MOISTURE SORPTION IN ARTIFICIALLY AGED WOOD-PLASTIC COMPOSITES

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Moisture sorption in wood-plastic composites (WPCs) affects their durability and dimensional stability. In certain outdoor exposures, the moisture properties of WPCs are altered due to e.g. cracks induced by swelling and shrinkage of the components, as well as UV degradation or biological attack. The aim of this work was to study the effect of different artificial ageing routes on the moisture sorption properties of WPCs. Extruded WPCs were prepared with either unmodified or acetylated wood and recycled high-density polyethylene (HDPE). The WPC samples were artificially aged involving water soaking, artificial weathering, and white- or brown-rot decay in different combinations. After the ageing, the samples were conditioned in either 65% or 90% relative humidity (RH) until equilibrium moisture content was reached. A dynamic moisture sorption analyzer was used to monitor the sorption rate of samples subjected to a climate change from 65% to 90% RH. Scanning electron microscopy was used to study the surface morphology of the aged composites. Results showed that the artificial weathering caused cracking of the HDPE matrix at the composite surface, as well as a wood-matrix debonding, resulting in an increased moisture sorption rate. The WPC samples subjected to white-rot decay showed the highest moisture sorption rate.

Keywords: *Wood-plastic composites; Acetylation; Artificial ageing; Moisture sorption; Diffusion; High-density polyethylene; Scanning electron microscopy*

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INTRODUCTION

Wood-plastic composites (WPCs) are used in a large variety of applications, most of which are for outdoor applications, e.g. decking, railing, and fencing (Smith and Wolcott 2006). When WPCs are used outdoors, they will be subjected to a climate with moisture- and temperature- fluctuations, as well as decay fungi and ultra violet (UV) radiation. WPCs are a combination of wood, in the form of fibers or particles, and a thermoplastic matrix. The thermoplastic matrices used are normally polyethylene (PE), polyvinyl chloride (PVC), or polypropylene (PP). The wood component is a hydrophilic phase, while the thermoplastic constitutes a hydrophobic phase. Because of this, moisture sorption of these composites will occur mainly in the wood component. The surface of the WPCs is usually smooth, and a thin surface layer consists, in general, of a high proportion of the polymer matrix. In an initial state of moisture exposure, this polymer-rich surface phase will retard the rate of moisture sorption, and the WPCs

therefore appear to be very moisture resistant. However, when the composite is subjected to UV radiation and/or water, this surface layer may be degraded, resulting in a decreased moisture resistance and a critical intrusion of water into the bulk of the material. When this degraded WPC is further exposed to decay fungi, the chemical composition is altered, also resulting in a changed moisture behavior of the composite.

Very low moisture content (MC) is required when processing wood and thermoplastics into WPCs, i.e. the wood component is normally dried to very low MC prior to extrusion, and any remaining moisture is ventilated out during processing. Hence, the resulting WPC contains a wood component that has a significantly lower MC than the equilibrium MC in most environments where the material is supposed to be used. Earlier studies on WPCs and moisture transport have shown that the initial MC of WPCs is very low and the rate of moisture uptake is slow (Jacoby et al. 2001; Johnson et al. 1999; Rowell et al. 2000; Shi et al. 2000). More recent studies have shown that the moisture distribution in WPCs is not uniformly distributed through the cross section, and there may be very high moisture levels close to the surface (Wang and Morrell 2004; Gnatowski 2009). These high moisture levels will provide an environment that is conducive for attack by fungi and microorganisms. In addition, and especially in the surface layer of WPCs, cyclic climate conditions may also cause dimensional changes of the inherently different wood and thermoplastic components. The effects of such dimensional changes may even be more pronounced in WPCs than in the isolated components, due to the fact that a moisture-induced swelling and shrinkage of the wood component may act in opposition to temperature-induced movements of the thermoplastic matrix, thus causing wood-matrix delamination.

