

Binderless Bio-based Composites Obtained by Thermo-compression of Walnut Shells Powder

Mathilde David,^{a,*} Quentin Charlier ^{a,*} and Julien Bras ^{a,b}

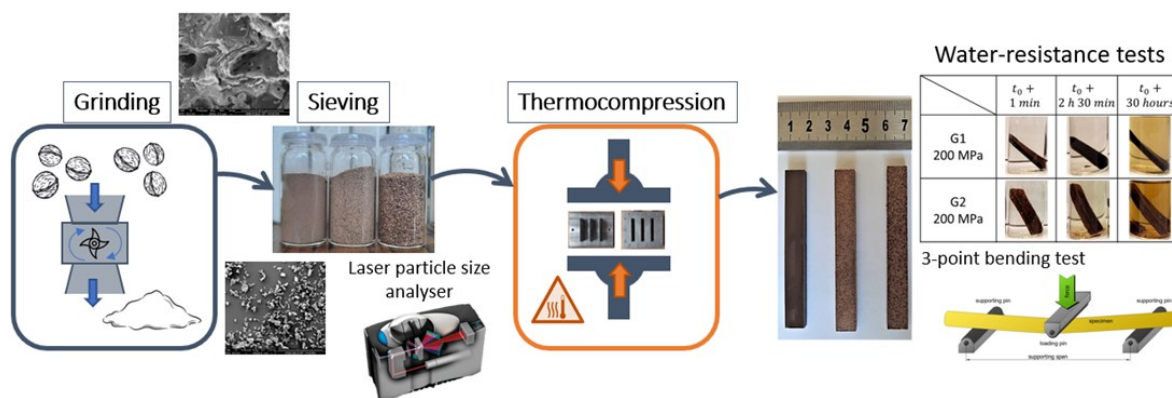
Contact information: *a*: Univ. Grenoble Alpes, CNRS, Grenoble INP, LGP2, F-38000 Grenoble, France;

b: Institut Universitaire de France (IUF), 75000 Paris, France;

* Corresponding author: quentin.charlier@grenoble-inp.fr

DOI: 10.15376/biores.21.3.6036-6049

GRAPHICAL ABSTRACT



Binderless Bio-based Composites Obtained by Thermo-compression of Walnut Shells Powder

Mathilde David,^{a,*} Quentin Charlier ^{a,*} and Julien Bras ^{a,b}

This study investigated the potential of dry processing methods to manufacture bio-based materials with reduced environmental impacts, which is in alignment with the energetic and ecological transitions global strategies. The increasing demand for eco-friendly materials drives research into bio-based composites. The mechanical properties were evaluated for binderless composites made from walnut shells, which are industrial bio-based by-products. Thermocompression moulding was used to fabricate the composites. Their mechanical behaviour and their resistance to water were tested. The composites showed a flexural strength of 16.9 MPa and a Young's modulus of 4.3 GPa. These findings suggest that walnut shell-based composites are viable alternatives for sustainable materials.

DOI: 10.15376/biores.21.3.6036-6049

Keywords: Walnut shells; Bio-based materials; Thermocompression molding; Mechanical testing

Contact information: a: Univ. Grenoble Alpes, CNRS, Grenoble INP, LGP2, F-38000 Grenoble, France;

b: Institut Universitaire de France (IUF), 75000 Paris, France;

* Corresponding author: quentin.charlier@grenoble-inp.fr

INTRODUCTION

Nowadays, daily used materials faces issues at different levels:

- Their sourcing relies too often on fossil resources, which face issues including oil depletion and the environmental impacts caused by oil extraction.
- They often have short service life, which raises their overall environmental footprint.
- They are mostly non-biodegradable, and they are not always recycled nor designed considering end of life. Moreover, they also raise concerns regarding micro-plastics effects on life on land and sea.

The shift toward eco-friendly materials is crucial to address environmental issues. Advancements in composite materials focus on factors such as material origin, energy consumption, recyclability, biodegradability, and applications. One way to improve the sustainability of daily used materials is to shift from oil sourcing to lignocellulosic biomass materials. This switch can lead to a more sustainable way of consumption.

In order to process lignocellulosic biomass, wet processing methods are commonly used, such as those for producing paper, cardboard, and cellulose microfibrils. However, these methods have significant drawbacks, particularly in terms of high energy costs associated with drying and the handling of large volumes of water. Another way that could be explored to process lignocellulosic biomass is dry processing methods, which can, under the right conditions, reduce energy consumption and simplify the processing steps.

This article explores ThermoCompression Molding (TCM) as a promising method, enabling direct dry processing of biomass. Studies have demonstrated that natural plant

fiber components can act as binders without additives, while producing materials at lab scale through TCM (Pintiaux *et al.* 2015; Hubbe *et al.* 2017).

Furthermore, bio-composites have successfully been made with TCM from native starch granules and wood fibers (Regazzi *et al.* 2019). Samples described in the cited work exhibited promising microstructural and mechanical properties, with starch fibers enhancing the overall performance when combined with wood fibers. Three-point bending tests showed a Young's modulus of 6 GPa, a flexural strength of 75 MPa, and a flexural strain at break of 6% for a bulk density of 1.25 g.cm⁻³. Additionally, cellulose nanofibrils molded under thermo-compression exhibited high structural integrity and stiffness (Rol *et al.* 2020). However, this dry biomass processing technique is not widely adopted, and data on the mechanical properties of resulting materials remain limited. Since biomass is more heterogeneous than traditional oil-sourced polymer matrices, a comprehensive understanding of how factors such as particle geometry and chemical composition affect the final properties of these materials becomes crucial. Variations in particle geometry and chemical composition, as observed in oil palm trunk and spruce bark panels, also play a critical role in determining the final material properties (Gao *et al.* 2011; Nishino *et al.* 1995).

In the frame of this study, walnut shells were selected because they are a byproduct in the production of walnuts, which is important in the region of Grenoble, France. Walnuts shell (WS) are classically made of 27.4 to 52.3 % of lignin (type SG), 25.6 to 34.5 % of cellulose, 22.1 to 27.6 % of hemicellulose, 9.9 to 12.5 % of extractives with almost half of polar extractives (4.6 % according to (Domingos *et al.* 2022)), and between 0.6 and 1.7% of ashes (Queirós *et al.* 2020). Their rich content in lignin, pectin and hemicellulose is expected to make it a good fit for the targeted process.

