DEVELOPMENT OF SUNFLOWER-BASED INSULATION MATERIALS COATED WITH GLYCEROL ESTERS TO PREVENT MICROBIAL GROWTH

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Abstract

It is now well known that, under specific environmental conditions, building materials may be the target of microbial proliferation. Their growth leads to the deterioration of both materials and indoor air quality (indirectly induced by the release of airborne microbial contaminants, including spores, fragments, toxins, mVOC, etc.). As bio-based building materials usually contain cellulose or derivatives, they are likely to be much more sensitive to such degradations. However, very few studies have shown precise hygrometric conditions that allow microbial growth and spread on this type of material. Glycerol esters are valuable by-products of agroindustry. Previous works have highlighted their significant antimicrobial effect. They are commonly used in the food industry as antimicrobial agents. They could be used as well to protect bio-based materials from microbial colonization. It would be an eco-friendly alternative, consistent with human health, to the classic ways of protecting bio-based materials against microorganisms. This study is included in a project that aims to (i) develop insulation materials from sunflower stalk and (ii) to study the antimicrobial efficiency of glycerol esters for the protection of such bio-based materials from microbial proliferation.Two types of insulation bio-based materials were designed from sunflower stalk particles. A “light” type was casted from pith and a “denser” one was casted from extruded bark, i.e. the depithed stalk. Physical, thermal and hygroscopic properties of the insulating panels (“light” type) were assessed (density, thermal conductivity, and vapor sorption isotherm). Optimum inhibitory concentrations of glycerol esters on two fungal strains were evaluated.

Keywords:

Insulation, bio-based materials, building, microbial growth, glycerol esters

1 INTRODUCTION

Under certain hygrometric conditions, building materials can become major target of microbial growth [Verdier 2014]. Their proliferation leads to the degradation of materials and may lead to the deterioration of air quality due to aerial particles (spores, fungal fragments, toxins ...) and volatile organic compounds produced by these microorganisms [Verdier 2016]. For several years, the World Health Organization and the Observatory of Indoor Air Quality in France have been raising awareness of the different types of indoor air pollution, including pollution of biological origin [CSHPF 2006; WHO 2009]. These two degradation issues (materials and indoor air) are all the more sensitive with bio-sourced materials, which contain a significant proportion of cellulose and / or derivatives that are nutrient sources promoting microbial growth.

Until 2011, cellulose-based insulation materials were treated with boron salts for their flame retardant and antimicrobial properties. A recent European Union directive bans the use of boric acid and salts as a biocidal agent because of their category 2 classification as reprotoxic agents [2009/94/EC 2009]. Today, the use of boron salts as flame retardants is still possible, if they are used without any biocidal claims. However, tolerated use is problematic from the point of view of health. "Greener" and healthier substitutes should be developed.

Recent works at LMDC and LCA were carried out to develop bio-based products based on certain glycerol esters that have shown significant antimicrobial effects [Mikhailenko 2015, Verdier 2017]. Glycerol esters have specific surface-active properties favoring their use in many fields (cosmetics, food, pharmaceutical, textile, etc.). They are made of a fatty acid connected to a glycerol molecule by an ester bond. Antimicrobial properties of glycerol esters have been studied for several years now and their disinfecting efficacy has been observed on a wide variety of microorganisms, including bacteria, yeasts, fungi and viruses [Desbois & Smith 2009]. These antimicrobial, microbicides and / or growth inhibiting properties are mainly governed by the structure and shape of the molecules, i.e. the length of the carbon chain and the presence of double bonds (saturated / unsaturated). The literature reveals a strong antimicrobial potential of these molecules but, to our knowledge, still no application to protect building materials. The use of this type of molecule is an innovative and environmentally friendly solution that can be used to protect bio-based insulation materials from microbial growth.

