solution is obtained. Then, a net amount of textile waste, rice husk and miscanthus particles are weighted according to each formulation. For the combined boards, particles and fibres are manually mixed for 10 min to obtain good dispersion of the raw materials. To this mixture 108 ml of chitosan binder is poured followed by manual mixing. Before molding, the mixtures are left to stand for 30 min to ensure the wetting of the reinforcements. The last step is composite molding manufacturing using a stainless steel mold of $200 \times 50 \times 70$ mm^3 coated with a self-adhesive backing Teflon sheet. After filling the mold with the mixture, a compacting step takes place at room temperature using manual press and a backing mold 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, drying for 19 h is carried out after dismantling the right and left edges of the mold in order to speed up drying. Finally, the composite is removed from the mold and then left in the oven for 12 h to carry out complete drying. Before testing, all samples were conditioned for 3 days in a climate-controlled room with a relative humidity of 50% and temperature of 23 °C.

2.3. Density and porosity measurements

The calculated density of the samples was obtained using the standard mass over volume formula. The actual density was measured on six samples of each formulation which were cut into $35 \times 15 \times 5$ mm^3, using the AccuPyc 133 Gas Pycnometer which injects Helium gas to fill the accessible pores while calculating

the volume of the gas at the outlet. Then, the porosity was estimated using the following equation 1

$$P = 1 - ((\rho\ calculated)/(\rho\ actual))$$

Where P is the porosity rate and ρ is the density of the sample.

2.4. Thermal conductivity properties

FP2C-NeoTIM device was used to determine the thermal conductivity (λ), effusivity (β) and diffusivity (α)of the composites with respectively a hot linear wire sensor (50 mm), a hot plane sensor (50 × 50 mm^2) and a ring sensor (diameter = 15.0 mm). Tests were conducted on six samples of each formulation having 200 × 50 × 17.5 mm^3 dimensions at room temperature.

The thermal phase difference (ϕ) was calculated using the equation below (equation 2):

$$\varphi = 0.023e \times \sqrt{\alpha}$$

Where e is the thickness of the material chosen here to be 0.12 m to represent a realistic building envelope and (α) is the measured thermal diffusivity.

The heat capacity (Cp) was calculated using the equation 3:

$$Cp = \beta 2/\lambda.\rho$$

Where λ is the thermal conductivity, β is the thermal effusivity and ρ is the density of the sample.

The thermal resistance (R) was calculated for a thickness of 0.12 m using the equation 4:

$$R = e/\lambda$$

2.5. Mechanical properties

The three-point flexural test was performed at room temperature on a ZWICK TH010 universal testing machine equipped with a 2.5 kN capacity load cell and the load speed was fixed at 2 mm/min [34]. The specimens of dimensions 200 × 50 × 17.5 m m^3 were placed between two supports at a distance of 120 mm according to the standard ASTM D790.

The compression test was performed on the MTS Criterion press model 45 with a 10 kN load cell and cross head speed of 10 mm/min [34]. The samples (50 × 50 × 17.5 mm^3) were compressed in the contrary direction than the pressure of the compacting was applied during the composites manufacturing.

Each mechanical measurement was done on four samples of each formulation. Results are presented via box plots showing clearly a statistical observation taking into consideration the values distributions of the four tests [35]. The circle and cube presented at the ends of the whiskers correspond to the extreme values (the minimum and maximum value), the lower and upper quartiles are presented in the bottom and top of each box while the band corresponds to the median position.

2.6. Scanning electron microscope (SEM) observations

Mm and Ms fibers were visualized at the microscopic scale with a magnification of × 300 and × 1000 using a scanning electron microscope (Hitachi S-4800) at an acceleration voltage of 10 kV. Samples are deposited on metal pads, glued with varnish and then metallized with carbon to reduce the phenomena of charge accumulation. The SEM is equipped with an energy dispersive X-ray spectroscopy which was used to determine the silica location on the miscanthus fibers surface.

3. Results and discussion

3.1. Density and porosity measurements

Fig. 2 shows photography of the different manufactured samples. Table 2 relates the porosity values according to the particle size, textile fibres content or the density of the prepared composites. All the produced composites have low density that ranged from 334 to 405 $Kg.m^{-3}$. These densities are compared to those of the glued coffee chaff [36], rice husk- Ecovio [5] and bagasse-wheat gluten [37] composites; whereas, they are greater than the densities obtained for big size M–T- chitosan biocomposites in our previous work (247–299 $kg.m^{-3}$) [34]. The results show the presence of high porosity rate for all composites. This porosity rate reaches 60% in presence of miscanthus alone and 70% by combining miscanthus or rice husk with textile fibres.

It is clear that the particle size affects slightly the density of the material but is affectless on its porosity. Larger particle size leads to lower composite panel density while having almost the same porosity. The addition of textile fibres reduces the density of composites having the same size of miscanthus (for example dM_s = 367.9 is greater than dM_s60 Tw 40) and increases the porosity rate (P (M_s = 60) is lower than P (M_s60 Tw40)).