Over the past decade, numerous studies have reported on the development of polymer-based bio-composites incorporating walnut shell particles as fillers, produced *via* thermo-compression. Improved tensile strength and thermal stability in polyurethane foams reinforced with walnut shells have been observed, especially when silane-treated (Członka *et al.* 2020). In PLA composites for food packaging, silane-functionalized walnut shells contribute to increase tensile strength and durability (Palaniyappan *et al.* 2024). On the other hand, by adding 20% of walnut shells in the matrix, it has been possible to decrease by 42% the thermal conductivity of the composites (Khantwal *et al.* 2016). Collectively, these studies underscore that walnut shell composites, particularly when surface-modified, consistently achieve enhanced mechanical properties across various polymer matrices.

However, the approach developed in this study is quite different from production of conventional polymer-based composites. Binderless composites utilize the natural self-bonding qualities of bio-elements such as lignin-based fibers or ground powders when exposed to heat and pressure. Bonding results from a combination of mechanisms. Above their glass transition temperature, biopolymers can flow and penetrate inside fibers or powder pores, creating mechanical interlocking upon cooling. Simultaneously, hydrogen bonds form between biopolymer and cellulose hydroxyl groups, while thermal cross-linking may occur in certain biopolymers (*e.g.*, proteins, starches), further strengthening adhesion (Hubbe *et al.* 2017). Thus, the objective of this study is to evaluate the capability of walnut shells to be shaped without binder by TCM and to assess the properties of the resulting materials.

To do so, different samples have been fabricated by varying the process parameters of TCM (pressure, temperature) and the morphology of walnut shells. Following this, the

mechanical properties of the fabricated materials were characterized by three-point bending tests. Scanning Electron Microscope (SEM) and Optical Microscope (OM) images of the composites were taken to analyze the structure. Water resistance tests were conducted. The properties of 100% walnut shell composites were then discussed and compared to conventional plastics and other materials obtained from similar approaches.

EXPERIMENTAL

Materials

Walnut shells (WS) from Grenoble Protected Designation of Origin (PDO) were provided by Cave Noisel, at Saint-Jean-en-Royans, France. The walnut shells came from the 2022 harvest. They were dried from October until they were sorted and cracked open in January 2023.

Methods

Walnut shells powder preparation and separation

The WS were ground at room temperature with a rotary knife mill SM100 provided by Retsch (Haan, Germany) during about a total of 60 min.

A series of 3 to 4 output grids were used in order to obtain various level of ground particles (respectively 4 mm, 1.5 mm, 750 μm , and 250 μm). These particles were then separated in size using 3 consecutive sieves (respectively 500 μm , 450 μm , and 75 μm). WS particles were divided into three populations:

- G1: the smallest powder used in this study, those that passed through the 75 μm holes diameter sieve;
- G2: the intermediate particles, those that had been blocked by the 75 μm holes diameter sieve but that had passed through the 425 μm openings;
- G3: the bigger particles used in this study, corresponding to the particles located in between the 425 μm and the 500 μm sieves.

Thermocompression of WS powder

Samples were prepared using a thermopress LabEcon 600 provided by Fontijne Grotnes BV (Rotterdam, Holland). Stainless steel moulds with cavities for the simultaneous production of three specimens of 80 by 10 mm² were selected for this study. WS particles were stored at least 24 h in a conditioned room at a temperature of 23 °C and a humidity percentage of 50%. The moisture content inside the particles was measured before the TCM and was in the range $6.26 \pm 0.05\%$ (w:w).

The WS particles were placed in the preheated mould with a total of 4 g spread in each mould cavity. After closing and placing the mould in the thermopress, a pre-compression force of 100 kN (240 MPa) during 10 min at the set temperature was applied on the mould. Afterward, the thermocompression was applied during 10 min at different temperatures and pressures. The non-hermetic mould design allowed moisture to escape during processing, precluding real-time moisture monitoring.

Once the thermocompression was finished (after 20 min), the mould was taken out of the thermopress, and the samples are retrieved from the cavities. The samples were then stored in a controlled environment (23 °C and 50% relative humidity).

Characterization

Granulometry

The WS granulometry was carried out with a CILAS 1190 laser particle size analyzer (CPS US, Inc., USA) in a wet dispersion (after magnetic steering in deionized water). As the studied particles were larger than 50 μm , the Fraunhofer theory was used. Mie theory was also used to evaluate the presence of smaller particles in the samples, in this case, cellulose diffraction index is used ($1.470 - 0.100 / 1.33 \text{ i}$), as suggested in the norm ISO 13320:2020. At least triplicates were performed and the most representative results is used for the discussion.

Chemical analysis

The chemical composition of the samples was determined using the Van Soest method, following the standards (“ISO 13906; Animal feeding stuffs — Determination of acid detergent fibre (ADF) and acid detergent lignin (ADL) contents” 2008) ISO 13906 and (“NF V18-122; Animal feed - Sequential determination of parietal constituents - Method using neutral and acidic detergents and sulphuric acid” 2008) NF V18-122. This method is based on the sequential solubilization of plant cell wall components using three detergent solutions, followed by ash determination *via* incineration. The procedure includes the following steps: 1 - Neutral Detergent Fiber (NDF) treatment: partial removal of pectins, 2 - Acid Detergent Fiber (ADF) treatment: removal of pectins and hemicelluloses, 3 - Acid Detergent Lignin (ADL) treatment: removal of pectins, hemicelluloses, and cellulose, 4 - Ashing (calcination): complete removal of organic matter, allowing quantification of the mineral fraction.

Mass loss after each treatment step was recorded in order to estimate the content of various cell wall components. It should be noted that the values obtained for pectins and hemicelluloses are approximations, as the Van Soest method does not specifically isolate these fractions but rather infers them from differential solubility.

