

MOISTURE SORPTION, BIOLOGICAL DURABILITY, AND MECHANICAL PERFORMANCE OF WPC CONTAINING MODIFIED WOOD AND POLYLACTATES

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Biological durability is an important feature for wood-plastic composites (WPC) intended for outdoor applications. One route to achieving WPC products with increased biological durability is to use wood preservative agents in the formulation of the WPC. Another option could be to use a chemically modified wood component that already exhibits increased resistance to biological degradation. There is also a need to use biobased thermoplastics made from renewable resources, which would decrease the dependency on petrochemically-produced thermoplastics in the future. The objective of this study was to examine moisture sorption properties, biological durability, and mechanical performance of injection-molded WPC samples based on acetylated or thermally modified wood components and a polylactate matrix. The biological durability was evaluated in a terrestrial microcosm (TMC) test according to ENV 807, followed by mechanical evaluation in a center point bending test. The moisture sorption properties were investigated via both water soaking and exposure in a high-humidity climate. Low or negligible mass losses were observed in the TMC test for all WPC samples. However, the mechanical evaluation after exposure in the TMC test showed 35-40% losses in both strength and stiffness for the WPC containing an unmodified wood component.

Keywords: Acetylation; Thermal modification; Polylactate; Moisture; Biological durability; Woodplastic composite

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INTRODUCTION

Wood-plastic composites (WPC) are a combination of wood in the form of flour, fibers, or particles, and a thermoplastic matrix. The first generations of WPC were considered to be very resistant to biological decay, and one reason for this was the slow moisture transport into the material achieved by the polymer matrix. However, the outermost layer of the composite has been shown capable of reaching moisture levels high enough to initiate biological decay (Wang and Morrell 2004; Gnatowski 2009; Ibach *et al.* 2011). To protect the composites against such attack, it is possible to use treatments with wood preservative agents when manufacturing the composites (Shirp *et al.* 2008). Another option would be to use a chemically modified wood component that already exhibits increased resistance to biological decay (Ibach and Clemons 2002, 2007; Hill 2006; Segerholm *et al.* 2007; Westin *et al.* 2008).

The commercial production of chemically modified wood has increased over the last decade. This production and further processing also leaves behind modified wood residuals in the form of shavings and sawdust, for example, which currently are used for energy production. One way to gain value from these residuals would be to further process them into fibers and flour to be used for the production of new durable biocomposites.

Two of the most studied and commercially available wood modification processes today are acetylation and thermal modification. Acetylation is a single-site reaction in which acetic anhydride is reacted with wood hydroxyl groups. The resulting wood material is fixed in a swollen state and exhibits good dimensional stability and resistance to decay by fungi and microorganisms (Rowell 2006). Thermal modification includes process steps with peak temperatures between 180 °C and 260 °C (Hill 2006), and the resulting material properties mainly depend on treating temperature, duration of treatment, wood species, and treatment atmosphere.

The development of biobased plastics, such as polylactates (PLA), has been progressing for many years, often showing products with acceptable mechanical and durability properties. The main area of application for PLA has been in packaging, though other emerging areas are automotive interiors and electronics. The outlook for the use of PLA in building products, such as WPC, will depend on long-term performance and price competitiveness. The competitiveness of PLA is expected to increase as alternative biomass feedstocks become available and as plants with higher production capacities are developed (Wolf *et al.* 2005). By continuing the work on combining modified wood residuals with a biobased thermoplastic polymer as a matrix (*e.g.*, Segerholm 2007; Westin *et al.* 2008; Segerholm *et al.* 2009, 2011), new durable biocomposites for building products can be developed.

WPC usually exhibit high levels of water repellency, mainly due to the thermoplastic-rich surface layer created during extrusion or injection-molding. The processing also disperses the wood component efficiently throughout the thermoplastic matrix. In order to simulate long-term field conditions when performing biological tests on WPC in the laboratory, it is necessary to expose the composites to moist conditions for long periods of time or to expose the material to moisture at an elevated temperature. This ensures an internal moisture content high enough to support fungal growth (Clemons and Ibach 2004; Defoirdt *et al.* 2010; Ibach *et al.* 2011). A higher temperature when exposing the composites with PLA to moisture might be a problem due to hydrolysis of the matrix material. In another study, Segerholm *et al.* (2011) studied the biological durability of WPC containing modified wood and a polylactate matrix in a single fungal strain test in accordance with a modified ASTM D1413 test. The resulting mass loss values from the test were very low to none; however, the test duration was short considering the slow moisture transport of this type of material.

