Impact of Mineral Fillers to the Moisture Resistance of Wood-Plastic Composites

TIINA HUUHILO, OSSI MARTIKKA, SVETLANA BUTYLINA AND TIMO KÄRKI*

Department of Mechanical Engineering, Lappeenranta University of Technology, Lappeenranta, P.O. Box 20, FINLAND, Tel: +358 5 432 1011. E-mail: timo.karki@lut.fi

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Abstract

The impact of mineral fillers to the moisture resistance of the wood-plastic composites (WPC) is studied. Five inorganic fillers were tested for the wood-plastic composites calcium carbonate, two different types of wollastonite, soapstone and talc. The amount of polypropylene, wood and mineral was held constant, only the mineral type was changed during the tests. The studied composites were also compared with a reference sample, which was manufactured without any mineral addition. All added minerals decreased the swelling and moisture absorption of the wood-plastic composite considerably. Also the density of the wood-plastic composites increased when minerals were added. Without any added mineral, clear openings could be seen in the composite structure in scanning electron microscope (SEM) pictures. These openings could work as pathways for water into the inner parts of the WPC and increase swelling. It could also be seen in the SEM pictures that when mineral was added, these pathways for moisture were closed. After three weeks soak/freeze/dry cycles, the bending strength of the reference sample decreased considerably more than the bending strength of the samples with added minerals. Of the studied minerals, talc was the most effective.

Key words: wood-plastic composite, mineral, moisture resistance

Introduction

The use of wood-plastic composites (WPC) has increased considerably in recent years. In most cases wood-plastic composites are manufactured from recyclable plastic and wood or other natural fibers, which make it ecological material. It is more durable, requires less maintenance and absorbs less moisture compared to timber (Klyosov 2007, Kuo et al. 2009). However, the moisture absorption of WPCs is still distinctive, and it is very important to decrease it as WPCs are often used outdoors as garden decking or window profiles (Huang et al. 2006). Moisture penetration has been found to decrease the mechanical properties of wood-plastic composites (Bledzki 1998, Huang et al. 2006).

A wood-plastic composite typically consists of polymers, wood fibers and coupling agents, which enhance the bonding between wood and plastic. The most often used polymers are polyethylene (PE), polyvinyl chloride (PVC) and polypropylene (PP). The amount of fibers varies according to the manufacturer, but usually the wood/plastic ratio varies between 50 and 80 (Pritchard 2004). Other additives like minerals, lubricants, colourants, UV stabilizers, flame retardants and antimicrobials are used to perform the process or to improve the properties of the end product. The mineral volume varies from 5 to 20%, and the lubricant quantity in WPC is usually up to 6%.

According to the literature (Wang and Morrell 2004) the larger particles of wood are less likely to be evenly coated with plastic, and they also present a more continuous pathway for moisture ingress. The moisture penetration increases when the amount of these pathways increases (Stark 2006). When some mineral is put in as an additive, these pathways are closed, and the moisture uptake slows down. The minerals will increase the density of the composite, but in the literature it is said that the higher the density, the lower the moisture content in WPC and the less swelling in the WPC boards (Klyosov 2007). According to the literature, the density of the composites can be decreased for example by adding foaming agents into the WPC (Reedy 2002, Rowell 2007). By adding minerals, the wood content can be reduced and in that way the tensile strength of the WPC can be increased. Some studies show that a decrease in the fiber content would improve the tensile strength (Xue et al. 2007) and a WPC with a higher wood content would absorb more water (Stark 2001).

Only a few composite manufacturers use mineral fillers, and they have big market potential. Mineral fillers like talc, calcium carbonate and wollastonite increase the bending strength and heat distortion capacity of the WPC and decrease creep under load. They also might improve the processing by absorbing moisture in the wood fibers and working as a lubricating agent (Sherman 2004). On the other hand, adding inorganic minerals might induce brittleness in the WPC (Godara et al. 2009), because the properties of the filled systems or composites are affected by the type and amount of mineral and also by its particle size. Also other properties, like particle shape and ability to absorb water, and mechanical properties like hardness affect the properties of the composite (Klyosov 2007).

The minerals most commonly used as plastic fillers are calcium carbonate and talc, but in WPC calcium carbonate is not used much. Other possible minerals in WPC are e.g. wollastonite. These minerals differ from each other by their chemical and physical properties.