The following parameters were thus estimated: 1 - Pectin content (approximated), 2 - Hemicellulose content (approximated), 3 - Cellulose content, 4 - Lignin content, 5 - Ash content (mineral matter). These characterizations were duplicated and the average was used for the discussion.

ThermoGravimetric analysis (TGA)

Thermogravimetric analysis was done using a TGA-DSC 3+ Melter Toledo device (Columbus, Ohio, USA). Analysis were done both in air and nitrogen environment. The temperature ranged between 25 °C and 900 °C at rate of 10 °C.min⁻¹. Archimedes thrust was considering by the device and alumina sample holder are used. An average mass of 8 mg per samples was used and triplicate measurements were performed. The graph presents the most representative curve.

Density measurement of thermocompressed WS

After at least 24 h in 50% RH and 23 °C, samples were weighted with an analytical balance ME204 (from Mettler Toledo, Greifensee, Switzerland) and their dimensions were measured with a precision caliper. These results were used to compute the composites densities.

Microscopy analysis

A Zeiss Axio Imager (Oberkochen, Germany), an optical microscope (OM), was used in transmission and in reflection mode to observe particles and composites.

A Quanta 200 Scanning Electron Microscope (SEM) provided by FEI (Hillsboro, Oregon USA) was used to take pictures at a smaller scale. This environmental tungsten SEM operate at 10 kV in secondary electron mode. Samples are previously metallized using a coating device to deposit a gold layer of 10 nm. In both cases, minimum 10 images per samples were obtained and the most representatives are used for the discussions.

Mechanical analysis

Three-point bending tests were performed based on the norm (“Wood-based panels. Determination of modulus of elasticity in bending and of bending strength” 1993) BS EN 310:1993 with some modifications, simply because some specimens could not follow the norm requirements in terms of dimensions. The support span was fixed at 64 ± 0.2 mm. A displacement velocity of $2 \text{ mm} \cdot \text{min}^{-1}$ was used. All measurements were done in triplicate. An Instron (Glenview, Illinois) 5965 universal testing machine with a 5 kN load cell capacity was used to perform the tests in a controlled environment (23°C and 50% relative humidity). Modulus of elasticity (*MOE*) were assessed using the norm recommendations,

$$MOE = \frac{l_1^3(F_2 - F_1)}{4bt^3(a_2 - a_1)} \quad (1)$$

where l_1 is the distance between the centers of the supports (mm), b is the width of the test piece (mm), t is the thickness of the test piece, $(F_2 - F_1)$ corresponds to the increment of the load on the straight-line portion of the load-deflection curve (N), F_1 shall be approximately 10% and F_2 shall be approximately 40% of the maximum load (N), and $a_2 - a_1$ is the increment of deflection at the mid-length of the test piece (corresponding to $(F_2 - F_1)$).

Samples bending strength are obtained thanks to,

$$MOR = \frac{3F_{\max} l_1}{2bt^2} \quad (2)$$

where $F_{\max}$ is the maximum load (N), and l_1 , b , and t are as mentioned above (mm).

Sample swelling in water and water resistance

Water resistance was assessed by water absorption measurements. Samples were immersed in deionized water and retrieved at different time: from 1 min to 30 h. Their thickness was measured with a caliper and their mass with a scale at each given time. The specimens were triplicated and conditioned at 23°C and relative humidity of 50% for at least 48 h before testing. The specimens were immersed in the same amount of distilled water. The thickness swelling and water absorption values were determined as follows,

$$\text{Thickness swelling (\%)} = \frac{t_i - t_0}{t_0} \times 100 \quad (3)$$

where t_0 and w_0 are the specimen initial thickness (mm) and weight (mg) and t_i and w_i are the specimen thickness (mm) and weight (mg) at time i .

RESULTS AND DISCUSSION

Walnut shells powder characterization

Fig. 1. Chemical characterization of walnut shell (WS) composites. Figure 1 presents an overview of the raw materials and the corresponding composite specimens fabricated for this study. The effect of particle size on composite properties was investigated using three distinct granulometries (G1, G2, and G3) of walnut shell particles.

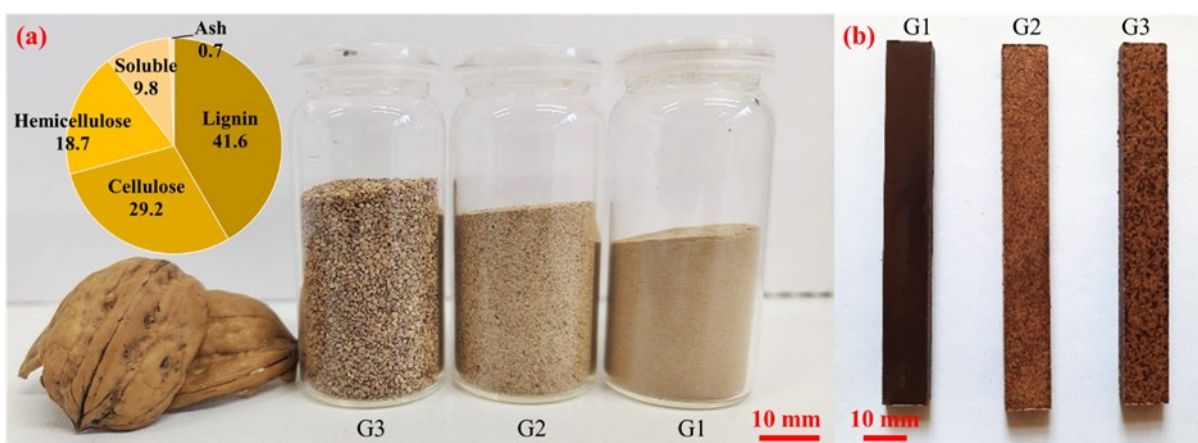


Fig. 1. Chemical characterization of walnut shell (WS) composites. (a) Raw WS and milled particles (G3, G2, G1); (b) composite samples (175 °C, 200 MPa) with different particle sizes (G3, G2, G1)

Once the grinding had been completed, optical microscope images were taken to observe the different WS particles obtained. It is clear that their shapes were non-spherical and heterogeneous. In Fig. 2, particles images, using optical microscopy (a), (b) and (c) and using MEB (d), (e) and (f) of the granulometry G1 ((a) and (d)), G2 ((b) and (e)) and G3 ((c) and (f)), SEM images of different particle sizes are presented.

