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Properties of extruded wood-plastic composites based on refiner wood fibres (TMP fibres) and hemp fibres

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Abstract

At present, wood particles (wood flour) with a low aspect ratio are mostly used as fillers in wood-plastic composites (WPC). Reinforcement of WPC and improved strength properties may be achieved by using real wood fibres with a high aspect ratio. WPC based on 70 % (wt.) refiner (TMP) wood fibres and mechanically processed hemp fibres were extruded in a two-step process. Eleven compounds based on the two natural fibre types were prepared using a thermokinetic mixer and extruded in a conical, counter-rotating twin-screw extruder. Additional formulation components were polypropylene fibres, maleic anhydride-modified polypropylene (MAPP) and lubricant. It was determined that compounding in a thermokinetic mixer is a useful step for processing of WPC with refiner and hemp fibres as little fibre damage occurred. However, during extrusion, both natural fibre types were severely shortened due to strong shear forces, and homogeneous dispersion of fibres in the matrix was not achieved. WPC based on hemp fibres displayed the best strength properties of the formulations tested. Current extruder screw and die configurations need to be modified to achieve improved fibre reinforcement and to create new, structurally demanding applications for WPC.

Using dynamic mechanical analysis, fibre-matrix adhesion of WPC was investigated, and activation energies for glass transition of selected formulations were calculated. Activation energy for formulations containing MAPP was higher than for WPC without MAPP. This indicates that better fibre-matrix adhesion was achieved in formulations with MAPP.

Eigenschaften von extrudierten Holz-Plastik-Werkstoffen auf Basis von Refiner-

- (TMP-) Fasern und Hanffasern
- Zusammenfassung

Zurzeit werden überwiegend Holzpartikel (Holzmehl) mit einem niedrigen Schlankheitsgrad Füllstoff Holz-Polymer-Werkstoffen (Wood-Plastic als in Composites, WPC) verwendet. Eine Verstärkung von WPC und verbesserte Festigkeitseigenschaften könnten durch die Verwendung echter Holzfasern mit einem hohen Schlankheitsgrad erreicht werden. WPC auf Basis von 70 Gew.% Refiner- (TMP-) Fasern und mechanisch aufgeschlossenen Hanffasern wurden in einem zweistufigen Prozess extrudiert. Elf Compounds, basierend auf den beiden Naturfasertypen, wurden mit einem Heizmischer hergestellt und auf einem konischen, gegenläufigen Doppelschneckenextruder weiterverarbeitet. Die weiteren Komponenten in den WPC-Formulierungen waren Polypropylenfasern, maleinsäureanhydrid-modifiziertes Polypropylen (MAPP) und Gleitmittel. Es wurde festgestellt, dass die Compoundierung im Heizmischer eine sinnvolle Methode zur Verarbeitung von WPC mit Refinerfasern und Hanffasern darstellt, da hierbei wenig Faserschädigung auftrat. Jedoch wurden beide Naturfasern aufgrund der starken Scherkräfte während der Extrusion deutlich verkürzt, und eine homogene Verteilung der Fasern in der Matrix wurde nicht erreicht. WPC auf Basis von Hanffasern wiesen die besten Festigkeitseigenschaften unter den getesteten Formulierungen auf. Das Design der Extruderschnecken und Werkzeuge sollte modifiziert werden, um eine verbesserte Faserverstärkung zu erzielen und um neue Anwendungen für WPC im konstruktiven Bereich zu ermöglichen.

Mit Hilfe der dynamisch-mechanischen Analyse (DMA) wurde die Faser-Matrix-Haftung der WPC untersucht, und die Aktivierungsenergien für den Glasübergang ausgewählter Formulierungen wurden berechnet. Die Aktivierungsenergie für Formulierungen mit MAPP war höher als für WPC ohne MAPP. Dies deutet darauf hin, dass bessere Faser-Matrix-Haftung in Formulierungen mit MAPP erzielt wurde.

1 Introduction

Most manufacturers of wood-plastic composites (WPC) use wood flour (particle size $300-500 \mu m$) in their formulations while often using the term wood fibres when referring to wood flour. This is confusing since wood flour is actually composed of fibre bundles, whereas wood fibre is an anatomical term and refers to a single fibre. Wood fibres are a) softwood tracheids (i.e., reinforcing and water-conducting elements); and b) hardwood libriform fibres and fibre tracheids (reinforcing elements only; water conduction is occurring in hardwood vessels). Tracheid length is up to 4.5 mm for pine wood with diameters of up to 0.046 mm (Lampert 1967). Therefore, pine wood fibres have an aspect ratio (ratio between fibre length and diameter) of up to 98. Wood fibres are usually longer in softwoods than in hardwoods.

