Short Term Scientific Mission (STSM)

Wood particle characterization in Wood-Polymer-Composites (WPC) processing

in the framework of COST Action FP1006:

Bringing new functions to wood through surface modification

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Report

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1. Purpose of the STSM

Wood-Polymer Composites (WPCs) are innovative hybrid materials and substitutes for many conventional product applications due to their 3-dimensional mouldability, durability and weather resistance. WPC can be formed by a thermoplastic process and consist of renewable materials (wood particles or natural fibres), mostly synthetic plastics, such as polypropylene, and additives. The manufacturing process is a decisive factor determining the specific material characteristics of WPC. Several approaches have demonstrated that wood fibre source and wood fibre length strongly influences mechanical properties (Bledzki, et al., 1998; Butylina, et al., 2011; Migneault, et al., 2008; Migneault, et al., 2009; Wolcott, et al., 1999). These properties might be improved by using wood particles/fibres with a distinctive aspect ratio (Stark, et al., 1997). Nevertheless, only a few trials have examined the particle length and geometry before and after processing. Also the impact of processing on wood particles was often just visually analysed (Radovanovic, 2007; Schirp, et al., 2010). In this study the fibre characteristics before and after processing and the interfacial adhesion between wood fibres and the polymer matrix are investigated, in which, among others, the fundamentals of bonding mechanisms via secondary interactions, crystallisation during processing and mechanical entanglement of the fibres are of major interest.

The purpose of the Short-Term Scientific Mission (STSM) was to investigate changes of molecular, nano- and microscale- interactions by means of appliance of different measuring techniques, such as optical fibre analysis, microscopy, microtomography, differential scanning calorimetry and solid-state nuclear magnetic resonance (NMR) spectroscopy. These measurements should help to understand the manufacturing and bonding process, in terms of fibre characteristics and chemical interactions.

2. Description of the work carried out during the STSM

In this research, properties of natural bonded wood fibre composites and their raw material source were investigated. The proposed species for the composite were Radiata Pine (*Pinus radiata*), Norway Spruce (*Picea abies*), Poplar (*Populus sp*) from short rotation coppice (SRC), willow (*Salix sp*) from short rotation coppice and two types of European beech (*Fagus sp*) wood sources. The material attributes, such as anatomical features and chemical compositions will be determined. The physical and mechanical properties of prototyped natural bonded fibre composites will be determined. Finally, the microstructure of this composite will be observed and discussed.

Moreover, composites containing stained fibre were also investigated via microscopy on their cross-, tangential- and longitudinal section. At Scion different preliminary procedures have been tested for WPC samples to work out a suitable preparation of samples for light microscopy.
Table 1: Methods, which are object of study for wood fibre/particle and composite characterization.

<table>
<thead>
<tr>
<th>No.</th>
<th>Method</th>
<th>Characteristics</th>
<th>Fibre characteristics and interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fibre analysis</td>
<td>Micro-scale 2-D Surface</td>
<td>Fibre characteristics and distribution</td>
</tr>
<tr>
<td>2.</td>
<td>Microscopy</td>
<td>Micro-scale 2-D Surface</td>
<td>Fibre characteristics and interactions</td>
</tr>
<tr>
<td>3.</td>
<td>Micro-tomography</td>
<td>Nano/micro-scale 3-D</td>
<td>Fibre characteristics and interactions</td>
</tr>
<tr>
<td>4.</td>
<td>Scanning electron microscopy (SEM)</td>
<td>Nano/micro-scale 2-D</td>
<td>Fibre characteristics and interactions</td>
</tr>
<tr>
<td>5.</td>
<td>Differential scanning calorimetry (DSC)</td>
<td>Molecular scale</td>
<td>Physical &amp; chemical phenomena Polymer /wood characteristics</td>
</tr>
<tr>
<td>6.</td>
<td>Solid state NMR</td>
<td>Molecular scale</td>
<td>Physical &amp; chemical phenomena Polymer /wood characteristics</td>
</tr>
</tbody>
</table>

Raw material preparation

Raw material source preparation was implemented in Göttingen and Rotorua. Raw particle sources from *Picea abies*, *Populus sp.*, *Willow sp.* and *Fagus sylvatica* have been prepared in Göttingen, whereas fibre material from *Pinus radiata* chips has been prepared in Rotorua. With regard to the composite specimens, composites based on different fibre types and fibre content have been prepared in Goettingen. Injection moulded dogbone-shaped specimen, containing a notable percentage of stained MDF fibres, has been prepared in Rotorua. A staining of wood fibres was assumed to be necessary for microtomography, in terms of proper fibre segmentation. In order to investigate these composites also via microscopy, the specimen have been polished in different steps, to achieve a smooth surface (XY,XZ and YZ plane).

