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Durability assessment of alkyl ketene dimer hydrophobic treatment of bio-based thermal insulation materials

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ABSTRACT

Bio-based composites are increasingly used as thermal insulation materials in construction due to sustainability and low thermal conductivity. However, their high moisture absorption can negatively affect performance and mould growth risk, shortening product lifespan. This study introduces alkyl ketene dimer (AKD) as an eco-friendly and economical solution for the hydrophobic treatment of two bio-based composites, mycelium and grass, to enhance their durability. We compare the physicochemical properties, hygrothermal performance, and mould growth resistance of bio-based composites before and after hydrophobic modification while evaluating their durability in simulated building envelopes across different climates. Results showed that the modified bio-based composites were well-grafted with AKD. The water absorption of bio-based composites significantly decreased after modification, and the mould growth resistance capacity of modified composites was significantly improved. Moreover, hygrothermal simulations reveal that AKD modification effectively enhances their suitability under different climate profiles, particularly when modified grass composites are applied.

1. Introduction

In the building field, thermal insulation materials play a role in achieving building energy efficiency (Kapoor and Singhal, 2024), by reducing heating and cooling loads under different climate zones. Current commercial insulation materials are mainly non-renewable materials such as glass wool, rock wool, polyurethane, polystyrene (expanded & extruded), and other novel materials and designs like aerogels and vacuum insulation panels (Zhao and Li, 2022). Although exhibiting good thermal insulation capacity, these traditional materials still have different levels of disadvantages: high production cost for aerogels; polluted environment for fossil fuel-based materials, complex processing, and toxic smoke release when polyurethane insulation materials combust and the like (Adhikary et al., 2021; Yuan et al., 2020).

In recent years, in the context of climate change and a series of low-carbon policies announced (Meckling and Allan, 2020), researchers in both academia and industry have been motivated to develop sustainable insulation materials of biomass origin (Raja et al., 2023; Savio et al., 2022). Grass is a fast and easy-growth plant. Some studies (Guna et al., 2019; Koh et al., 2022; Lu et al., 2023) have explored the potential of manufacturing grass fibers into composites for thermal insulation. These studies confirm that such composites have comparable hygroscopic, acoustic, and thermal insulation properties with commercial insulation materials. In addition, mycelium composites are comprised of organic fiber wastes through mycelium binding (Jones et al., 2017). A lot of literature (Schritt et al., 2021; Zhang et al., 2023, 2022) has reported that mycelium composites can be exploited as insulation materials given that they feature excellent thermal performance, low density, biodegradability, low-carbon footprint, and cheap (Zhang et al., 2021). Appels et al. (2019) manufactured the mycelium composites with different substrates: straw, sawdust, and cotton, and found that the mycelium composites are feasible as foam-like and natural materials in terms of density and elastic modulus. Besides, mycelium composites with multiscale hierarchical porous structures, constructed by randomly disordered poplar and birch sawdust, were found that lower thermal conductivity and high mechanical properties (Zhang et al., 2023). Despite these promising attributes, the critical disadvantage of such composites is that their high susceptibility to mould growth in humidity environments attributed to their hydrophilic nature adversely affects their durability and limits their practical application in some structural

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materials such as panelling, flooring, and furniture (Jones et al., 2020; Koh et al., 2022).

To address this, various hydrophobic modification treatments have been undertaken to alter the moisture absorption characteristic of bio-based composites. For example, Al Abdallah et al. (2022) used silane coupling agents to treat date palm wood fibers toward water resistance of bio-based thermal insulation materials. The results showed that the silane treatment can effectively improve the hydrophobicity of the composites. Kumar et al. (2016) investigated the hydrophobic modification on the wood fibrous insulator surface using octadecyltrichlorosilane (OTS). They found that the modified wood fibers have higher resistance to fungi growth and condensate adsorption. These treatments achieve different levels of the hydrophobic effect, but they simultaneously bring some disadvantages: nonuniform coating, poor durability of the hydrophobic modification effect, and expensive modified agents. Thus, looking for a cost-effective hydrophobic modification agent is urgent for improving mould resistance capacity of bio-based composites.

Alkyl ketene dimer (AKD) as a reactive sizing agent, due to its low cost (1–10 €/kg), low dosage, and low toxicity has been widely applied in papermaking to enhance paper hydrophobicity (Cao et al., 2022; Oh et al., 2022). AKD has been reported to endow cellulose with high hydrophobicity by reacting with hydroxyl groups of cellulose, forming covalent bonds (β-keto ester linkages) and non-covalent hydrogen bonding, and introducing two long alkyl chains (Adenekan and Hutton-Prager, 2019). However, to our knowledge, this AKD hydrophobic treatment has not yet been used in bio-based thermal insulation composites to prevent mould growth risk. Furthermore, the effect of this hydrophobic treatment on their hygrothermal properties has not been investigated.

Thus, this work aims to investigate the effect of using AKD hydrophobic treatment to enhance the durability of bio-based composites based on the hygrothermal properties but also mould growth resistance capacity. Here, two common bio-based composites, grass and mycelium composites, as thermal insulation materials were concerned. We investigate the physicochemical properties, hygroscopic properties, thermal performance, and mould growth resistance after applying AKD modification. A simulated building envelope is presented to assess durability by analyzing the hygric properties and mould growth risk in different climates for years. The results found in this study provide insights into effectively upgrading the durability of common grass and mycelium composites through AKD modification, resulting in accelerating their practical application as thermal insulation materials.

2. Experimental section

2.1. Materials

In this work, mycelium and grass bio-based composites were supplied by Fairm (the Netherlands) and Gramitherm (Belgium), respectively. The thickness in both mycelium and grass composites was measured at 35 mm and 60 mm, respectively. The physical appearances of both composites are characterized in Fig. A.1. The mycelium composites mainly consist of Dutch agricultural biomass including miscanthus, flax, and straw bounded together by the fungal mycelium growth as the natural connector. For the grass composites, 72% grass fibers, 20% jute fibers from waste cocoa and coffee sacks, and partially waste polyester fibers are bounded through air laying and thermal press processes. The commercial Alkyl ketene dimer (AKD) emulsion was provided by Kemira ora (Finland) and the physical properties of the emulsion are shown in Table A.1.