On an industrial scale, wood fibres and wood fibre bundles may be obtained by thermomechanical pulping (TMP) or refining of wood chips. Refiner wood fibres (TMP fibres) are produced for the manufacture of medium-density fibreboard (MDF), for papermaking and for compression-moulding of parts used in automotive applications. During the refining process, wood chips are continuously added to a digester via a plug screw. After softening of the wood, the material is ground between two refiner discs to extract fibres and fibre bundles from the wood matrix. During refining, the structural integrity of the middle lamella which contains the highest concentration of lignin across the cell wall and acts as glue for the wood matrix is weakened, and the lignin is softened and plasticized. After refining, fibres are dried in a tube drier and collected for further processing. In Europe, softwoods are primarily used for mechanical refining due to availability and high fibre aspect ratio which result in good mechanical properties of fibreboards. With regard to costs, refiner wood fibres are significantly cheaper than hemp fibres or cellulose fibres (e.g., sulfite or kraft fibres). Refiner wood fibres produced in MDF plants are not commercially available at present as they are usually processed on-site immediately following the refining step. If refiner wood fibres can meet expectations pertaining to reinforcement of thermoplastics, their commercial availability should be expected.

Size distribution of fibres after the refining process is heterogeneous, and in addition to fibres, very fine particles are obtained. Generally, fibre / particle lengths after

refining are between 20 μ m and 4500 μ m with widths between less than 1 μ m and 80 μ m (Lohmann 2003). Overall, aspect ratio of softwood refiner fibres is approximately 25 (Gehrmann et al. 2004) while aspect ratio of commercial pine wood flour (mesh size between 20 and 140, i.e., between 0.85 mm and 0.106 mm) is between 3.4 and 4.5 only (Stark and Rowlands 2003). Hence, refiner wood fibres have good potential for reinforcement of WPC due to their high aspect ratio. In addition, modification of fibre surfaces during the refining process may lead to improved fibre-matrix adhesion.

At present, WPC based on refiner wood fibres have been processed by roll milling (Miller et al. 1995), injection-moulding (Stark 1999, Stark and Rowlands 2003, Pickering and Ji 2004, Warnes et al. 2005, Specht 2007), and hot-pressing of panels (Gehrmann et al. 2003, 2004, Marutzky et al. 2005; Michaud et al. 2005, Zhang et al. 2007). In addition to refiner wood fibres, other fibre types were also used: Bledzki et al. (2007) used hemp fibres which were converted into TMP fibres at the Fraunhofer-Institute for Wood Research for injection-moulding of hemp-fibre-PP-composites. It was found that thermokinetic mixing of refiner hemp fibres and PP was a fibre-friendly compounding technique and that better mechanical properties were obtained compared to compounding using a twin-screw extruder.

Migneault et al. (2008) extruded WPC based on CTMP fibres in a two-step process, however, fibres used were very short (between 0.196 mm and 0.481 mm). Profile extrusion of WPC based on long (up to 5 mm) refiner fibres represents a challenge due to problems related to feeding of the fibres into the extruder and fibre damage caused by the severe shear forces occurring in the twin-screw extruder. Gehrmann et al. (2003, 2004) performed extrusion trials with WPC based on longer refiner fibres; however, results for mechanical properties reported are based on panels that were hot-pressed immediately following extrusion of round WPC strands (Gehrmann 2008).

Difficulties related to fibre feeding into extruders may be overcome by using a pelletization technique (Warnes et al. 2005, Bengtsson et al. 2007) or a fibre mat forming process (Reußmann and Thole 2006). The differences in the approach taken by Scion as described by Warnes et al. (2005) compared to our approach are substantial: Scion used a much lower amount of fibres (40 weight-%), and they used a pelletizing technique and injection-moulding. In this study it is believed that direct

extrusion of natural fibres (no compounding) is required to exploit the full potential of natural fibres and to provide an economic incentive for the use of natural fibres. The use of a crammer feeder (Gehrmann et al. 2004) may be a suitable method for feeding of compounds based on fibres and possibly also for a one-step, direct extrusion process without prior compounding of fibres.

In addition to investigations related to processing issues and testing of mechanical and physical composite properties, the present study was undertaken to perform dynamic mechanical analysis (DMA) with the extruded WPC based on wood refiner fibres and hemp fibres. DMA is a useful tool to investigate wood, wood-based products, and WPC (Salmén 1984, Kelley et al. 1987, Son et al. 2003) and has also been employed to study the effects of wood decay fungi on WPC (Schirp and Wolcott 2006).

In summary, the overall objective of this study was to use refiner wood fibres and mechanically processed hemp fibres for manufacturing of WPC and to determine mechanical and physical properties of the composites. Wood flour was used to serve as a reference. In detail, the following objectives were pursued:

- Development of a compounding process suitable for long (5 mm) refiner wood fibres and hemp fibres for further processing in a conical, counter-rotating extruder while using a high amount of fibres (70 wt%);
- Partial substitution of hemp fibres with refiner wood fibres to determine possible changes in resulting WPC properties and to achieve raw-material cost-savings;
- Visual observation of natural fibre geometries after compounding and after extrusion;
- Investigation of the composite interphase using dynamic mechanical analysis (DMA) and determination of activation energies for glass transition.