3.2. Thermal conductivity properties

Thermal conductivity (λ), diffusivity (α), effusivity (β), phase difference (ϕ), thermal capacity (Cp) and thermal resistance (R) values of the prepared composites are presented in Table 3. Since a material is considered an insulating one when its thermal conductivity is <1 $W.m^{-1}.K^{-1}$ [38,39], all the composites of this study can be qualified as insulators with thermal conductivities varying between 0.076 and 0.084 $W.m^{-1}.K^{-1}$. The thermal conductivity of porous materials is governed by the voids presents in samples. These voids are occurring from fibers packing [40]. More the porosity rate increases, more the conductivity values decreases and more the density of the composite increases, more the conductivity values increases. This behaviour is clearly shown in Fig. 3. Composites containing Rh (Rh60 TW40) present the lowest thermal conductivity (0.076 $W.m^{-1}.K^{-1}$) despite their highest density and porosity rate which may indicate that conductivity is more influenced by porosity than density. This behaviour can be also related to the hydrophobicity of the silicified (SiO_2) outer epidermis cells of rice husks which prevents the chitosan solution from entering and filling the open pores of the husk [41]. The thermal conductivity of Rh60Tw40 composites is comparable with rice husk/Ecovio composites [5], rice husk/polyurethane composites [4]. It seems that particle size may affect the thermal conductivity in a way that when size increases, conductivity values decreases; it could be related to the compaction and alignment of the fibers during the compression. This will only be clearly shown with the two particle sizes used in this study ($\lambda(M_s)$ = 0.084 $W.m^{-1}.K^{-1}$; $\lambda(M_m)$ = 0.08 $W.m^{-1}.K^{-1}$) if we compare the results with those of our previous work, in which the conductivity of miscanthus/chitosan biocomposites was 0.07 $W.m^{-1}.K^{-1}$ for taller (2–6 mm) miscanthus fibers size [34]. Moreover, it seems that textile wastes addition doesn't affect the conductivity of the composite panels. Comparing to literature for the same density range (300–400 $Kg.m^{-3}$) of building bio-based insulation materials, thermal conductivities obtained in this study are similar to those of wood fibers/textile waste fibres composites (0.078–0.089 $W.m^{-1}.K^{-1}$) [15] but higher than those of binderless coconut husk insulation board (0.048–0.068 $W.m^{-1}.K^{-1}$), binderless bagasse insulation board (0.052–0.057 $W.m^{-1}.K^{-1}$) and binderless cotton stalk fiberborad (0.072–0.075 $W.m^{-1}.K^{-1}$) [42,43].

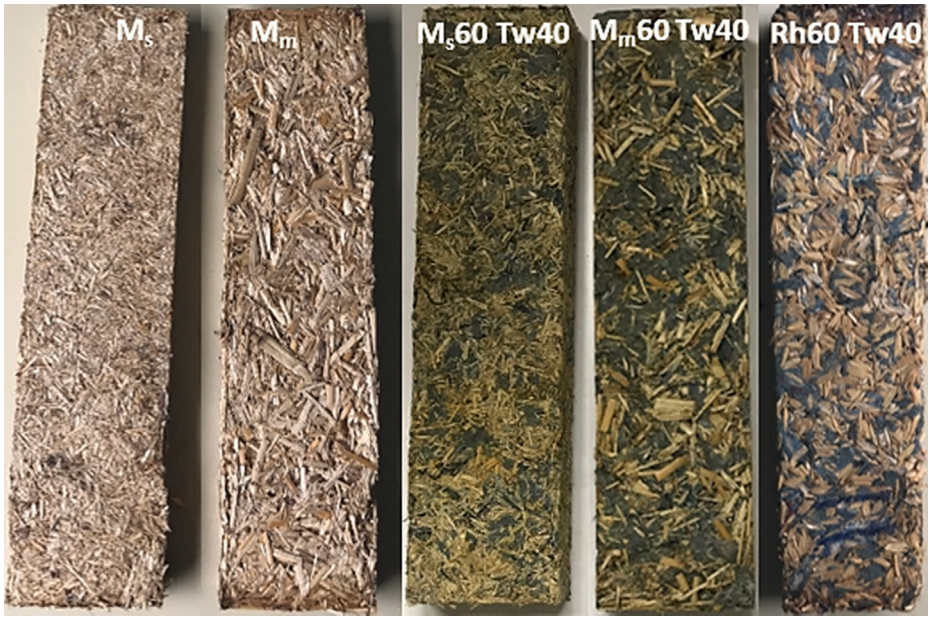


Fig. 2. Photography of the different processed composites.

Table 2
Density and porosity values of the composites.

	Density (Kg.m^{-3})	Porosity (%)
M_s	367.9 ± 1	60.0
M_m	354.0 ± 6	59.6
M_s60 Tw40	356.7 ± 8	72.1
M_m60 Tw40	334.4 ± 8	71.8
Rh60 TW40	405.0 ± 6	73.0

On the other hand, α is also an important parameter which measures the capacity of heat transfer through a material and its ability to store thermal energy. Lower values mean that heat passes slowly through a material.

In general, insulators have low thermal diffusivity. Regarding the bio-composites of this study, they all have low α values (<5. 10^{-07} m^2s^{-1}). The obtained values remain lower than those obtained by our other previous studies [15,34]. However, it can be noted that the addition of textile fibers accompanied higher

Table 3
Thermal properties of the different bio-composites.

Sample	λ (W.m^{-1}.K^{-1})	A (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 Tw40	0.081 ± 0.004	4.6 ± 0.7	166 ± 14	4.1	965	1.50
M_m60 Tw40	0.079 ± 0.002	4.2 ± 0.3	176 ± 6	4.3	1167	1.52
Rh60 TW40	0.076 ± 0.005	4.4 ± 0.6	176 ± 2	4.2	1006	1.58