There are three groups of wood-decaying fungi that normally attack wood: brown-, white-, and soft-rot. Brown-rot fungi degrade mainly hemicelluloses and cellulose, white- rot fungi degrade mainly lignin, but also hemicelluloses and cellulose, and soft-rot fungi degrade all cell wall polymers. A study of red maple wood (Anagnost and Smith 1997) showed a decrease in hygroscopicity in brown-rot decayed wood, while the hygroscopicity of white-rot decayed wood went unaltered. Papadopoulos (20 1 1) studied the sorption behavior of acetylated pine subjected to decay. Brown-rot-decayed acetylated wood showed a decrease in hygroscopicity. White-rot-decayed acetylated pine showed a decrease in hygroscopicity for relative humidity (RH) lower than 70 to 80%, whereas higher RH resulted in an increased hygroscopicity.

If the surface layer of WPCs is degraded by accelerated ageing in a weather-ometer, the rate of moisture uptake is increased, but it is still much slower compared to that of solid wood (Segerholm et al. 2007). In WPCs most of the cell lumens of the wood component are filled with polymer or compressed or collapsed, resulting in a low overall porosity, e.g. 2-5% (Cheng et al. 2009) compared with values of 60 to 70% for many types of softwood. Therefore, most of the moisture transport in the composite will be in the form of bound water diffusion. It is expected that exposure of WPCs to weathering by UV radiation and to decay fungi will decrease their moisture resistance (Ibach et al. 2004). Decay from brown- and white- rot fungi would most likely penetrate deeper into the material, thus altering the diffusion properties of the bulk material compared with that of the alternation caused by weathering. If the wood component is chemically modified to reduce its hygroscopicity, the rate and extent of moisture sorption of the composite, as

well as degree of attack by decay fungi, should be greatly decreased (Ibach and Clemons 2002). Acetylation is one such modification known to greatly decrease the rate and degree of moisture sorption in wood (Rowel1 2006).

The objective of this work was to study the effect of different artificial ageing routes on the water vapor sorption properties of extruded WPCs. The artificial ageing procedures of interest were: soaking in water, UV weathering, white-rot decay, and brown-rot decay. The WPCs were prepared with two different wood components: unmodified and acetylated western pine. The overall aim of the study is to achieve a better understanding of the durability properties of WPCs in outdoor applications. In order to focus on the surface properties of the composites, the study was performed on thin specimens prepared from the surface region of the material.

EXPERIMENTAL

WPC Preparation

Ground wood components were supplied by American Wood Fiber (Schofield, WI) and had a nominal size of 40 mesh. The wood species was a western pine mixture, i.e. a commercial blend of different pines. The thermoplastic matrix was a high-density polyethylene (HDPE) from recycled milk bottles (Muehlstein and Co., Inc., Roswell, GA). Half of the wood component was oven-dried and then acetylated by boiling it in acetic anhydride for 4 hours. Average acetyl content was determined by HPLC to be 22% for the acetylated wood, and 2.3% for the unmodified wood, according to the method described by Ibach et al. (2000).

A 32-mm, twin-screw extruder (D-TEX extruder, Davis Standard, Pawcatuck, CT) and related gravimetric feed system (Accurate, Whitewater, WI) were used to compound and produce WPC profiles of rectangular cross sections (3 mm x 13 mm). Melt temperature was between 170 and 180°C and the die pressure was about 5 MPa, the screw speed was 30 rpm. Before the extrusion process, both the unmodified and the acetylated wood components were dried to a MC value below 1%. Nine percent TR-251 lubricant (Struktol Company of America, Stow, Ohio) was added to the formulation to prevent tearing of the material when exiting the die. Samples of 100 mm in length were cut from the extruded profiles.

Artificial Ageing

The following four procedures were used to artificially age the sample profiles:

1. Room temperature (22°C) water soaking for 2 weeks (S)
2. Artificial weathering for 1000 hours, followed by room temperature (22°C) water soaking for 2 weeks (WS)
3. Artificial weathering for 1000 hours and room temperature (22°C) water soaking for 2 weeks, followed by a modified soil block test procedure based on ASTM D1413 with *Trametes versicolor,* a white-rot fungus (WS wr)
4. Artificial weathering for 1000 hours and room temperature (22°C) water soaking for 2 weeks, followed by a modified soil block test procedure based on ASTM D1413 with Gloeophyllum trabeum, a brown-rot fungus (WS br)