2 Materials and Methods

2.1 Materials

Refiner wood (thermomechanical pulp / TMP) fibres were produced at the Fraunhofer-Institute for Wood Research (Wilhelm-Klauditz-Institute, WKI) using a laboratory-scale 12 inch (30.5 cm) double disc refiner (Andritz, Graz, Austria). Scots pine wood chips were steamed at 150 °C for 5 minutes at 5 bar pressure. Fibres were discharged through a blow-line without resin application and dried in a tube drier. Wood moisture content of the fibres after drying was approximately 10 % (wt).

Wood flour (Lignocel® BK 40/90, particle size 300 – 500 µm, J. Rettenmaier & Söhne GmbH + Co. KG, city, country) was used as reference filler material.

Retted and mechanically processed hemp fibres (type KFS fine, average fibre length 10 – 20 mm, initial moisture content of 10 % (wt)) were provided by Badische Naturfaseraufbereitung GmbH (BAFA), Malsch, Germany.

Polypropylene (PP) fibres (Asota Ges.m.b.H, Linz, Austria) used had a length of 6 mm and a melt flow index (MFI) of 10-12 g/10 min and contained ethylene as a copolymer. In addition, isotactic PP fibres without a copolymer were used (Belgian Fibres, Mouscron, Belgium; 6 mm length, MFI 13 g/10min).

A low-molecular, maleic anhydride-modified PP (MAPP; Licocene® PP MA 6252, Clariant GmbH, Gersthofen, Germany) was used as coupling agent. MAPP was supplied in granular form, with a high graft content of 7 % maleic anhydride and a melting point of approx. 140 °C. An ester wax-based lubricant (Licomont® ET 141, Clariant GmbH, Gersthofen, melting point between 76 °C und 81 °C) provided in flake form was used to improve extrudability.

2.2 Compounding and extrusion

Wood refiner fibres and hemp fibres were either used separately or in various mixtures (Table 1). Compounds based on wood flour were prepared to serve as reference. The weight percentage of wood refiner fibres, hemp fibres or wood flour was kept constant at 70%. Two compounds based on PP fibres, type Belgian fibres, were prepared for dynamic mechanical analysis (DMA) because these fibres consisted of PP only (no copolymer like in Asota fibres). Prior to compounding, both types of fibres and the wood flour were dried at 100 °C until a moisture content of less than 6% (wt) was obtained. A thermokinetic mixer (type TSHK 100, Papenmeier / Lödige, Paderborn) was used for preparation of compounds. A plough-blade mixer (type FM 130 DS, Lödige, Paderborn) was used for cooling and further granulating of

the compounds. The moisture content of the prepared compounds was approx. 1% (wt).

Compounds were extruded into tape profiles (4 mm x 40 mm) on a 58 mm, conical, counter-rotating twin-screw extruder (Cincinnati Titan 58). A crammer feeder (type KSW, Kreyenborg GmbH, Münster, Germany) was used to add the compounds into the extruder. Extrusion temperatures were between 150 °C and 170 °C.

2.3 Isolation and characterisation of natural fibres and wood flour following processing

Natural fibres and wood flour were extracted from the thermoplastic matrix following compounding and following extrusion to determine the effect of processing on fibre geometry. Extraction was performed as follows: 3 g of compounded or extruded material were added into a 250 ml round bottom flask which was subsequently filled with 100 ml of xylene (boiling point 145 °C). The sample was boiled under reflux for two hours in a Soxhlet extractor. After complete dissolution of PP, wood fibres and particles were obtained by filtering the solution through a glass frit (porosity 2) using a vacuum pump. Glass frits were dried in an oven at 105 °C. Geometry of extracted fibres and particles was optically evaluated using a digital camera.

2.4 Determination of mechanical and physical properties of extruded WPC

Specimens for mechanical and physical property testing were machined by conventional techniques. The largest sample dimension was coincident with the extrusion direction. Composite surface layer was not removed because sample thickness required for testing was 4 mm and therefore coincident with extruded tape profiles. After cutting, specimens were conditioned to constant weight (less than 1% change during 24 hours) at 20°C and 65% relative humidity and weighed to the nearest 0.001 g. Flexural strength and modulus of elasticity (MOE) of ten specimens per formulation (sample size $80 \times 10 \times 4 \text{ mm}^3$) were determined according to modified DIN EN 310 (modification consists in sample size) using a three-point bending test on a universal testing machine (Zwick 1474); support span was 64 mm and test speed was 3 mm per min. Tensile strength and MOE of ten specimens per formulation were determined on dumb-bell shaped specimens (type 1B) according to DIN EN ISO 527-2 on a universal testing machine (Zwick 1474); test speed was 2 mm per min. Charpy impact bending strength of ten specimens per formulation was

determined on a pendulum-type test machine (Zwick, type 5102) equipped with a 1 J - pendulum according to DIN EN ISO 179-1 for unnotched specimens (type 1) in flatwise impact direction; specimen size was identical with specimen size for flexural strength tests. Support span was 62 mm.