2.2. Methodology and relevant characterizations

The durability of mycelium and grass composites under AKD hydrophobic modification was evaluated. In particular, the basic physiochemical properties, hygrothermal performances, and mould growth risk of both composites are tested using the following methodology (Fig. A.2).

2.2.1. Hydrophobic modification

Before the modification, mycelium composites (15 cm × 10 cm × 3.5 cm) and grass composites (15 cm × 10 cm × 6 cm) underwent an oven-drying process at 60 °C for 8 h Subsequently, the dried composites were immersed in a 2.4% AKD emulsion for 12 h and then taken out. Following this, they were positioned in a fume hood to facilitate the evaporation of excess water before being transferred to an oven set at 105 °C for 6 h to promote the reaction between the fibers and AKD. Finally, the modified composites were cooled down to room temperature and seal-bagged for end use.

2.2.2. Performance characterization

2.2.2.1. Density and porosity. True density (ρ_{true}) measurements were conducted on a helium pycnometer (Micromeritics AccuPyc II 1340). Each composite was milled into the powder to break the existing pores/voids and directly filled in a sample cell (10 cm^3 vol size). The bulk density ($\rho_{apparent}$) of each composite was directly calculated according to the shape volume. The total porosity ∅ of the composites was calculated with:

$$\varnothing = 1 - \frac{\rho_{apparent}}{\rho_{true}} . \quad \text{(Eq. (1))}$$

Where $\rho_{apparent}$ is bulk density in dry conditions and ρ_{true} is true density in dry conditions.

2.2.2.2. Fourier Transform Infrared Spectroscopy (FTIR). The Perkin-Elmer spectrometer (Varian 3100) was employed to analyze the surface chemistry of as-received/modified composites. The wavenumber ranges from 4000 to 400 cm^{-1} with 30 scans per spectrum and a resolution of 1 cm^{-1}.

2.2.2.3. Optical microscope. The surface topography of the composites before and after modification was observed using a Zeiss optical microscope with a Camera/Director Axiocam 305.

2.2.2.4. Microscopic characterization. To better understand variations of the microstructural and surface composition of the composites before and after the AKD modification, a scanning electron microscope (SEM, Thermo Fisher Phenom Pro-X) was used with energy dispersive spectrometry (EDS). The investigated composites were split into small pieces, bound on carbon tape, and sputter-coated with Au under vacuum conditions. The prepared samples were observed under the SEM at an accelerating voltage of 15 kV.

2.2.2.5. Water absorption/wettability characterization. According to the literature, the water absorption capacity *(WAC)* of both as-received and modified composites was tested through the weight difference between dry and saturation humidity conditions. Specifically, the unmodified/modified composites were initially dried and weighted (w_{dried}) before being saturated in water for 48 hours. After that, the composite samples were taken out, lightly blotted with a cloth to remove extra surface water, and finally weighted (w_{sat}). The water absorption capacity of the composites was calculated using:

$$WAC = \frac{w_{Sat} - w_{dried}}{w_{dried}} . \quad \text{(Eq. (2))}$$

Where w_{sat}.is wet weight, and w_{dried} is dried.

The wettability of investigated composites was evaluated and compared using the sessile drop method (Water contact angle measuring instrument, Dataphysics OCA30). The measurement was performed with an accuracy of 0.1° reading.

2.2.2.6. Hygroscopic properties. Given the high porosity resulting from the cellulosic fibers, the sorption isotherms (adsorption and desorption phases) of the bio-based composites are a very important characteristic. Protocols on sorption isotherms measurements are detailed in the supplementary information and are in conformity with the recommended standard (American Society of Testing and Materials, 2017). The setup schematic of the measurement is described in Fig. A.3. The water vapor diffusion resistance factor μ is tested using the wet/dry cup methods following the standard NF EN ISO 12572 (European Union and International Organization for Standardization, 2001). Detailed steps involved in the sample test are described in the supplementary information.

2.2.2.7. Thermal properties. In this study, thermal conductivity λ [W/(m*k)] was measured using the transient line source method equipped with a thermal needle probe (AP ISOMET heat transfer analyzer model 2104). The measurement device has an accuracy of 5%. The conditions of the thermal conductivity measurement are described in the supplementary information. The values tested are the average of 5 trials.

2.2.2.8. Mould growth resistance. The hydrophobic modification on the mould growth resistance was assessed using the European Assessment Document EAD 040005-00-1201 (European Organization for Technical Assessment, 2015). Specifically, the tested bio-based composites were placed into desiccators filled with water to expose them to a higher humidity. The specimens were inspected at 0, 30, and 60 days later. The mould growth on unmodified/modified bio-based composites was observed with the naked eye and using an optical microscope (Zeiss) at different magnifications, following ISO 846 (International Organization for Standardization, 2019).

2.2.3. Durability assessment of the composites

To evaluate the durability of the as-received/modified bio-based composites as the insulation layer within cavity walls in realistic weather conditions, a heat and moisture transport software WUFI Pro 6 with plug-in Bio component (WUFI@Team, 1995) was employed to simulate the hygrothermal performance and mould growth risk of the composites in ten years. The analysis is focused on the interfaced bio-based composite layers next to the exterior and interior sides. Within WUFI Pro 6, the non-steady heat and moisture transport process can be calculated by following coupled equations:

$$\frac{\partial H}{\partial T}\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[\lambda\frac{\partial T}{\partial x}\right] + h_v\frac{\partial}{\partial x}\left[\frac{\delta}{\mu}\frac{\partial p}{\partial x}\right] \quad \text{(Eq. 3)}$$

and

$$\rho_w\frac{\partial w}{\partial \varphi}\frac{\partial \varphi}{\partial t} = \frac{\partial}{\partial x}\left[\rho_w D_w\frac{\partial w}{\partial \varphi}\frac{\partial \varphi}{\partial x}\right] + \frac{\partial}{\partial x}\left[\frac{\delta}{\mu}\frac{\partial p}{\partial x}\right], \quad \text{(Eq. (4))}$$

respectively, in which H (J·m^{-3}) is the enthalpy, λ ($W·m^{-1}·K^{-1}$) is the thermal conductivity, T (°C) the temperature, h_v (J·kg^{-1}) the evaporation enthalpy of water, p (Pa) the water vapor partial pressure, μ (dimensionless) the vapor diffusion resistance factor, ρ_w (kg·m^{-3}) the density of water, δ (kg·m^{-1}·s^{-1}·Pa^{-1}) the water vapor diffusion coefficient in air, D_w ($m^2·s^{-1}$) the liquid transport coefficient, and φ (dimensionless) the relative humidity RH.