The objective of this study was to examine the moisture sorption properties, biological durability, and mechanical performance of injection-molded WPC samples based on acetylated or thermally modified wood components and a polylactate matrix. The wood components used were in the form of both wood flour and wood fiber intended for medium density fiberboard (MDF). The biological durability was evaluated through a terrestrial microcosms (TMC) test in accordance with ENV 807, including a water soaking preconditioning procedure. The moisture sorption properties were investigated via both water soaking and exposure to a high-humidity climate. To achieve

complementary durability information, the study also included an evaluation of the mechanical performances of the samples after being exposed in the TMC test.

EXPERIMENTAL

Wood Material

The wood flour batches were produced from thermally modified Norway spruce (*Picea abies*) or acetylated Scots pine sapwood (*Pinus sylvestris*) by means of a two-step grinding process involving a disk flaker (Bezner®) and a knife ring mill (Condux®). The thermally modified solid wood was supplied by Stora Enso Oy and modified according to the Thermowood D procedure (Anonymous 2003). The acetylated solid wood was produced in a 0.67 m³ pilot plant reactor according to Rowell *et al.* (1986), and the degree of acetylation, expressed as wood acetyl content, was about 20%. The MDF softwood fibers for acetylation were supplied by Kronospan, UK. The acetylation of the MDF softwood fibers was carried out in liquid phase by BP Chemicals in 100 kg batches as part of an earlier European Commission project (AIR 3-CT94-2000), and the degree of acetylation, expressed as wood acetyl content, was about 20%. The corresponding unmodified MDF softwood fibers were supplied by Valbopan®, Portugal.

Wood Plastic Composites

The matrix material used in this study was a PLA-polymer (Nature Works R 4042D, NatureWorks LLC, Minnesota, USA). Prior to compounding, the wood components were dried at 105 °C overnight, and the PLA granules were dried in a Gerco granule dryer at 80 °C for at least 5 hours using pre-dried air. The wood components and PLA were compounded at 50 wt.-% using a Berstorff ZE 40-38D twin screw extruder. The polymer granules were fed upstream to the extruder by calibrated volumetric feeding using a K-Tron KCL-KT20. The wood components were fed downstream to the extruder with a K-Tron 332P volumetric feeder and a Berstorff side feeder, except for the acetylated MDF fibers, which were fed by hand at the barrel element just downstream from the side feeder. For the hand feeding, the amounts to be fed in one minute were prepared in containers prior to drying. The resulting compounded material was collected, cooled in a water bath for about 5 minutes, air-dried overnight, and granulated. The granules were dried overnight at 60 °C in a vacuum oven and injection-molded into the flexural test specimens using a Demag ERGOtech 25-80 Compact injection-molding machine. The rectangular specimens measured 80 x 10 x 4 mm³. Results from an earlier study on these materials showed that the wood component was well dispersed throughout the specimens for all samples (Galland 2009).

Water Vapor Sorption Test

Five specimens of each sample were exposed in a climate room set at 90% relative humidity (RH) and a temperature of 27 °C. The weight gain was then monitored at certain intervals for 20 months.

Preconditioning Prior to Laboratory Decay Test

For each of the three terrestrial microcosms (TMCs), 12 specimens from each of the five injection-molded samples were preconditioned via leaching for two weeks in de-ionized water with water exchange every weekday, followed by two weeks of soaking in

deionized water at room temperature. Eight specimens of each sample were directly inserted into each test soil after the preconditioning, and four specimens were inserted into the sterilized test soils to be used to calculate the corrected mass loss. Five specimens of each sample were dried in a convection oven at 50 °C for one week for the purpose of measuring the moisture contents after the preconditioning procedure. Scots pine (*Pinus sylvestris*) control specimens measuring 100 x 10 x 5 mm³ were dried over-night prior to insertion in the test soils.