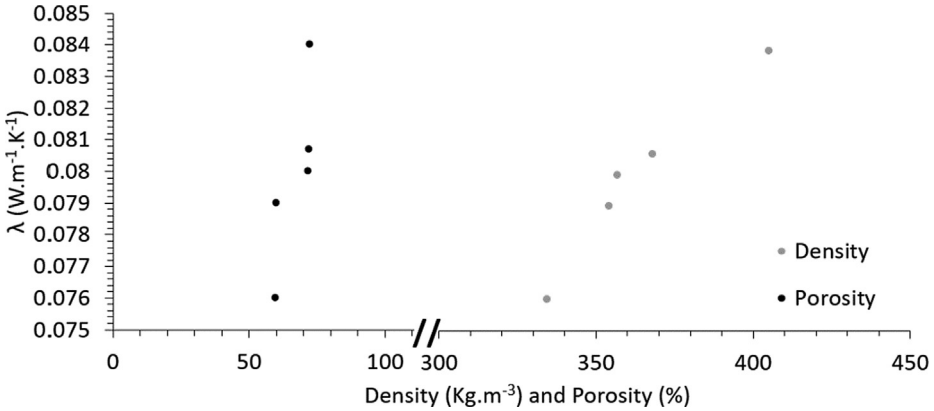


Fig. 3. Thermal conductivity as a function of density and porosity rate of biocomposites.

porosity content gives higher α values (Tables 2 and 3) indicating an increasing in heat transfers, heat moves more quickly, and that no relationships between α and density or fibers size can be found.

Whereas, the thermal energy exchange with the environment of the materials is characterized by their effusivity. It is clear that β possesses an inverse behavior to that observed for α. β values decrease with the addition of Tw. Moreover, β values seems to be increased in presence of higher fibres particle size. The lowest thermal effusivity is detected for the M_s60 Tw40 composite having a value of 166 ± 17 $W.s^{1/2}m^{-2}K^{-1}$. β is similar for Rh60 Tw40 and M_m60 Tw40 biocomposites having almost same particle size. It should be noted that no linear behavior is observed between β and density or porosity.

Moreover, ϕ (which ranged between 4.1 and 4.6 h) and Cp (Which ranged between 946 and 1167 $Jkg^{-1}K^{-1}$) of the composite panels are relatively high which make them good insulators because it takes time for them to absorb heat before they can transfer it after heating up. It seems that the composites with small particle size have the least thermal capacity (M_s and M_s60 Tw40) while no significant change is noted for the phase difference between the manufactured composites. The thermal resistance (R) calculated from the given thickness of the biocomposite is inversely proportional to the conductivity. The higher R, the better the insulation. R values are almost very close for the various composite panels. No relationship is found between R and density or porosity or fibers size.

3.3. Mechanical properties

3.3.1. Bending properties

Fig. 4 represent the different bending properties: A) Young's modulus, B) maximum stress and C) elongation at maximum stress respectively compared to some results from literature.

It can be observed that the highest median Young's modulus value (69 MPa) corresponds to the formulation containing small miscanthus fibres (M_s). It can be noted that the rigidity of the composite panels significantly decreased about 62% when medium size miscanthus particles (M_m) are used. This obtained rigidity (26 MPa) is very close to that obtained by El Hage et al. 2018 (29 ± 5 MPa) [34] (Fig. 4A-1) where bigger fibers size where used (2–6 cm) in the conception of 247 ± 8 kgm^{-3} composite panels. This behavior could be linked to the size of the miscanthus particles which limit the wettability of the fibres while impacting the fibre/matrix interface. Thus, much higher rigidity values could be achieved using miscanthus fibers having particle size <1 cm. Adefisan et al. [25] found also a comparative behaviour to this study, where it seems that composites reinforced with < 0,5 mm bamboo fibers recorded significantly higher moduli than those made from < 2 mm particles (Fig. 4A-2 and A-3). Authors suggests a better interfacial bonding between the shorter bamboo fibers and the plastic matrix. Furthermore, the replacement of 40 wt% of M_s fibres by textile fibres (Tw) did not impact severely the rigidity value. Thus, the modulus median value (65 MPa) of M_s60 Tw40 was slightly lowered by 6% in comparison to M_s samples. However, while replacing 40 wt% of M_m by Tw (M_m60 Tw40) a significant increasing of about 21% in modulus median value was obtained. This observation is in accordance to that obtained by our previous work [34] where mixing of miscanthus having high particle size (2–6 cm) and textile fibers (50 wt%) showed to be very promising. This could also be also related to the wettability factor where it is improved in presence of textile fibres. Textile fibers were assumed to be highly hydrophilic in comparaison to natural wood fibers [15]. Moreover, Rh60 Tw40 composites feature the lowest median modulus (17 MPa). This observation is not only caused by fibers size but mainly related to the hydrophobic nature of Rh [41] which make it less wettable leading to a poor fibres/matrix adhesion and lower rigidity. The highest median values of bending maximum