Water absorption and volume change of eight specimens per formulation (sample size $50 \times 40 \times 4 \text{ mm}^3$) were determined according to modified DIN EN 317. Specimens were measured, weighed, and submerged in water. After 7, 14 and 21 days, specimens were retrieved and blotted dry with paper towels. Water uptake (w) of specimens was determined using the following equation:

$$w = \frac{w_{wet} - w_{original}}{w_{original}} \cdot 100$$
 (%)

where w_{wet} = weight after submersion and $w_{original}$ = initial weight after equilibration at 20 °C and 65% relative humidity.

Volume change (v) of specimens was determined using the following equation:

$$v = \frac{v_{wet} - v_{original}}{v_{original}} \cdot 100$$
 (%)

where v_{wet} = volume after submersion and $v_{original}$ = initial volume after equilibration at 20 °C and 65% relative humidity.

2.5 Dynamic mechanical analysis

Dynamic mechanical analysis was conducted in dual cantilever mode in a Tritec 2000 analyzer (PerkinElmer; formerly Triton Technology Ltd, Keyworth, United Kingdom). Specimen dimensions within clamped supports were $35 \times 6 \times 2 \text{ mm}^3$. Dynamic temperature scans from -40° C to $+100^{\circ}$ C were conducted with selected specimens at sequential frequencies of 0.1 Hz, 1 Hz and 10 Hz and with an amplitude of 50 µm. Prior to beginning of measurements, specimens were cooled to below -40° C using liquid nitrogen. When a temperature of -40° C was reached, measurements were started using a constant heating rate of 2 K/min. DMA was performed using pure PP and WPC formulations 10 und 11 (Table 1) because these

 formulations contained pure PP (Belgian Fibres) as a matrix material (no copolymer like in Asota-Fibres). Three specimens per formulation were tested.

The activation energy for the glass transition (B-transition) of WPC was calculated using the Arrhenius equation (Turi 1997):

$$k = A_e \exp\left[-\frac{E_a}{RT}\right]$$

where k = rate constant or test frequency; A_e = frequency factor; R = ideal gas constant; 8.314 J/(mol K); T = temperature (K); E_a = activation energy. The peak temperatures of E" at different frequencies were determined using Tritec 2000 DMA software.

3 Results and Discussion

3.1 Characterization of natural fibres and wood flour following processing

Structure of natural fibres and wood flour after compounding as well as after extrusion was observed using WPC containing 70% refiner wood fibres or hemp fibres or wood flour. Following compounding in the thermokinetic mixer, structure and initial high aspect ratio of refiner wood fibres were maintained with fibre lengths of up to 5 mm (compare Figures 1 and 3). After extrusion, refiner fibre length and aspect ratio were significantly reduced (Figure 4) due to the high shear forces occurring during extrusion. The same observation was made for WPC compounds and extruded profiles based on mechanically processed hemp fibres (figures not shown). In addition, hemp fibres were strongly entangled and could not be isolated after extraction from the thermoplastic matrix. In contrast to the two natural fibres used, low aspect ratio of the wood flour was not significantly changed after compounding and extrusion (Figures 2, 5 and 6). Mechanical damage to the wood flour particles during extrusion appears to be insignificant compared to damage observed for the natural fibres. These results confirm investigations by Specht (2007) who determined severe reductions of natural fibre aspect ratios during processing in a counterrotating twin-screw extruder. Fibre damage occurring during twin-screw extrusion was also found to be more severe compared to other compounding methods, i.e., use of a Palltruder[®] or thermokinetic mixer (Specht 2007).

In addition to screw design, die geometry has an influence on resulting fibre structure. In our extrusion trials, a relatively large amount of material was forced through a small die (4 mm x 40 mm). The Titan 58 extruder works usually with a recommended throughput of about 100 kg /h. However, the implemented throughput was only a small part of that. This caused a very long residence time and should be partially the reason for fibre damage. It is likely that fibre damage can be reduced when using a much larger die and when using a co-rotating extruder instead of a counter-rotating extruder. These issues are currently under investigation.

