Wood Plastic Composites made from Modified Wood - Aspects on Moisture Sorption, Micromorphology and Durability

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WOOD PLASTIC COMPOSITES MADE FROM MODIFIED WOOD

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Abstract

Wood plastic composite (WPC) materials have seen a continuous market growth worldwide in the last decade. So-called extruded WPC profiles are today mainly used in outdoor applications, e.g. decking, railing and fencing. In outdoor conditions, moisture sorption in the wood component combined with temperature induced movements of the polymer matrix causes deformations of such composites. On the macroscopic scale this may lead to unacceptable warp, cup and bow of the WPC products, but on a microscopic scale, the movements will cause interfacial cracks between the particles and the matrix, resulting in little or no ability to transfer and re-distribute loads throughout the material. Moisture within the composite will also allow fungi and micro organisms to attack the wood particles.

The conceptual idea of this work is to use a chemically modified wood component in WPCs to enhance their long term performance. These chemically modified wood particles exhibit reduced susceptibility to moisture, resulting in better dimensional stability and a higher resistance to biological degradation as compared to that of unmodified wood. The objective of this thesis is to study the effects of using modified wood in WPCs on their moisture sorption behaviour, micromorphology and microbiological durability. The modification methods used were acetylation, heat treatment and furfurylation.

Equilibrium moisture content (EMC) and sorption behaviour of WPCs were determined by water vapour sorption experiments. The use of thin sections of the composites enabled EMC to be reached within a comparably short time span. The micromorphology was studied by LV-SEM (low vacuum-scanning electron microscope) using a specially designed sample preparation technique based on UV laser. The biological durability was evaluated by laboratory fungal test methods.

The moisture sorption experiments showed lower moisture levels for all the composites when modified wood particles were used. This was also reflected in the micromorphological studies where pronounced wood-plastic interfacial cracks were formed due to moisture movement in the composites with unmodified wood particles. The sample preparation technique by UV laser proved to be a powerful tool for preparing surfaces for micromorphological studies without adding mechanical defects caused by the sample preparation technique itself. Results from the durability test showed that WPCs with modified wood particles are highly resistant to decay by fungi.

Keywords: Wood plastic composites, WPC, acetylation, heat treatment, furfurylation, moisture sorption, micromorphology, decay, UV laser, soil tests.
Sammanfattning (in Swedish)

Användningen av så kallade trä-plastkompositer (eng. wood plastic composites, WPCs) har ökat avsevärt de senaste åren, framför allt inom byggnadsmaterialsektorn i Nordamerika. Det största användningsområdet för WPC är i utomhusapplikationer som till exempel altandäck, räcken och staket. Vid användning utomhus blir dessa material utsatta för fukt- och temperaturvariationer. Fuktvariationer i materialet innebär att träkomponenten krymper eller sväller, medan temperaturvariationerna innebär att termoplastmatrisen krymper eller sväller.


Syftet med detta arbete är att studera effekten av att använda kemiskt modifierade trämaterial i WPC och att utröna inverkan på egenskaper kopplade till kompositernas beständighet. De trämodifieringar som har använts är acetylering, värmbehandling och furfurylering. Dessa kemiska modifieringar resulterar i trämaterial som är mindre fuktkänsliga än omodifierat trä vilket i sin tur medför en ökad dimensionsstabilitet och större motståndskraft mot biologisk nedbrytning.

Sorptionsexperimenten visade att kompositerna med en modifierad träkomponent uppvisar en signifikant reducerad fuktupptagning. Detta avspeglade sig även i den mikromorfologiska analysen där delaminering i trä-plast-gränsskikten uppstod, på grund av fuktrörelser för kompositerna med en omodifierad träkomponent. I de mikromorfologiska studierna framgick det tydligt att UV laser-teknik är en mycket värdefull provberedningsteknik för denna typ av material, eftersom mekaniskt introducerade artefakter på grund av provberedningen kan undvikas. Tester gällande rötbeständighet visade i sin tur tydligt att den mikrobiologiska nedbrytningen minskade signifikant genom användning av de modifierade träkomponenterna.
Preface

This work has been carried out at Kungliga Tekniska Högskolan, Avd för Byggnadsmaterial (KTH – Royal Institute of Technology, Division of Building Materials). The thesis is a part of two SP Trätek managed projects, EcoComp (Dnr 2003-00993) and ECOMBO (Dnr 2003-02700). The scope of these projects is to supply a development of a new generation of eco-efficient and durable wood plastic composites. The projects are included in the research platform Gröna material financed by VINNOVA (Swedish Governmental Agency for Innovation Systems). The ECOMBO project is also included in the Finnish-Swedish research program Wood Material Science and Engineering (2003–2007).