The purpose of this paper is to present some preliminary results from a project that aims to (i) develop and evaluate thermal and hygroscopic properties of two new types of bio-based insulation materials made of sunflower stalk, a by-product of sunflower cultivation, and (ii) investigate the antimicrobial performances of an innovative product formulated using glycerol esters that could be used to protect insulation materials. At first, the casting methodology by cold compaction is presented. Subsequently, the study provides a synthesis of the first results obtained on (a) the determination of inhibitory concentrations of glycerol ester products and (b) the thermal and hygroscopic properties of insulation samples made of sunflower pith.

2 MATERIALS AND METHODS

2.1 Insulation sunflower-based materials

Insulation materials were designed with sunflower stalk. A mechanical process developed by the AGROMAT technological transfer hall of LCA was carried out to separate pith from bark. A “light” insulation material (≈ 50 kg/m^3) was casted using pith (d < 2.5 mm) and a “denser” one was casted using extrusion-refined bark (≈ 250 kg/m^3). Samples were formulated with water and a starchy binder, then compression-molded at ambient temperature in different metallic molds. The proportions are presented in Table 1.

Tab. 6: Mix proportions of insulation materials

	Aggregates (% dry mass)	Binder (% dry mass)	Binder Dilution (%)
Pith	90.9	9.1	2.5
Bark	87.0	13.0	4.0

The casting protocol was as follows for both materials:

- Mixing manually sunflower aggregates and binder in dry state
- Incorporation of warm water (≈ 60-70°C) and maintain mixing until the water is homogeneously distributed in the mixture
- Incorporation of the mixture inside the corresponding mold (a baking paper is placed in the bottom of the mold and on the surface of the piston to prevent the mixture from sticking to the mold)
- Compaction with piston under cold hydraulic press for 90 sec per sample
- Removal from mold and drying at 40 °C inside a ventilated oven until mass stabilization.

Tab. 7: Apparent densities of samples (mean ± s.d.).

Material	Type of sample	Density (kg/m^3)
Bark	Rectangular. prism	232.5 ±2.6
	Plate	261.9 ±13.7
Pith	Rectangular. prism	44.1 ±0.1
	Plate	44.1 ±0.1

Apparent densities of samples after mass stabilization in ambient air (21 °C, ≈ 50% RH) are presented in Tab.2. Pith- and bark-based prismatic samples are visible in *Fig. 1* and *Fig. 2*.

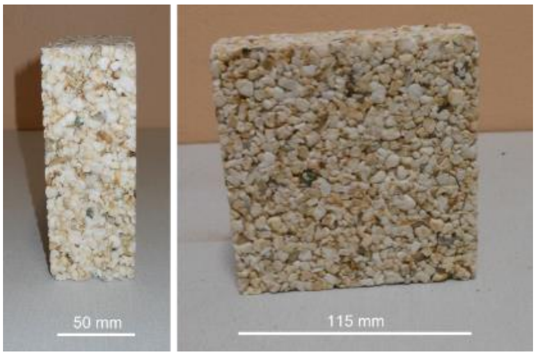

Fig. 1: Prismatic pith-based samples.

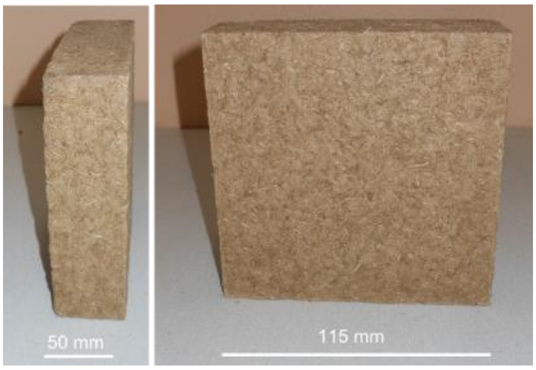

Fig. 2: Prismatic bark-based samples.