Talc is a hydrated magnesium silicate and it has a complex chemical composition; $Mg_3Si_4O_{10}(OH)_2$. It is a rather soft material, and its Mohs hardness is 1. Calcium carbonate ($CaCO_3$) is harder and its Moh's hardness is 3-4. Talc and calcite have different types of structures. Talc particles have a platy shape, which improves stiffening, and calcium carbonate has a rhombohedral, blocky morphology (Dombrowski et al. 2005).

Wollastonite is fibrous mineral and its aspect ratio is typically between 3 and 20, with a particle length of 8-650 μm. The general composition of wollastonite is CaO (40-50%) and SiO_2 (40-50%). The formulation also contains minor fractions of Fe_2O_3, Al_2O_3, MgO, MnO and TiO_2 (Klyosov 2007). Moh's hardness of wollastonite is 4.5. Because of its acicular crystal habit and relatively high hardness, wollastonite gives polymer composites reinforcing properties (Meng and Dou 2008).

In this study, different inorganic fillers were added into a wood-plastic composite, and the moisture resistance of the WPC was studied. The used minerals were calcium carbonate, two different types of wollastonite, talc and soapstone. The amount of wood, polypropylene and coupling agent was held constant. The results were also compared with a composite manufactured without any mineral adding.

The fourth mineral filler used in this study was soapstone. Soapstone is often used as a raw material for fireplaces and also as other kinds of decoration stone. The basic minerals of soapstone are talc and carbonate minerals, like magnesite, dolomite and calcite. Its color is blueish, greenish or yellowish grey. Soapstone is extremely soft material due to the talc it contains and it is highly heat-resistant. The objective of this study was to understand how different mineral fillers affect the structure and moisture resistance of WPC.

Materials and methods

Materials

The thermoplastic matrix in the composite was polypropylene supplied by Ineos Polyolefins by the trade name Eltex P HY001P. The melt flow index of the PP was 45 g/10min (230°C), the melting point was 161°C, and the density was 910 kg/m^3. The used coupling agent was maleated polypropylene (MAPP) (OREVAC® CA 100, by Arkema) with a melt flow index of 10 g/10min (190°C) and a melting point of 167°C. The wood fiber was conifer sawdust from our own laboratory, and the specific gravity of the fiber was 158 g/dm^3. According to the sieve analysis, the weighted average for the fiber size was 1.6 mm. The used lubricating agent was Struktol TPW 113.

Five inorganic fillers were obtained and their mechanical properties were characterized. The studied fillers were calcium carbonate, calcite FC2,5 (Nordkalk Inc.), two different types of wollastonite, FW400 and HARWoll7 (Nordkalk Inc.), soapstone (Tulikivi Inc.), and talc, Finntalc M30 (Mondo minerals). The soapstone was not a commercial product but waste dust from a process line at Tulikivi Inc. The physical and mechanical properties of the inorganic fillers are presented in Table 1.

Table 1. Characteristics of the used fillers; calcium carbonate, wollastonite, soapstone and talc

	Bulk density g/cm^3	Density g/cm^3	Moh's hardness	Median particle size d50%, μm	Top cut particle size d90%, μm
$CaCO_3$ (FC 2,5)	0.52	2.70	3.0	1.4	7.0
WOll (FW400)	0.75	2.94	4.5	10.6	40.0
WOll (HARWoll7)	0.29	2.94	4.5	9.8	36.6
Soapstone		2.98	2.5	19.8	91.4
Talc (Finntalc M30)	0.75	2.75	1.0	14.5	37.4

WPC manufacturing

The composite recipe was maintained constant: 20% by weight of inorganic filler, 44% of wood fiber and 30% of plastic. The remainder was 3% of coupling agent (MAPP) and 3% of lubricant. In the control sample without any mineral, the mineral amount was replaced with wood, meaning that the wood amount was higher, 75%. The control samples contained 22% of plastic and the coupling agent (MAPP) amount was the same as in the composites containing minerals, 3%. Hollow-shape decking boards were produced in a counter-rotating twin-screw extruder Weber CE7.2. The temperature of the mixing zone in the barrel was maintained at 190 °C, and the die temperature was maintained at approximately 180 °C. The screw speed was maintained at 13 rpm. About 25 m of final product was made from each composite type, and the samples were taken by random sampling from it.

Measurements

The particle size of the fillers was analyzed with an LS 13 320 Laser Diffraction Particle Size Analyzer with the Tornado (Dry Powder Module) System. Scanning electron microscope (SEM) pictures were performed with a JEOL-JSM 5600LV scanning electron microscope operating at 20.0 keV. Because the composite material is not conductive, the sample surface had to be covered with a thin gold layer before testing.