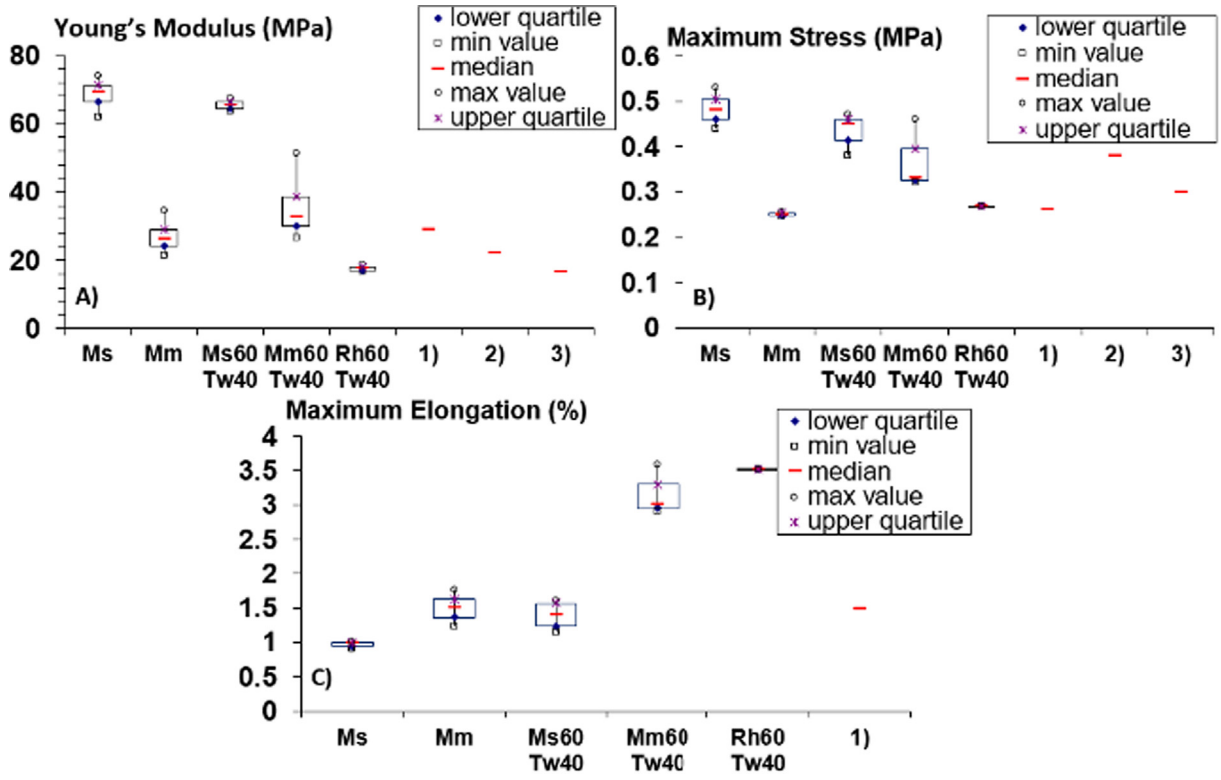


Fig. 4. Bending results: A) Young's modulus (MPa), B) maximum stress (MPa) and C) Maximum elongation (%); 1) EL HAGE et al. 2018 (miscanthus 2–6 cm) [34], 2) Adefisan et al. 2019, fiber size < 0.5 mm, (×10^2 Mpa) [25] and 3) Adefisan et al. 2019, fiber size < 0.2 mm, (×10^2 Mpa) [25].

stress also corresponds to the 2 formulations containing small miscanthus particles (M_s: 0.48 MPa and M_s60 Tw 40: 0.43 MPa) (Fig. 4B). The stress drops in the presence of medium-sized miscanthus M_m: 0.25 MPa (48%), M_m60 Tw40: 0.33 MPa (31%), rice husk Rh60 Tw40: 0.27 MPa (44%) and higher miscanthus fibers size (2–6 mm):0.27 MPa ([34] Fig. 4B-1). Same behaviour is observed by Adefisan et al. [25] for bamboo reinforced composites where a significant higher flexural strengths is obtained using lesser fibers size (<2 mm – Fig. 4B-1 and B-2). It should be noted that stress is improved by the addition of Tw only in presence of M_m. This observation is in agreement with our previous work [34] where 2–6 mm size miscanthus fibers where replaced by 50 wt% of Tw for the conception of lower density composite panels. However, this observation is not valid for low miscanthus particle size which could be related to the increasing in the wettability behavior of the miscanthus fibers which limits the influence of Tw on this mechanical parameter. The lowest median value for the elongation at maximum stress (0.99%) corresponds to the M_s composite panels (Fig. 4C). This value increases slightly with Tw addition and particle size increasing [34] (Fig. 4C-1), to reaches a median value of 3.2–3.5% for M_m60 Tw40 and Rh60 Tw40.

3.3.2. Compression properties

Young's modulus, maximum stress and deformation at maximum stress in vertical compressive mode are presented in Fig. 5. A scheme is added in Fig. 5 showing the direction in which the sample was tested. The same trend seen in bending tests is observed for all the composite panels in terms of Young's modulus and maximum stress for the compression tests. The modulus values in compressive mode are twice lower than those obtained in flexural mode. The highest modulus and maximum stress values (Fig. 5A–B) were found for M_s composite panels (36 MPa and 0.64 MPa respectively) in comparaison with M_m composite panels and miscanthus composites (Fig. 5A-1 and Fig. 5B-1) having 2–6 cm fiber size [34]. The median values of modulus and maximum stress decreased slightly for M_s60 Tw40 (28% and 12%) and dropped significantly for M_m (71% and 62% respectively), for M_m60 Tw40 (67% and 48% respectively) and Rh (78% and 60% respectively) in comparison to M_s. However, same behavior is also observed like in bending results for modulus and maximum stress values which increased for M_m60 Tw40 in comparison to M_m. This result confirms again that in the case of using M_m rigidity is increased by the addition of 40 wt% of a higher wettability Tw fibers.

On the other hand, concerning the densification strain (Fig. 5C) at the maximum stress, we can note a similarity of results for all formulations. The mean median value of the various materials is 0.22 ± 0.01%.

In conclusion to the results obtained in compression and bending tests it becomes clearer that the elastic modulus in bending and compression increases with decreasing miscanthus particle size by creating better interfacial bending [30] with chitosan matrix. These results are in agreement with those obtained for rice straw/polypropylene composite [44] where authors found a decrease in strength of PP composites as the particle size increases (20 MPa for 18–35 mesh straw and 15.6 MPa for 325 mesh straw) and wood/PP where a clear increase of 50% in strength and 23% of rigidity is obtained for smaller particle size (0.25 mm) in comparison to higher one (0.42 mm) [30]. However, to understand more clearly about the size effect of miscanthus fibres on the different properties of the chitosan-based composites, SEM analysis were performed on the surface of Mm and Ms fibres. SEM micrographs of Ms and Mm are presented in Fig. 6. It is clear from the micrograph of Mm the presence of silica nodules (confirmed by the EDX analysis) on the outer layer of the miscanthus surface which are not clearly visible in the micrographs of Ms. These hydrophobic nodular aggregates of the outer epidermis cells seems to prevent the wettability of the chitosan solution in these fibres and lead to bad interface in a similar behaviour of the rice husk [41]. However, for the small size miscanthus fibres Ms, in the absence of these nodules, the hydrophobicity of the fibres decreases, and more pores are shown in their outer structure leading to better