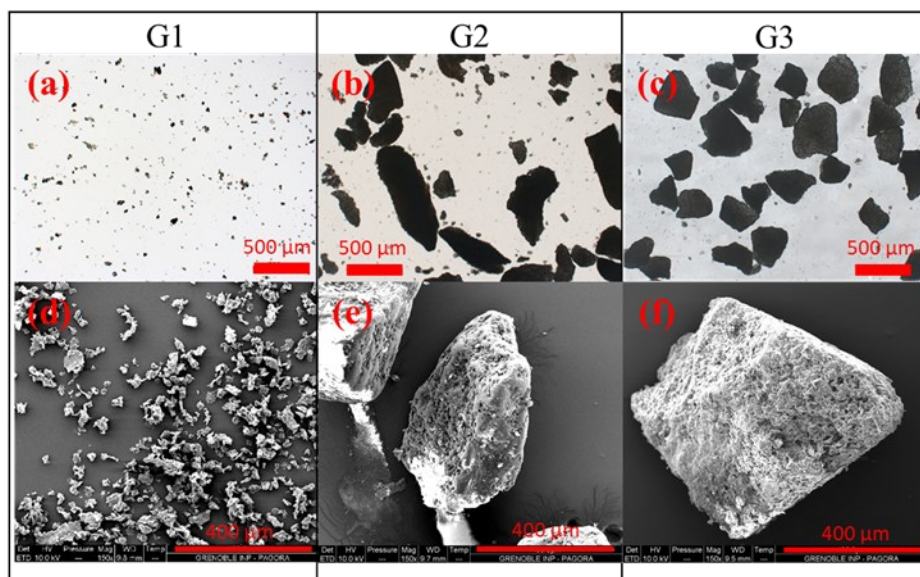


Fig. 2. Particle morphology of granulometries G1 (a, d), G2 (b, e), and G3 (c, f) observed by optical microscopy (a-c) and SEM (d-f)

These images allow a better understanding of the initial structures of the particles. The granulometry results obtained by granulometry (Fig. 3) assume that the analyzed particles are spherical. Diameters at 50% were respectively $625 \pm 4 \mu\text{m}$, $449 \pm 3 \mu\text{m}$, $31.77 \pm 0.09 \mu\text{m}$, for G3, G2, and G1. Nonetheless, the maximum diameters measured by the particle size analyzer were bigger than the sieve mesh sizes used. This may imply that the particles analyzed were not spherical, which confirms the observations of MO and SEM images. This can explain why the obtained density function did not look exactly like a Gaussian curve. Particles G2 and G3 had close mean diameters and their density functions were superimposed (Fig. 2).

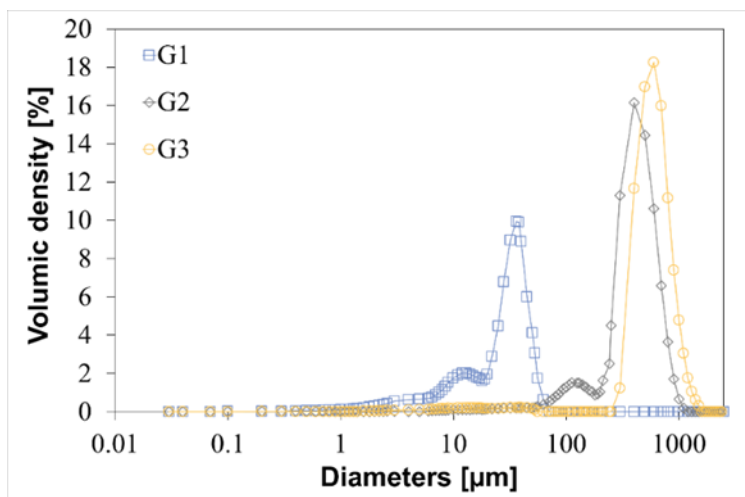


Fig. 3. Size repartition of walnut shells particles: Fraunhofer methods for G1, G2, and G3 particles

Chemical composition of WS particles prior to size fractionation

The walnut shell particles showed a composition dominated by lignin (41.6%), with significant amounts of cellulose (29.2%) and hemicelluloses (18.7%). Soluble compounds accounted for 9.8%, and ash content was measured at 0.7%. These values are consistent with the ranges reported in the literature, confirming the reliability of the analysis (Domingos *et al.* 2022). A slightly lower hemicellulose content and similar levels of extractives and ash were observed (Domingos *et al.* 2022), which may result from natural variability in the raw material or differences in extraction procedures. The high lignin content reflects the inherent rigidity of walnut shells.

All TGA curves displayed an initial decrease in mass close to 100°C corresponding to the water contained in the WS particles. The amount of water in G1 particles seems to have been higher than in particles G2 and G3, as indicated by the more pronounced initial mass loss. This was attributed to a higher specific surface area, making cellulose and hemicellulose more accessible. Until 200°C the relative mass was stable. Particles did not deteriorate below this temperature. No differences can be seen on the nitrogen TGA curve. All sizes of particles seem to have exhibited the same thermal behavior in a nitrogen environment. The inflection points were similar to each other, and respectively in between 339.6 and 351.3°C for the smallest to the biggest particles. On the other hand, the TGA curve obtained in air (Fig. 3) showed more distinctly that smaller particles were more sensitives to high temperatures. The smallest particles inflection point corresponded to a temperature of 300.8°C , whereas the inflection point of the bigger ones was 340.5°C .

The distinct thermal behavior of G1 particles may be linked to their higher water retention capacity, as evidenced by the initial mass loss observed during TGA. This greater hygroscopicity could result from a more porous structure or a higher content of hydrophilic constituents such as hemicelluloses or pectins. Additionally, the higher surface area-to-volume ratio of smaller particles could enhance oxidative reactions in air, making them more thermally sensitive. These factors suggest that G1 particles exhibit a unique physicochemical profile that could influence their suitability for thermochemical conversion processes.

