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ENGINEERED WOOD MATERIAL WITH BIO-BASED PHASE CHANGE MATERIAL AND MICRONISED COPPER FOR BUILDING APPLICATIONS

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Abstract:
In this study, pine sapwood was first impregnated with micronized copper (Cu) solution at concentrations of 5 and 10%, the samples then dried and impregnated with ethyl palmitate as a bio-based phase change material (BPCM). The leakage test showed slightly less leakage in this scenario compare to controls without copper. The mould test showed using copper solution, significattly improves the resistance of the composites to mould growth. Thermal tests showed using BPCM improves thermal conductivity and thermal mass of the composites, enabling them to store and release energy within the temperature range of 20-25ºC. It is observed that the copper did not improve thermal conductivity, and 5% copper showed the best performance in thermal mass improvement.

Key words: *bio-based PCMs; mould test; micronized copper treatment; Scots pine sapwood; thermal energy storage; thermal properties.*

INTRODUCTION

Originating from renewable resources, recyclable, and possessing high ratio of strength to density, wood becomes an inevitable part of building industry, which is confirmed by increasing application of timber in single - and multi - floor buildings (Hepburn et al. 2019, Ramage et al. 2017). Traditionally used building materials including concrete, metals, polymers and plastics contributes to environmental, health problems and non-recyclable wastes. The above demonstrates the bright future of wood materials in construction industry. However, wood materials have some inherited drawbacks, e.g. biological deterioration related to mould growth and release of mycotoxins affect the occupants in buildings (Abbott 2002, Nazari et al. 2022), emphasizing the importance of material selection and living climate. Residential buildings are the main consumers of thermal energy. In addition, low thermal mass of wood due to relatively low density and specific heat capacity limits wood's resiliency to temperature fluctuation, and thus extra energy is needed to provide comfort environment in the buildings.

Engineering wood properties can introduce challenges and advantages to overcome the above mentioned issues. Today micronized copper serves as a highly effective wood protection formulation to protect the material against degrading microorganisms and mould fungi producing mycotoxins. Micronized copper has been widely used for wood protection since its introduction in USA in 2006 (Karunasekera 2017). Bio-based phase change materials (BPCMs) can improve thermal properties of wood materials introducing the ability to absorb, store and release thermal energy and thus, controlling temperature fluctuations inside the building, i.e. using the thermal energy more efficiently (Nazari et al. 2022a, Nazari et al. 2022b).

Wood materials in various forms, e.g. wood fibers, flour, solid wood, delignified wood and more are considered as a cheap and porous bio-resource for encapsulation of BPCMs. BPCMs incorporated in solid wood can serve for manufacturing of flooring (Mathis et al. 2018) with novel properties. Mathis et al. (2018) impregnated oak and sugar maple wood for flooring with a commercial microencapsulated BPCM (Nextek29) and revealed an improvement in the thermal mass with 77% compared to the untreated wood. Wood

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materials combined and engineered with BPCMs (e.g. eutectic mixtures of fatty acids and esters) have been topic of certain studies with solid wood, and composites of wood fibers (Temiz et al. 2020, Nazari et al. 2023). Therefore, there is a potential for solid wood impregnated with BPCMs as an option for wood flooring and for wood fibers with BPCM for wallboards.

The above approach still needs more research to eliminate the inherited disadvantages of wood, namely its low thermal mass, bio-degradability and leakage of the BPCM from wood structure after impregnation. The idea of the present study is to use micronized copper solution together with a BPCM incorporated in a commonly used wood specie to *a)* minimize the leakage of the BPCM; *b)* improve the wood's resistance against discoloration fungi (stain and moulds) and *c)* improve wood's thermal properties. According to our knowledge, the mentioned questions and solution introduced in this study have rarely been studied together and comprehensively.

MATERIAL, METHOD, EQUIPMENT

Sapwood samples of Scots pine (*Pinus sylvestris* L.) with dimensions of 9×90×90mm were used throughout the study. Micro - and nano - size particles of basic copper carbonate ($CuCO_3 \times Cu(OH)_2$) called "micronized copper" was used as a protective formulation. Ethyl palmitate (EP) purchased from Sigma-Aldrich was used as BPCM.