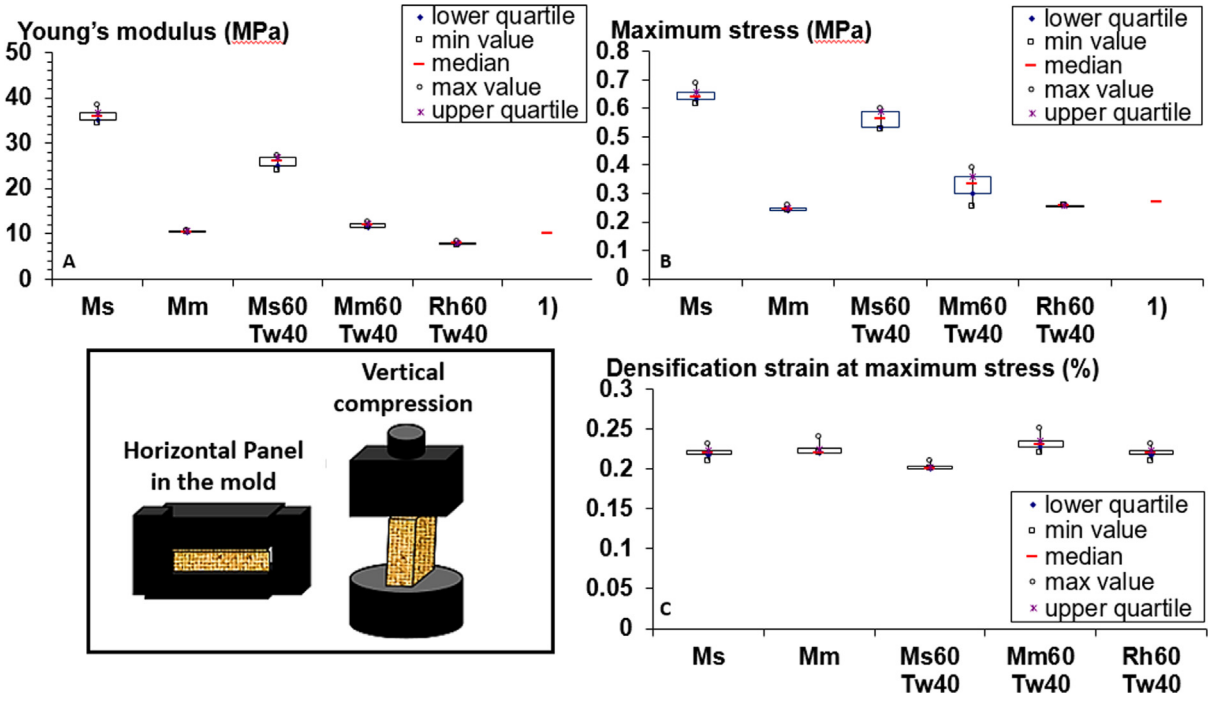


Fig. 5. Compressive results: A) Young's modulus (MPa), B) maximum stress and C) Densification strain at maximum stress (%);1) EL HAGE et al. 2018 (miscanthus 2–6 cm) [34].