The WPC density was determined according to the EN ISO 1183-1 standard. The moisture content was measured according to ISO 16979. Thickness swelling and water absorption were determined according to EN ISO 317. The moisture resistance under cyclic test conditions was determined according to the standard EN 321, and the three-point tests were carried out according to the EN ISO 310 standard after three weeks soak/freeze/dry cycles.

For the density, moisture, thickness swelling and water absorption measurements, average of twenty measurements was calculated, except for the three-point tests, where average of ten measurements was calculated.

Results

The used inorganic fillers were medium sized particles, except for calcium carbonate, which had small sized particles, (Table 1). The length-to-diameter ratio (L/D) for the wollastonite is quite high because of the acicular nature of the wollastonite. This makes it difficult to measure the particle size accurately. The aspect ratios for the two used wollastonites were different. According to the manufacturer, the L/D ratio for FW400 wollastonite is 3-5:1 and for HARWoll7 wollastonite the ratio is higher than 10:1. A microscopic picture of the used wood particles can be seen in Figure 1 a), where the rather large particle size of the used sawdust, over 1.6 mm is visible. SEM pictures of the studied minerals are presented in Figure 1 b)-f). Also the variable particle shapes of the mineral qualities can be seen in the figure: spherical for calcium carbonate, acicular for wollastonites, platy for soapstone and talc.

Figure 2 shows the water absorption and swelling that happened during 28 days of immersion in water baths. As seen in the figure, both water absorption and thickness swelling happened during the immersion, but mineral adding significantly diminished water absorption into the composites. When mineral was not added into the WPC, maximum thickness swelling was reached after the first 7 days of immersion in the water bath. After 28 days, the thickness swelling was 10% and water absorption 33% for the composite without mineral addition. With added minerals, the thickness

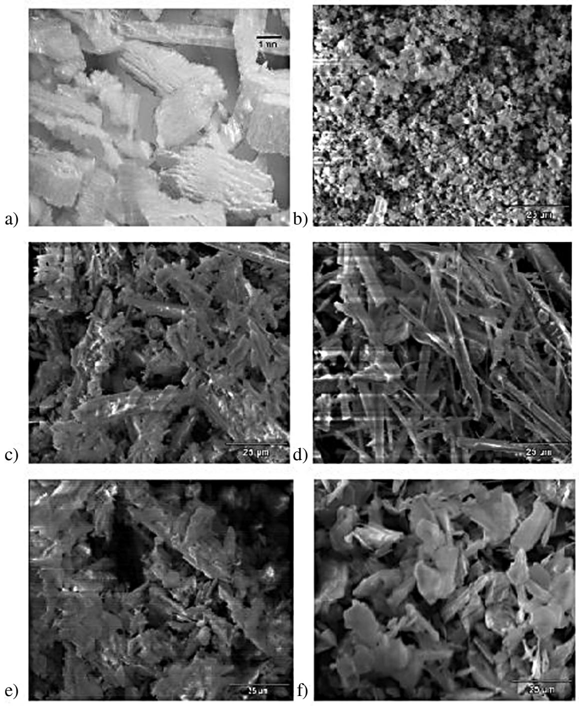

Figure 1. a) Microscopic photograph of the used conifer fiber (x12.6) and SEM pictures of the mineral particles (x1000): b) calcium carbonate FC2,5 c) WollastoniteI FW400, d) WollastoniteII HARWoll7, e) soapstone, and f) talc, Finntalc M30

swelling varied between 4-6% and the water absorption was between 11-16%. It can also be seen that the mineral type has an effect on the water absorption and

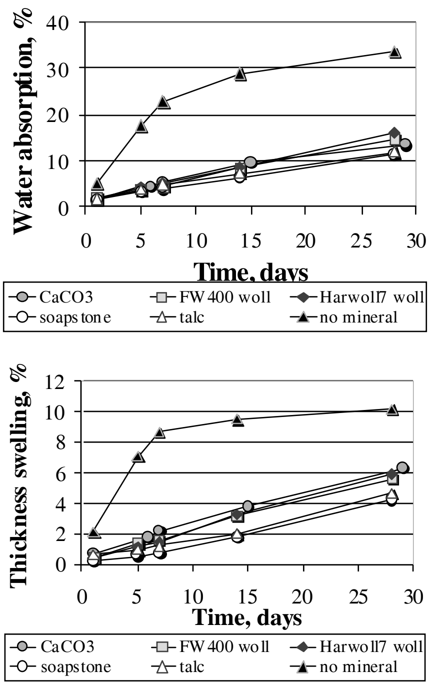

Figure 2. Water absorption and thickness swelling of the composites during 28 days (EN ISO 317)

thickness swelling. Adding minerals made the composites heavier. The density of the reference sample without any mineral was 1.04 g/cm3, but after adding minerals the densities ranged between 1.17 and 1.21 g/cm^3.