The artificial weathering of the specimens included cycles with 102 minutes of UV light exposure and 18 minutes of simultaneous water spray and UV light in an Atlas 6500 XEII Weather-Ometer. This instrument uses a xenon lamp combined with an advanced filter system specially designed to simulate solar radiation for accelerated weathering tests. A borosilicate inner and outer filter was used in this case, which results in an irradiance of 52 W/m^2 on the specimens. The modified soil block test was done according to the procedures presented by Clemons and Ibach (2004) and Ibach and Clemons (2007). These procedures are based on the ASTM D 1413 test method, where sterile soil is inoculated with a fungal strain, and thereafter, solid wood veneers are put on the soil as feeder strips. The samples are then placed on the feeder strips after two weeks, and the bottles are put in a controlled climate in 27°C and 70% RH for twelve weeks, after which the specimens are cleaned, dried, and weighed for mass loss. The method deviates from the ASTM standard D 1413 in three ways: the standard is written for solid wood, the sample size is different from the normal sample size, and the bottles are used horizontally to allow a longer specimen for mechanical testing. The type of artificial ageing of the WPC samples and their abbreviations are listed in Table 1. Any fungal mycelium was wiped off the samples, which had been artificially aged in the soil block test (3 and 4). After all artificial ageing procedures, the samples were dried at 105°C.

Table 1. WPC Samples and Type of Artificial Ageing

Notation for material and artificial ageing	HDPE (wt-%)	Wood component	Wood content (wt-%)	Lubricant (wt-%)	Artificial ageing	Average mass loss due to artificial ageing*
U1	41	Unmodified	50	9	S	0.7
U2	41	Unmodified	50	9	WS	4.7
U3	41	Unmodified	50	9	WS wr	10.9
U4	41	Unmodified	50	9	WS br	14.0
A1	41	Acetylated	50	9	S	-0.1
A2	41	Acetylated	50	9	WS	2.5
A3	41	Acetylated	50	9	WS wr	3.2
A4	41	Acetylated	50	9	WS br	4.2

*Data from Ibach and Clemons (2007)

The moisture, UV, and biological resistance of the artificially aged WPCs, according to the procedures described above, have been reported in Ibach and Clemons (2007).

Characterizations

Equilibrium moisture content determination at 65% and 90% relative humidity

WPC specimens with a thickness of 1 mm were cut lengthwise from the outer artificially aged surface of the 3 mm thick WPC samples. A knife was then used to section out specimens measuring 1x13 mm^2 in cross section and 6.5 mm in length (i.e. parallel to the extrusion direction). Twenty specimens were prepared from each of the eight samples, as presented in Table 1. The specimens were separated into two groups and either placed in climate chamber with 65% RH and 27°C, or in a climate chamber

with 90% RH and 27°C. Their weight gain was monitored until equilibrium **MC** was reached.

Dynamic water vapor sorption analysis

For the dynamic sorption measurements, equilibrated specimens were taken from the 65% RH room and sealed with aluminum tape on all surfaces except the original outer surface of the material. The specimens were then mounted in the measuring chamber of a dynamic moisture sorption analyzer (IGAsorp, Hiden Isochema, Warrington, UK). In this equipment, the climate is controlled by two airstreams, of which one airstream is dry and the other is saturated. The two airstreams are then mixed to achieve the desired RH, in this study initially set at 65% and then raised to 90% RH. The velocity of the airstream passing the specimen was about 2 mm/min, and the temperature in the chamber was set to 27°C. The weight of the specimen was continuously recorded by a microbalance with a resolution of 0.1 µg. After the test, the specimens were dried at 105°C to determine the dry weight of the materials.

Surface evaluation

The specimen surfaces were evaluated in a scanning electron microscope (SEM, Hitachi Tabletop Microscope TM-1000) to distinguish morphological differences of the surfaces as a result of the different types of artificial ageing procedures.