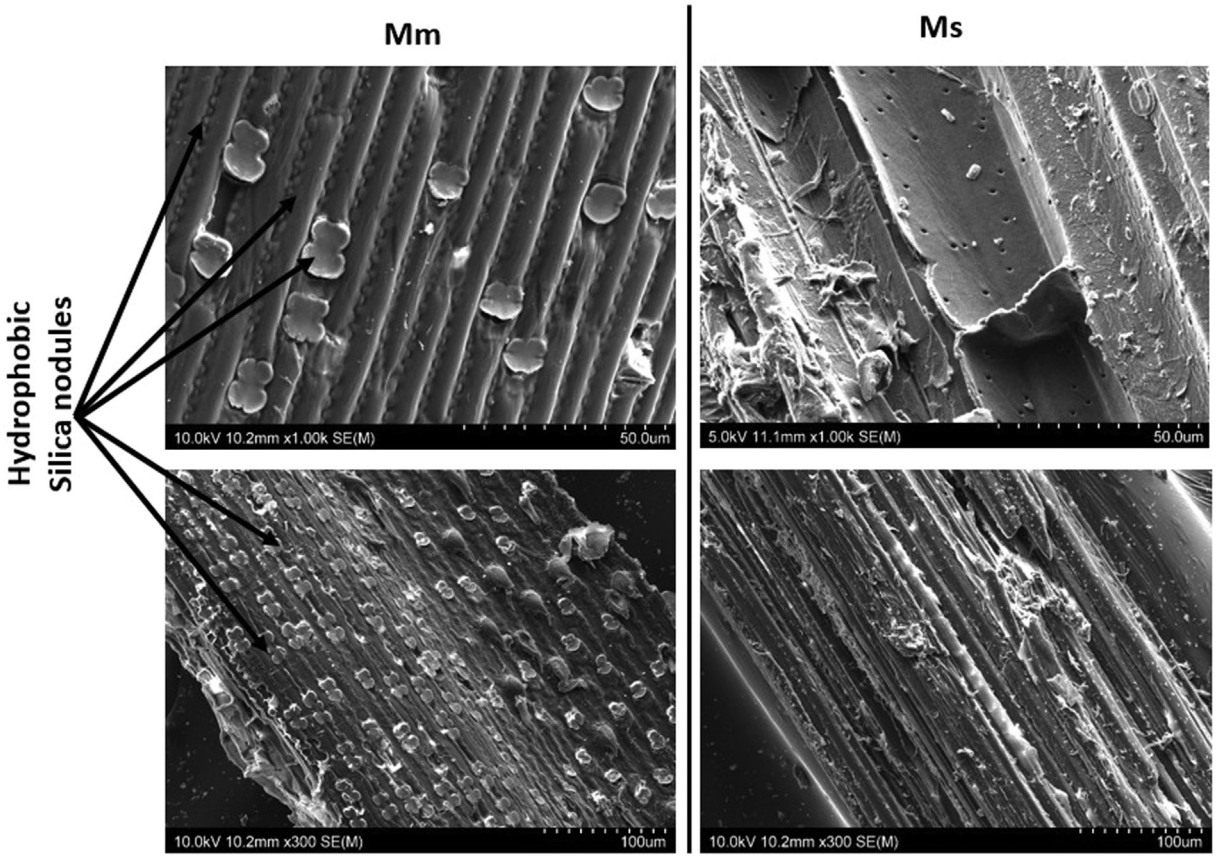


Fig. 6. SEM micrographs of Mm and Ms fibres.

absorption of the chitosan therefore a better adhesion of the manufactured composites. Finally, we can note that according to European construction specifications (DIN 4108–10) the maximum compressive and bending stress must be greater than 0.02 MPa for thermal insulation. The various formulations of this study, more precisely those which contain small size miscanthus (M_s) largely exceed this threshold value indicated in this standard (32 times superior in compression and 25 times superior in bending).

4. Conclusion

The main goal of this work was to evaluate the reinforcements particle size on the thermal and mechanical properties of insulating composites for building industry using renewable resources. We performed a careful analysis by preparing different composite panels having high porosity rate which reaches values of 60–75% and high density which ranged between 350 and 400 $Kg.m^{-3}$.

Based on the results of this investigation, miscanthus fibres alone or mixed with textile wastes and rice husks mixed with textile wastes could be considered as potential sources of natural and low-cost reinforcements for insulating composites.

It emerges from this study that the size and the nature of the used fibers influence the various final properties of the composite panels. Based on the thermal results, it has been shown that all the prepared composites are considered as insulating materials (0.076–0.0874 $W.m^{-1}.K^{-1}$) despite their high density (350–400 $Kg.m^{-3}$). We demonstrated that thermal conductivity increased with porosity decreasing and density increasing, and that porosity is the property that have a greater impact on this thermal parameter. Moreover, a linear relationship was only found for λ and β compared to particles size. Results showed an increasing of λ and β values with the addition of M_m particles. Furthermore, from bending and compressive analysis, results confirm that highest rigidity and stress are found for composites with M_s fibers which decreased significantly in presence of bigger particles size (M_m). This has been linked to the better wettability of M_s with the chitosanic matrix which has been confirmed by SEM observations of the two sizes of miscanthus fibres. However, it was concluded for the hybrid composites composed of two kind of fibers that the replacement of 40 wt% of miscanthus fibers by Tw increases the rigidity and stress for the less wettable M_m fibers but slightly decreases the rigidity and stress for the more wettable M_s fibers. Also, it was seen that fibers size increasing and Tw addition induce plastique behavior to the composites in bending analysis.

Finally, this work confirms a successful development of green biocomposites mainly composed of short miscanthus fibers (Ms < 1 mm) alone or mixed with Tw possessing very good mechanical and thermal properties. Further development of this research would be to study the fire, swelling, aging and sound insulation behaviours of the different panels produced.

CRediT authorship contribution statement

Yasmina Khalaf: Methodology, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Peter Hajj:** Methodology, Investigation, Writing - original draft, Writing - review & editing. **Yuliya Mihaylova:** Conceptualization, Supervision. **A. Bergeret:** Conceptualization, Supervision. **Patrick Lacroix:** Conceptualization, Supervision. **Roland El Hage:** Conceptualiza-

tion, Writing - original draft, Writing - review & editing, Supervision, Visualization, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This project was supported by the National Council for Scientific Research in Lebanon CNRS-L and Lebanese University (NOMISOL-2018/2020). The authors gratefully acknowledge EARL GozennAr and Le Relais companies for supplying freely the reinforcement used in this work. The authors would also like to thank Nisrine AARAJ-KHOURY and Maria Moussa for their help in some technical development and characterizations.