3.2 Mechanical and physical properties of extruded WPC

3.2.1 Flexural strength properties

Flexural strength was highest for WPC containing hemp fibres and MAPP (34 N/mm²), followed by WPC containing wood flour and MAPP (30 N/mm²; Figure 7). WPC based on refiner wood fibres and MAPP displayed lower flexural strength (24 N/mm²). Refiner fibres were more severely damaged during extrusion than hemp fibres. This is probably due to the initially higher fibre length of the hemp fibres compared to the refiner fibres resulting in a lower potential for fibre shortening and damage.

Another observation was that the composites with hemp and no MAPP displayed similar strength values to the WPC with wood flour and no MAPP and that strength values of WPC with refiner fibres and no MAPP were lowest overall. This indicates that both wood and hemp fibres were not well dispersed in the thermoplastic matrix. When fibres are used without effective dispersion, the potential benefits of improved mechanical properties are negated (Wolcott and Englund 1999).

Overall, the use of MAPP resulted in improved flexural strength compared to uncoupled formulations (Figure 7) which is a well-known effect (Woodhams et al. 1984, Dalväg et al. 1985, Felix et al. 1993, Stark and Rowlands 2003). Flexural strength due to application of MAPP was improved by 126 % for the hemp fibre-based WPC, by 109 % for the wood fibre-based WPC and by 88 % for the wood flour-based WPC.

Flexural strength of formulations increased with increasing amount of hemp fibres used (Figure 8). In addition to processing effects, morphological aspects and chemical composition of the hemp fibres may account for the observed differences in

strength properties between WPC with refiner wood fibres and hemp fibres. With regard to morphology, microfibril angle of the secondary cell wall (S2) of hemp fibres is lower (2°; Reußmann 2003 and references therein) than microfibril angle of the wood fibre (10 to 30 °; Walther 2006). A low microfibril angle leads to a high degree of orientation of cellulose chains. This in turn leads to high values in strength properties. In addition, hemp fibres contain more cellulose (60-72%) and less lignin (2-5%) than wood (Walther 2006) and therefore display better strength properties than wood fibres.

Gehrmann et al. (2004) determined flexural strength values of approximately 80 N/mm² for WPC based on refiner wood fibres; however, WPC were manufactured by pressing panels (Gehrmann 2008) which lead to a high degree of fibre orientation, and different formulations were used.

Schirp and Wolcott (2005) used a slit die for extrusion similar to the die used in the present study and reported flexural strength of approx. 14.7 N/mm² for formulations containing 70% wood flour. Formulations by Schirp and Wolcott (2005) also included phenolic and methyl di-isocyanate resins which are highly effective coupling agents in WPC; this means that flexural strength values obtained in the present study using refiner wood fibres (24 N/mm², including MAPP) are very promising.

Migneault et al. (2008) reported flexural strength values of up to 44 N/mm² for extruded WPC based on short CTMP white birch fibres, however, the amount of fibres used was not more than 40% (wt). It was also determined that flexural strength increased with increasing fibre length.

With regard to flexural MOE, in this study, the use of refiner fibres and hemp fibres did not lead to an improvement compared to wood flour, despite the use of MAPP as a coupling agent (Figure 9). This indicates that fibres were shortened and not uniformly dispersed in the matrix during extrusion. Strength and stiffness increases can be realized with increasing fibre length if (1) adhesion between wood fibres and the plastic matrix is good; (2) fibres are uniformly dispersed in the matrix; and (3) fibres are adequately oriented (Migneault et al. 2008).

Flexural MOE increased with increasing amounts of hemp fibres used in WPC formulations (results not shown). Flexural MOE for the formulation with 70% wood refiner fibres and without hemp fibres was 3,309 N/mm². When 70% hemp fibres

were used and wood refiner fibres were omitted, flexural MOE increased to 4,582 $\ensuremath{\text{N/mm}^2}\xspace$

3.2.2 Tensile strength properties

Maximum tensile strength of approx. 13 N/mm² was achieved using either 70% hemp fibres or wood flour (Figure 10) whereas the use of wood refiner fibres resulted in lower tensile strength (approx. 10 N/mm²). Higher values for tensile strength of hemp fibre-WPC can likely be explained with the lower microfibril angle of the secondary cell wall in hemp as well as the higher cellulose content of hemp fibres compared to wood (compare previous section).

With increasing amounts of hemp fibres used in the formulations, no apparent trend was observed with regard to tensile strength of WPC (data not shown). This result has not yet been explained, and further experiments are required.

Application of MAPP resulted in significant increases in tensile strength. Tensile strength was increased by 107% for WPC based on wood flour, by 198% for WPC based on hemp fibres and by 212% for WPC based on wood fibres.