3. Description of the main results obtained

The overall goal was to evaluate methods for wood fibre/particle characterization in wood-polymer composites and investigate wood fibre/particle and polymer matrix interactions. The fundamental bonding along the fibre/particle polypropylene interfaces was investigated to clearly understand the material on the one hand and effects of different wood fibre/particle sources on the other hand.

*Dynamic image analysis (DIA)*

In a first step, the length and shape of wood particles were examined before compounding using a dynamic optical particle analyser. Therefore, the analyser (QICPIC, Sympatec GmbH, Germany) was connected to a vibrating chute (VIBRI, Sympatec GmbH, Germany) and a particle disperser (RODOS, Sympatec GmbH, Germany). The particles were dispersed in air.
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and transported in a laminar air stream, passing a laser light and an optical detector. The detector collected a 2D image of each particle with a size between 10 µm to 20 000 µm.

Particle length (length of fibre, LEFI) was analysed via using a skeletonisation algorithm determining the shortest distance between the farthest endings. The projected area of the particle (equal projection area, EQPC) was divided by the total length of all skeleton sections, which coincided with the particle diameter (diameter of fibre, DIFI). In this respect, the evaluation of the particles was determined by statistical intervals (x_{10}, x_{50}, x_{90}). The x_{50} was determined as the arithmetic mean. The x_{10} and x_{90} were determined as auxiliary interval parameters to represent the shortest and longest particles of the population, respectively. Aspect ratios (AR) were calculated by dividing the mean LEFI by the mean DIFI. The particle distribution was calculated as the relative amount (%) of each class and summarised cumulatively based on LEFI.

Table 1: Fibre length and aspect ratio of the different wood particle sources produced.

<table>
<thead>
<tr>
<th>LABEL</th>
<th>NO. OF PARTICLES ANALYSED</th>
<th>x_{10}-VALUE (µm)</th>
<th>x_{50}-VALUE (µm)</th>
<th>x_{90}-VALUE (µm)</th>
<th>AR (for x_{50})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech wood I</td>
<td>1 845 224</td>
<td>31</td>
<td>134</td>
<td>735</td>
<td>2.9</td>
</tr>
<tr>
<td>Beech wood II</td>
<td>5 223 421</td>
<td>29</td>
<td>105</td>
<td>539</td>
<td>2.4</td>
</tr>
<tr>
<td>Poplar spec.</td>
<td>2 951 871</td>
<td>31</td>
<td>112</td>
<td>645</td>
<td>2.6</td>
</tr>
<tr>
<td>Willow spec.</td>
<td>1 108 573</td>
<td>37</td>
<td>154</td>
<td>567</td>
<td>2.9</td>
</tr>
<tr>
<td>Norway spruce</td>
<td>2 424 451</td>
<td>37</td>
<td>152</td>
<td>609</td>
<td>3.3</td>
</tr>
<tr>
<td>Industrial sawdust (C100)</td>
<td>3 749 146</td>
<td>29</td>
<td>96</td>
<td>297</td>
<td>2.5</td>
</tr>
<tr>
<td>Woodforce</td>
<td>14 822</td>
<td>169</td>
<td>1157</td>
<td>2845</td>
<td>13.5</td>
</tr>
</tbody>
</table>

The characterization of fibre/ particle material used for the production of fibre composites will be analysed in Goettingen and is not finished yet. The purpose has to be to study the difference in fibre length/ diameter before and after processing using different measurement techniques.

**Reflectance light microscopy**

For qualitative and quantitative evaluation, the fibre polypropylene composites containing 1 wt% stained fibres were investigated by reflective light microscopy using a Leica stereo microscope MZ12 (see Fig.1). All images were taken at a field of view of 2048 x 1536 pixels and a pixel size of 0.2 µm. To investigate the fibre orientation inside the injected specimen, the samples were polished to reach the desired depth. In addition to the XY plane, two transverse cross sections in XZ and YZ planes were analysed to obtain a 3D overview of fibre orientation.

Unstained fibres within the composites could be identified in reflectance measurements as white, bright objects. Reflectance measurements were very effective in displaying the
outlines of fibres. The stained fibres in particular were easily identifiable by their darker colour.

Fig. 2. Light micrographs of fibre polypropylene composites: (A) XZ plane; (B) XY plane; (C) YZ plane. The stained fibres are revealed in a darker colour.