References

[1] L. Gustavsson, R. Sathre, Variability in energy and carbon dioxide balances of wood and concrete building materials, Build. Environ. 41 (7) (2006) 940–951, https://doi.org/10.1016/j.buildenv.2005.04.008.
[2] Z. Liu, S.Z. Erhan, D.E. Akin, F.E. Barton, "Green" composites from renewable resources: preparation of epoxidized soybean oil and flax fiber composites, J. Agric. Food Chem. 54 (2006) 2134–2137, https://doi.org/10.1021/jf0526745.
[3] V.I.E. Ajiwe, C.A. Okeke, S.C. Ekwuozor, I.C. Uba, Pilot plant for production of ceiling boards from rice husks, Bioresour. Technol. 66 (1998) 41–43, https://doi.org/10.1016/S0960-8524(98)00023-6.
[4] C. Buratti, E. Belloni, E. Lascaro, F. Merli, P. Ricciardi, Rice husk panels for building applications: thermal, acoustic and environmental characterization and comparison with other innovative recycled waste materials, Constr. Build. Mater. 171 (2018) 338–349, https://doi.org/10.1016/j.conbuildmat.2018.03.089.
[5] R. Muthuraj, C. Lacoste, P. Lacroix, A. Bergeret, Sustainable thermal insulation biocomposites from rice husk, wheat husk, wood fi bers and textile waste fi bers: elaboration and performances evaluation, Ind. Crop. Prod. 135 (2019) 238–245, https://doi.org/10.1016/j.indcrop.2019.04.053.
[6] A. Sorensen, P. Teller, T. Hilstrom, B. Ahring, Hydrolysis of Miscanthus for bioethanol production using dilute acid presoaking combined with wet explosion pre-treatment and enzymatic treatment, Bioresour. Technol. 99 (14) (2008) 6602–6607, https://doi.org/10.1016/j.biortech.2007.09.091.
[7] J. Eitzinger, C.h. Kössler, Microclimatological characteristics of a miscanthus (Miscanthus cv. giganteus) stand during stable conditions at night in the nonvegetative winter period, Theor. Appl. Climatol. 72 (3-4) (2002) 245–257, https://doi.org/10.1007/s00704-002-0681-9.
[8] R. Muthuraj, M. Misra, A.K. Mohanty, Biodegradable biocomposites from poly (butylene adipate-co-terephthalate) and miscanthus: Preparation, compatibilization, and performance evaluation, J. Appl. Polym. Sci. 134 (43) (2017) 45448, https://doi.org/10.1002/app.45448.
[9] R. Muthuraj, M. Misra, A.K. Mohanty, Injection molded sustainable biocomposites from poly(butylene succinate) bioplastic and perennial grass, ACS Sustain. Chem. Eng. 3 (11) (2015) 2767–2776, https://doi.org/10.1021/acssuschemeng.5b00646.
[10] R.M. Johnson, N. Tucker, S. Barnes, Impact performance of Miscanthus/Novamont Mater-Bi® biocomposites, Polym. Test. 22 (2) (2003) 209–215, https://doi.org/10.1016/S0142-9418(02)00084-3.
[11] A. Eschenhagen, M. Raj, N. Rodrigo, A. Zamora, L. Labonne, P. Evon, H. Welemane, Investigation of miscanthus and sunflower stalk fiber-reinforced composites for insulation applications, Adv. Civ. Eng. 2019 (2019) 1–7, https://doi.org/10.1155/2019/9328087.
[12] A. Briga-Sá, D. Nascimento, N. Teixeira, J. Pinto, F. Caldeira, H. Varum, A. Paiva, Textile waste as an alternative thermal insulation building material solution, Constr. Build. Mater. 38 (2013) 155–160, https://doi.org/10.1016/j.conbuildmat.2012.08.037.
[13] F. Asdrubali, F. D'Alessandro, S. Schiavoni, A review of unconventional sustainable building insulation materials, Sustain. Mater. Technol. 4 (2015) 1–17, https://doi.org/10.1016/j.susmat.2015.05.002.
[14] C. Rubino, S. Liuzzi, F. Martellotta, Preliminary investigation on the acoustic properties of absorbers made of recycled textile fibers Preliminary investigation on the acoustic properties of absorbers made of recycled textile fibers, Proc. 23rd Int. Congr. Acoust. (2019).
[15] C. Lacoste, R. El, A. Bergeret, S. Corn, P. Lacroix, Sodium alginate adhesives as binders in wood fi bers / textile waste fi bers biocomposites for building insulation, Carbohydr. Polym. 184 (2018) 1–8, https://doi.org/10.1016/j.carbpol.2017.12.019.
[16] A. Pizzi, Wood products and green chemistry, Ann. For. Sci. 73 (1) (2016) 185–203, https://doi.org/10.1007/s13595-014-0448-3.
[17] P. Antov, V. Savov, N. Neykov, Sustainable bio-based adhesives for eco-friendly wood sustainable bio-based adhesives for eco-friendly wood composites a review, Wood Res. 65 (1) (2020) 051–062.
[18] N. Mati-Baouche, H. De Baynast, A. Lebert, S. Sun, C.J.S. Lopez-Mingo, P. Leclaire, P. Michaud, Mechanical, thermal and acoustical characterizations of an insulating bio-based composite made from sunflower stalks particles and chitosan, Ind. Crops Prod. 58 (2014) 244–250, https://doi.org/10.1016/j.indcrop.2014.04.022.
[19] P.K. Dutta, D. Joydeep, V.S. Tripathi, Chitin and chitosan: properties and applications, J. Sci. Ind. Res. (India) 63 (2004) 20–31, https://doi.org/10.1016/j.progpolymsci.2006.06.001.
[20] M.A. Barbosa, P.L. Granja, C.C. Barrias, I.F. Amaral, Polysaccharides as scaffolds for bone regeneration, Itbm-Rbm 26 (3) (2005) 212–217, https://doi.org/10.1016/j.rbmret.2005.04.006.
[21] L. Illum, I. Jabbal-Gill, M. Hinchcliffe, A.N. Fisher, S.S. Davis, Chitosan as a novel nasal delivery system for vaccines, Adv. Drug Deliv. Rev. 51 (1-3) (2001) 81–96.
[22] A.K. Patel, P. Michaud, E. Petit, H. de Baynast, M. Grédiac, J.-D. Mathias, Development of a chitosan-based adhesive. Application to wood bonding, J. Appl. Polym. Sci. 127 (6) (2013) 5014–5021, https://doi.org/10.1002/app.38097.
[23] D. Belley, Détermination des propriétés de transfert de chaleur et de masse des panneaux de fibres de bois, 2009.
[24] W.Z.W. Mohamed, A. Baharum, I. Ahmad, I. Abdullah, N.E. Zakaria, Effects of fiber size and fiber content on mechanical and physical properties of mengkuang reinforced thermoplastic natural rubber composites, BioResources 13 (2018) 2945–2959, https://doi.org/10.15376/biores.13.2.2945-2959.
[25] O.O. Adefisan, A.G. McDonald, Evaluation of the strength, sorption and thermal properties of bamboo plastic composites, Maderas Cienc y Tecnol 21 (2019) 3–14, https://doi.org/10.4067/S0718-221X2019005000101.
[26] L. Aliotta, V. Gigante, M.-B. Coltelli, P. Cinelli, A. Lazzeri, M. Seggiani, Thermo-mechanical properties of PLA/short flax fiber biocomposites, Appl. Sci. 9(18) (2019) 9. https://doi.org/10.3390/app9183797.
[27] D. Jagadeesh, P. Sudhakara, C.V. Prasad, H.J. Kim, J.I. Song, A study on the mechanical properties of bio composites from renewable agro-waste/poly (lactic acid), J. Biobased Mater. Bioenergy 7 (1) (2013) 163–168, https://doi.org/10.1166/jbmb.2013.1277.
[28] A.O. Ameh, M.T. Isa, I. Sanusi, Effect of particle size and concentration on the mechanical properties of polyester/date palm seed particulate composites, Leonardo Electron. J. Pract. Technol. 14 (2015) 65–78.
[29] M. Kociszewski, C. Gozdecki, A. Wilczyński, S. Zajchowski, J. Mirowski, Effect of industrial wood particle size on mechanical properties of wood-polyvinyl chloride composites, Eur. J. Wood Wood Prod. 70 (2012) 113–118, https://doi.org/10.1007/s00107-011-0531-5.
[30] A. Nourbakhsh, A. Karegarfard, A. Ashori, A. Nourbakhsh, Effects of particle size and coupling agent concentration on mechanical properties of particulate-filled polymer composites, J. Thermoplast. Compos. Mater. 23 (2) (2010) 169–174, https://doi.org/10.1177/0892705709340962.
[31] P. Rebolledo, A. Cloutier, M.C. Yemele, Effect of density and fiber size on porosity and thermal conductivity of fiberboard mats, Fibers 6 (2018) 1–17, https://doi.org/10.3390/fib6040081.
[32] M.A. Tahir, H.V. Tafreshi, S.A. Hosseini, B. Pourdeyhimi, Modeling the role of microstructural parameters in radiative heat transfer through disordered fibrous media, Int. J. Heat Mass Transf. 53 (21-22) (2010) 4629–4637, https://doi.org/10.1016/j.ijheatmasstransfer.2010.06.030.
[33] J. Yang, H. Wu, M. Wang, Y. Liang, Prediction and optimization of radiative thermal properties of nano TiO2 assembled fibrous insulations, Int. J. Heat Mass Transf. 117 (2018) 729–739, https://doi.org/10.1016/j.ijheatmasstransfer.2017.09.069.
[34] R. El Hage, Y. Khalaf, C. Lacoste, M. Nakhl, P. Lacroix, A. Bergeret, A flame retarded chitosan binder for insulating miscanthus/recycled textile fibers reinforced biocomposites, J. Appl. Polym. Sci. 136 (13) (2019) 47306, https://doi.org/10.1002/app.v136.1310.1002/app.47306.
[35] R. Mcgill, J.W. Tukey, W.A. Larsen, Variations of box plots, Am. Stat. 32 (1) (1978) 12–16, https://doi.org/10.1080/00031305.1978.10479236.
[36] P. Ricciardi, F. Torchia, E. Belloni, E. Lascaro, C. Buratti, Environmental characterisation of coffee chaff, a new recycled material for building applications, Constr. Build. Mater. 147 (2017) 185–193, https://doi.org/10.1016/j.conbuildmat.2017.04.114.
[37] V. Guna, M. Ilangovan, C. Hu, K. Venkatesh, N. Reddy, Valorization of sugarcane bagasse by developing completely biodegradable composites for industrial applications, Ind. Crops Prod. 131 (2019) 25–31, https://doi.org/10.1016/j.indcrop.2019.01.011.
[38] B.P. Jelle, Traditional, state-of-the-art and future thermal building insulation materials and solutions - properties, requirements and possibilities, Energy Build. 43 (10) (2011) 2549–2563, https://doi.org/10.1016/j.enbuild.2011.05.015.