I would like to dedicate my thanks to VINNOVA and the participating companies within EcoComp and ECOMBO for their belief in this area of research and their financial contribution.

An acknowledgement is addressed to FORMAS for their financial support (Dnr 24.3/2003-0690) regarding the development of the UV laser technique for sample preparation used in this work, as well as the Knut and Alice Wallenberg foundation (Dnr KAW 1998.0130) for funding the UV laser laboratory. SP and SP Trätek is also acknowledged for providing important research infrastructure in the form of laboratory facilities and office space. Financial support for the last phase of this thesis was obtained from EcoBuild – an Institute Excellence Centre which was formed at SP Trätek in collaboration with KTH in December 2006.

I wish to express my sincere gratitude to my supervising group at KTH and SP Trätek consisting of Prof. Ove Söderström, Dr. Magnus Wålinder, Dr. Pia Larsson Brelid, and Dr. Mats Westin for their enthusiasm and support. Ove has been a solid foundation for discussions regarding theory on moisture movements in materials and he has been a great driving force for getting this thesis finished. Magnus has been the enthusiastic motor with great knowledge within the area of wood and wood plastic composites and giving me the inspiration to this field of research. Pia, with her knowledge in wood chemistry and chemical modification, has been of outmost importance for giving me as a non chemist insight in those matters. Mats has contributed with his over all view of the area and knowledge in the biological testing procedures.

My colleagues at KTH Building materials M.Sc. Lars Elof Bryne and Dr. Stéphane Hameury are greatly acknowledged, Lars Elof for the discussions and close work, Stéphane for the discussions about science in general. A large recognition is sent to Dr. Harald Brelid at Chalmers University for his involvement in reading and commenting on the thesis and the manuscripts. I am also grateful for the assistance in preparing specimens by UV laser and supervision with the LV-SEM by Joachim Seltman and Dr. Jan-Erik Lindqvist.
respectively. I would also like to express my thanks to the staff at SP Trätek for fruitful discussions and guidance when needed. The Biofibre Materials Centre (BiMaC) is also acknowledged for providing me a platform of researchers and students within closely related field of research. I would also like to thank the administrative staff at KTH, Building Sciences for creating a stimulating and friendly environment.

I would also like to acknowledge the research collaborators within EcoComp, Dr. Pernilla Walkenström and Dr. Bengt Hagström at IFP Research, and tekn. Lic. Birgitha Nyström at SICOMP, for their valuable input in this project, especially regarding processing, polymer technology and evaluation of the mechanical performance of WPCs.

A special thank is expressed to Prof. Roger M Rowell for his unique experience about chemical wood modification and encouraging thoughts and comments about the thesis and manuscripts. His and Judy’s involvement in my work has made it even more motivating and I am looking forward to continue our collaboration.

Finally, I would like to express my profound gratitude to my other half, Johanna for her support and understanding and to my son, Pontus for reminding me that there also are other important things in life.

Stockholm, November 2007

Kristoffer Segerholm
List of papers

This Licentiate thesis is based on the following research and conference articles, which are referred to in the text by their roman numerals:


The progress of this work has also been presented at the following international conferences:


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1. Introduction

1.1 General context of the thesis

Wood plastic composites (WPCs) have been accepted for many outdoor applications. This material is marketed as durable and maintenance free, although the material has shown a lack in long term durability. The primary cause of the insufficient durability of today’s WPCs is related to moisture sorption in their wood component. This will yield dimensional instability of the composites. Moisture within the material also provides a foundation for fungi and microorganisms to attack and degrade the wood component of the composite material.

Several, not new, modification methods for wood are emerging on the market, for example acetylation, furfurylation and heat treatment (cf. e.g. Hill 2007). The common characteristics for these modifications are their reduced susceptibility to moisture and increased dimensional stability. In this thesis, the basic idea is to use chemically modified wood based on the modification routes acetylation, furfurylation and heat treatment as wood component in WPCs. By introducing wood particles from these modifications in the composites, the moisture induced movements of the composites can be kept to a minimum and the long term performance of the composite can be improved greatly. The objectives of this thesis are then to study the susceptibility to moisture, micromorphology and durability of these composites.

1.2 Background

In this work, the abbreviation WPC stands for wood plastic composites and is defined as a thermoplastic-wood-reinforced composite with more than 50 % by weight of wood material (e.g. wood particles, sawdust or wood flour). This group of materials has seen a remarkable growth within the building material sector over the last decade, especially on the North American market, see examples of WPC products in Figure 1. The WPC decking market in North America has grown from less than 1 % in the mid nineties to over 10 % in 2003, and is expected to reach +20 % in the end of this decade. Regarding the use of WPC, it has been estimated that Europe is 5-10 years behind North America, but the products are now established and a similar growth could be expected over the next few years in Europe (Anonymous 2003b). The annual market is predicted to reach 270,000 tonnes in Europe and 1.7 million tonnes in North America by year 2010 (Vogt et al. 2006).