The profiles of temperature (T) and relative humidity (RH) are set as the boundary conditions:

$$T_{indoor}(time) = 20\,^{\circ}\mathrm{C} \quad \text{(Eq. (5))}$$

$$RH_{indoor}(time) = \mathrm{ISO13788}\ \textit{with humidity class}\ 3\ (ISO13788,\ 2012). \quad \text{(Eq. (6))}$$

$$T_{outdoor}(time) = \textit{Climate profile}. \quad \text{(Eq. (7))}$$

$$RH_{outdoor}(time) = \textit{Climate profile}. \quad \text{(Eq. (8))}$$

In this study, the design of the assembly wall was based on the most common solid brick cavity wall type. Specifically, the masonry exterior walls (2 × 110 mm) within filling the tested bio-based composites (60 mm) and air layer (40 mm), as illustrated in Fig. A.4. To evaluate the durability of the bio-based composite specimens confronting different climates, eight distinct climate zones distributed in the world were selected as input for the hygrothermal modeling. Table. A.2 summarizes the annual weather conditions including temperature, humidity, wind speed, and rainfall precipitation for all eight locations. The hygrothermal simulation runs for ten years and the data of the final year is extracted for special analysis on hygric content on both interior and exterior surfaces of bio-based composites using WUFI Pro 6. Moreover, according to the hygrothermal results, the mould growth risk is assessed using WUFI Bio 4.0 plug-in component.

3. Results and discussion

3.1. Physic-chemical properties and bio-hygrothermal performances of bio-based composites

3.1.1. Physical properties

The physical properties of bio-based composites, which are affected by the type of natural fibers, chemical characteristics, and manufacturing processing, directly determine their insulation performance. To understand the physical property variance, basic important properties such as thermal conductivity, specific heat, bulk density, apparent density, and porosity of as-received and modified bio-based composites are tested (Table A.3). Although highly different, these basic physical properties can meet the requirements of traditional insulation materials with comparable thermal conductivity in the range of 0.03–0.06 W/m*K. Compared to the mycelium composites, the grass composites have lower thermal conductivity, and higher porosity regardless of the modification treatment. This indicates that grass composites possess better insulation performance. Similarly, after the AKD modification, the general insulation performance has improved in comparison with their as-received mycelium and grass, respectively. Regarding thermal conductivity property, the value of mycelium composites was reduced by 5.13% and the grass composites dropped to about 6%. However, the porosity of modified composites gets slightly decreased because the formation of AKD wax membrane can cover the voids of the fiber surface and pores between the interwoven fibers (Huang et al., 2018). Despite this, the AKD wax deposited on the fiber surfaces potentially increased thermal insulation performance by increasing the thickness of average fibers, which can be observed via optical microscope imaging (Fig. 1).

Therefore, the morphology of the composite is distinctively different before and after AKD modification. In the case of as-received mycelium composites, the loose and fogging-white mycelium ligaments were covered on the fiber surfaces. While the milky-white substances from dried AKD wax and mycelium ligaments are observed on the surfaces of the modified mycelium composites. In terms of the grass composites, the semi-transparent white wax was coated on the fiber surface after the modification. Noticeably, the surface color becomes yellow after the AKD modification. This is related to the AKD dispersion solution. One of the dispersions, cationic starch, gets yellow after the water molecules removal during the drying process (Frinhani and Oliveira, 2006), thus resulting in composite yellowing.

Furthermore, the fiber surface micromorphology of both composites becomes smoother after the AKD modification, which can be observed via SEM images (Fig. A.5). It is interesting to note that residual AKD wax was attached to grass fiber surfaces. These findings are in line with the optical microscope observation.

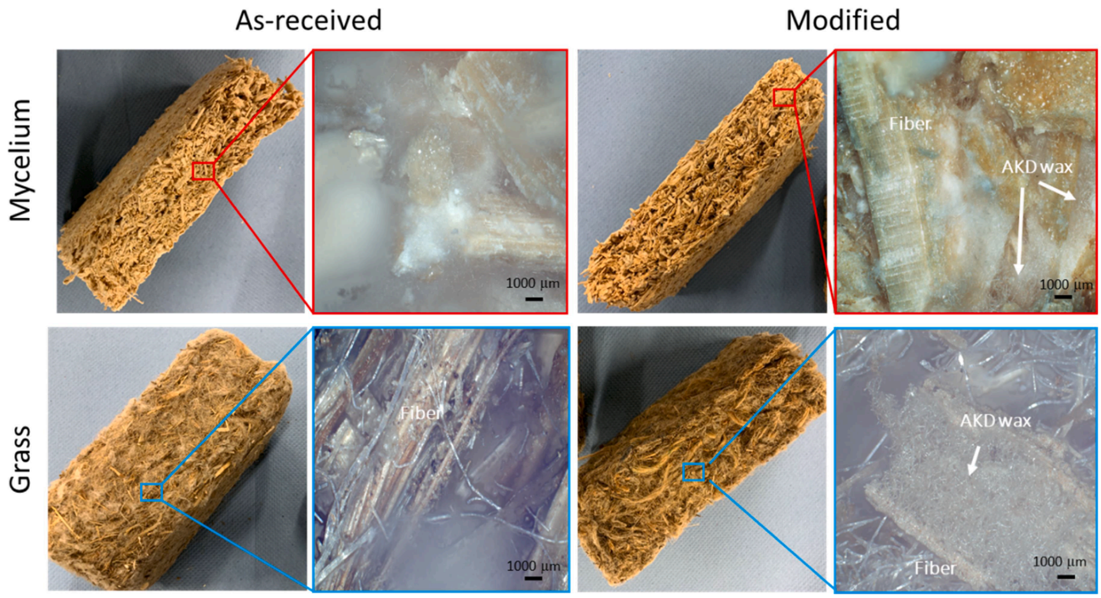

Fig. 1. Morphologies of mycelium composites and grass composites before and after the AKD modification.