2.2 Glycerol esters

Glycerol esters used in this study are derivatives of biodiesel production [Mikhailenko 2015] supplied by Kemerid. The product used in this paper, refered as XUG, consisted of glyceryl mono undecylenate (50-60 %), glyceryl di undecylenate (35-45 %), glyceryl tri undecylenate (1-5 %) and undecylenic acid. The content of the latter is 0.5-2 % for washed XUG and 10-15% for unwashed XUG. Several concentrations of XUG were diluted in water and spray on sample with a trigger spray bottle. Quantity was controlled by mass measurement. As the XUG presents surfactant properties, its viscosity is temperature dependent. In order to carry out a repeatable covering method, the XUG and samples were conditioned in an air-conditioned room at 23 ± 1.5 °C before each application.

2.3 Thermal conductivity

Thermal conductivity was evaluated according to two methodologies: hot wire [ASTM D 5930-97 2001] RILEM AAC 11-3, and guarded hot plate [NF EN 12664 2001; NF EN 12667 2001]. The hot wire device used includes an FP2C power supply and associated software. It measures conductivities ranging from 0.02 to 5 W.m^{-1}.K^{-1}. All measurements were made in an air-conditioned room (21 °C), with a power set at 0.1 W for an acquisition time of 60 s. Before each test, samples were stored in the test room for approximately 45 min – 1 h in order to be stabilized at room temperature. This stable state was then verified (the temperature difference must be less than 0.2 °C for 60 s). The guarded hot plate test was carried out with a λ-Meter EP500 at three temperatures (10 °C, 23 °C and 35 °C) with a difference of 10 K between the plates. Before each test, samples were conditioned at different relative humidities until mass stabilization (5 %, 50 %, 60 %, and 93 %) ± 5 % RH. For both methods, 4 rectangular prisms (15 x 15 x 5) cm^3 were tested.

2.4 Sorption isotherms (DVS method)

The sorption isotherms of the materials were evaluated by the Dynamic Vapour Sorption (DVS) method, previously described in [Cagnon 2014; Bui 2017; Laborel-Préneron 2018]. For each test, five samples (1.5 ± 0.5 g) were tested to be representative of the material. Before testing, samples were dried at 50°C in the DVS for 3 h. Tests were carried out at 23°C. Relative humidity was regulated in successive stages from 0 to 95 % by steps of 20 % (15 % for the last). The mass stabilisation criterion (d_m/d_t) to go to the next step was chosen ≤ 5.10^{-4} min^{-1} over a ten-minute period [Cagnon 2014]. The water content was calculated as the ratio of the mass of water contained in the sample to the mass of the dry sample (at 0 % RH).

2.5 Inhibitory concentration test

In order to evaluate the optimal concentration of XUG to protect material from microbial proliferation, a growth test was carried out on two fungal strains. As fatty acids also show antimicrobial properties [Bergsson 2002; Valentin 2012; Shi 2016], tests were carried out with three products: undecylenic acid, unwashed XUG (XUG + undecylenic acid), and washed XUG. Fungal strains used in this study are part of the FCBA Bordeaux's collection. The strains *Aspergillus niger,* commonly identified on indoor building materials [Verdier 2014], and *Trichoderma viride,* known to be more resistant to chemical treatment*,* were propagated on malt/agar (4 %: 2 %) plates incubated at 22°C and 70 %RH. The test was carried out on malt/agar medium supplemented prior solidification with washed XUG, unwashed XUG or undecylenic acid at several concentrations. One plug of each strain was put on supplemented medium to evaluate the ability of each molecule to affect fungal growth. Experiments were carried out in three independent biological repeats. Agar plates were incubated at 22 °C and 70 % of relative humidity until complete growth. Radial growth was evaluated regularly during the experiment.

3 RESULTS AND DISCUSSION

3.1 Antimicrobial performances

Fig. 3 shows the growth of *T. viride* and *A. niger* in contact with undecylenic acid, unwashed XUG or washed XUG. It should be noted that these tests were carried out in order to identify the most effective concentrations in a relatively short period of time. This is why tests were carried out on nutrient media that promote microbial growth. They do not reflect any antimicrobial activity that the products could have on an insulating material in real-world conditions.