RESULTS AND DISCUSSION

Equilibrium Moisture Contents at 65% and 90% RH

Figure 1 shows the equilibrium MC of the WPC samples after two months of exposure in the 65% and 90% RH climates. As can be seen, in both climates, distinctly higher equilibrium MC was observed for the composites with the unmodified wood component, compared with those with the acetylated wood component. A number of additional trends could also be observed for the composites, depending on the type of wood component and type of artificial ageing procedure. For the WPCs with unmodified wood, lower equilibrium MC was observed in both climates for the samples, which had been artificially aged including the biological decay by brown- or white-rot fungus. This is probably due to the relatively high wood mass loss in these samples caused by the fungal decay (Table 1). On the contrary, for the WPCs with acetylated wood, higher equilibrium MC was observed for the samples that had been artificially aged including the biological decay by brown- or white- rot fungus. It should be remembered that in this case, the composites have been subjected to artificial weathering and water soaking, followed by an exposure to white- and brown- rot fungi, and only slight mass losses due to decay were recorded. In the climate with 90% RH, the equilibrium MC of the composites with acetylated wood was essentially the same for the samples aged by UV alone, and the samples also including white-rot and brown-rot fungus exposure (ageing procedures A2-4). It is known that UV radiation removes acetyl groups in the surface region of acetylated wood (Rowell 2006), and hence the artificial weathering may have reduced the effect of acetylation in the surface of these samples. The weathering

procedure will also degrade the thermoplastic matrix at the surface of the WPC that is changing its surface morphology, which may create new possible water sorption sites.

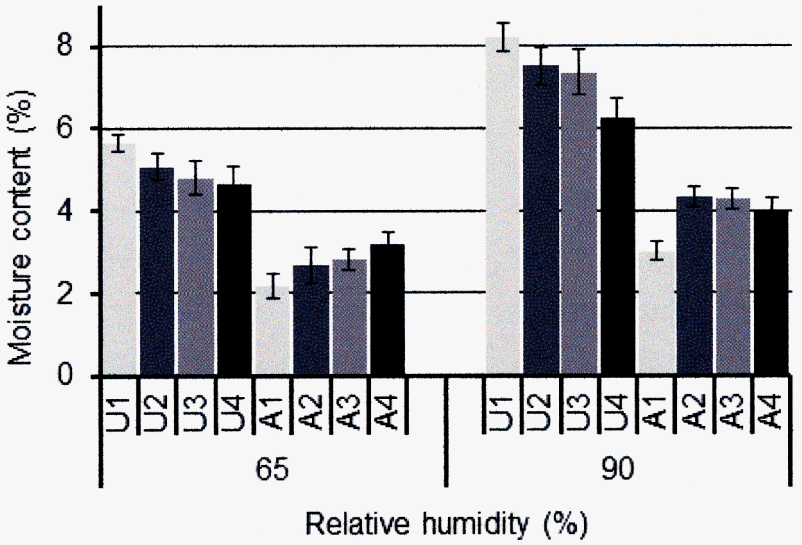

Fig. 1. Equilibrium moisture content of the WPC samples in either 65% or 90% relative humidity

Dynamic Water Vapor Sorption Properties

Figures 2a and 2b show the results from measurements using the dynamic moisture sorption analyzer. The results are presented as weight gain versus the square root of time for the different WPC specimens, which first have been equilibrated at 65% RH and then exposed to climate of 90% RH. An external resistance, due to moisture convection and the boundary layer at the composite surface could cause the apparent initial time lag of the graphs in Fig. 2. The rate of moisture sorption, as well as the extent of moisture gain, also varied greatly in the composites depending on both the type of artificial ageing and the type of wood component. The WPCs artificially aged by weathering and water soaking followed by white-rot fungus exposure, showed the most rapid weight gain, which was valid for composites with both the unmodified and the acetylated wood component. This result is in agreement with the observations made by Papadopoulos (2011). As expected, the extent and rate of the moisture gain were, however, significantly greater in the composites with unmodified wood, The WPC samples that had been artificially aged by weathering and water soaking and the samples aged by weathering and water soaking followed by brown-rot fungus exposure both showed approximately the same extent and rate of moisture gain, and again, the rate and extent was greater in the samples with unmodified wood. Both samples aged solely by water soaking showed the lowest moisture sorption rate. This was evidently due to the clearly undamaged polymer rich surface of both these samples, as presented in the next section. The samples with acetylated wood aged solely by water soaking showed the over-all lowest moisture sorption rate.