Laboratory Decay Tests in Terrestrial Microcosms Test (ENV 807)

The injection-molded specimens and the solid wood control specimens were buried to $\frac{3}{4}$ of their length in three types of TMC soils according to an expanded version of the European test standard ENV 807. The soils were: a compost soil (TMC 1), soil from the Simlångsdalen test field (TMC 2), and soil from a mixed forest (TMC 3). The compost soil was a 50/50 mixture of soil with high activity of both tunneling bacteria and soft rot and soil from household waste. The compost soil mix had a pH of 7.4 and a water holding capacity (WHC) of 102%. The soil from the test field in Simlångsdalen was a sandy soil with dominating brown-rot decay mainly caused by *Leucogyrophana pinastri*. The Simlångsdalen soil had pH 5.2 and WHC 20%. The forest soil was from the test field in Ingvallsbenning, in which there is high activity from the white-rot fungus *Asterostroma cervicolor*. The forest soil had pH 4.6 and WHC 130%. Specimens were removed from the soils after 32 weeks for the TMC1 and after 56 weeks for the TMC2 and TMC3 soils. A small brush was used to remove excess soil on the surface of the specimens. The specimens were dried at 50 °C in a convection oven for one week, after which the specimens were weighed and the mass loss was calculated. The mass losses of the specimens from the sterile soils were used to calculate the corrected mass loss, or mass loss solely caused by the biological degradation, *i.e.*, the mass loss due to leaching was subtracted.

Mechanical Test

The specimens from the laboratory decay tests as well as two reference specimens not tested for decay were conditioned at 22 °C and in 65% relative humidity prior to mechanical evaluation in a center point bending test. For the mechanical evaluation EN ISO 178:2010 was followed, a universal testing machine (model Alwetron TCT50, Lorentzen & Wettre, Sweden) was used, the span length was 64 mm, and the crosshead speed was 2 mm/min for determining both strength and stiffness.

Scanning Electron Microscope Evaluation

After the ENV 807 test, the composite surfaces were evaluated with a scanning electron microscope (SEM, Hitachi Tabletop Microscope TM-1000, Krefeld, Germany) to distinguish any morphological differences of the surfaces that resulted from the different soil types and/or different wood components.

RESULTS

Water Vapor Sorption Test

Figure 1 shows the rate and extent of the moisture weight gain for PLA alone and for the composite samples. The composite with unmodified MDF fibers showed the

fastest moisture sorption rate and the highest level of moisture weight gain of all of the composites. The composites with thermally modified wood flour showed the next highest level of moisture uptake, followed by the acetylated MDF fibers and flour. As expected, pure PLA showed a distinctly lower rate of moisture uptake and the lowest level of moisture weight gain when compared to the composites. It is notable that even after 20 months at 90% RH and at 27 °C, all of the composites were still gaining moisture.

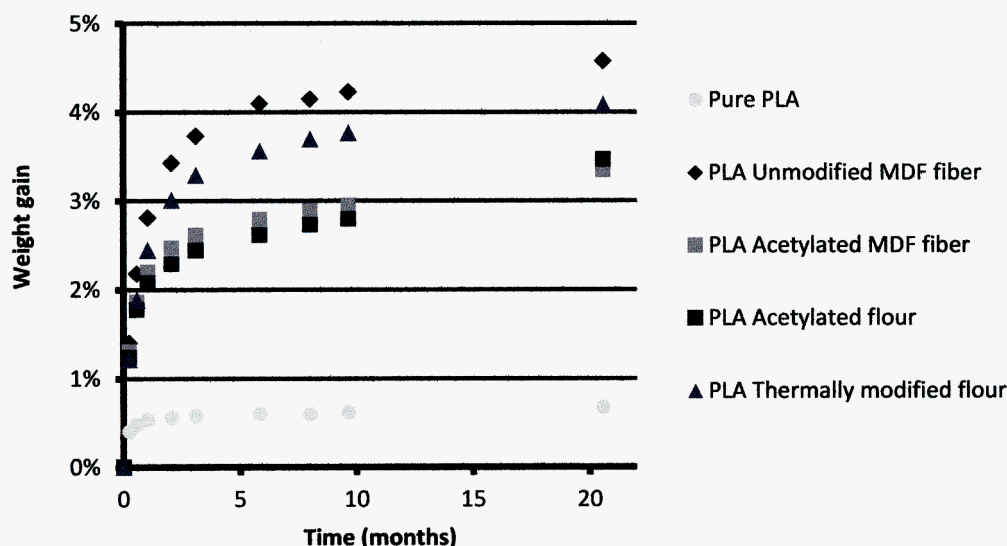


Fig. 1. Water vapor sorption for pure PLA and for the composite samples exposed to a climate of 90% relative humidity and at 27 °C for 20 months

Preconditioning Prior to Terrestrial Microcosms Test

The preconditioning by water soaking of the samples resulted in different weight gains depending on the type of wood component in the composites (see Table 1). The pure PLA specimens did not gain any weight during the soaking. The highest average moisture content, 3.7%, was observed for the samples with unmodified MDF fibers.