Under the extrusion conditions used in this study, initially high aspect ratios of both fibre types used did not result in high tensile strength. Higher tensile strength was reported by other authors (e.g., Stark and Rowlands 2003, Gehrmann et al. 2003), however, it has to be stressed that in most other studies, wood refiner fibres were processed differently and used in different weight percentages. Stark and Rowlands (2003) reported tensile strength values of up to 52 N/mm² for injection-moulded WPC based on refiner wood fibres. Gehrmann et al. (2003) manufactured WPC panels using wood refiner fibres and determined tensile strength values of 47 N/mm².

Considering that tensile strength of pine wood fibres is between approximately 400 N/mm² and 1400 N/mm² (Groom et al. 2002) and that tensile strength of hemp fibres is about 1000 N/mm² (Snell et al. 1997), tensile strength of WPC based on these fibres is relatively low. Several factors may account for this observation, e.g., mechanical and thermal fibre damage during processing, insufficient fibre-matrix adhesion and load transfer from matrix to fibres, and inhomogeneous dispersion and orientation of fibres (Wolcott and Englund 1999, Migneault et al. 2008).

 Results for tensile MOE are not shown due to high standard deviation in the values determined. A possible explanation is that tensile MOE may be more sensitive to inhomogeneous dispersion of fibres and MAPP in the thermoplastic matrix than flexural MOE. Lack of fibre orientation may also have contributed to variation in the values determined for tensile MOE.

3.2.3 Charpy impact bending strength

Highest impact bending strength was obtained when hemp fibres and MAPP were used (3.4 N/mm², Figure 11). With increasing amounts of hemp fibres, impact bending strength increased (results not shown). Only slight differences in impact bending strength of WPC based on wood refiner fibres and wood flour were observed. Overall, the use of MAPP has lead to improved impact bending strength; however, improvements due to MAPP were not nearly as high as for flexural and tensile strengths. Impact bending strength was increased by 28% for refiner fibre-based WPC, by 25% for hemp fibre-based WPC and by 18% for wood flour-based WPC due to the application of MAPP.

It is expected that impact bending strength values can be optimized using various strategies. Gehrmann et al. (2004) report values of approximately 10 kJ/m² for WPC panels based on refiner wood fibres, and Migneault et al. (2008) state values of up to 6 kJ/m^2 for extruded WPC based on short CTMP fibres.

3.2.4 Water absorption and volume change of WPC

Water absorption of composites was still on-going after 21 days, however, the largest amount of water had been absorbed within the first 14 days of water storage (Figure 12). The formulation containing hemp fibres and MAPP absorbed the least amount of water (approx. 22% by wt.). Overall, the application of MAPP caused a reduction in water uptake which is a well-known effect (Bledzki et al. 1998). Maleic anhydride grafted on synthetic polymers such as polypropylene forms covalent ester linkages and hydrogen bonds when reacting with hydroxyl groups at the cellulose interface (Felix and Gatenholm 1991). As MAPP couples the polar surfaces of the wood to the unpolar polypropylene, the repulsion forces between these two materials are

lowered. This leads to a decrease in voids within the composites and hence, blocks the pathways for water penetration.

Overall, the highest reduction of water uptake due to MAPP was observed for the WPC with wood flour (29% reduction). This effect was not as pronounced for WPC with hemp fibres and refiner wood fibres, which indicates that the coupling agent may have been better dispersed in formulations with wood flour than in formulations containing fibres.

Water absorption of WPC produced in this study appears high, however, water absorption of commercial WPC products has been shown to be as high as 40% with maximum water absorption reached after 21 days only (Gnatowski 2005). In addition, large water uptake would be expected because the test samples had small thicknesses.

The higher the percentage of hemp fibres used in the formulations, the lower the water uptake (results not shown). This observation can be explained by the differences in chemical composition of hemp and wood fibres; hemp fibres contain only 11-19 % (hydrophilic) hemicelluloses (Walther 2006) while wood fibres contain up to 30% hemicelluloses (Sjöström 1993). In addition, it has to be considered that the chemical composition of the wood fibres was changed during the refining process. During thermomechanical pulping, low-molecular carbohydrates and part of the lignin are solubilised. The total amount of water-soluble and gaseous substances produced during thermomechanical pulping is approx. 5% of the wood dry weight (Lohmann 2003).

Figure 13 shows the volume change of WPC following water storage. WPC with wood refiner fibres and MAPP displayed the lowest volume change (19 %), followed by WPC with hemp fibres and MAPP and WPC with wood flour and MAPP. As with water uptake, volume change was significantly reduced due to the use of MAPP. The higher the proportion of hemp fibres in the formulations, the higher the volume change (results not shown).

3.3 Dynamic mechanical analysis of extruded WPC

The effect of the coupling agent (MAPP) on the WPC interphase was investigated using DMA. Storage modulus E' and loss modulus E' of formulations with 35% wood refiner fibres and 35% hemp fibres and with or without MAPP are shown in Figure 14.