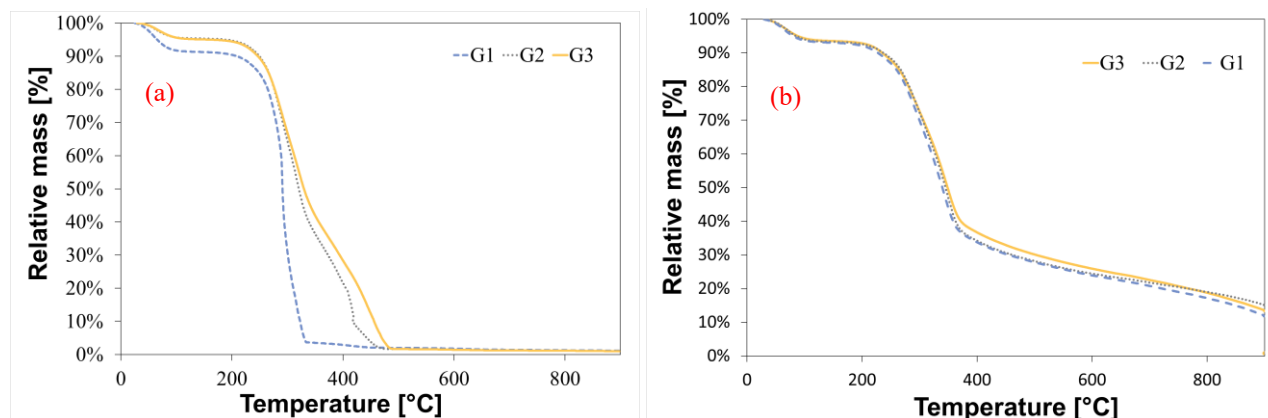


Fig. 4. Thermogravimetric curves of walnut shells particles in air (a) and nitrogen (b)

Structural properties of thermocompressed WS composites

Walnut shell (WS) composites were then produced by thermocompression with the different powder specimens, testing different temperatures.

Optical and SEM images showed good composite homogeneity. Within the composites, individual WS particles could be distinguished by their color variations. These chromatic differences likely arise from compositional variations among the WS particles, which may depend on their origin within the walnut shell (inner vs. outer layers) and the inherent variability between individual walnuts.

It is possible that smaller particles contain a relatively higher lignin content. This assumption is supported by previous studies that have demonstrated a correlation between particle size and chemical composition in lignocellulosic biomass: finer particles often exhibit increased concentrations of lignin and ash, along with altered thermal decomposition behaviors compared to coarser fractions (Mawardi *et al.* 2021). Such differences may arise from the higher surface area-to-volume ratio and selective fragmentation during grinding processes. Moreover, the composite density did not seem to depend on the temperature, the pressure, or the particles sizes during the TCM.

The mean WS composites final density was $1.27 \pm 0.04 \text{ kg.mm}^{-3}$. The composite absolute density was relatively high compared to particleboard (average density between 650 and 750 kg.mm^{-3} according to ANSI A208). This value also positioned the material within the upper range of binderless lignocellulosic composites, and even slightly higher than most values found for walnut shell-based composites (1.03 to 1.20 g.cm^{-3}) (Khantwal *et al.* 2016; Pintiaux *et al.* 2015; Rol *et al.* 2020).

Moreover, the composite density did not seem to depend on the pressure, especially with the fine WS powder (G3), as can be seen on the graph below (Fig. 5).

At 175 °C (Fig. 5a), the composite density depended more on the particle size than on the applied pressure (respectively 1.34 ± 0.02 , 1.28 ± 0.03 and 1.23 ± 0.01 kg.mm⁻³ for G1, G2 and G3).

At 200 MPa (Fig. 5b), the density increased with the temperature and the particle size from 1.23 ± 0.03 kg.mm⁻³ at 150 °C for G3 up to 1.30 ± 0.01 kg.mm⁻³ for G2 at 200 °C.

The degree of densification increases with decreasing particle size due to improved packing. Concurrently, higher processing temperatures enable the reorganization of amorphous regions into more ordered structures (Hubbe *et al.* 2017).

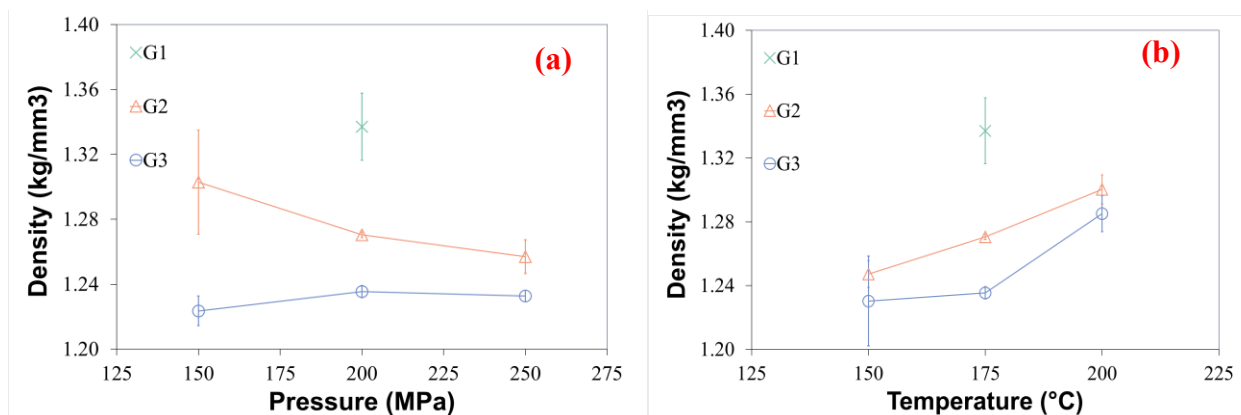


Fig. 5. Influence of pressure (a) and temperature (b) on the composites final density at (a) 175 °C and (b) 200 MPa

Influence of particle size, temperature and pressure on mechanical properties of thermopressed WS composites

Figure 6 presents the bending characteristic curves of the three composite groups. All samples exhibited brittle behavior, characterized by low strain at break and a sudden stress drop after reaching the maximum load.