The demand for new environmentally friendly building materials is likely to increase as a consequence of the recent restrictions regarding chemicals used for impregnation treatment of wood. WPC is one alternative option. This product is more expensive than conventional preservative treated wood, but the
manufacturers promote their products as maintenance-free and highly durable with lack of cracking and splintering, often offering a 10-years warranty (Clemons 2002). However, the first generation of WPCs has shown to lack in long time durability, and failures have led to class action law suits (Morris and Cooper 1998). Laboratory soil block tests have shown weight losses of 3-8 % due to fungal degradation of WPCs after 12 weeks exposure (Clemons and Ibach 2002, Ibach et al. 2003). The mechanical durability has been evaluated for WPC products for use in naval waterfront applications, and it was there concluded that moisture ingress into the composite can reduce strength up to 50 % (Smith and Pooler 2000).

Figure 1. Left: Examples of extruded wood plastic composites (WPCs). Right: Example of WPC application for an outdoor staircase.

To minimize these problems due to dimensional instability and micro-organism attack and to increase the number of WPC products with high quality in exterior applications, improvements are needed. Moisture is one of the key reasons for lack in both mechanical durability and resistance towards decay by fungi. To improve the durability and resistance to decay of the WPCs it is possible to introduce a chemically modified wood component into the composite that will increase both dimensional stability and resistance to biological attack.

New durable products of modified solid wood have emerged on the market during the last few years. This increased interest depends on the restricted use of toxic preservatives due to an increased environmental concern, but also a wish for a reduced need for maintenance. Several environmentally friendly methods for chemical modification of wood have been developed, most of them are not new, but have previously failed to gain commercial interest. Three wood modification methods, which recently have been commercialized are acetylation,
furfurylation and heat treatment (see e.g. Hill et al. 2007). Acetylation of wood has work dating back to 1928 (Rowell 1983) and the early work on acetylation solid wood was performed by Stamm and Tarkow in 1947 and 1950 (Stamm and Tarkow 1947, Tarkow et al. 1946). The research concerning furfurylation was initiated by Stamm in the early 1950s. Most of the early work was performed by his student Goldstein (cf. e.g. Goldstein 1955, Goldstein and Dreher 1960). Heat treatment is reported back to Tiemann in 1915 (Hill 2007) who discovered that heat treated wood showed reduced moisture sorption with relative low reductions in strength. The reduced moisture sorption of heat treated wood depends on the initial thermal degradation of the hemicelluloses (Stamm 1964), which are the most hygroscopic constituents in the wood. These modification methods have been extensively studied in the literature throughout the years and several improvements have been made since the early work. In the recent book by Hill (2007), these and other modifications are thoroughly described.

In the present investigation, the conceptual idea is to use residuals from the production of modified wood, such as sawdust, shavings or boards rejected due to cracks or discolouration. This will mean that no additional wood resources are used and the waste products are turned into value added products. The wood particles used in conventional WPCs often originate from planer shavings or sawdust. The producers of WPCs normally use commercial wood flour, which has a broad particle size distribution and it is therefore difficult to predict the properties of the WPCs products. Typical particle sizes used in WPCs are 10-80 mesh (Clemons 2002). Stark and Rowlands (2003) have in a comparative study on the effects of particle size concluded that it is the particle shape, not the size, which has the greatest influence on strength and stiffness. A more slender particle will redistribute and transfer stresses better between the particles and the matrix. Therefore, the process for wood particle preparation should be designed to give particles with high length to width ratio.

One of the most critical aspects of WPCs is the high hygro sensitivity of the wood component. Moisture uptake is slow in WPC, even when immersed in water, but continues over a long period of time. The rate and extent of moisture uptake increases when the wood part exceeds 50 % of the composite (Rowell 2005). Wang and Morrell (2004) have shown that moisture will not penetrate deep into the material, but the moisture levels close to the surface are very high. A moist environment will swell the wood particles close to the surface, and the particles will shrink upon drying. This will cause stresses within the material and create microcracks, which will expose more particles deeper into the material. This swelling and shrinkage will also cause cracks at the interfaces between the wood particles and the matrix. Abdul Khalil et al. (2002) have shown reduced thickness swelling and moisture levels of the composites by using acetylated Acacia magnum as wood component. The amount of wood in that study was between 20 and 50 % by weight.
Resistance to biological decay has been studied in laboratory tests, both in single fungi test jars and also in soil boxes with a variety of different fungi and microorganisms (Westin et al. 2006, Ibach et al. 2003, Clemons and Ibach 2002). Current standards for fungal resistance have been developed for testing solid wood. The slow moisture uptake of WPCs makes it inappropriate to use those standard test methods directly. Modifications of such test procedures are needed. Pre-treatment to increase the initial moisture content has been used, but still there is need for further refinement (Ibach et al. 2003, Clemons and Ibach 2002).