Table 1. Moisture Content of Composites After Soaking in Water for Two Weeks

Material	Moisture Content After Soaking %
Pure PLA	-0.1
PLA - Unmodified MDF fiber	3.7
PLA - Acetylated MDF fiber	2.2
PLA - Acetylated flour	2.3
PLA - Thermally modified flour	2.4

*The standard deviations were less than 0.05% for all samples,

Terrestrial Microcosms Test (ENV 807)

The activity of the soil from Simlångsdalen (TMC2) and the forest soil (TMC3) was very low. Therefore, the specimens in those soils were moved to a new soil from Simlångsdalen (TMC2) and to a new forest soil (TMC3), both with higher activity. The presented results (Table 2) are after 32 weeks in the new soil for TMC2 and TMC3 (56 weeks in total) and after 32 weeks in the compost soil for TMC1. The pine control specimens in all three soils had mass losses between 31.4 and 34.5%, indicating good fungal activity. The pure PLA specimens showed little to no mass loss. All the composite samples had mass losses lower than 1%. The small negative mass losses, *i.e.*, mass gains, obtained for some samples could be due to a small amount of soil residue that was still left on the specimens.

Table 2. Corrected Mass Loss after 32 Weeks for the Compost Soil (TMC 1) and after 56 Weeks of Exposure in the Soils from Simlångsdalen (TMC 2) and Forest Soil (TMC 3), Tested According to ENV 807.

Material	Mass Loss (%)		
	TMC1	TMC2	TMC3
Pine sapwood control	31.4	31.5	34.5
Pure PLA	0.0	0.0	0.0
PLA - Unmodified MDF fiber	0.8	-0.2	0.7
PLA - Acetylated MDF fiber	0.0	0.0	0.0
PLA - Acetylated dour	-0.1	0.0	-0.2
PLA - Thermally modified flour	0.0	-0.5	-0.6

*The standard deviation was 0.0% for all samples except for the PLA–UnmodifiedMDF fiber, which were 0.4%, 0.1%, and 0.2%, respectively.

Mechanical Evaluation

The preconditioning of the specimens slightly increased the stiffness (MOE) compared to the non-preconditioned reference for all samples (Fig. 2). However, the preconditioning lowered the strength (MOR) for all the composite samples except for the pure PLA samples, in which strength was increased (Fig. 3). Losses in MOR for all the composite samples with wood components when subjected to preconditioning including water soaking indicated poor interaction between the PLA and the wood component.

Figure 2 shows the stiffness of all the samples tested. The samples with modified wood components show small losses in stiffness after the TMC test; however, all of them had a stiffness greater than 6 GPa after the TMC testing. The sample with an unmodified wood component showed a large reduction in stiffness after the TMC test. The TMC test had little or no effect on the strength of the composite samples, except for the composite sample with unmodified MDF fiber, which showed a large reduction in strength due to the TMC test (Fig. 3).

