Bio-Based Phase Change Materials for Wooden Building Applications

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Abstract: Solid wood can serve multifunctionality for energy savings in buildings. The study reveals the results of biodeterioration and degradation of solid Scots pine wood used to incorporate single or multicomponent fatty acid mixtures as bio-based phase change materials (BPCMs). The sapwood samples were impregnated with capric acid (CA), methyl palmitate (MP), lauryl alcohol (LA) and a mixture of coconut oil fatty acids and linoleic acid (CoFA-LA). The samples were tested against subterranean termites by an Italian species (*Reticulitermes lucifugus*), the wood boring beetle *Hylotrupes bajulus* and mold through a discoloration test. Tested against termites, the impregnated samples were significantly less susceptible to the attack than the controls, i.e., the tested BPCMs were resistant to *R. lucifugus*. The only test with MP terminated at the moment against *H. bajulus* showed positive results with no larvae surviving. The mold discoloration test revealed that the wood impregnated with CoFA-LA was identically susceptible to mold discoloration when compared to the control, nonimpregnated samples. This pioneer study verifies that solid wood employed for the encapsulation of BPCMs for building purposes can serve identically or somewhat better than similar wooden building elements regarding attacks of the above microorganisms and insects. Such multifunctional building elements will be tested further in a pilot scale building to characterize better the durability aspects of the new materials.

Keywords: bio-based phase change materials; energy savings; fatty acids; *H. bajulus*; mold test; Scots pine; termites

1. Introduction

Living in a time of changes and initiatives for a harmonic human existence, we strive to develop sustainable products to replace materials with high environmental footprints. In recent years, the matter has been internationalized, and innovative projects on the versatile use of wood are driven by the sustainability and climate mitigation debate. Apparently, the market needs niche innovative wood products, revised manufacturing processes and research transfers to reproduce specific approaches and replicate successful processing. Some examples are novel wood-based packaging with significantly improved properties, using horticultural side stream fibers, bio-based adhesives for fiber-based products, new...
wood-engineered construction materials and many more. The innovative research on wood and wood-based materials addresses EU policies and targets, e.g., European Green Deal (EGD), Circular Economy Action Plan (CEAP), Industrial Strategy, Bio-economy and Forest Strategies and Chemicals Strategy for Sustainability and Climate Policy. The United Nations (UN) Sustainable Development Goals (SDG) are also addressed, namely goal 9: “Industry, innovation and infrastructure”, 11: “Sustainable cities and communities” and 12: “Responsible consumption and production”, by developing novel sustainable solutions and creating new business opportunities responding to population growth and demand for housing.

Bio-based materials from renewable sources have become an inevitable part in building and construction applications. Wood is one of the most common renewable and available materials for the construction industry. Therefore, use of timber and other wood-based materials has experienced growth during the last decade in single and multi-floor buildings due to the high ratio of strength to density, thus bringing renewability, sustainability and climate benefits [1–3]. However, wood has a moderate density and specific heat capacity and cannot absorb and store excessive energy inside buildings or control temperature fluctuations in buildings [4]. In order to handle this problem with wood and wood-based materials used in the construction industry, one promising approach is to incorporate bio-based phase changing materials (BPCMs) into wood cells, thus making a smart bio-composite for energy storage and management in buildings [5].

Phase-change materials (PCM) are organic or inorganic substances that undergo melting and solidifying at certain temperatures, accompanied by storing and releasing energy (heat); thus, PCMs are classified as latent heat storage (LHS) materials. PCMs have been known for more than thousands of years and used in various applications for cooling and the accumulation of heat, predominantly in solar installations. The wide temperature range offered by a huge number of commercial PCM nowadays opens up a new approach for building insulation and heat storage. BPCMs are PCMs of natural origin.

Since no single material possesses ideal properties for thermal storage, an adequate PCM system design can combine several substances, e.g., water–salt eutectic solutions, a mixture of two or more fatty acids or PCM–metal combinations. The classification, merits and disadvantages of PCM have been extensively studied [6,7].

Hydrates of inorganic salts (e.g., K$_2$HPO$_4$, FeBr$_3$ and Mn(NO$_3$)$_2$) are cheap and available substrates with a LHS capacity of 100–296 kJ/kg, high thermal conductivity and nonflammability. Paraffins, fatty acids and polyethylene glycol (PEG) are representatives of the group of organic PCM; they are also cheap and available, chemically stable, safe to use and some of them recyclable, while the flammability and low thermal conductivity of these materials is a problem. Paraffins have high LHS (170–269 kJ/kg), are derived from fossil crude oil and are nonbiodegradable. In contrast, fatty acids are extracted from animal fat or plant oils (i.e., from renewables) but have a lower LHS capacity (150–200 kJ/kg). Eutectic combinations of materials can have a sharp melting point, an average LHS capacity of 150 kJ/kg and are less studied than the others. The advantage of this group is the option to design a desirable temperature range of action depending on the application.