Figure 3 shows SEM pictures of the studied wood-plastic composites. In Figure 3 a) is the reference composite without any mineral adding, and the openings between plastic and wood fibers are clearly visible. Through these open pathways, the moisture can penetrate the component structure. In Figure 3, the minerals are packed tightly between the wood fibers. The mineral adding has closed the pathways and the structure is denser.

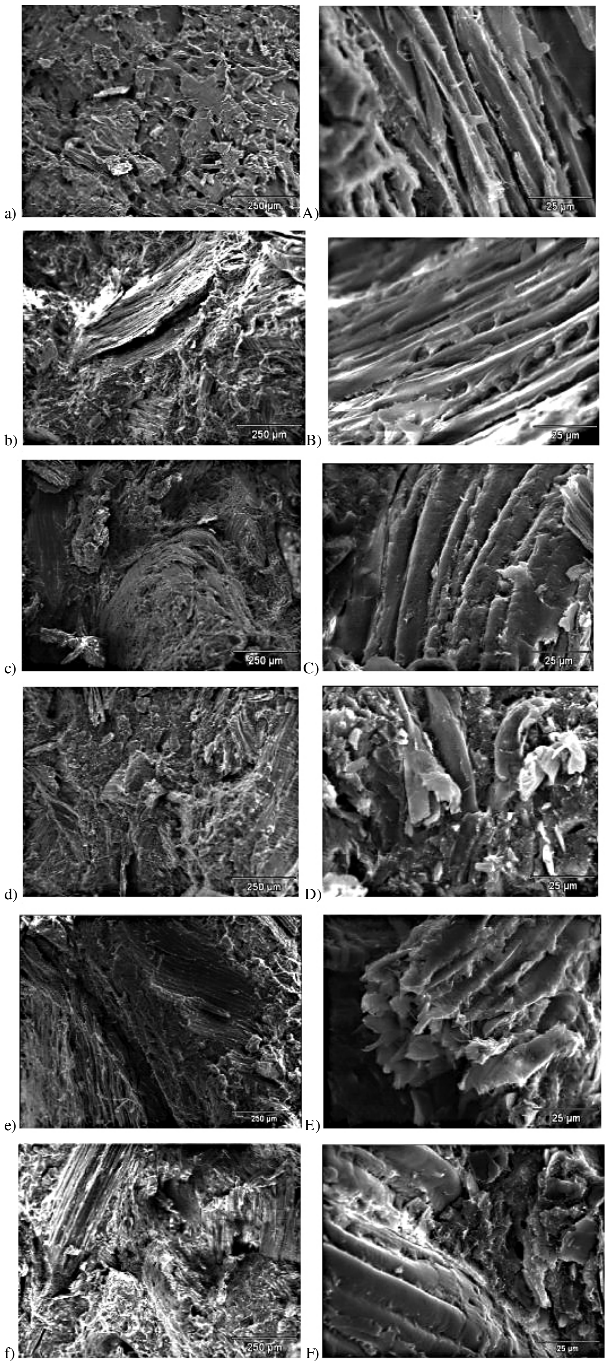

Figure 3. SEM pictures of the composites (magnification x100 and x1000): a) and A) reference composite with no mineral, b) and B) calcium carbonate FC2,5, c) and C) WollastoniteI FW400, d) and D) WollastoniteII HARWoll7, e) and E) soapstone, and f) and F) talc Finntalc M30

During the manufacturing process, the mineral adding diminished the enlargement of the initial composite board profiles. The reference sample without any mineral swelled by 8% compared to the die profile, whereas in the samples with mineral addition only 1% swelling or shrinking in the profiles occurred, so the boards stayed better at the die profile. In the manufacturing process, the WPC boards were pulled along a roll table to the cutting unit, and during the pulling the boards might have got thinner because of stretching. However, in the manufacturing process no clear difference between the different minerals or mineral particle structure was found.