All these morphology observations suggest that the AKD was covered on the surfaces of fibers within the bio-based composites. To better and deeply understand the chemical reaction mechanism in the modifying process, we analyzed the variation of chemical function groups and element ratio of the fiber surfaces in the following section.

3.1.2. Chemical analyses

The surface OH groups of cellulosic fiber are the dominant reason for the hydrophilicity of bio-based composites. To alter the hydrophilic nature, hydrophobic groups are often introduced on the fiber surfaces. Hence, in this study, the AKD with long-carbon chains (about 12–17 carbon) are grafted on the OH groups of the fibers, as illustrated in Fig. 2a. The linkage reactions between AKD and OH groups consist of two ways: hydrogen-bonded and covalently bonded (Adenekan and Hutton-Prager, 2019). The FTIR spectra curves of as-received and modified composites in this study are displayed in Fig. 2b and corresponding characteristic peaks are listed in Table A.4. All investigated composites have similar spectra curves because of similar studied bodies: cellulosic fibers. For example, the cellulosic characteristic peaks at 2925 cm^{-1}, 2850 cm^{-1}, and hemicellulose peak at 1728 cm^{-1} are found in all spectra curves. However, the intensity of some peaks is distinct. In the case of mycelium composites, The broad peat at about 3330 cm^{-1} represents the OH stretching: intermolecular hydrogen bonds and intramolecular hydrogen bonds (Liang and Marchessault, 1959). After AKD modification, the peak in mycelium composites became flatter, indicating that AKD molecules were primarily covalently bonded to the cellulose molecules. This resulted in a reduction in the number of hydrogen bonds generated by both the cellulose molecules themselves and their interaction with water molecules. In contrast, the peak in the grass composites became thinner and steeper, implying that the combination between AKD molecules and grass cellulose OH was mainly hydrogen bonded. Additionally, the intensities of the peaks at 2920 cm^{-1} and 2850 cm^{-1}, corresponding to C—H antisymmetric stretching and C—H symmetric strength, increased in both modified composites due to the introduction of long-chain alkyl groups. Furthermore, the presence of broken lactone ring peaks at 1703 cm^{-1} in both modified composites indicated that reactive AKD molecules were chemically grafted onto the cellulosic molecules. However, the peak at 1845 cm-1 suggests the presence of partially unreacted AKD on the fiber surfaces.

In addition, the C/O element ratio on the fiber surfaces is an important parameter for identifying surface group variation (Fig. 2c). Before AKD modification, the C/O ratio, at about 1, was approximately consistent with that of cellulose molecules: $(C_6H_{12}O_6)_n$. However, after the modification, the C/O ratio increased to approximately 2, attributed to the long-chain alkyl group from AKD, thereby confirming the presence of AKD on the modified bio-based composites.

Consequently, both FTIR and EDS findings suggest that AKD, with a hydrophobic role, has been successfully grafted onto the bio-based composites through hydrogen bonding and covalent bonding. Therefore, in the following section, the hydrophobic effect in both composites was investigated.

3.1.3. Hygroscopic properties

The hygroscopic property of bio-based composites plays a key role in the insulation materials. Here, we studied some important hygroscopic properties, i.e., water vapor resistance factor μ, water absorption capacity, and water contact angle results of the bio-based composites. The results are listed in Table 1. The μ factor value of the mycelium composite is twice that of the grass composite regardless of under dry or wet cup conditions. This distinct μ factor between them is attributed to different apparent densities and thicknesses (Sonderegger and Niemz, 2009). However, a neglect influence of the AKD modification under the same condition was found for the μ factor of the composites. In terms of water absorption capacity, AKD modification reduces the hydrophilic nature of the composites, which results in a close to half-time reduction in water absorption weight, and a more noticeable decrease was observed in the case of grass composites, up to 50.1%. The reduced hydrophilic behavior is also further confirmed by the water contact angle test through the sessile drop method (Fig. A.6) and such relatively substantial alteration is observed in grass composites.

In addition, both as-received composites exhibited a typical sigmoidal profile and significant hysteresis phenomenon between adsorption and desorption phases (Fig. A.7). These are the common features of hygroscopic bio-based composite materials (Alioua et al., 2019; Vololonirina et al., 2014). Specifically, as-received grass composites have a more distinct hysteresis phenomenon at around 75% RH than their counterpart mycelium composites. The smaller pores within the grass composites accelerate the moisture absorption kinetic and maintain the moisture content due to the capillary force role (Yunnus, 2010). This explanation is also confirmed by the morphology observation (see Fig. 1). However, after AKD modification, the non-typical sigmodal profiles, and low hysteresis features are shown in two