For comparison, results for pure PP (Belgian Fibres) are included. The maximum of the loss modulus is at approximately 0°C which corresponds to the glass transition (β-transition) temperature (T_G) of the polypropylene matrix (Boyd 1985). A second maximum of the loss modulus is indicated at approximately 60°C for the formulation containing MAPP. This second maximum is referred to as α-relaxation and is characteristic for semi-crystalline polymers such as PP; at this temperature, amorphous components in the crystalline phase achieve higher mobility (Gedde 1995, Harper 2003).

Overall, it is apparent that the maximum of the loss modulus is higher for the formulation with MAPP than for the formulation without coupling agent. This means that the use of the coupling agent resulted in improved adhesion of the fibres to the thermoplastic matrix.

The maximum of the loss modulus for the PP matrix is below the maxima of the two WPC formulations. Increased loss modulus and hence, increased temperatures for glass transition of WPC compared to pure PP are due to reduced mobility of the polymer chains caused by the addition of fibres to the thermoplastic matrix (George et al. 1996).

Activation energies for glass transition (β-transition) were calculated by determining maximum temperatures of the loss modulus at different frequencies and by rearranging the Arrhenius equation (Turi 1997). Activation energy refers to the energy required to facilitate a reaction between two molecules or the energy required to cause a molecule of a polymer chain segment to jump from its present position to a nearby hole (Son et al. 2003). Figure 15 shows the Arrhenius plots for the extruded WPC without MAPP; similar plots were prepared for formulations with MAPP. Activation energy for glass transition in formulations containing MAPP was higher (480 kJ/mol) than for formulations without MAPP (418 kJ/mol) which indicates improved interfacial adhesion due to the coupling agent (Son et al. 2003). Values determined for activation energy are in the same range as values reported by Son et al. (2003) for a WPC formulation containing 60% pine wood flour, 38% PP and 2% MAPP (373 kJ/mol).

4 Conclusion

To our knowledge, this is the first published feasibility study in which long refiner wood fibres and hemp fibres were used in a large amount (70 weight-%) for WPC extrusion and without a pelletizing step. It was surprising to see that extruded WPC containing wood or hemp fibre without MAPP did not display improved strength compared with composites containing wood flour. This goes against composite strength theory, with larger aspect ratios leading to improved stress transfer from matrix to fibre. Consequently, this is an indication of poor fibre dispersion in the polymer matrix.

When MAPP was used, flexural strength values of WPC with hemp fibres were slightly superior to those of the WPC with wood flour. This indicates that there is a benefit when using high aspect ratio-fibres as compared to wood flour. Additional experiments are currently on the way to determine aspect ratios of wood flour, wood fibres and hemp fibres before and after processing and to shed more light on the role of fibre attrition during processing. At this stage, the most important conclusion is that adding hemp or wood fibres to improve mechanical properties is not beneficial if the processing conditions are not optimal. The use of a co-rotating twin-screw extruder with large screw diameter may lead to a reduction in fibre damage. If challenges related to fibre damage during extrusion can be overcome, optimum fibre length for refiner fibres will need to be determined. Achieving optimum refiner fibre length during extrusion should result in new, structurally demanding applications for WPC.

Fibre-matrix adhesion in selected WPC formulations was investigated using dynamic mechanical analysis, and activation energies for glass transition were calculated. It was determined that stronger fibre-matrix adhesion was achieved in formulations containing maleic-anhydride-modified polypropylene.

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Figure 1: Refiner wood fibres before compounding. Abb. 1 Refinerfasern vor der Compoundierung.



Figure 2: Wood flour before compounding.

Abb. 2 Holzmehl vor der Compoundierung.



Figure 3: Extracted refiner wood fibres after compounding in a thermokinetic mixer (compound 1: 70% refiner wood fibres; 25.5% polypropylene fibres; 3% MAPP; 1.5% lubricant).

Abb. 3 Extrahierte Refinerfasern nach der Compoundierung im Heizmischer (Compound 1: 70% Refinerfasern; 25,5% Polypropylenfasern; 3% MAPP; 1,5% Gleitmittel).

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Figure 4: Extracted refiner wood fibres after extrusion (compound 1: 70 % refiner wood fibres; 25.5 % polypropylene fibres; 3 % MAPP; 1.5 % lubricant).

Abb. 4 Extrahierte Refinerfasern nach der Extrusion (Compound 1: 70% Refinerfasern; 25,5% Polypropylenfasern; 3% MAPP; 1,5% Gleitmittel).



Figure 5: Extracted wood flour after compounding in a thermokinetic mixer (compound 8: 70 % wood flour; 25.5 % polypropylene fibres; 3 % MAPP; 1.5 % lubricant).

Abb. 5 Extrahiertes Holzmehl nach der Compoundierung im Heizmischer (Compound 8: 70% Holzmehl; 25,5% Polypropylenfasern; 3% MAPP; 1,5% Gleitmittel).