As can be seen from the 2 top diagrams, 5 % of undecylenic acid are sufficient to inhibit growth of *A. niger* whereas 10 % are not enough to inhibit the growth of *T. vinide*. The results obtain from unwashed XUG (two middle diagrams) show that 5 % of the mix is sufficient to inhibit the growth of *A. niger* and 20% is sufficient to inhibit the growth of *T. vinide*. Regarding washed XUG (two bottom diagrams) at 5 % and 10 %, growth is limited for 6 days for *A. niger* and *T. vinide*. Both fungi grow again after 8 days. 20 % of washed XUG seem sufficient to inhibit growth for 8 days. These results show a synergic effect of XUG and undecylenic acid as the best inhibition performances were observed with 5 % and 20 % of the mix on *A. niger* and *T. vinide*, respectively. Surprisingly, undecylenic acid was more efficient on *A. niger* than washed XUG and conversely washed XUG was more efficient on *T. vinide* than undecylenic acid. These findings suggest that their antimicrobial actions are governed by different mechanisms.

3.2 Thermal and hygric performance

Thermal conductivity: λ

Fig. 4 provides the experimental data of thermal conductivity obtained on samples with the two methods (hot wire and guarded hot plate), depending on the relative humidity of samples. It can be seen that both methods lead to significantly close values of λ for samples that were kept at 5 % RH, 50 % RH and 60 % RH. Since experiment with the guarded hot plate is relatively long (more than 10 hours for 3 measurement temperatures), samples were weighed before and after experiments in order to evaluate water migration: for RH from 5 % to 60 %, maximum mass variation did not exceed 3.5 %. At 93 % RH, mass losses were observed from 14 to 17 %. Interestingly, λ values at 93%RH were significantly different between hot wire and hot plate measurements, 52.0×10^{-3} W/(m.K) vs 40.4×10^{-3} W/(m.K), respectively. The thermal conductivity assessed by the hot wire method at 93%RH is significantly higher than the values assessed at lower humidity, which seems intuitive because the increase of water content in a sample tends to increase its conductivity. However, such increase was not observed with the guarded hot plate method. Experiments are currently carried out on samples embedded with cellophane. The thermal conductivity measured on the first sample at 23 °C, 93 % RH was 48.3×10^{-3} W/(m.K), i.e. almost 20 % higher than without the cellophane, which is closer to values obtain with the hot wire. As mentioned in [Amziane 2017] and confirmed by the observed mass variations, it is important to bear in mind the possible bias induced by water migration inside sample near 100 % RH when using the guarded hot plate method for long-time measurements. In those particular cases, embedding samples in cellophane could be a way to prevent water migration. Otherwise, the hot wire method should be used instead.

A comparison of experimental λ obtained on pith and bark samples and other insulation materials from the literature is set out in *Fig. 5*.