Comparing the different plane areas of the composite, as seen in Fig. 2, there is an obvious strong difference between stained and unstained fibres. Moreover, as stated by Bourmaud (Bourmaud, et al., 2013) for flax fibre composites, an fibre alignment along the mould flow is expected. Overall, the fibre distribution seems to be quite homogeneous and the composites show no areas with great voids.

Fig. 3. Illustration of fibre segmentation: (A) XZ plane; (B) XY plane; (C) YZ plane.
In Fig. 3 the segmentation process of the stained fibres is displayed. The quantitative analysis of the fibre orientation and distribution is still on-going and might detect differences in distribution that are not visible to the naked eye.

**X-ray microtomography**

The X-ray microtomographic images were acquired using a phoenix nanotom® S. The dimension of the sample was 10 mm x 4 mm x 170 mm. The used sensor resolution was 7.5 μm.

In Fig. 4 the distribution of segmented stained wood fibres is depicted in 3D by way of example. On the ortho slices in the back, the air fraction is visualised in black, whereas wood particles and polypropylene matrix are light grey and dark grey, respectively. A phase segmentation of stained fibres was successful. However, a separation between unstained fibres and polypropylene was not feasible, due to their similar absorption rates and correspondingly illustrated grey values.

Minor voids were present in the inner core of the composite, but difficult to detect due to their small size. These voids could be related to the fibre mixture and the inclusion of gas, which is probably caused by remaining moisture within the composite compound or thermal degradation during processing. The quantitative analysis of the fibre length, orientation and distribution is still on-going.
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Scanning electron microscopy (SEM)
The analysis of the fibre/wood flour polypropylene composites is currently in progress.

Differential scanning calorimetry (DSC)
The evaluation of the polymer and fibre/wood flour polypropylene composites analysis is currently on-going.

Solid state NMR
Solid-state NMR is a powerful and versatile technique for studying structural and dynamic properties of solids. Moreover, it was an important analysis tool in organic and inorganic chemistry and a valuable tool to study local dynamics, kinetics, and thermodynamics of a variety of systems. NMR is extremely sensitive to the location of light atoms, such as hydrogen, providing information on the strength and orientation of hydrogen bonds. Additionally, NMR can provide useful information on static crystal structures, which are highly important for the characterisation of thermoplastic composites containing natural fibres/particles. Furthermore, NMR is also a uniquely applicable method for measurement of porosity, particularly for porous systems containing partially filled cell pores or for dual-phase systems. Unfortunately, no final results had materialized at the time of preparing this report.

4. Future collaboration with the host institution
The evaluation of the microtomography and microscopy images is currently in progress and the mechanical tests are not completed yet. Hence, the collaboration is still on-going. Although, the results look very promising, it is planned to extend the area investigated by microtomography to illustrate the fibre orientation and melt flow characteristics in the entire injection moulded composite. As the collaboration between the university of Göttingen and Scion was very productive and well organized, further projects are planned in the future.

5. Foreseen publications/articles resulting from the STSM
Once the evaluation of the results is completed, it is planned to publish the results in a journal.
Results are supposed to be published in an adequate journal such as:
- Journal of Composite Science and Technology
- European Journal of Wood and Wood Products
- Composites: Part A
- Journal of Applied Polymer Science

6. Gain of knowledge
Based on the results of fibre analysis and the effect of processing, suitable methods for fibre and interface characterization could be identified.

Potential effects of fibre interaction in combination with processing-induced effects on fibre orientation, distribution and fibre length could be investigated on a molecular-, nano- and...
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micro-scale. In future investigations, findings could be verified by implementing adapted processing techniques with subsequent macroscopic testing.

Due to the intensive preparation of specimens as well as time consuming measurements, it is not possible to communicate further results. However, initial evaluations of fibre orientation within the examined materials show promising results. Some of the findings seem to be in accordance to former work (Bourmaud, et al., 2013).

I personally got a detailed view into preparation techniques of thermoplastic specimen dedicated for microscopic or NMR evaluation. In addition, I had the opportunity to learn much about material characteristics, whereas all conclusions from Solid state NMR are based on chemically interactions within and between the materials, respectively.

Currently, there are still some experiments which have to be accomplished, focusing on fibre as well as composite characterisation.

7. Confirmation of the host institution of the successful execution of the STSM

The confirmation is sent in a separate PDF.

8. Further comments

I would like to warmly thank the staff at Scion for the great time I had, especially Alan Dickson, David Sandquist, Stefan Hill, Marie Joo Le Guen, Damien Even and Warren Grigsby. Everyone was very helpful and thank you very much for all the good discussions we had. They made it possible to gain as much knowledge as possible during my visit at Scion. Moreover, I would like to thank the COST FP1006 committee for financial support.

9. References