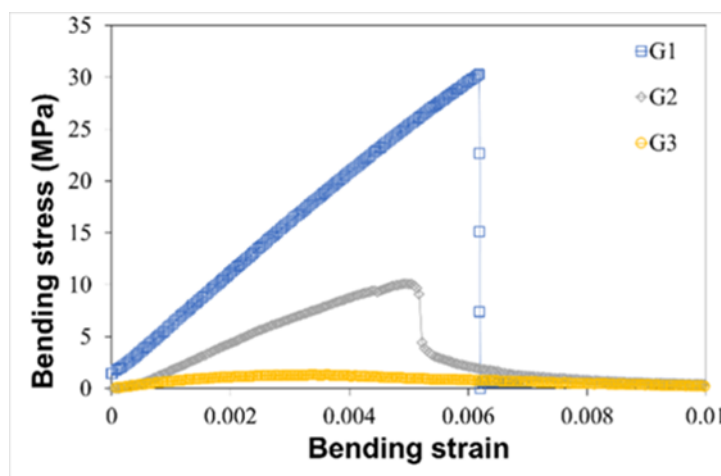


Fig. 6. Examples of Stress - Strain curves of the different composites

The initial slope of the curves, corresponding to the flexural modulus, was highest for G1 (the smallest particle size) and decreased with increasing particle size. The area under the curves, which reflects the energy absorbed before failure, remained low for all groups, with

a slightly higher value observed for G2. A limited pseudo-ductile behavior can be noted in G2, as shown by a short plateau before fracture. Samples exhibited early failure at very low flexural strain, confirming the brittle behavior of walnut shell powder composites. Fractured samples showed predominantly interparticle debonding, indicating that interfacial bonding strength rather than particle strength limits mechanical performance.

Particles size and the compression temperature were key parameters (Fig. 5 to 8). An increase in temperature led to an increase in the modulus. When increasing the temperature from 150 to 200 °C at 200 MPa, the density decreased by 4.3% and the MOE rose by a factor of 2.4 (for example, with particles G2). However, above 200 °C (*i.e.* 225 °C), it was not possible anymore to obtain composite samples for the tested pressures. At 225 °C, compressed particles started to flow out of the mold through die clearances (≤ 0.15 mm) and became significantly darker, resulting in deformed samples resembling the mold imprint rather than testable specimens. On the other hand, it seems that increasing the pressure did not improve the composite final density and mechanical properties as it was expected.

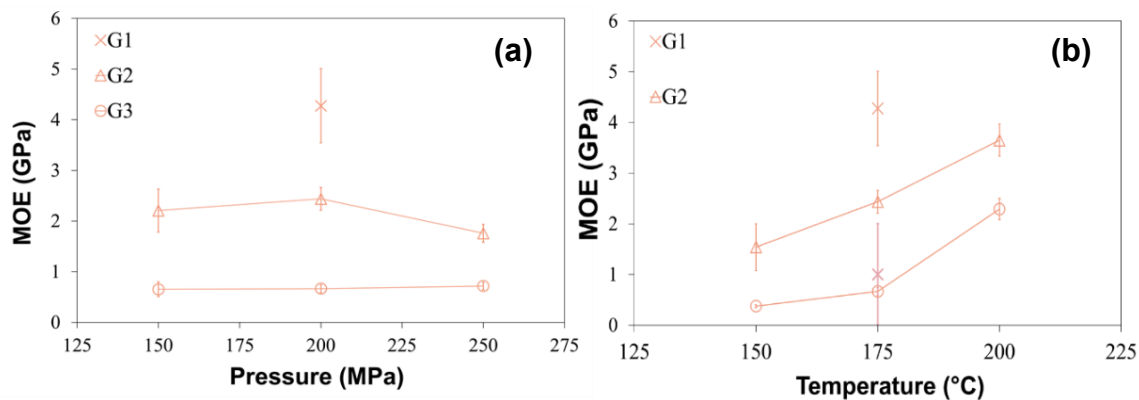


Fig. 7. Influence of the pressure and temperature on the module of elasticity at 175°C for (a) and at 200 MPa (b)

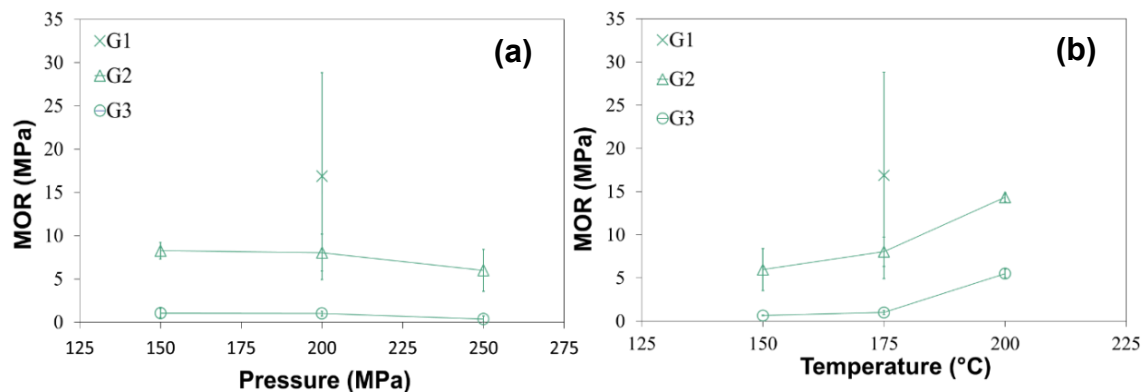


Fig. 8. Influence of the pressure and temperature on the module of rupture at 175°C for (a) and at 200 MPa (b)

By increasing the pressure from 150 to 250 MPa (for particles G2 at 175°C), the density was decreased by 3.5%. Concerning mechanical properties, the MOE was decreased by 26% and the MOR by 38%. Indeed, the pressures used in this study (150 to 250 MPa) were already significantly higher than those typically employed for conventional bio-based materials processing, such as particleboard (1 to 5 MPa) or molded cellulose (0.5

to 1 MPa) (Pintiaux *et al.* 2015; Zhang *et al.* 2015; Tajuddin *et al.* 2016; Pizzi *et al.* 2020; Hubbe *et al.* 2023). This necessity for elevated pressures stems from the dry processing route, which, in the absence of water, requires substantially higher mechanical forces to achieve adequate particle bonding and densification compared to wet-forming processes.