Apart from the most intensive use of PCM for heat storage in solar installations, energy savings and better living comfort have been aimed for when integrating PCMs in buildings. Research in the field started in the 1980s when PCMs were combined with gypsum, lightweight concrete and wood to increase the LHS capacity of the matrix by more than 100% [8]. However, intensive exploitation of the concept of PCM in buildings started in years 2004–2012 when 90% of the contributions were published. Gypsum, concrete [9] and plaster impregnated with PCM prevailed among the studied matrix materials from this time period [10,11].

The majority of the attempts to macro-encapsulate or apply PCM by immersion have been ineffective, and thus, none of these products have reached the market. Micro-encapsulated PCMs [12] have made PCMs more accessible to the building industry, e.g., the microencapsulation of PCM into concrete as an easy and economical way. Molecular
encapsulation is another technology [13] allowing a very high concentration of PCMs within a polymer compound. Apparently, PCMs perform best in small volumes, and thus, they are usually encapsulated in cells [14]. Some important requirements of the cells are heat conductivity and mechanical strength to withstand frequent PCM volume changes. The cell should also be water impermeable to eliminate the wetting, drying and leaching of PCM. This probably explains why wood cells have not been used previously for the encapsulation of PCMs. A vast number of wood and wood-based building materials are intended for use class (UC) 1 or 2, i.e., under roof but still exposed to moisture changes (UC 2) and susceptible to insects, termites of the standard EN 335 and EN 599 [15,16] and mold and stain deterioration according to the American Wood Protection Association (AWPA) Standard E24-21 [17]. Due to its chemical composition and anatomical structure, wood is sensitive to moisture and a nutrient of the microorganisms [18]. In addition, health problems related to mold growth and the release of mycotoxins affect the occupants in buildings [19] which emphasizes the importance of material selection and living climates. The above is particularly important when BPCMs are going to be introduced as heat storage solutions in buildings. Although the BPCMs are normally encapsulated in various forms and materials, they are always used in indoor environments, and thus, the susceptibility of the composites to the biological deterioration and degradation typical for UC 1 and 2 should always be considered [20]. The aim of the present research is to study the biological resistance of Scots pine wood impregnated with four different BPCMs to Coleoptera spp. (beetles), Isoptera spp. (termites) and the growth of some common mold fungi, e.g., Aureobasidium pullulans (de. Bary) Arnaud 1918, Aspergillus niger v. Tiegh and Penicillium brevicompactum Dierckx) [20,21].

The risk of mold growth on building materials can be minimized when the expected level of relative humidity and temperature in the building is known. Mathematical models have been developed [22] and can be used to predict the risk of mold growth. Examples of calculated mold growth limit levels are shown in the literature [23], where the critical humidity level at 22 °C is 75% < RHcrit ≤ 80% and 85% < RHcrit ≤ 90% at 10 °C. The conditions in the present test with CoFA-LA impregnated in Scots pine sapwood are significantly more favorable for mold growth compared to the publications above. Despite the fact that the indoor climate in buildings can hardly reach these levels, the mold test proved that the susceptibility to mold of untreated wood, which is frequently used as wood-engineered building elements, and the susceptibility of building materials based on solid wood for the encapsulation of BPCMs are identical.

According to our knowledge, no studies investigating the resistance of BPCMs to the above biological invasive organisms have been performed. The compounds of the BPCMs in the present study, i.e., the fatty acids, can be utilized by the organisms as nutrients in a similar manner as the available soluble low-molecular sugars on the sample surface. Thus, the investigation of the hypothesis is sound, and the present study tries to cover the durability and performance aspects concerning insects, termites and mold fungi as potential degraders when a BPCM is incorporated into solid wood.

2. Materials and Methods

2.1. Materials

Scots pine (Pinus sylvestris), sapwood, dimensions 15 × 25 × 50 mm, six replicates for treatment and reference controls, were used for termites and the insect H. bajulus.

Four fatty acids serving as BPCMs, namely capric acid (CA), methyl palmitate (MP), lauryl alcohol (LA) and a mixture of coconut oil fatty acids and linoleic acid (CoFA-LA), were selected and studied. Capric acid with formula CH₃(CH₂)₈COOH (known also as decanoic acid) and a purity ≥ 98.0% has a melting temperature range from 27 to 32 °C, molecular weight of 172.27 g/mol and density of 0.893 g/mL (at 25 °C). Methyl palmitate (C₁₇H₃₄O₂), purity of 99.0%, has a molecular weight of 270.45 g/mol and melting point of 29 °C. Lauryl alcohol (C₁₂H₂₅O) is an organic fatty alcohol with a melting temperature within the human thermal comfort range (25 °C) and a latent heat fusion of 205.4 J/g.
The fourth BPCM was composed of coconut oil fatty acids (CoFA) and linoleic acid (LA) mixed in a ratio of 80:20 [24]. Scots pine (Pinus sylvestris L.) wood samples with dimensions of $9 \times 90 \times 90$ mm along the grain and without visible defects were used throughout the study for mold tests. The fatty acids above were purchased from Sigma-Aldrich, Milan, Italy.