Incorporation of micronized copper and BPCM into wood

Micronized copper solutions were prepared by weighing and adding water to the micronized particles to reach 5 and 10% concentration. The solutions were then impregnated into the wood samples in an impregnation autoclave using 10min vacuum of 350mbar and 6bar pressure for 1h. The copper impregnated wood samples were stored into conditioning room to reach 12% moisture content. After the conditioning, the samples were impregnated with EP by a vacuum-pressure process in an autoclave, following the procedure below; The autoclave temperature was set to 60ºC to ensure melting of the BPCM. The samples were immersed in the EP and a vacuum of 350mbar for 10min followed by 6bar pressure for 1h was applied. After the impregnation, the samples were conditioned in a cold room (10°C) for one week and weighed prior to the leaching tests. The samples were leached in an oven set to 35ºC for 24h and the final weight was recorded after the process.

Mould discolouration test

The susceptibility of the composites to mould growth and discolouration was tested according to the American Wood Protection Association Standard E24-06 (2015). Three mould 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 mould spore suspension was prepared and inoculated on the sterilized soil in a plastic chamber. After inoculation, the chamber was incubated in a climate room at 20°C for 2 weeks. Afterwards, untreated, copper-treated with and without BPCM wood samples were put in the chamber hanging approximately 5cm above the soil. The climate in the chamber was maintained at 25°C and the relative humidity (RH) was 95%. After 8 weeks of exposure, the mould growth on the sample surfaces (90×90mm) was classified by visual examination according to a scale from 0 (no visible growth) to 5 (very abundant growth, 100% coverage).

Thermal behavior of the materials

The same T-history method reported in refs. (Nazari et al. 2022a, Nazari et al. 2022b, Nazari et al. 2023), was used to monitor temperature profile of several samples simultaneously over time, illustrating melting/freezing point and degree of supercooling. The samples were thermally insulated using 10mm thickness ARMAFLEX insulation material. K-type thermocouples placed at the centerline and in the middle of the samples were used to record temperature changes over time. For cold and hot ambient climate, two chambers were employed, the former used for cold ambient climate fixed at 10ºC, while the latter chamber was used for hot ambient climate set at 35ºC. The chamber's temperatures were recorded with two separate thermocouples. Samples were first preheated at 35ºC, and then quickly transferred into the chamber at 10ºC and the temperature profile was recorded. Once the equilibrium temperature was reached (ca. 3h) the samples were transferred back to 35ºC and the temperature changes were recorded.

Two methods of thermal conductivity measurement were used to study the effect of micronized copper on thermal conductivity. A heat flow meter method reported in refs. (Nazari et al. 2022a, Nazari et al. 2023) was used using a steady state measurement. Thermal conductivity along the thickness of samples was measured in an insulated box. Two thermocouples of K - and T- type used to measure the temperature at the both surfaces of the samples. A heat flux meter type FHF03 supplied from Hukseflux, the Netherlands was used to measure the heat flux at the surface exposed to cold environment. A transient approach was further used to compare the result of the copper-impregnated samples to untreated samples, i.e. to study the effect of copper on the thermal conductivity. A Hot Disk TPS 3500 with sensor type of 5501 F1 Kapton (radius 6.4mm) which uses a standard isotropic hot disk method was employed. Each transient measurement run for 40sec with heating power of 60-100mW.