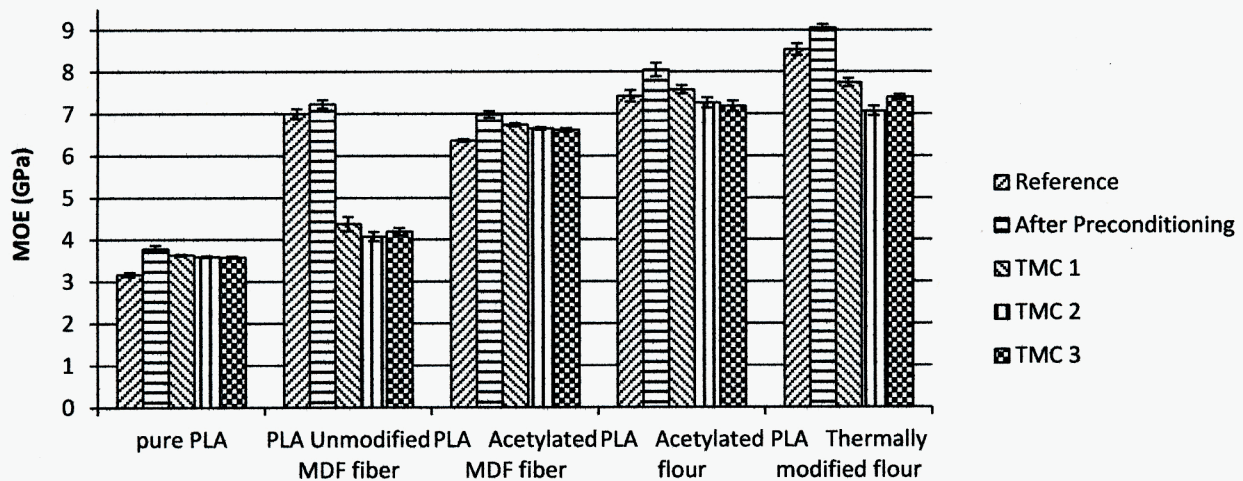


Fig. 2. Modulus of elasticity for pure PLA and for the composite samples after water soaking and TMC exposure according to ENV 807

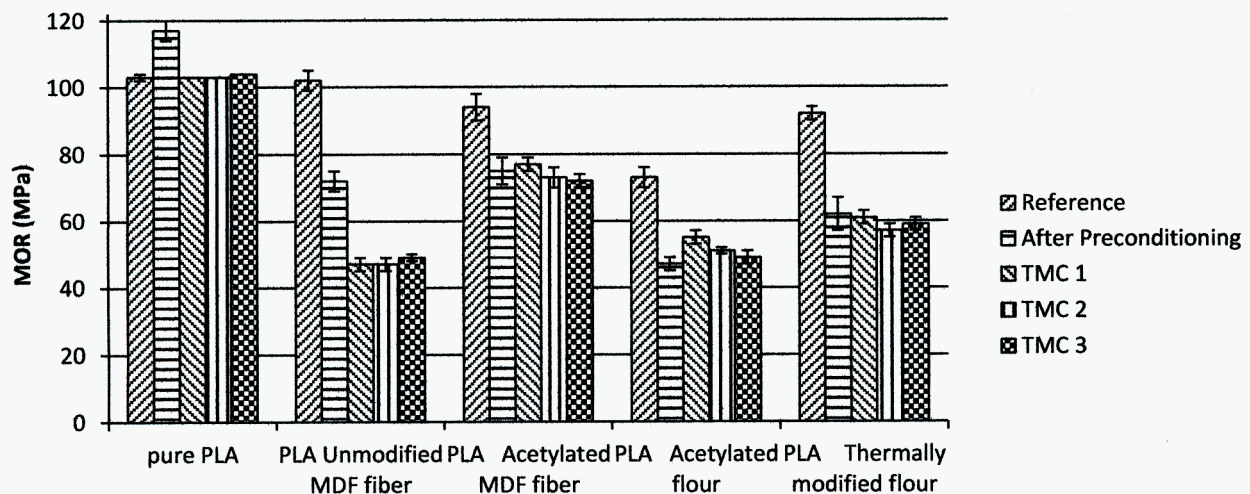


Fig. 3. Modulus of rupture for pure PLA and for the composite samples after water soaking and TMC exposure according to ENV 807

Scanning Electron Microscope Evaluation

Figure 4 shows micrographs of the surface of the PLA composites with unmodified MDF fibers. The left micrograph is a specimen that was only subjected to the preconditioning prior to the laboratory decay test, while the right micrograph is a specimen after the TMC test in the compost soil. The composites with unmodified MDF fiber showed surface cracking after the TMC test in all three soils. Small surface cracks were also visible in the composite samples with acetylated and thermally modified wood flour, most likely caused by the moisture-induced movement of the relatively large wood components in the wood flour composites.