1.3 Objectives

The objective of this thesis is to:

1. Study the use of three types of chemically modified wood components (acetylation, furfurylation and heat treatment) in two types of thermoplastics (polypropylene and cellulose acetate propionate).

2. Study micromorphological changes in modified and un-modified WPCs due to both water vapour and liquid water exposure.

3. Study biological durability of modified and un-modified wood materials in WPCs using both a soil jar test and a terrestrial microcosm test.
2. Materials and methods

2.1 Wood raw material

Three types of modified wood materials were used in this study: acetylation, heat treatment and furfurylation. A brief description of these methods is given in the following sections.

Acetylation

Modification of wood by acetylation is a single site reaction where one acetyl group is replacing one hydroxyl group in the cell wall polymers. In the modification procedure, the wood material is impregnated with acetic anhydride and then reacted at elevated temperature. The only by-product produced is acetic acid. The resulting modified wood material exhibits increased dimensional stability, maintained strength, decreased equilibrium moisture content (EMC), and superior resistance to biological degradation (Larsson Brelid 1998). The method of acetylation used in this work was performed by A-Cell Acetyl Cellulosics AB in their pilot plant according to a simplified procedure without use of any catalyst or co-solvent in the reaction (Rowell et al. 1986, Larsson Brelid 1998). The acetylation level of the wood material used in this study was approximately 18-23 % expressed as wood acetyl content.

Thermal modification

Thermal modification of wood results in a colour change and a partial degradation of the cell wall polymers. The hemicelluloses are the most affected constituents. The resulting material exhibits a higher dimensional stability, a reduced hygroscopicity and improved resistance to microbial decay. There are four major heat treatment methods in Europe today; Thermo Wood, Oil Heat Treatment, Plato Wood and Retification. These four are similar in that solid wood is subjected to a temperature of around 200 °C for several hours in a low oxygen atmosphere (Rapp 2001). In this work, Norway spruce modified according to the ThermoWood D (Anonymous 2003a) procedure has been used. This process has a peak temperature of 212 °C.

Furfurylation

The furfurylation of wood involves treatment with furfuryl alcohol, which is pressure impregnated into the wood and then polymerized within the cell wall. The resulting material exhibits high dimensional stability, improved mechanical behaviour, except for impact resistance, and improved resistance to fungal decay (Lande et al. 2004). In this study, the furfurylation of Radiata pine has been carried out according to Lande et al. (2004) in an industrial pilot plant of Wood Polymer Technologies ASA (WPT).
2.2 Preparation of wood particles

The basic idea is to use residuals from the production of modified wood. The commercial production of this modified material is, however, still low therefore in this study the wood particles have been prepared from modified solid wood boards, ground into particles in a two step process at SP Trätek in Stockholm, Sweden. First the solid wood boards were fed into a disk flaker (Figure 2, left), turning the wood boards into thin veneers. Thereafter, the thin veneers were fed into a knife ring mill (Figure 2, right) chopping the veneers into particles. The particles obtained were then characterized by sieving analysis and microscopic analysis.

Figure 2. The two step grinding process, disk flaker (left) and knife ring mill (right).

2.3 Polymer matrices

Two inherently different thermoplastics were used as matrices in this study, polypropylene (PP) and cellulose acetate propionate (CAP). The PP used in this study was BE160MO from Borealis for injection moulded composites and Moplen HF 500N from Basell Polyolefins for extruded composites. CAP is a partially biobased matrix and the one used was Tenite™ Propionate 360A4000016 supplied from Eastman Chemicals.
2.4 Manufacturing of composites

Two types of samples were prepared in this study: injection moulded dumbbell shaped WPCs with a wood/polymer ratio of 50/50 by weight, and a high wood content extruded square hollow profile, with a wood/polymer ratio of 70/30 by weight. These two manufacturing methods differ both in process and also in the final product. In injection moulding, the material is melted by a single screw and high pressure is built up. Then the molten material is injected into a mould of the final shape and rapidly cooled. In extrusion, the material is heated in screws and pressed through a die, shaped like the final cross section of the extruded board. The extruder used in this study consists of rotating cones instead of screws (Conenor Ltd.). Table 1 shows all the material combinations used in this study and Figure 3 shows an example of the extruded WPC profiles.