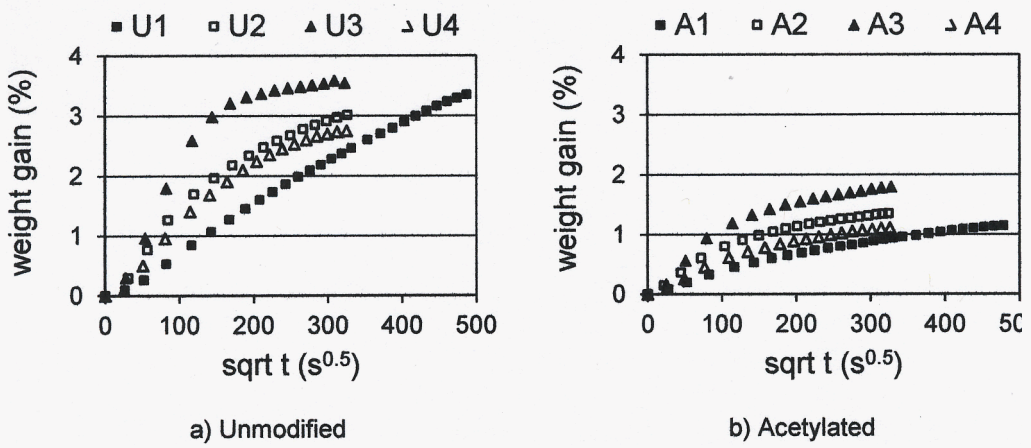

Fig. 2. Weight gain versus square root of time when relative humidity is raised from 65% to 90% for WPC specimens with unmodified (a) and acetylated (b) wood component. The legend correspond to the artificial ageing procedures as water soaking (U1, A1), weathering (U2, A2), white-rot (U3, A3), and brown-rot (U4, A4)

Surface Evaluation in Scanning Electron Microscope

Figure 3a shows a SEM micrograph of the surface of a WPC specimen with an unmodified wood component and aged solely by water soaking. As shown, this specimen had a smooth polymer surface with some areas where wood component are present at the surface. Figure 3b shows a micrograph of a WPC specimen with an unmodified wood component aged by both weathering and water soaking. Clearly, in this case, major cracks can be observed in the polymer matrix as well as wood-matrix delamination. A similar behavior as shown in Fig. 3 could also be observed in the corresponding samples with an acetylated wood component.

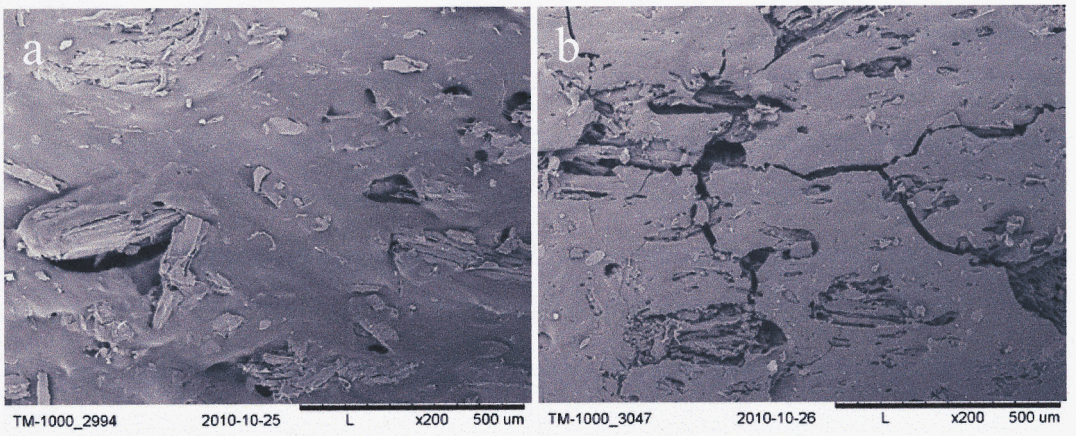

Fig. 3. Scanning electron microscope micrographs of the surface of WPC specimens with an unmodified wood component, artificially aged by a) water soaking (U1) and b) weathering followed by water soaking (U2)

Figure 4 shows SEM micrographs of WPC specimens aged by weathering and water soaking, followed by white-rot fungus exposure. As can be seen, fungal hyphae

were clearly visible on the surface and in the cavities for composites with both unmodified (Fig. 4a, c) and acetylated wood (Fig. 4b, d). However, this was more pronounced for the composites with the unmodified wood. The degradation of the wood component at the surface was evidently more severe for the samples with unmodified wood, in good agreement with the mass loss data presented in Table 1.