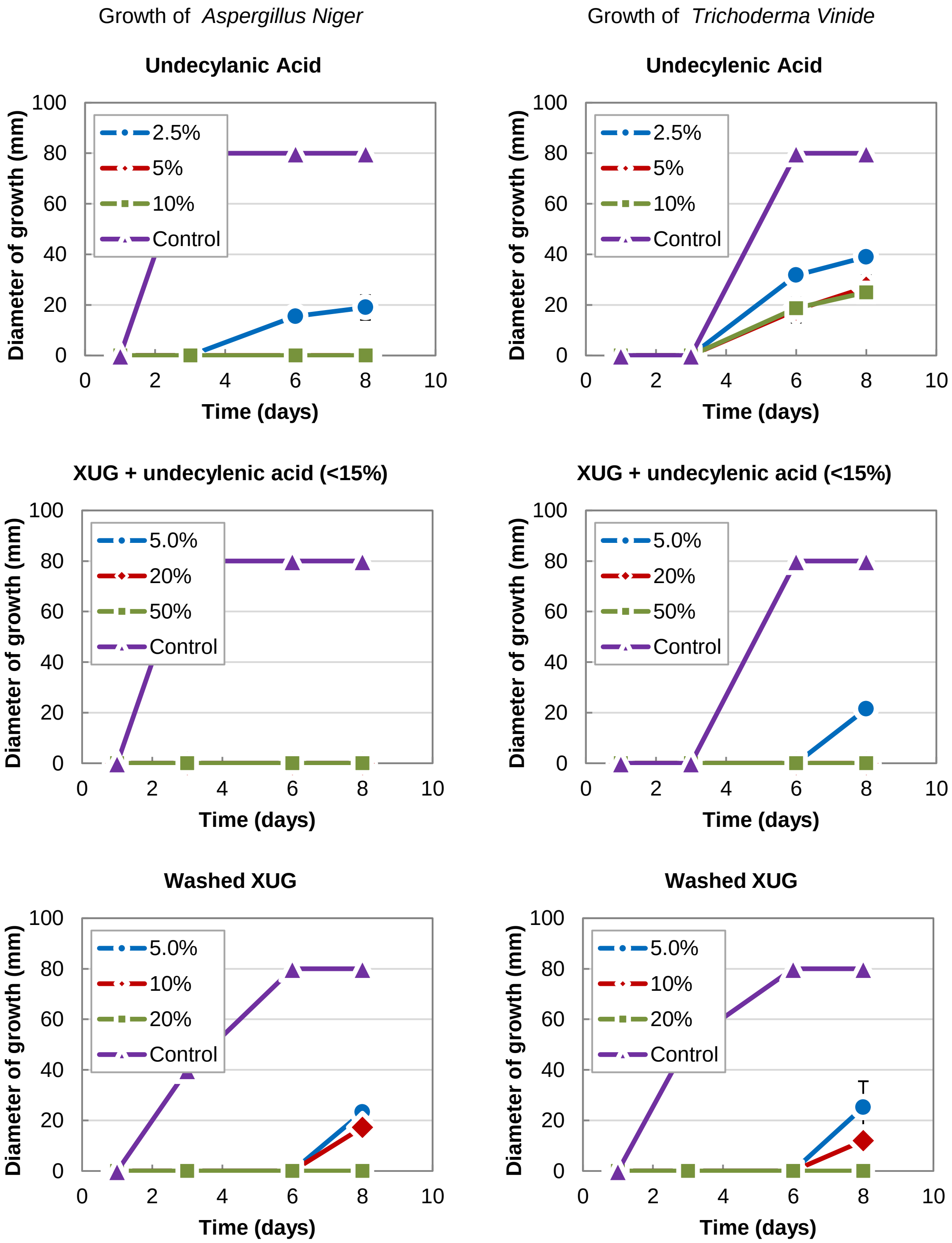

Fig. 3: Results of the inhibitory concentration test of different products on A. niger *(left) and* T. vinide *(right).*

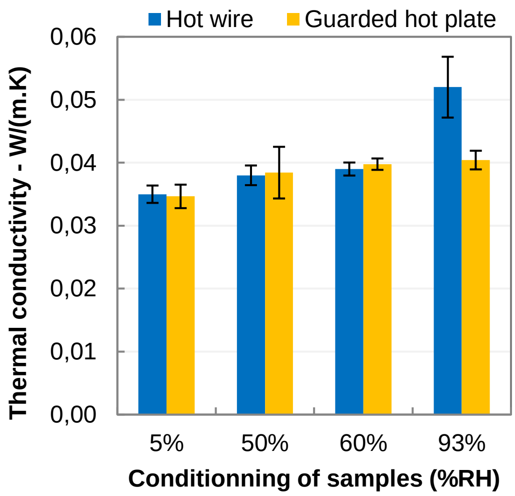

Fig. 4: Thermal conductivity of insulation materials made with sunflower pith. Mean ±2σ (n=4).