Table 1. Overview of the material combinations used in this study.

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer matrix</th>
<th>Wood material</th>
<th>Process</th>
<th>%Wood content</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP</td>
<td>Acetylated pine</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>PP</td>
<td>Heat treated spruce</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>PP</td>
<td>Furfurylated pine</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>PP</td>
<td>Unmodified pine</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>-</td>
<td>Inj. mould</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>CAP</td>
<td>Acetylated pine</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>CAP</td>
<td>Heat treated spruce</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>CAP</td>
<td>Furfurylated pine</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>CAP</td>
<td>Unmodified pine</td>
<td>Inj. mould</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>CAP</td>
<td>-</td>
<td>Inj. mould</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>PP</td>
<td>Acetylated pine</td>
<td>Extruded</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>PP</td>
<td>Heat treated spruce</td>
<td>Extruded</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>PP</td>
<td>Furfurylated pine</td>
<td>Extruded</td>
<td>70</td>
</tr>
<tr>
<td>14</td>
<td>PP</td>
<td>Unmodified pine</td>
<td>Extruded</td>
<td>70</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>Acetylated pine</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>Heat treated spruce</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>17</td>
<td>-</td>
<td>Furfurylated pine</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>-</td>
<td>Unmodified pine</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>
2.5 Wood Particles – Before and after processing into composites

The particles that go into the process may be very different in shape and size as compared to the particles in the composites. This is caused by the thermal and mechanical forces in the compounding and extrusion of the material. It is therefore interesting to analyse the particles before and after processing to evaluate the magnitude of size reduction and changes in shape. The particles in the composites were therefore isolated using xylene in a soxtech extractor (Figure 4). The particles prior to processing into composites and the extracted particles were analyzed (length and width) in an optical microscope, and the length to width ratio of the particles was calculated.

Figure 3. Example of extruded WPC profiles with external dimensions 600 x 400 mm² used in this study.

Figure 4. Soxtech extraction apparatus.
2.6 Water vapour sorption

Moisture uptake by WPC is a critical feature, since the presence of moisture allows for biological attack by fungi. For intended outdoor applications of this material, it is unavoidable to have moisture present. Therefore, it is crucial to keep the moisture levels in the material at a minimum.

All materials in Table 1 were divided into two groups: one was subjected to accelerated ageing in a weatherometer for 500h with cycling 102 minutes of water spray followed by 18 minutes of water spray and UV-light and the other group was left as controls. The accelerated ageing is normally used when preconditioning specimens for biological testing. A more detailed description of the accelerated ageing is given in Paper II.

To be able to reach equilibrium moisture content (EMC) within a comparable short time span, thin sections/veneers from the surface layer of all the material combinations (Table 1) were prepared using a planer and a bandsaw, the specimen dimensions were 25 x 10 x 2 mm\(^3\). All sides except the original outer surface of the material were sealed using aluminium tape. The specimen where then placed in a controlled climate (22 °C, 80 % relative humidity) and the weight gain was recorded at different time intervals. The test setup for the water vapour sorption is shown in Figure 5. The test was run for 12 months after which the test was terminated and the specimens were dried at 105 °C to be able to calculate the weight gain into moisture content (MC) of the WPC and its wood component.

![Figure 5](image)

**Figure 5.** Setup for the water vapour sorption experiments, 1) specimens, 2) balance, 3) logger for temperature and relative humidity.
2.7 Water sorption, Micromorphology and UV laser technique

By immersing the WPC into water, the wood component in the WPC will swell and deform the composite. When the WPC dries, the wood component in the composite will shrink and cracks in the material will be visible. This method of testing is very harsh, but is reality if the material would be used in waterfront applications or in other moist environments. The main focus of this part of the study is to examine the micromorphology of the material, i.e. to observe the material on a microscopic scale and to see the effects of using a modified wood component on swelling and shrinkage in the WPC. For these studies a low vacuum-scanning electron microscope (LV-SEM) was used. By using the low vacuum mode, no sputtering of the surface is required and it has been possible to acquire micrographs of the specimens before and after immersing them into water. This part of the study did not include furfurylated wood particles and not CAP.