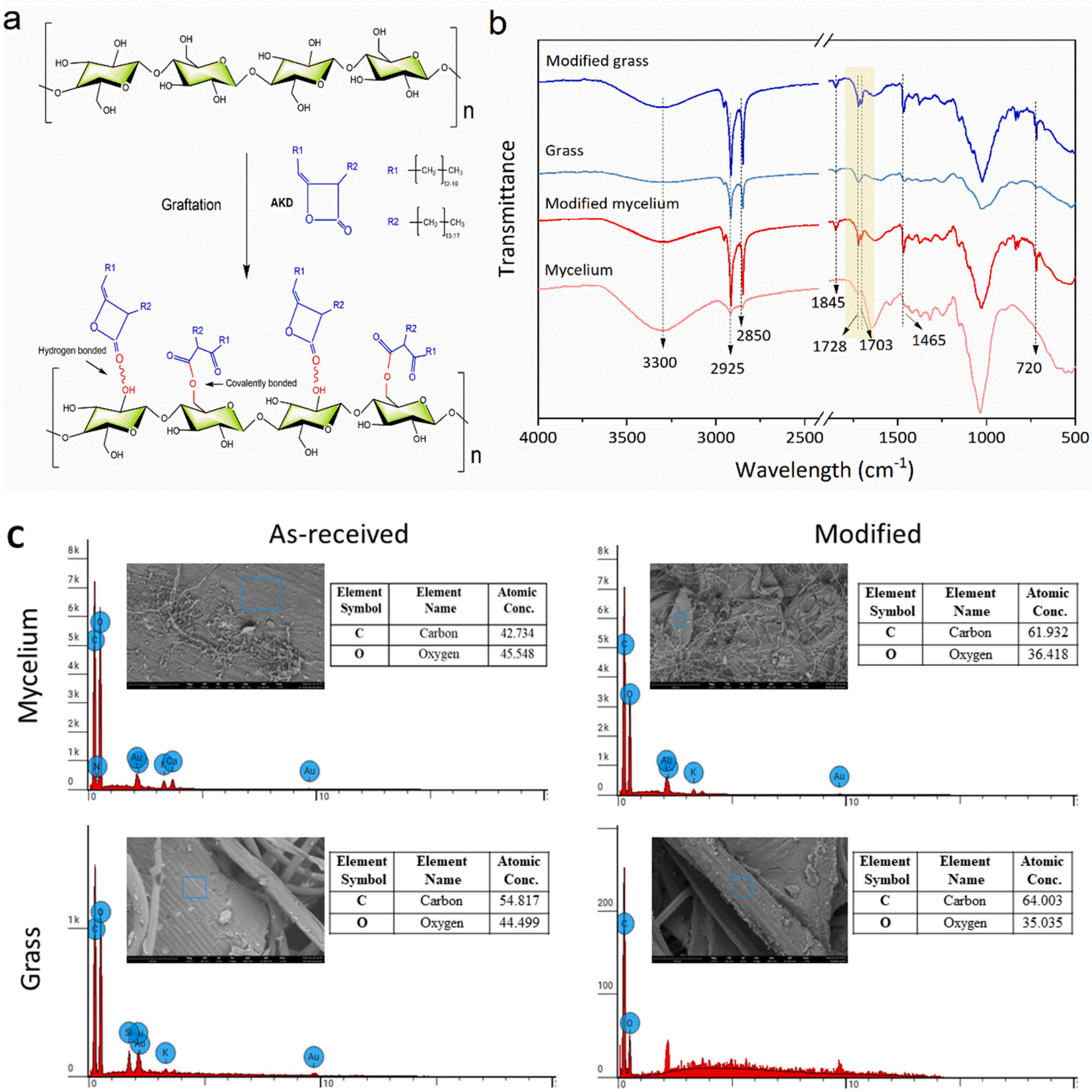

Fig. 2. Hydrophobic mechanism for bio-based composites humidity resistance: a, molecular grafting reaction of AKD on different composites cellulose. b, the FTIR spectra of as-received/modified bio-based composites. and c, the C/O element ratio variation before and after the modification.

Table 1
Hygroscopic properties of unmodified and modified bio-based composites.

		As-received mycelium	Modified mycelium	As-received grass	Modified grass
Water Vapour Resistance Factor μ	"Dry cup" condition	4.0	4.0	1.9	2.0
	"Wet cup" condition	3.1	3.3	1.4	1.5
Water absorption capacity (*WAC*, %)		451	269	776	387
WAC decrement (%)		40.4		50.1	
Water contact angle (°)		82±1	108±1	45±5	115±2

composites because of the hydrophilic alteration of the cellulosic fibers and pores filled with AKD wax.

In summary, AKD modification comprehensively reduces the hygroscopic properties of bio-based composites, especially grass composites. The reduced hygroscopic behavior will likely affect the thermal conductivity (Hurtado et al., 2016) and mould growth (Koh, C.H. et al., 2022; Viitanen et al., 2010), so next, we investigate the correlation between thermal conductivity and hygroscopic moisture (Section 3.1.4), as well as the association between the mould growth risk and hygroscopic moisture (Section 3.1.5), respectively.

3.1.4. *Thermal properties*

Thermal conductivity λ, is the most direct reflection of thermal insulation materials. A study of changes in the thermal conductivity for two composites before and after the modification at various RH conditions (related to moisture content) is summarized (Fig. 3). These results

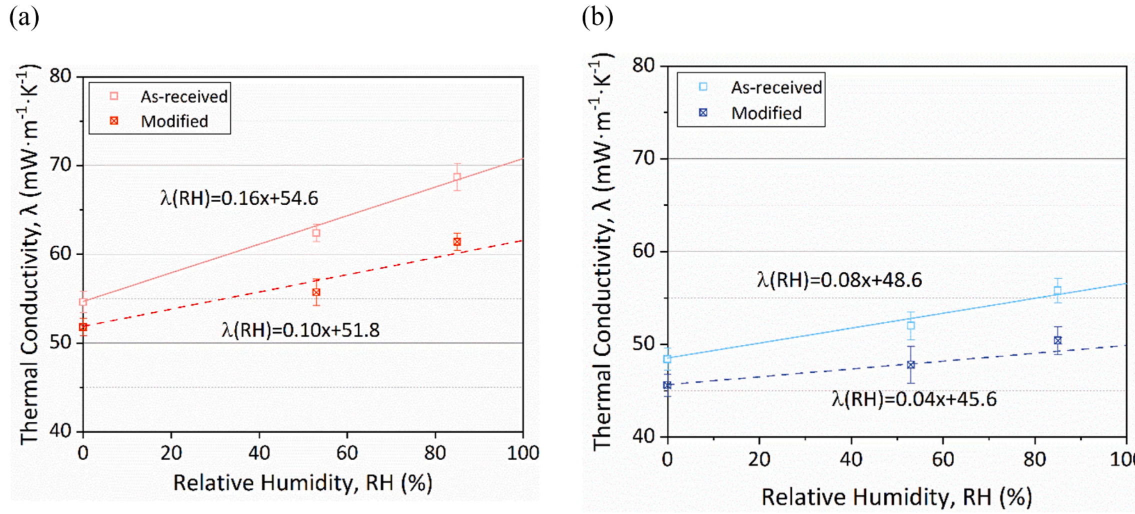

Fig. 3. Thermal conductivity λ VS relative humidity RH for mycelium composites (a): as-received and modified, and grass composites (b): as-received and modified.