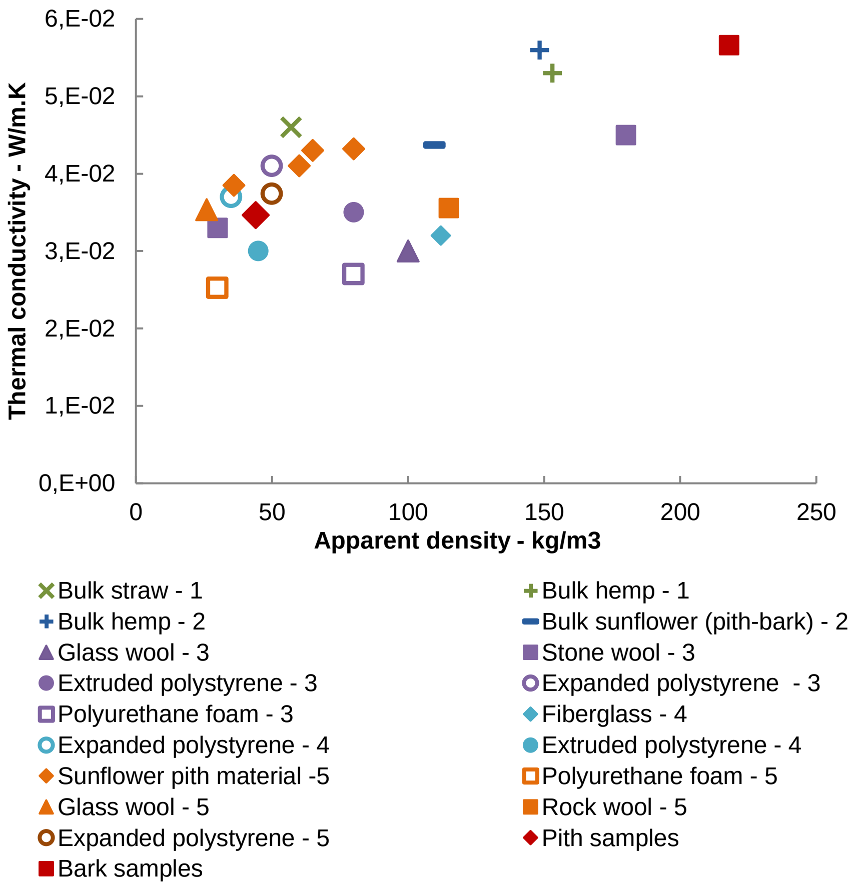

Fig. 5: Thermal conductivity of pith samples and of comparable insulation materials from the litterature measured around 21-25°C. 1-(Aurélie Laborel-Préneron et al. 2018); 2-(Verdier et al. 2012); 3-(Papadopoulos 2005); 4-(Al-Homoud 2005); 5-(Vandenbossche et al. 2012).

The thermal conductivity of pith samples is similar to those of stone wool and expanded polystyrene, highlighting their interest of use as insulation material. Thermal conductivity of bark samples is higher than other materials, which is consistent with its higher density, but is in the range of common insulation materials.

Sorption Isotherms

Sorption isotherms of pith samples covered or not with XUG (20 %) are presented in *Fig. 6*. The curve of pith samples (green curve) is typical of isotherms obtained with a macroporous adsorbent, which correspond to a Type II isotherm according to the IUPAC classification [Sing 1985]. The isotherm represents unrestricted monolayer-multilayer adsorption. A strong increase in water content was observed at high RH likely due to capillary condensation [Sing 1985]. The curve is close to the sorption isotherms of sunflower pith bulk particles (orange curve) measured by [Magniont 2010] with a DVS method. At 80 % RH and 95 % RH, the water content was close to 20 % and 40 % in mass, respectively. As Magniont underlined, the density of pith is very low (30-50 kg/m^3), so is the volume fraction of adsorbed water. An implication of this is the thermal properties of pith materials should be less impacted by water variation than expected by reading the ***Fig. 6***. Concerning the isotherm of samples covered with XUG (blue curve), the adding of XUG on samples lowered water contents by about 5 % from 20 to 80 % RH. At 95 % RH, the water content was similar to that of pith samples. According to these data, we can infer that the XUG restricts the monolayer adsorption of water probably by decreasing Van der Waals forces but does not affect the capillary condensation.