Specimen preparation by UV laser

There are several ways of studying the micromorphology of a material. One way is to look at a fracture surface and from that draw conclusions regarding the internal structure of the material. However, when looking at a fractured surface, you only view the weakest part of the material and not the actual inner structure of the material. Preparation by microtome is another technique used for preparing surfaces for studies in SEM, but this and other cutting preparation techniques are doubtful, because of the introduced artefacts by the mechanical forces applied by the preparation technique itself. Balasuria et al. (2001) have used a preparation technique involving polishing of the surface. That may seem to be a gentle preparation technique, but also in this case mechanical forces have been applied to the material, which makes it inappropriate to use in this study. Therefore, a sample preparation technique based on UV laser for preparing specimens was used in the present work. This technique was developed at KTH in the early nineties (Seltman 1995, Stehr et al. 1998). The laser used was a pulsing UV excimer laser (LAMBDA PHYSIK LTD 210 ICC) and applied the wavelength 248 nm. Each pulse corresponds to 1 J/cm² energy and the frequency was varied between 1 and 100 Hz. Figure 6 shows the UV laser laboratory set-up. Specimens were prepared by the UV laser to the dimensions 20 x 5 x 1 mm³.

Reference micrographs were acquired in the LV-SEM of all the specimens before they were subjected to a wetting-drying cycle. All specimens were immersed in distilled water for one week. The weight gain was recorded and the specimens were dried at 105 °C until no more weight loss was recorded. The initial and final moisture contents were then calculated. The specimens were finally inserted in the LV-SEM again and new micrographs were acquired and compared with the reference micrographs.
2.8 Biological durability

Durability has been tested in two different tests. The first one is a “soil jar test” according to the AWPA E10 standard, in which the specimens are placed with feeder strips on sterile soil and then inoculated with a specific fungi. This testing procedure is further described in Paper I. The second test procedure is a terrestrial microcosm (TMC) test according to an expanded version of the European test standard ENV 807. In this test, the specimens are placed in soil boxes with three different soils with a variety of active wood decaying organisms. The soil types used in this study were: 1) a compost soil which was a mixture of 2/3 of a soil with high activity of both tunnelling bacteria and soft rot and 1/3 of Borås municipal compost from a mix of household and garden waste; 2) soil from Simlångsdalen test field, a sandy soil with dominating brown rot decay; and 3) forest soil, where 50 % of the soil was from the test field in Ingvallsbenning (with high activity of white rot fungi: *Asterostroma cervicolor*) and 50 % from a mixed forest soil from near Ås in Norway with similar pH and water holding capacity. This test is further described in Paper III. All the specimens have been subjected to a pre-ageing procedure according to EN84 prior to both of the durability tests.
3. Results and discussion

3.1 Wood particle size and shape

The particles obtained from the grinding process differed greatly between the three types of modified wood. This is a result of the changes made of the wood properties during the modifications. The furfurylated wood was ground to finer particles as compared to the unmodified wood. Acetylated wood on the other hand, yielded more particles in the larger fractions according to the sieve analysis. The heat treated particles only slightly differed from the unmodified particles according to sieve analysis. The results from the sieve analysis can be seen in Figure 7. The sieve analysis only gives an indication of the size distribution of the particles and it is hard to conclude the reason for the differences based on this analysis alone. Therefore, a microscopic analysis of the particles was performed as a complement to the sieve analysis.

![Figure 7. Results from sieve analysis.](image)

The microscopic analysis showed that there were large differences in shape of the particles from each type of modification procedure. The shape of the particles is important, since the stresses in the material will be better distributed in the composite material the more slender the particles are. The average length to width (l/w) ratios are presented with their respective length and width in Table 2. As can be seen, the l/w ratio of unmodified particles was 4.6. For acetylated and
furffurylated particles the ratios were 6.6 and 7 respectively, and in the case of the heat treated particles the ratio was almost 10.

**Table 2.** Average length and width of the wood particles prior to processing into composites.

<table>
<thead>
<tr>
<th></th>
<th>Unmodified</th>
<th>Heat treated</th>
<th>Acetylated</th>
<th>Furfurylated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (μm)</td>
<td>619</td>
<td>451</td>
<td>405</td>
<td>601</td>
</tr>
<tr>
<td>Width (μm)</td>
<td>164</td>
<td>65</td>
<td>69</td>
<td>121</td>
</tr>
<tr>
<td>Length/width ratio (-)</td>
<td>4,6</td>
<td>9,8</td>
<td>6,6</td>
<td>7,0</td>
</tr>
</tbody>
</table>

Figure 8 shows micrographs of the 35-60 mesh fraction of unmodified particles and heat treated particles. The micrographs clearly show that the heat treated particles are more nail shaped as compared to the unmodified particles. The particles have also been analysed after the composite processing by extracting the particles from the matrix and thereafter observing them in microscope. These observations showed that the processing of the composites resulted in severe degradation in both length and width of all the particles types. An important conclusion was, however, that a higher degree in slenderness of the modified particles as compared with that of the unmodified particles, was maintained after the processing steps. Data for the acetylated and unmodified particles are presented in Paper II.