2.2. Impregnation of Wood Samples with BPCMs

The wood samples were conditioned for 2 weeks at 23 °C and 70% relative humidity (RH) before impregnation. The impregnation of CA, MP and LA was carried out in a vacuum oven under a pressure of 850 mbar at 45 °C for 3 h.

The wood samples were impregnated with CoFA-LA in an autoclave at temperature of 60 °C to ensure the melting and penetration of the BPCM in a vacuum pressure process. The samples were immersed in the melted CoFA-LA and a vacuum of 350 mbar for 10 min, followed by 6 bar pressure for 1 h. The weight percentage gain (WPG) achieved for CoFA-LA was 95%, i.e., close to full cell impregnation. For CA, MP and LA, the WPG was 56%, 73% and 55%, respectively.

After impregnation, the samples were conditioned at room climate for 3 weeks, and the mass was recorded prior to a leaching test. To assess the leaching rate, the impregnated samples were placed in a climate chamber at 35 °C (i.e., higher temperature than the melting one) for 24 h.

2.3. Biological Test Methods

2.3.1. Termite Test

To evaluate the resistance of BPCM-treated and control samples against subterranean termites, an Italian species, Reticulitermes lucifugus was employed in accordance with the European normative EN 117:2012 [25]. In the test, based on an artificial mini-colony, 250 workers with some soldiers and nymphs in a ratio depending on the original colony were let in contact with the BPCM impregnated samples for eight weeks or until all termites in the treated samples died. Six BPCM impregnated wood samples were used per treatment together, with nine untreated reference controls.

The validity of the test was based on the percentage of workers in contact with the untreated Scots pine samples; the test is considered valid when the survival rate is 50%. The evaluation of degradation was based on a four-grade ranking that considers the extension and the depth of gallery excavates by termites in the wood and the number of termites that survived. The results can also be expressed as a durability class as reported in the EN 350:2016 [26]. When the grade of attack is 0 or 1 for more than 90% of the samples, and the remaining 10% have attack grades not more than 2, the treatment is durable. When the rankings 3 or 4 are less than 50%, the durability class is moderately durable, and when the same ranking grades are equal to or more than 50%, the durability class is nondurable.

2.3.2. Insect Test

The resistance of the control and BPCM-treated samples against the wood boring beetle Hylotrupes bajulus was tested in accordance with the EN 47:2016 (with some modifications) [27] using newborn larvae hatched not more than 3 days ago. Six larvae were used for the wood samples, and the evaluation was assessed by means of a X-ray analysis. The duration of the test performed with newborn larvae was 12 weeks. The assessment was based on the survival of the larvae in the treated wood sample. The evaluation can be performed through a X-ray analysis after 4 weeks. The X-ray source was a Gilardoni Radiolight, Italy at 50 KV and 3 mA for 5 min as the time exposed to X-rays on phosphorus-active plates and the digital scanner NDT HD CR 35 DÜRR, Bietigheim-Bissingen, Germany.

2.3.3. Mold Test

The susceptibility of only CoFA-LA impregnated samples to mold growth and discoloration was tested in accordance with American Wood Protection Association Standard
Three mold fungi (Aureobasidium pullulans (d. By.) Arnaud, Aspergillus niger v. Tiegh and Penicillium brevicompactum Dierckx) were chosen and grown on 2.5% malt extract agar for three weeks. A mixed mold spore suspension was then prepared and inoculated on the sterilized soil in a plastic chamber. After inoculation, the chamber was incubated in a room at 20 °C for 2 weeks. Afterwards, nonimpregnated and impregnated samples with CoFA-LA were put inside the chamber hanging approximately 5 cm above the soil. The climate in the chamber was maintained at 25 °C with a relative humidity higher than 95%. After 2, 4, 6 and 8 weeks of exposure, the mold growth on the sample surfaces (90 × 90 mm) was classified by visual examination according to a scale from 0 (no visible growth) to 5 (very abundant growth, 100% coverage).

3. Results

3.1. Termite Test

The results of the test are shown in Table 1.