As can be seen in Fig. 7 and 8, the WS composite made out of smaller particles sizes (G1) achieved higher MOE and MOR than the composite made out of bigger ones (G2, G3). Regarding the MOE, at 175 °C and 200 MPa it ranged from 0.66 GPa for G3 to 2.44 GPa for G2, and 4.28 GPa for G1. Reducing the mean particle size by 95% led to a significant improvement in stiffness, with the MOE increasing by a factor of 3.7. Smaller WS particle size led to higher MOE and MOR. These MOE values placed the best-performing WS composites well above many binderless bio-composites found in the literature, including those reported by Gao *et al.* (2011) or Rol *et al.* (2020), and they were even comparable to the upper range of values cited by (Regazzi *et al.* 2019) for high-density samples. While ultimate strengths (MOR) were lower than those of conventional composites containing synthetic adhesives, the values obtained were comparable to those reported for other binderless materials and walnut shell-based composites (Palaniyappan *et al.* 2024), demonstrating the feasibility of binder-free processing for this type of biomass.

Influence of immersion in water on WS composite dimensions

Among the tested samples, only those made from G1 and G2 walnut shell particles withstood immersion for more than 30 seconds. G3 samples (the biggest particles) disintegrated quickly into the water. G1 samples (smallest particles) remained intact even after 30 h in water, whereas G2 samples (intermediate size) failed after 1 h (200 MPa, 175 °C) and 5.5 h (250 MPa, 175 °C), allowing only thickness swelling to be evaluated. The water surrounding the G2 samples developed a noticeable brown coloration, which was attributed to the higher release of extractives. This effect is likely due to the less cohesive structure of G2 composites, which facilitates the leaching of soluble compounds. In contrast, G1 samples, limited the release of extractives, resulting in less water discoloration.

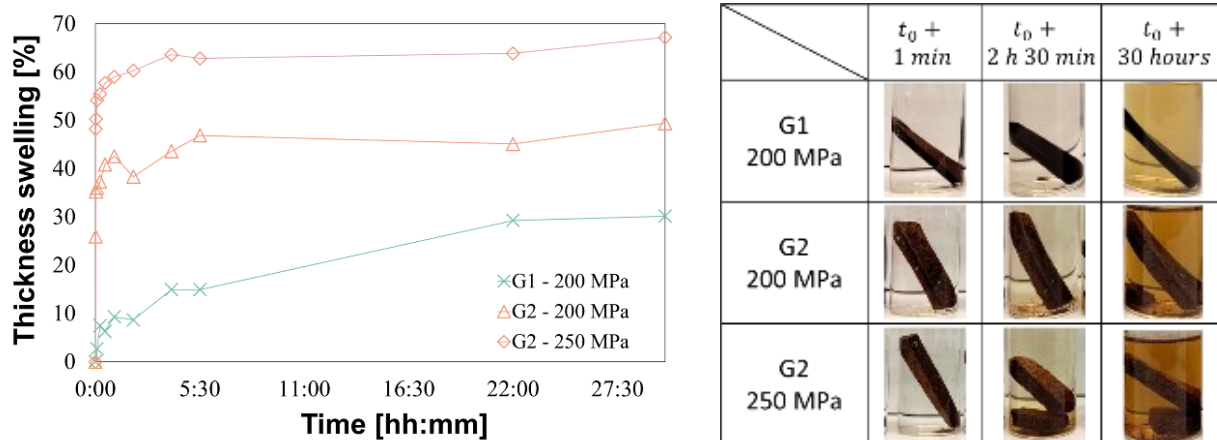


Fig. 9. Water resistance observations and results; (a) thickness swelling evolution over time; (b) samples pictures at different times for samples made at 175°C

Swelling was faster for G2. G1 exhibited a gradual, steady increase in water uptake, indicating a compact, hydrophobic structure. After 30 hours, G1's thickness swelling reached about 30%, compared to 50% and 70% for G2 samples at 200 MPa and 250 MPa, respectively. Overall, G1 composites demonstrated better water resistance compared to G2,

maintaining structural integrity with more limited swelling. However, the observed thickness swelling, even for G1 (around 30%), remained significant and may restrict the use of these materials in applications requiring dimensional stability under prolonged water exposure.

The link between mechanical and hygroscopic properties was obvious in the contrasting properties of composites made from smallest and intermediate size particles. Samples made from the smallest particles were denser and had a more cohesive structure. This not only enhanced its mechanical strength but also limited water penetration, resulting in gradual swelling and better water resistance. Conversely, samples made with intermediate size particles exhibited lower mechanical properties and were more susceptible to water absorption and swelling, which compromised their mechanical integrity. These findings emphasize that optimizing particle size and processing conditions is essential to achieving a balance between mechanical strength and moisture resistance in composite materials.

CONCLUSIONS

100% binderless composites were successfully produced from an industrial biobased by-product, the walnut shell (WS) by thermocompression, using varying particle sizes ($625 \pm 4 \mu\text{m}$, $449 \pm 3 \mu\text{m}$, $31.77 \pm 0.09 \mu\text{m}$), temperatures (150, 175, 200 °C), and pressures (150, 200, 250 MPa). The use of such high pressures (150 to 250 MPa) is inherent to the dry, binderless processing approach and represents a requirement for successful composite formation.

1. The (WS), rich in lignin and cellulose, demonstrated good compatibility with this process. The best mechanical performance was achieved with the smallest particles ($<75 \mu\text{m}$), reaching 4.3 GPa for the module of elasticity (MOE) and 16.9 MPa for the module of rupture (MOR). These values are comparable to those reported for other binderless lignocellulosic materials.
2. Cohesiveness demonstrated by immersion in water was also influenced by particle size: finer particles resulted in lower swelling and better integrity after immersion.