![Micrographs](image_url)

**Figure 8.** Micrograph of unmodified (left) and heat treated (right) particles within 35-60 mesh fraction. The white bar represents 500 μm.
3.2 Water vapour sorption

The moisture sorption of the materials was slow, especially for the unaged composites with PP as matrix, which did not reach EMC during the time of the test. All the WPCs with modified wood showed reduced moisture uptake as compared with the reference WPCs.

Some of the sorption graphs are presented in Figure 9. In these graphs MC is plotted versus time for the injection moulded material with PP as matrix. The left graph includes unaged materials and the right graph includes materials subjected to accelerated ageing before testing. There are two important results in these graphs. One is the moisture levels, where the EMC of the composites was significantly lowered by the introduction of a modified wood component. The composite with acetylated wood component has an EMC which was less than 50% of the EMC for the reference composite with unmodified wood. The other important result from this test was the observed difference between the unaged and aged materials. The sorption of the unaged material was very slow and the unaged composite with unmodified wood was still not in equilibrium after 500 days of sorption. The sorption behaviour of the aged material was completely different. Moisture uptake was more rapid and almost as fast as for the composites with CAP as matrix. CAP is expected to have a more rapid moisture uptake since the matrix itself is hygroscopic. A conceivable reason for this altered behaviour is probably due to degradation of the polymer rich surface caused by the accelerated ageing. Consequently, the surface has become porous and the particles inside the material have become more easily accessible to moisture.

Figure 9. Sorption curves for polypropylene based WPCs; moisture content versus time without pre-ageing (left graph) and with pre-ageing (top graph), composites with a) unmodified, b) furfurylated, c) heat treated, and d) acetylated wood component.
3.3 Micromorphology LV-SEM

By means of the sample preparation by the UV laser technique, micromorphology of the interior of the materials is revealed without introducing any mechanical induced artefacts. This preparation method was therefore a powerful tool for studying the micromorphology and the response of the wood thermoplastic interface when subjected to moisture changes. The soaking of the extruded specimens resulted in pronounced differences in MC as shown in Table 3. These large differences were also reflected in the appearance of the particles in the composites. The extruded reference composites with 70 % unmodified wood component showed interfacial cracks formed around most of the particles (cf. Figure 10) after a soaking and drying cycle. The composites with modified wood had a much lower EMC than the composites with unmodified wood which also was reflected in the micromorphological analysis. No or few interfacial cracks were formed between the modified particles and the matrix after a soaking and drying cycle. This is exemplified in Figure 11 in which the appearance of WPC containing acetylated wood before and after water soaking cycle is shown.

Table 3. Moisture content of the WPCs before and after soaking.

<table>
<thead>
<tr>
<th>Material combination (30/70) w/w</th>
<th>Initial MC [%]</th>
<th>Final MC [%]</th>
<th>Final MC based on wood component [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/unmodified</td>
<td>3.2</td>
<td>24.1</td>
<td>34.4</td>
</tr>
<tr>
<td>PP/acetylated</td>
<td>1.4</td>
<td>8.1</td>
<td>11.6</td>
</tr>
<tr>
<td>PP/heat treated</td>
<td>2.5</td>
<td>15.2</td>
<td>21.7</td>
</tr>
</tbody>
</table>

If the moisture sorption fluctuations are kept to a minimum, the stress induced swelling and shrinkage of the wood component will be smaller. This will improve the mechanical durability of the WPCs by keeping the interfaces between the wood component and the matrix intact.
Figure 10. SEM micrographs of a polypropylene based WPC with 70 % unmodified wood, before soaking cycle (upper micrograph) and after soaking cycle (lower micrograph).
Figure 11. SEM micrographs of a polypropylene based WPC with 70 % acetylated wood, before soaking cycle (upper micrograph) and after soaking cycle (lower micrograph).
3.4 Biological durability

The results from the two biological tests showed that the mass losses of the composites made using modified wood were significantly lower as compared to that of the composites with unmodified wood. Some results from the terrestrial microcosms on the extruded materials according to an expanded ENV 807 test are presented in Figure 12. The results are from 40 weeks of exposure in three types of soils. The composites with unmodified wood had a mass loss (ML) of almost 10 % in the soil with high activity of soft rot and around 5 % in the other two soils. There was fungal decay of the WPCs with unmodified wood in all soil types as revealed by microscopic analysis. The ML in the composites with heat treated wood component was 2.5-3 % for all soils, although no decay of the specimens could be revealed by microscopic analysis. WPCs with acetylated wood component only had a slight ML of around 0.5 %. These results are presented in more detail in Papers I and III. The ML for composites with furfurylated wood component was excluded due to failures in the sample preparation procedure.