illustrate that the thermal conductivity increased with relative humidity, with a generally linear trend, which is in accordance with data in the literature (Koh et al., 2022; Vololonirina et al., 2014). Meanwhile, the linear results are as input for following hygrothermal modeling using WUFI software. In addition, the thermal conductivity λ at various RH was tested with the thermal needle probe under steady-state conditions. The composites after AKD modification show an overall lower thermal conductivity under different RH compared with their corresponding as-received ones. This indicates that AKD introduction can improve the thermal insulation capacity of bio-based composites by reducing hygroscopic moisture. Among all studied composites, modified grass composites have the lowest value of thermal conductivity (47.9 $mW{\cdot}m^{-1}{\cdot}K^{-1}$), followed by as-received grass composites (52.1 $mW{\cdot}m^{-1}{\cdot}K^{-1}$) and slightly higher value (56.3 $mW{\cdot}m^{-1}{\cdot}K^{-1}$) of modified mycelium composites, while as-received mycelium composites have the highest thermal conductivity, at the mean value of 61.9 $mW{\cdot}m^{-1}{\cdot}K^{-1}$. According to these comparative results, grass composites with lower thermal conductivity are recommended, in particular with AKD-modified. Furthermore, these values of conductivity are lower than those of reported other organic insulation materials such as about 105 $mW{\cdot}m^{-1}{\cdot}K^{-1}$ for wood chip board and 70 $mW{\cdot}m^{-1}{\cdot}K^{-1}$ for wood wool board (Domínguez-Muñoz et al., 2010).

3.1.5. Mould growth risk

Another moisture-dependent mould growth risk is a key criterion to evaluate the durability of bio-based composites. In this study, the tested bio-based composite samples are subjected to high humidity conditions to inspect the mould growth for two months (60 days). Besides the visual inspection, the mould indexes also called the *VTT* model based on laboratory studies (Viitanen et al., 2015), were employed here to quantify the intensity of the mould growth. The photos and their partially magnified microscope images at 0, 30, and 60 days are illustrated in Fig. 4, and corresponding quantitative results are listed in Table A.5.

By the end of the initial 30 days, with the naked eye, a small but significant portion of mould growth on the surface of as-received mycelium composites, while no obvious mould growth is exhibited on the surfaces of the other three composites including as-received grass composites. According to this, three investigated composites such as modified mycelium composites and both as-received and modified grass composites have good mould-resistance capacity and are suitable to use as insulation components. However, by the end of the 60 days, the as-received mycelium composites have been fully covered by the mould hyphae and intensive spores, but only minor mould hyphae have begun to grow on the surface of modified mycelium composites. In terms of grass composites, a certain area portation of mould with spores visually has been grown on the surface of as-received grass composites, while no mould growth is visibly found on the surface of modified grass composites. These comparative results indicate that AKD hydrophobic modification makes the bio-based composites very resistant to mould growth. This aligns with the literature where the hydrophobic treatment using Octadecyltrichlorosilane (OTS) is resistant to microorganisms attack and against mould growth on the wood fibrous thermal insulator (Kumar et al., 2016). Additionally, compared to mycelium composites, grass composites exhibited better mould-resistance capacity, which also has been found in the previous study (Koh et al., 2022). This is because higher ratios of lignin and wax against sugar content (cellulose-hemicellulose cellulose and hemicellulose) of grass fibers protect their sugar content from attacking by microorganisms and thus delay their degradation into simple sugars that could provide some nutrition for mould growth (Kamarullah et al., 2015; Koh et al., 2023; Komuraiah et al., 2014).

Consequently, following AKD modification, both composites, particularly the grass composites, have improved mould-resistant capabilities. In addition, considering future practical applications, it is necessary to evaluate the durability of bio-based composites used as insulation materials under distinct climates in the next section.

3.2. Durability assessment of using bio-based composites simulated as the insulation layer

3.2.1. Hygric performance of the bio-based composite layer

The hygric content of bio-based composites has a positive correlation with mould growth risk that can negatively determine their durability (Ali et al., 2016; Ryu et al., 2015; Xue et al., 2022). Thus, the moisture contents of two interfaces to both exterior and interior sides of tested bio-based composites are computed considering these interfaces are readily points for moisture accumulation. The simulation period is preset ten years and the hygric results of the final year are extracted and plotted in Fig. A.8. Moreover, to assess the different climate suitability of tested bio-based composites that expand their future application spread, eight distinct climate types i.e., Cfb, Aw, Dwb, Bsh, Csa, Bwh, Cfa, and Dfc distributed in the world are selected (see Table A.2).