RESULTS AND DISCUSSION

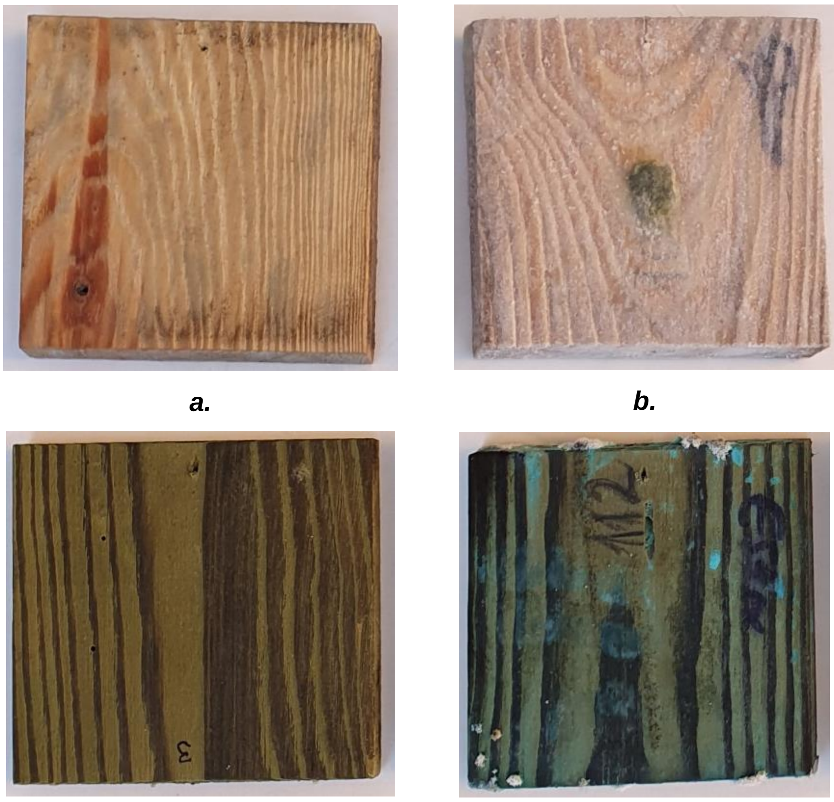
Impregnation and leaching of BPCM

The used impregnation schedule for incorporation of BPCM into copper-impregnated samples led to reaching WPG of 86% into 10% copper-treated and 90% into 5% copper-treated samples, which is similar to impregnation of pine samples with BPCM but without micronized copper. The leaching test showed that after 24h in the oven set to 35ºC, 8% of the BPCM leached out from the copper-impregnated samples (at 5 and 10% retention) which is slightly lower than that for pine wood samples without micronized copper impregnation i.e. 10%. This may be due to the presence of copper in wood structure (cell walls) assisting the wood to keep the BPCM inside the cell lumens.

Mould discolouration of the composites

The intention of the mould test was to study and compare the susceptibility of untreated samples, copper-treated and in both cases with BPCM composites to mould growth. The selected mould fungi are very common and grow well on pine (Bjurman 1994). The laboratory test was performed at 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.

As shown in Fig. 1, there is a significant difference between the mould growth on the untreated and copper-treated samples of the wood specie. Pine sample is discolored to rate 4 after 8 weeks while the copper-treated one is 0 showing that the mould does not grow on the surface of the copper-treated samples. This is clearly due to toxic nature of copper solution for mould fungi. After incorporation of BPCM in the wood, it seems that mould grows better in presence of BPCM on the surface, this is probably due to the fact that the used BPCM is used by mould fungi as a nutrient. The untreated wood with BPCM reached rate 5, while the copper-treated one with BPCM reached rate 2 after 8 weeks of exposure.



a. b. c. d.

Fig. 1.
The appearance of surfaces after 8 weeks exposure to mold fungi: a-Pine, b-Pine/BPCM, c-Pine/Cu10%, d-Pine/BPCM/Cu10%.

Thermal behavior of the composites

The measured thermal conductivity of pine and copper-treated pine with heat flowmeter showed average of 0.12W/m K in both cases. The result obtained from transient measurement of TPS was higher but still was the same for both cases. Incorporation of BPCM in the wood materials (WPG 80%) resulted in increment in thermal conductivity reaching value of 0.2W/m K for pine/BPCM and pine/BPCM/Cu10% measured with heat flowmeter method, in this case also the measured value with TPS was higher but the same for composites with and without copper treatment. It was expected that copper treatment would improve thermal conductivity of the composites but the result confirmed that the copper treatment does not increase the thermal conductivity, and this might be due to the chemical composition of copper solution.

Fig. 2 shows the temperature profile versus time for the samples during the cooling (Fig. 2a) and heating process (Fig. 2b). When the samples from the oven set to 35ºC transferred to the climate chamber set to 10ºC, the materials' temperature decrease from the starting temperature at 35ºC and continues to decease with the time until it reaches the chamber's temperature (10ºC). During this cooling process, phase change transition is observed for all composites of Pine/BPCM and those with copper treatment. It is also observed that the pure BPCM experiences supercooling which cools down to 20ºC, while fully solidifies at 21.7ºC showing 1.7ºC supercooling, however, this problem is not observed after incorporating into the wood materials. The solidification temperature for all composites is 20ºC. During the heating process, when the materials transferred back from climate chamber at 10ºC to the oven at 35ºC (Fig. 2b), the BPCM inside the composites start to melt, and it is observed that the melting temperature for all composites is 25ºC.