![Figure 12. Mass loss of extruded material with 70 % wood content after 40 weeks of exposure according to an expanded ENV 807 test. The soils are denoted by their dominating fungal strain.](image)

The mass loss due to brown rot decay in the AWPA E10 test with the brown rot fungi *Poria placenta* of four WPC materials and reference solid pine sapwood are presented in Table 4. Both of the WPCs with acetylated wood component showed promising results with a very low mass loss. The WPCs with unmodified
wood had a mass loss of 6 and 9 % (based on wood mass) depending on the matrix used. This reveals that the WPCs with acetylated wood component are very resistant to decay, both when exposed to single fungal strains in the AWPA E10 test and also when exposed to a variety of active wood decaying organisms tested in the expanded ENV 807 test. The mechanism for the greatly improved fungal resistance of acetylated wood is not yet fully understood. One theory for this is the lowering of moisture content in the cell wall, however, it is also possible that the replacement of hydroxyl groups with acetyl groups interferes with the specific enzyme-substrate recognition mechanism. More research on this is needed to make definite conclusions (Rowell et al. 2007).

Table 4. Mass loss of injection moulded WPC with unmodified and acetylated wood component due to brown rot decay by *Poria placenta* in the AWPA E10 test.

<table>
<thead>
<tr>
<th>Polymer Matrix</th>
<th>Wood material</th>
<th>Process</th>
<th>% wood content</th>
<th>Based on:</th>
<th>Total mass</th>
<th>Wood mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>Pine Sapwood</td>
<td></td>
<td>100</td>
<td>47</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>Unmod. wood</td>
<td>Inj. moulded</td>
<td>50</td>
<td>4</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>Acetyl. wood</td>
<td>Inj. moulded</td>
<td>50</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>CAP</td>
<td>Unmod. wood</td>
<td>Inj. moulded</td>
<td>50</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>CAP</td>
<td>Acetyl. wood</td>
<td>Inj. moulded</td>
<td>50</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusions

Wood plastic composites (WPCs) made using unmodified wood material have been shown to lack in long-term durability. Moisture enters the composite through the wood component. The time-scale for this uptake can be several years depending on the amount of wood used in the material. In other words, it is only a question of time before moisture enters the material, resulting in dimensional changes (swelling) and a moisture content high enough to allow attack by fungi or other micro-organisms. The results presented in this thesis show that by using chemically modified wood components in WPCs, even with as high wood content as 70 %, the moisture levels can be lowered which will lead to less swelling and shrinkage of the wood component and no or slight attack by fungi. In other words, by using a modified wood component in WPCs, it is possible to use a higher wood weight percent in the composites with maintained long-term performance. That is using less thermoplastic matrix, which often is several times more expensive as compared to the wood component.
5. Ongoing and future work

This thesis is since year 2007 a part of a WPC project within EcoBuild an Institute Excellence Centre at SP Trätek (see www.ecobuild.se). Future studies will in this case involve so-called in-situ micro tensile tests in LV-SEM (see example in Figure 13), where thin WPC sections are loaded in tension while achieving micrographs. By this procedure in combination with an image correlation technique it is possible to study the deformations in the material and to see how the strains are distributed around the particles. This could increase the understanding of the effect of particle size and shape as well as adhesion properties between the matrix and the particles in wood based composites.

Field tests, both in- and above ground as well as marine testing are also ongoing within EcoBuild, but have still not been evaluated. However, preliminary results show that large improvements regarding durability can be achieved by the use of chemically modified wood particles in WPC.

Figure 13. SEM (left image) with load cell (right image) mounted for micro tensile testing.
6. References


Appended papers (I-III)

Division of the work in the appended papers:


Segerholm initiated the work. Segerholm performed the sorption experiments, Westin performed the durability tests, and mutually the authors interpreted the results. Segerholm wrote the paper.

II. Segerholm, B.K., P. Walkenström, B. Nyström, M.E.P. Wålinder & P. Larsson Brelid. “Micromorphology, moisture sorption and mechanical properties of a biocomposite based on acetylated wood particles and cellulose ester”.

The consortium of Ecocomp initiated the work. Segerholm performed the sorption and micromorphological experiments, Walkenström performed the mechanical experiments, Nyström performed the particle characterisation, and mutually the authors interpreted the results. Segerholm wrote most of the paper.


Segerholm initiated the work. Segerholm performed the sorption experiments, Westin and Alfredsen performed the durability tests and Segerholm interpreted the results. Segerholm wrote the paper.