Across all climate types, both modified bio-based composites exhibit relatively lower average moisture content regardless of which interface compared to their original ones. In other words, AKD modification can effectively prevent the moisture content from retaining inside the bio-based composites, consequently potentially delaying the mould growth risk and improving durability. Interestingly, the grass

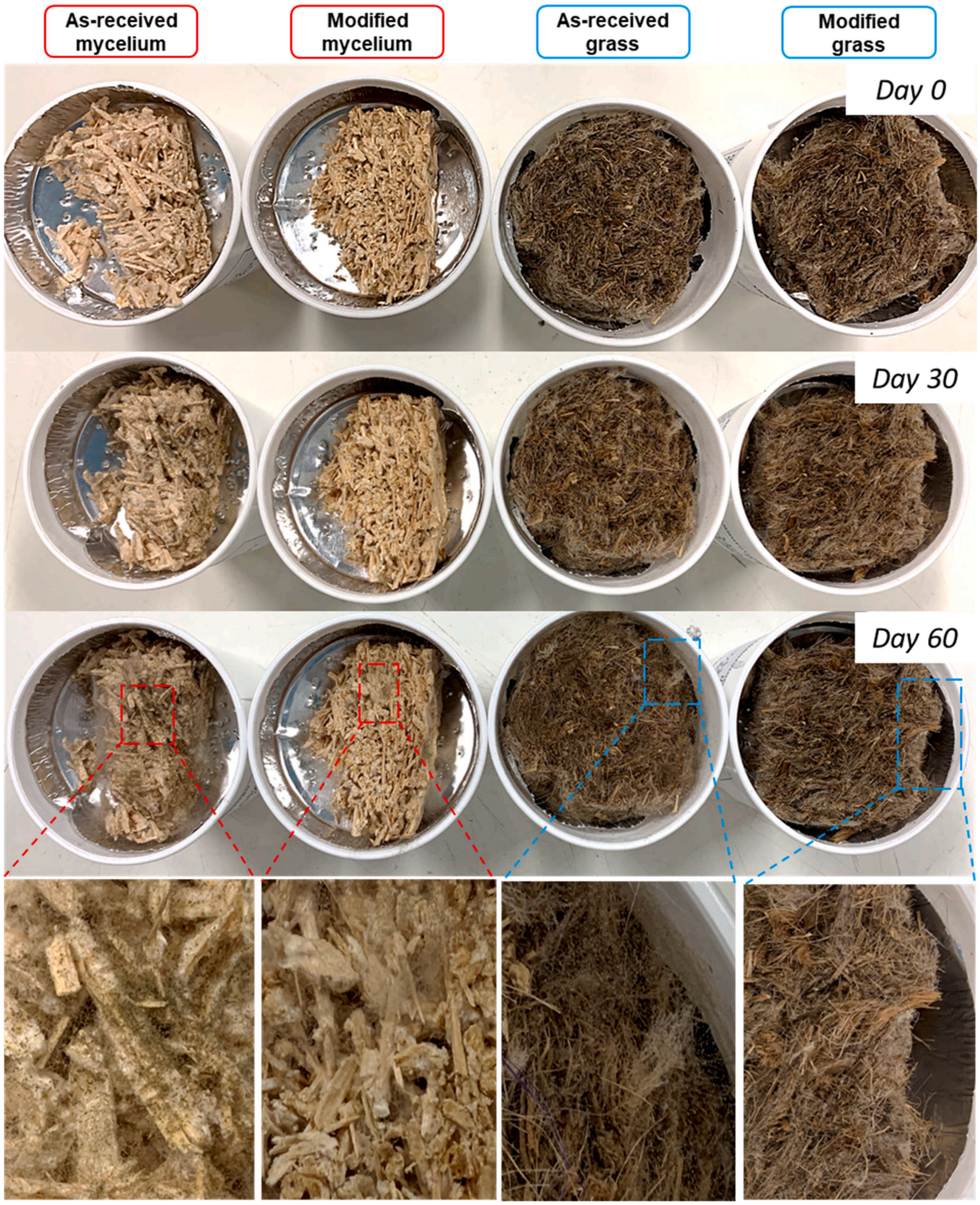

Fig. 4. Mould resistance tests on the mycelium and grass composites (as received and modified). Photos and magnificent optical microphotos are taken on day 60.

composites exhibit higher average moisture content than the mycelium composites under most climate types except for Aw (Hainan). This result is in agreement with their water absorption capacity likely due to smaller size pores and higher porosity of grass composites and the opposite for mycelium composites (Table A.3 & Table 1). Only considering this point of simulated moisture content, therefore, it seems that modified mycelium composites slightly lower the risk potential of mould growth than modified grass composites. However, in fact, besides the moisture content factor, other factors i.e., sorption-desorption rate, fiber types (the ratio of lignin and wax to cellulose and hemicellulose), and binder type influence the mould growth. So next, we use WUFI-Bio to more directly and more accurately predict the mould growth risk.

3.2.2. *Mould growth risk evaluation*

Fig. 5 summarizes mould growth risk simulated results of the bio-based composites within the assembly walls under selected distinct climates using WUFI-Bio. Within this simulation, the mould growth rate above 239 mm/year represents an unacceptable risk level, while below 176 mm/year represents no risk, and the value between them represents a possible risk and requires a specific evaluation.

Based on the internal comparison of between as-received and modified mycelium composites in Fig. 5a and between as-received and modified in Fig. 5c, these results support the hypothesis that the reduced hygric property in bio-based composites, which resulted from AKD hydrophobic modification, contribute to their higher resistance to mould growth compared to their as-received ones. According to Fig. 5a and b. out of the eight cases that represent typical climates, modified mycelium