The figure shows that during both cooling and heating processes, untreated pine sample reached the equilibrium temperature faster than the impregnated ones. This is due to the improvement in thermal mass of the composites with BPCM. The BPCM has enabled the composites to store energy in terms of latent heat and release energy in the temperature range of 20-25ºC, thus postponing the equilibrium time as clarified in the figure with the rectangular shape. Improvement of thermal mass enables materials to absorb and store more energy during heating and release more energy during cooling process, leading to delay for reaching the ambient temperature. It is also observed that 5% copper treated sample showed better result due to the fact that in this case the impregnation uptake was slightly higher than untreated pine and that with 10% copper. Furthermore, copper treated samples in both cases leached slightly less BPCM compared to untreated samples, therefore the final remaining BPCM inside the copper-treated samples were slightly more.

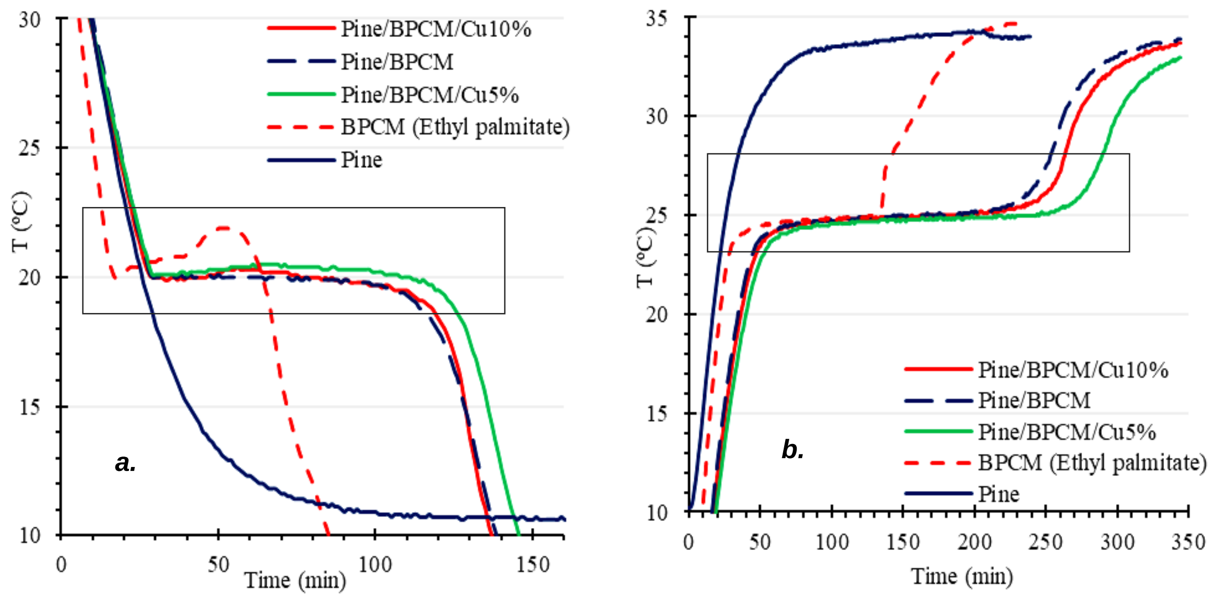


Fig. 2.
T-history curves over cooling/heating cycle for: a-cooling and b-heating.

CONCLUSIONS

Scots pine sapwood impregnated with micronized copper solution and a BPCM showed improvement in resistance to mould growth and thermal mass for building applications. The important findings of the study are summarized as:

- Micronized copper impregnated wood showed a relatively better performance in keeping BPCM in its structure, compare to untreated one. Copper treated wood showed 8% leakage while it was around 10% for untreated wood.
- Copper treatment did not improve thermal conductivity, but in terms of thermal mass and ability to keep temperature constant, 5% copper in the wood structure with BPCM showed a better performance compare to 10% treatment and untreated woods with BPCM.
- The mould test showed that the growth of moulds is much less on the surface of copper-treated woods compare to untreated ones. The study of mould growth on Wood/Cu/BPCM composite showed that although the BPCM can serve as nutrient for mould fungi, in the presences of copper it did not growth on the composite.

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