Table 1. Tested BPCMs, number of treated wood replicates evaluated according to EN 117 and the survival percentage.

| BPCM    | Replicates (n) | Evaluation EN 117 | Survival (%) |
|---------|----------------|-------------------|--------------|
| CA      | 6              | 0                 | 0.0          |
| MP      | 6              | 1                 | 0.2          |
| LA      | 6              | 1                 | 13.9         |
| CoFA-LA | 6              | 0                 | 0.0          |
| CS      | 9              | 4                 | 67.3         |

CA = capric acid, MP = methyl palmitate, LA = lauryl alcohol, CoFA-LA = mixture of coconuts oil fatty acids and linoleic acid and CS = control samples.

The results can also be expressed as a durability class (DC) in accordance with the EN 350:2016 [26]. The test results confirmed that the four BPCM formulations are not susceptible to termite attack when impregnated in Scots pine sapwood, i.e., the material is durable, while the untreated controls are nondurable. As shown in Table 1, the survival rate of termites on the control samples is more than 50%. In Figure 1a,b, there are images of the controls and of a BCPM CoFA-LA at the end of the test. In the figure, there are signs of the decay of termites in the Figure 1a control samples and no sign at all in the Figure 1b CoFA-LA impregnated samples.

3.2. Insect Test

Table 2 shows the final results of the test with Hylotrupes bajulus L.
3.3. Mold Discoloration

The laboratory test for mold discoloration was performed at the optimal temperature and relative humidity for growth of the selected fungi. Another intention was to evaluate the laboratory test as an accelerated predictor of the discoloration process in practice. The average growth of the test fungi is shown in Table 3 and Figure 2.

Table 3. Ratings of mold growth and discoloration in nonimpregnated and samples impregnated with CoFA-LA (0 = no visible growth, 1 = covering up to 10% of the surface, 2 = covering between 10% and 30%, 3 = covering between 30% and 70%, 4 = more than 70% of the surface and 5 = 100% coverage).

| Wood and Treatment            | 2 Weeks | 4 Weeks | 6 Weeks | 8 Weeks |
|-------------------------------|---------|---------|---------|---------|
| Untreated Scots pine sapwood  | 2       | 2       | 3       | 4       |
| Scots pine CoFA-LA at WPG 95%| 1       | 2       | 3       | 4       |

All the BPCMs treatments are resistant to attack of the newborn larvae of *H. bajulus* L., even if the survival of CS is only 50% of the initial larva number instead of 70%, as requested by the standard.

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Figure 2. Illustration of mold discoloration for the tested samples: (a) nonimpregnated Scots pine and (b) Scots pine impregnated with CoFA-LA at 95% WPG.

Nonimpregnated pine is susceptible to mold growth, reaching a rate of 4 after 8 weeks of exposure; the susceptibility to mold growth can be related to the amount of available low-molecular sugars on the wood surface, e.g., glucose, fructose and sucrose [29,30]. A similar susceptibility to mold growth on pine has been observed recently [31].

After impregnation with CoFA-LA, the mold discoloration susceptibility of the wood impregnated with BPCM was similar, but the speed of the discoloration slowed down in the first 2 weeks. The growth rates for both the treated and untreated Scots pine samples after 8 weeks of exposure were 4 (Table 3).

After the impregnation of wood with a mixture of fatty acids, the surface is enriched and ready for mold growth. The BPCM can play some role as a water-repellent formulation.
in the wood, but it can only postpone the moisture adsorption. It has been demonstrated that the most common airborne fungal genera *Cladosporium* spp., *Penicillium* spp. and *Aspergillus* spp. and nonsporulating molds [32,33] found in indoor environments are restricted by the availability of moisture. However, this was not the case with CoFA-LA impregnated in Scots pine, and the mold discoloration on the wood–BPCM material was identical compared to the nonimpregnated wood.

The high WPG can also contribute negatively to the results because of some leaching during the test. Thus, the effect of retention must be also considered, presumeing that a lower WPG can perform better.

4. Conclusions

Scot pine sapwood was impregnated with four fatty acid types of BPCMs, namely capric acid (CA), methyl palmitate (MP), lauryl alcohol (LA) and CoFA-LA composed of coconut oil fatty acids (CoFA) and linoleic acid (LA), in order to produce a smart bio-composite for building applications. Biological tests, including termite, insect and mold discoloration, were conducted. The main findings of the work are that the tested BPCMs were durable against subterranean termites of the Italian species *Reticulitermes lucifugus*. Only in one case (LA) did we observe a few termites that survived on the treated samples. All the BPCMs were resistant to *H. bajulus* newborn larvae before the end of the test at 4 weeks.

The mold susceptibility test showed that the appearance and growth of mold are related to critical levels of moisture and temperature. The results showed that CoFA-LA treated samples can serve identically to the untreated wood in terms of mold discoloration.

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