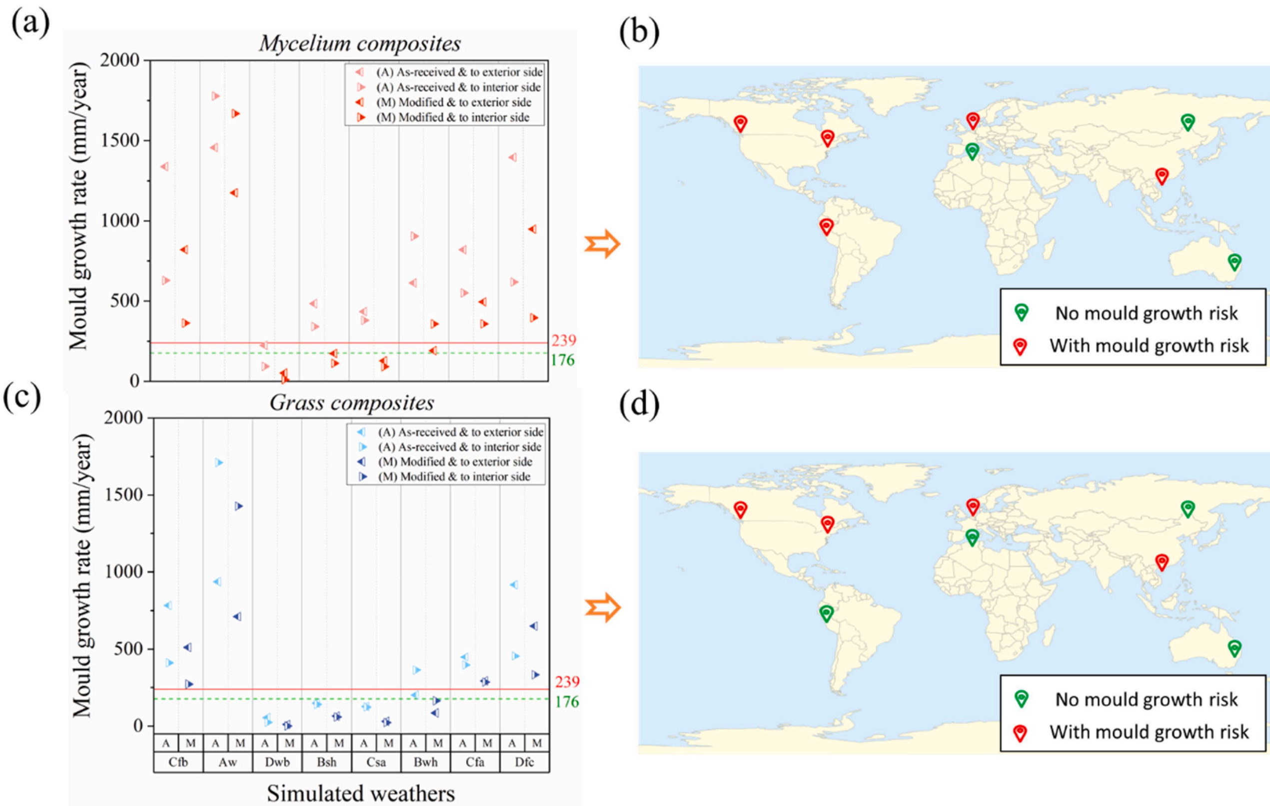

Fig. 5. Simulated results of bio-based composites as the insulated layer (a) mould growth rate of two interfaces of mycelium composites (as-received & modified) to both exterior and interior sides under distinct climate types, (b) their mould growth risk evaluation in corresponding locations, (c) mould growth rate of two interfaces of grass composites (as-received & modified) to both exterior and interior sides under distinct climate types and (d) their mould growth risk evaluation in corresponding locations.

composites can be applied to three climate types: Dwb (Heilongjiang), Bsh (New South Wales), and Csa (Alger), in which their values are almost all below the green line (176 mm/year) with no mould growth risk. Whereas only the Dwb (Heilongjiang) case is possibly suited for original mycelium composites because the mould growth risk of the interface to the exterior is between the thresholds. Similar behavior is found in the grass composites (Fig. 5c and d). For modified grass composites, up to four climate cases have no mould growth risk. Besides the three climate cases above, the additional Bwh (Lima) case can be suited for modified grass composites. However, this Bwh (Lima) case could not be suited for original grass composites as the mould growth rate of their interface to the interior side is exceedingly over the mould growth threshold. To sum up, these findings indicate that AKD hydrophobic modification can not only effectively decrease the mould growth risk, enhancing the durability of bio-based composites, but also broaden the climate suitability range and application range of the bio-based composites when used as insulation materials in multi-assembly walls.

4. Conclusion and recommendations

In this present work, two distinct mycelium and grass bio-based composites were modified by AKD to improve the hydrophobicity of the cellulosic composites, and their effects on the hygrothermal performance and mould growth behaviour were studied. Additionally, the study evaluates the durability of the bio-based composites layer within assembly walls under different climate types by analyzing hygric property and mould growth risk using a bio-hygrothermal simulation approach. Based on the results, we want to highlight the main findings:

- The long-chain alkyl groups of AKD were successfully grafted on the fiber surfaces via hydrogen-bonded and covalent-bonded between the lactone ring of AKD and cellulosic OH groups, thereby achieving a hydrophobic effect.
- The AKD modification can lower the water absorption capacity of bio-based composites, reaching a decrement of 50.1% when used on grass composites.
- The thermal conductivity of bio-based composites after AKD modification can be significantly reduced, especially under high relative humidity.
- In terms of mould growth risk, it is better to use AKD-modified composites than as-received ones due to lower hygric properties.
- When adopting bio-based composites to apply within simulated assembly walls, the AKD modification can increase their suitability to distinct climate types, e.g., Dwb, Bsh, and Csa.

To conclude, both modified bio-based composites, in particular modified grass composites, demonstrate significant potential as thermal insulation materials, characterized by lower hygric performance, lower thermal conductivities, higher mould-resistance ability, and better suitability to climate types compared to as-received composites.

Several future research points can be drawn from this study. First, the feasibility of AKD-modified bio-based composites used within real assembly walls and under real weather conditions needs to be investigated. Secondly, the cost of modifying bio-based composites and its impact on the environment could be necessary to consider. Thirdly, fiber type and components can impact the hygrothermal properties and mould growth risk of their composite materials, which is one interesting research direction. The exploration of these research points could effectively accelerate the practical application of bio-based composites in the building field.

CRediT authorship contribution statement

Helong Song: Writing – original draft, Methodology, Data curation. **Koh Chuen Hon:** Writing – review & editing, Methodology, Data curation. **Florent Gauvin:** Writing – review & editing, Supervision. **Samuel Pantaleo:** Methodology. **Felix Berger:** Methodology. **Wei Chen:** Writing – review & editing. **H.J.H. Brouwers:** Writing – review & editing, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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