Such results are very promising in view of the goal to valorize 100% binderless bio-based by-product materials for numerous applications such as particleboard or structural composites. To further enhance ductility, future developments could include the addition of bio-based plasticizers such as PHBH, in line with a fully sustainable material strategy. Particle surface modification through simple grafting approaches could further enhance mechanical and hygroscopic properties. Future iterative optimization of these composites would benefit from long-term durability testing (cyclic hygrothermal exposure, creep) to progressively refine material performance.

ACKNOWLEDGMENTS

This work was supported by the Agence Nationale de la Recherche (ANR-23-CE43-0002). LGP2 is part of the LabEx Tec 21 (Investissements d'Avenir - grant agreement n°ANR-11-LABX-0030) and of PolyNat Carnot Institute (Investissements

d'Avenir - grant agreement n° ANR-16-CARN-0025-01) and of the Cross Disciplinary Program Glyco@Alps (Investissements d'avenir – Grant agreement ANR-15-IDEX-02).

REFERENCES CITED

- BS EN 310 (1993). "Wood-based panels. Determination of modulus of elasticity in bending and of bending strength," British Standards Institution, London.
- Członka, S., Strąkowska, A., and Kairytė, A. (2020). "Effect of walnut shells and silanized walnut shells on the mechanical and thermal properties of rigid polyurethane foams," *Polymer Testing* 87, article 106534. <https://doi.org/10.1016/j.polymertesting.2020.106534>
- Domingos, I., Ferreira, J., Cruz-Lopes, L. P., and Esteves, B. (2022). "Liquefaction and chemical composition of walnut shells," *Open Agriculture* 7(1), 249-256. <https://doi.org/10.1515/opag-2022-0072>
- Gao, Z., Wang, X.-M., Wan, H., and Brunette, G. (2011). "Binderless panels made with black spruce bark," *BioResources* 6(4), 3960-3972. <https://doi.org/10.15376/biores.6.4.3960-3972>
- Hubbe, M. A., Pizzi, A., Zhang, H., and Halis, R. (2017). "Critical links governing performance of self-binding and natural binders for hot-pressed reconstituted lignocellulosic board without added formaldehyde: A review," *BioResources* 13(1), 2049-2115. <https://doi.org/10.15376/biores.13.1.Hubbe>
- Hubbe, M. A., Trovagunta, R., Zambrano, F., Tiller, P., and Jardim, J. (2023). "Self-assembly fundamentals in the reconstruction of lignocellulosic materials: A review," *BioResources* 18(2), 4262-4331. <https://doi.org/10.15376/biores.18.2.Hubbe>
- ISO 13906; "Animal feeding stuffs — Determination of acid detergent fibre (ADF) and acid detergent lignin (ADL) contents." (2008).
- Khantwal, R., Gupta, G., and Negi, R. S. (2016). "Walnut shell reinforced composite: A review," *International Journal of Scientific Engineer and Research* 7(5), 179-189.
- Mawardi, I., Aprilia, S., Faisal, M., and Rizal, S. (2021). "Characterization of Thermal bio-insulation materials based on oil palm wood: The effect of hybridization and particle size," *Polymers* 13(19), article 3287. <https://doi.org/10.3390/polym13193287>
- NF V18-122 (2008). "Animal feed - Sequential determination of parietal constituents - Method using neutral and acidic detergents and sulphuric acid," Saint-Denis, France: AFNOR (Association Française de Normalisation).
- Nishino, T., Takano, K., and Nakamae, K. (1995). "Elastic modulus of the crystalline regions of cellulose polymorphs," *Journal of Polymer Science Part B: Polymer Physics* 33(11), 1647-1651. <https://doi.org/10.1002/polb.1995.090331110>
- Palaniyappan, S., Sivakumar, N. K., Bodaghi, M., Rahaman, M., and Pandiaraj, S. (2024). "Preparation and performance evaluation of 3D printed Poly Lactic Acid composites reinforced with silane functionalized walnut shell for food packaging applications," *Food Packaging and Shelf Life* 41, article 101226. <https://doi.org/10.1016/j.fpsl.2023.101226>
- Pintiaux, T., Viet, D., Vandenbossche, V., Rigal, L., and Rouilly, A. (2015). "Binderless materials obtained by thermo-compressive processing of lignocellulosic fibers: A comprehensive review," *BioResources* 10(1), 1915-1963. <https://doi.org/10.15376/biores.10.1.Pintiaux>

- Pizzi, A., Papadopoulos, A. N., and Policardi, F. (2020). "Wood composites and their polymer binders," *Polymers* 12(5), article 1115. <https://doi.org/10.3390/polym12051115>
- Queirós, C. S. G. P., Cardoso, S., Lourenço, A., Ferreira, J., Miranda, I., Lourenço, M. J. V., and Pereira, H. (2020). "Characterization of walnut, almond, and pine nut shells regarding chemical composition and extract composition," *Biomass Conversion and Biorefinery* 10(1), 175-188. <https://doi.org/10.1007/s13399-019-00424-2>
- Regazzi, A., Teil, M., Dumont, P. J. J., Harthong, B., Imbault, D., Peyroux, R., and Putaux, J. L. (2019). "Microstructural and mechanical properties of biocomposites made of native starch granules and wood fibers," *Composites Science and Technology* 182, article 107755. <https://doi.org/10.1016/j.compscitech.2019.107755>
- Rol, F., Rouilly, A., and Bras, J. (2020). "Thermo-compression of cellulose nanofibrils," *Cellulose* 27(1), 25-40. <https://doi.org/10.1007/s10570-019-02720-6>
- Tajuddin, M., Ahmad, Z., and Ismail, H. (2016). "A review of natural fibers and processing operations for the production of binderless boards," *BioResources* 11(2), 5600-5617. <https://doi.org/10.15376/biores.11.2.Tajuddin>
- Zhang, D., Zhang, A., and Xue, L. (2015). "A review of preparation of binderless fiberboards and its self-bonding mechanism," *Wood Science and Technology* 49(4), 661-679. <https://doi.org/10.1007/s00226-015-0728-6>

Article submitted: February 3, 2026; Peer review completed: March 7, 2026; Revised version received and accepted: April 24, 2026; Published: May 18, 2026.

DOI: 10.15376/biores.21.3.6036-6049