Figure 5 shows SEM micrographs of WPC specimens subjected to weathering and water soaking, followed by brown-rot fungus exposure. In this case, the wood component at the surface had been heavily degraded, leaving only imprints of the wood structure on the polymer matrix. Fibrous structures are also present at the surface, built up by polymer matrix. The fibrous structure was created during processing of the material through lumen filling of the wood cells, and those wood cells had been degraded, leaving only the polymer matrix in a fibrous structure.

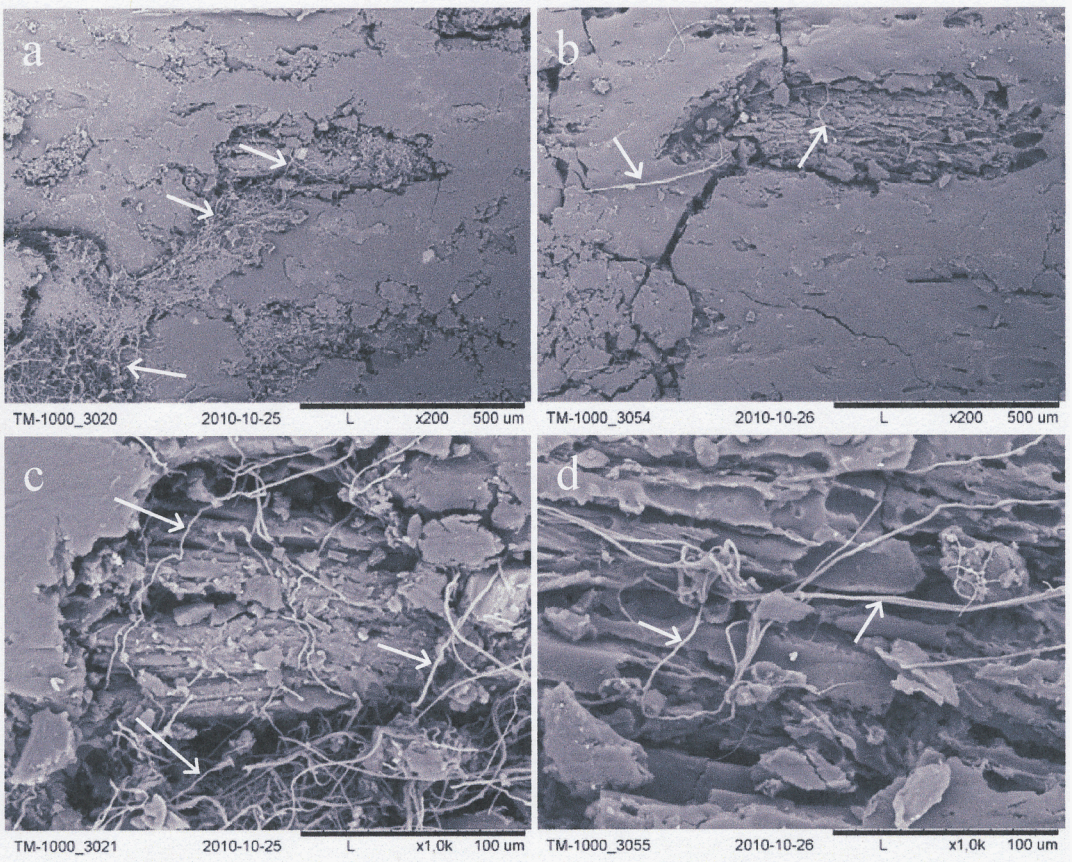

Figure 4. Scanning electron microscope micrographs at two different magnifications of the surface of WPC specimens with an unmodified (a, c) and acetylated (b, d) wood component, artificially aged by weathering, water soaking, and followed by a whit&-rot fungus exposure (U3, A3). White arrows indicate fungal hyphae.