[39] A. Abdou, I. Budaiwi, The variation of thermal conductivity of fibrous insulation materials under different levels of moisture content, Constr. Build. Mater. 43 (2013) 533–544, https://doi.org/10.1016/j.conbuildmat.2013.02.058.
[40] J. Khedari, B. Suttisonk, N. Pratinthong, J. Hirunlabh, New lightweight composite construction materials with low thermal conductivity, Cem. Concr. Compos. 23 (1) (2001) 65–70, https://doi.org/10.1016/S0958-9465(00)00072-X.
[41] B.D. Park, S. Gon Wi, K. Ho Lee, A.P. Singh, T.H. Yoon, K.Y. Soo, Characterization of anatomical features and silica distribution in rice husk using microscopic and micro-analytical techniques, Biomass Bioenergy 25 (2003) 319–327, https://doi.org/10.1016/S0961-9534(03)00014-X.
[42] S. Panyakaew, S. Fotios, New thermal insulation boards made from coconut husk and bagasse, Energy Build. 43 (2011) 1732–1739.
[43] X. yan Zhou, F. Zheng, H. guan Li, C. long Lu, An environment-friendly thermal insulation material from cotton stalk fibers, Energy Build. 42 (2010) 1070–1074. https://doi.org/10.1016/j.enbuild.2010.01.020.
[44] N.L.E. Wahyuni, B. Soeswanto, H. Aulia, R.A. Fadhilah, The effects of rice straw weight fraction and particle size on thermal conductivity and mechanical properties of polypropylene composite, J. Phys. Conf. Ser. (2019) 1295. https://doi.org/10.1088/1742-6596/1295/1/012067.