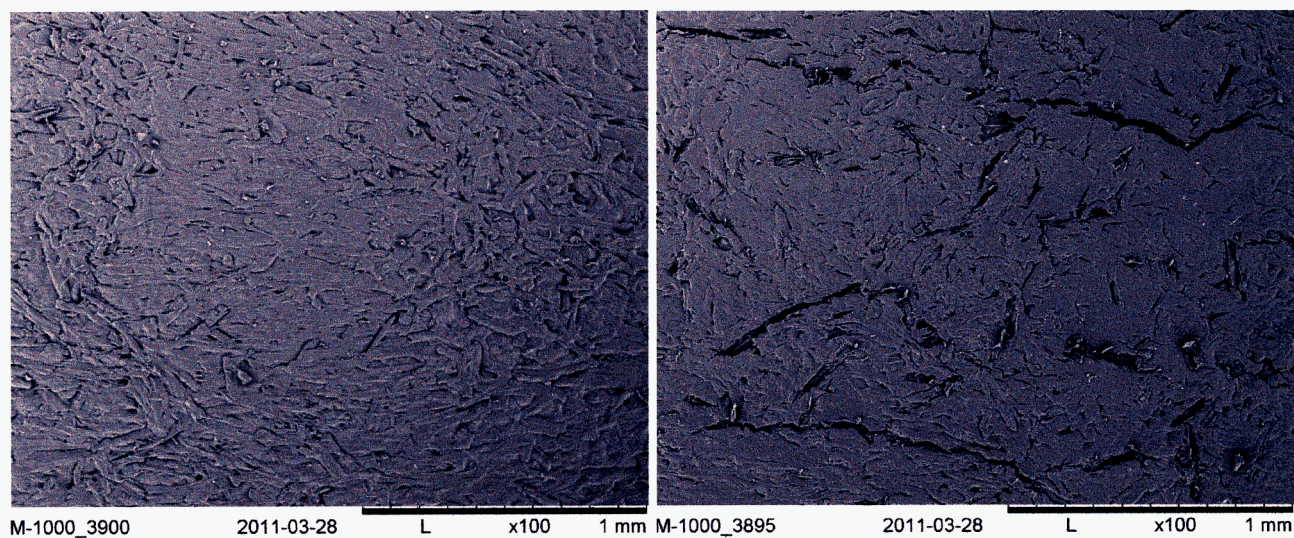


Fig. 4. PLA-unmodified MDF fiber subjected to preconditioning with water (left) and after exposure to compost soil in a TMC (right)

DISCUSSION

The water vapor sorption test showed that the moisture uptake of all the composites and the pure PLA was very slow and that the rate was further slowed after approximately 6 months. The highest moisture content was obtained for the materials with unmodified MDF fiber. Testing for biological durability in terrestrial microcosms resulted in very small mass losses; however, the mass loss results obtained in this study were insufficient to allow conclusions on the biological durability of the composites solely on the basis of mass losses.

The mechanical evaluation of the decay tested material showed three distinct trends. First, the moisture soaking and drying at 50 °C had a slight stiffening effect on all the composites; the reason for this is unclear but could be related to an annealing effect of the PLA already at 50 °C. Second the strengths of the composites were lower after the moisture soaking and drying for all the composites with wood components, and this reduction in strength due to moisture soaking indicated weak interaction between the wood components and the thermoplastic matrix. Third, the stiffness was greatly reduced for the composites with unmodified MDF fiber after the decay tests in all three of the test soils.

The SEM evaluation also revealed severe surface cracking for the composites with unmodified MDF fibers after the decay tests. The composites with acetylated and thermally modified flour also showed some surface cracks, whereas the pure PLA and the composites with acetylated MDF fiber showed no surface cracks. The surface cracking is believed to be related to the moisture-induced movements of the wood components, where the unmodified MDF fibers have the largest relative movements. The acetylated and thermally modified flour had reduced moisture-induced movement due to the modification, but their larger size compared to the fibers led to large deformations around the larger particles.

Under the circumstances tested, the PLA used was not affected mechanically by the moisture soaking and decay testing in the terrestrial microcosms. However, with the addition of a hygroscopic wood component, the moisture greatly influenced the strength of the composite. And furthermore, the stiffness of the composites containing unmodified MDF fibers was greatly reduced after all the decay tests, whereas the stiffness of the composites with modified wood component was maintained or only slightly reduced.

CONCLUSIONS

1. Low or negligible mass losses were observed for all composites exposed to decay testing. In contrast, the mechanical evaluation after the decay test showed large losses in both stiffness and strength for the composites with unmodified MDF fiber.
2. It is evident that a mechanical evaluation after decay testing may provide additional important information about critical factors such as moisture intrusion in WPC, which strongly affects the long-term behavior and durability of the composites.
3. The modified wood components that were used resulted in high decay resistance of the composites; however, the strength losses due to moisture sorption suggest that the compatibility between the PLA and the different wood components needs to be improved.

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