Figure 4 shows the change in the bending strength after three weeks of soak/freeze/dry cycles. The bending strength was measured before and after the soak/freeze/dry cycles. Before the cycles, there was not much difference between the components, and the strengths varied between 22.6 and 23.9 MPa. After the soak/freeze/dry cycles, the bending strength varied from 6.0 (no mineral) to 20.3 MPa (talc). Clear conclusions can be drawn from the experiments; the bending strength decreased over 70 percent with the WPC with no added mineral. When minerals were added to the WPC, the boards were found to become more resistant to the soak/freeze/dry cyclic treatment. The 20% drop of the bending strength was found for all the WPCs with minerals, except that with the added talc, for which the 12% reduction of the bending strength was found. This shows that talc has a clear influence on the bending strength of WPC.

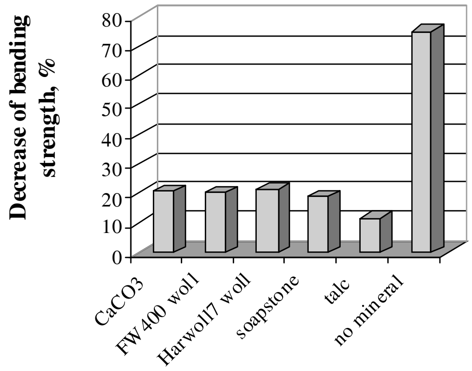

Figure 4. Decrease in bending strength after three weeks soak/freeze/dry cycles (EN ISO 310)

Discussion and conclusions

In this study, the effect of five different minerals on the moisture-resistance of wood-plastic composites was examined. The studied minerals were calcium carbonate, two different types of wollastonite, soapstone and talc.

Mineral adding had a clear effect on the water absorption and thickness swelling of the studied wood-plastic composites. The reference composite with no added mineral absorbed considerably more water, and the swelling happened already during the first week in water bath. This result was as expected, as according to literature 30% talc adding would cut the moisture absorption to half (Shutt 2004). The used wood particles had a rather rough form, which could affect the WPC quality. If the wood had been in smaller chips or even as flour, more bonding between wood and MAPP could have formed. Adding a mineral clearly improves the resistance of a wood-plastic composite against moisture by closing the pathways for water in the composite. Mineral adding also diminishes the swelling of the WPC at the manufacturing stage, which would make the manufacturing more accurate.

After three weeks of soak/freeze/dry cycles, the bending strength of the reference sample with no mineral weakened a lot more than the bending strength of the samples with added minerals. At the same time, also the density of the WPC increased remarkably.

Soapstone and talc are hydrophobic by nature, and the composites having these minerals as fillers were least swollen in the tests. Both wollastonite and calcium carbonate are hydrophilic by nature, and in the study these composites had the weakest water resistance of the mineral-filled composites. Of the studied minerals, talc was the most effective one.

Fungal growth and weather resistance should be kept down in composites. In many WPC types, the fungus growing caused by the moisture content is decreased by adding different chemicals, like zinc borate (Morrell 2009). The results of this study show that with minerals the moisture content in WPC can be decreased in an environmental way, and there would be no need to add extra chemicals.

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ВЛИЯНИЕ МИНЕРАЛЬНЫХ НАПОЛНИТЕЛЕЙ НА УСТОЙЧИВОСТЬ ДРЕВЕСНО-ПЛАСТИКОВЫХ КОМПОЗИТОВ К ВЛАГОПОГЛОЩЕНИЮ

Тиина Хуухило, Осси Мартика, Светлана Бутылина и Тиимо Кэерки

Резюме

Целью данного исследования было изучение влияния минеральных наполнителей на устойчивость древесно-пластиковых композитов к влагопоглощению. В работе были использованы пять наполнителей неорганической природы: карбонат кальция, две разновидности волластонита, мыльный камень и тальк. Количество полипропилена, древесного волокна и минерального наполнителя были одинаковыми для всех изученных композитов. Для сравнения использовался образец древесно-пластикового композита, не содержащий минерального наполнителя. Все минеральные наполнители приводили к значительному снижению абсорбции влаги и набухания композитных материалов. В тоже время плотность композитных материалов увеличивалась при добавлении минеральных наполнителей. Изображения, полученные с помощью сканнирующего электронного микроскопа, показали наличие открытых пор в структуре композита без минерального наполнителя. Пористая структура способствует проникновению влаги во внутренние слои композитного материала. Электронная микроскопия показала, что добавление минеральных наполнителей приводит к блокированию пор. Прочность при изгибе, определенная в конце циклического теста на устойчивость композитов к вымачиванию-замораживанию-оттаиванию, была выше для композитов с минеральными наполнителями. Тальк был наиболее эффективным среди изученных минеральных наполнителей.

Ключевые слова: древесно-пластиковые композиты, минеральные наполнители, влагоустойчивость