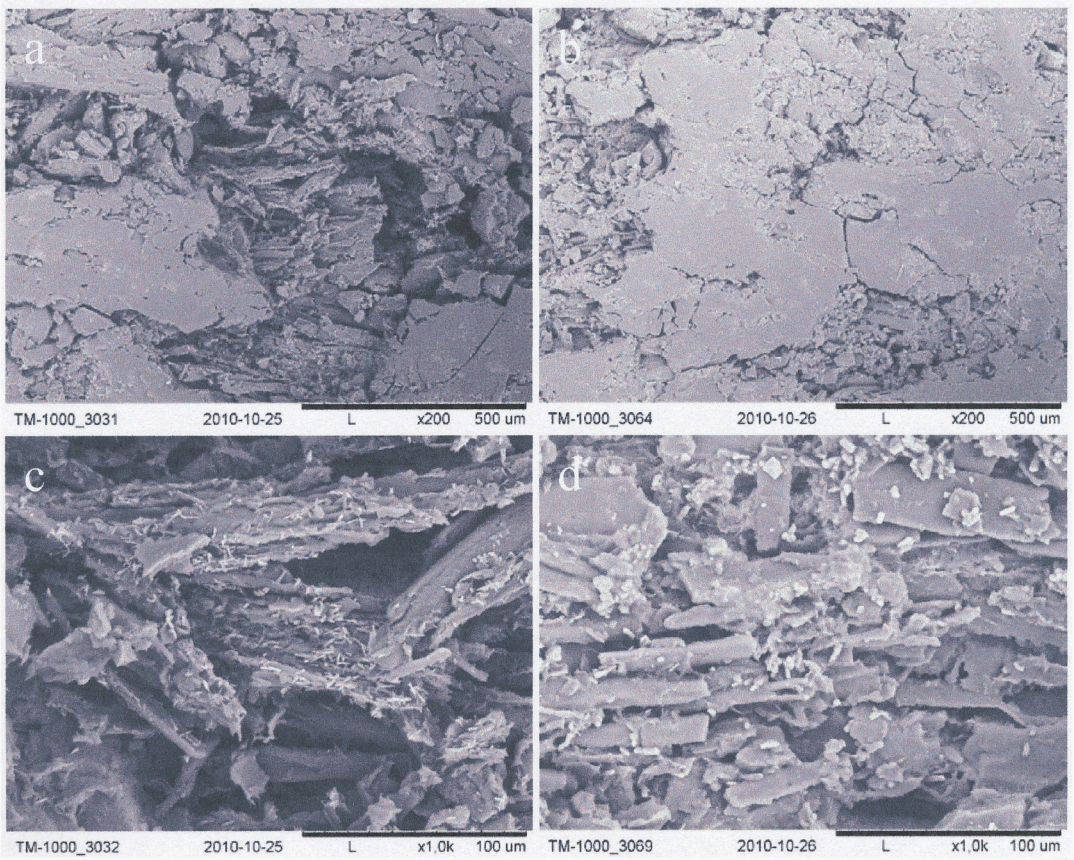

Fig. 5. Scanning electron microscope micrographs at twa different magnifications of the surface of WPC specimens with an unmodified (a, c) and acetylated (b, d) wood component, artificially aged by weathering, water soaking, and followed by a brown-rot fungus exposure (U4, A4)

This SEM evaluation of the specimen surfaces was in good agreement with the observed differences in sorption behavior between the samples aged by weathering and water soaking and the samples aged solely by water soaking. For the latter sample, the polymer matrix at the surface was still intact, and the major path for moisture sorption into the material was through the wood component at the surface, resulting in a much lower moisture transport rate compared to the weathered specimens, which had a degraded polymer matrix at the surface, creating new pathways for the moisture transport.

CONCLUSIONS

1. The artificial weathering of the WPCs caused matrix cracking at the surface, and a wood-matrix delamination, resulting in an increased moisture sorption rate.
2. The use of an acetylated wood component in the WPCs decreased the moisture sorption rate and the amount of sorbed moisture when compared to that of the composites with an unmodified wood component.

3. The WPC samples subjected to artificial ageing involving white-rot decay showed the highest moisture sorption rate for both the composites with an unmodified and an acetylated wood component.
4. The SEM evaluation showed that fungal hyphae were able to grow on WPCs with both the unmodified and acetylated wood.
5. The WPCs with the acetylated wood showed some fungal hyphae around the wood component, whereas the composites with unmodified wood were completely overgrown by fungal hyphae.

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