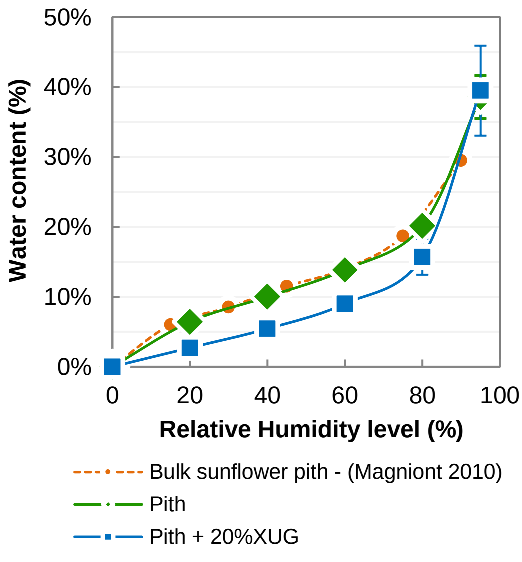

Fig. 6: Sorption isotherm of pith samples. Mean ±2σ (n=5).

4 CONCLUSION

The first aim of the present research was to develop and to evaluate thermal and hygroscopic properties of two new types of bio-based insulation materials made of sunflower stalk, a by-product of sunflower cultivation. The second aim was to investigate the antimicrobial performances of an innovative product formulated using glycerol esters that could be used to protect insulation materials. A light type of insulation (50 kg/m^3) including sunflower pith and a denser one (250 kg/m^3) including sunflower bark were casted by a compaction method with a cold hydraulic press. As the production of XUG generate undecylenic acid residues, a preliminary test was carried out to evaluate their respective antimicrobial performances. Results shown different antimicrobial behaviors, depending on the nature of the tested microorganism: inhibitory effects of washed XUG were similar on *A. niger* and on *T. vinide* whereas undecylenic acid shown a higher inhibitory effect on *A. niger* but a lower effect on *T. vinide* than the washed XUG. The better inhibitory effect was observed for the XUG containing undecylenic acid on both microorganisms. These results support the antimicrobial performance observed in previous work [Verdier 2017] and are encouraging with regard to the use of XUG as a protection product from microbial growth. Further tests will be conducted on the insulating materials for several weeks in conditions favoring microbial growth.

Thermal conductivity and sorption isotherms of insulation materials made with pith were evaluated. Thermal conductivity varied from 34.7x10^{-3} W/(m.K) to 52.0x10^{-3} W/(m.K) for relative humidity ranging from 5 % to 93 %. These values are close to those from commercial insulation materials such as expanded polystyrene or glass wool, which encourage further studies. The experiments also highlighted a bias induced by water migration during long-time measurements on the guarded hot plate for relative humidity close to 100 %. In such particular cases, something must be used to prevent water migration without altered the thermal conductivity measurement. Otherwise, the hot wire method may be used. Sorption isotherms obtained by DVS method showed that the hydric behavior of pith samples is that of a macroporous material. It should be remembered that the water content in % mass is to be related to the low density of pith material. It can therefore be assumed that their thermal insulation properties should not be that much impacted by humidity. Adding XUG on the material has a water adsorption reducing effect for relative humidities ranging from 20 % to 80 %.

The results presented in this paper come from a project focused on the development of these two insulation materials and on the XUG. Experiments are still ongoing on the thermal and hygroscopic properties of bark-based insulation and the antimicrobial performance of XUG coated on materials. Subsequently, a comparison will be conducted to observe in more details the effect of XUG on the thermal and hygroscopic properties of the two materials.

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