Figure 6: Extracted wood flour after extrusion (compound 8: 70 % wood flour; 25.5 % polypropylene fibres; 3 % MAPP; 1.5 % lubricant).

Abb. 6 Extrahiertes Holzmehl nach der Extrusion (Compound 8: 70% Holzmehl; 25,5% Polypropylenfasern; 3% MAPP; 1,5% Gleitmittel).

□ RF 70%, PP 28,5%, MAPP 0%
 □ HF 70%, PP 28,5%, MAPP 0%
 □ HF 70%, PP 28,5%, MAPP 0%
 □ WF 70%, PP 28,5%, MAPP 0%
 □ WF 70%, PP 25,5%, MAPP 3%



Figure 7: Flexural strength of extruded WPC based on 70% refiner wood fibres (RF), hemp fibres (HF) and wood flour (WF). Each formulation contained 1.5% lubricant. Abb. 7 Biegefestigkeit extrudierter WPC auf Basis von 70% Holz-Refinerfasern (RF), Hanffasern (HF) und Holzmehl (WF). Jede Formulierung enthielt 1,5% Gleitmittel.



Figure 8: Flexural strength of extruded WPC with 70% (wt) natural fibre and various proportions of refiner wood fibres (RF) and hemp fibres (HF). Each formulation contained 3% MAPP and 1.5% lubricant. Polypropylene represents the remaining component in each formulation. Abb. 8 Biegefestigkeit extrudierter WPC mit 70 Gew.% Naturfasern und unterschiedlichen Anteilen an Holz-Refinerfasern (RF) und Hanffasern (HF). Jede Formulierung enthielt 3% MAPP und 1,5% Gleitmittel. Der restliche Anteil an den Formulierungen besteht aus Polypropylen.

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□ RF 70%, PP 28,5%, MAPP 0%
□ HF 70%, PP 28,5%, MAPP 0%
□ HF 70%, PP 28,5%, MAPP 0%
□ WF 70%, PP 28,5%, MAPP 0%
□ WF 70%, PP 25,5%, MAPP 3%



Figure 9: Flexural MOE of extruded WPC based on 70% wood refiner fibres (RF), hemp fibres (HF) and wood flour (WF). Each formulation contained 1.5% lubricant. Abb. 9 Biege-E-Modul extrudierter WPC auf Basis von 70% Holz-Refinerfasern (RF), Hanffasern (HF) und Holzmehl (WF). Jede Formulierung enthielt 1,5% Gleitmittel.



Figure 10: Tensile strength of extruded WPC based on 70% wood refiner fibres (RF), hemp fibres (HF) and wood flour (WF). Each formulation contained 1.5% lubricant. Abb. 10 Zugfestigkeit extrudierter WPC auf Basis von 70% Holz-Refinerfasern (RF), Hanffasern (HF) und Holzmehl (WF). Jede Formulierung enthielt 1,5% Gleitmittel.



Figure 11: Impact bending strength of extruded WPC based on 70% refiner wood fibres (RF), hemp fibres (HF) and wood flour (WF). Each formulation contained 1.5% lubricant. Abb. 11 Schlagzähigkeit extrudierter WPC auf Basis von 70% Holz-Refinerfasern (RF), Hanffasern (HF) und Holzmehl (WF). Jede Formulierung enthielt 1,5% Gleitmittel.



 →
 RF 70%, PP 28,5%, MAPP 0%
 →
 RF 70%, PP 25,5%, MAPP 3%
 →
 HF 70%, PP 28,5%, MAPP 0%

 →
 HF 70%, PP 25,5%, MAPP 3%
 →
 WF 70%, PP 28,5%, MAPP 3%
 →
 WF 70%, PP 28,5%, MAPP 3%

Figure 12: Water uptake of extruded WPC based on 70% refiner wood fibres (RF), hemp fibres (HF) and wood flour (WF). Each formulation contained 1.5% lubricant. Abb. 12 Wasseraufnahme extrudierter WPC auf Basis von 70% Holz-Refinerfasern (RF), Hanffasern (HF) und Holzmehl (WF). Jede Formulierung enthielt 1,5% Gleitmittel.



60



Figure 13: Volume change of extruded WPC based on 70% refiner wood fibres (RF), hemp fibres (HF) and wood flour (WF). Each formulation contained 1.5% lubricant. Abb. 13 Volumenveränderung extrudierter WPC auf Basis von 70% Holz-Refinerfasern (RF), Hanffasern (HF) und Holzmehl (WF). Jede Formulierung enthielt 1,5% Gleitmittel.



Figure 14: Storage modulus E' and loss modulus E'' of formulations 10 und 11 and PP at a frequency of 1 Hz.

Abb. 14 Speichermodul E' und Verlustmodul E' der Formulierungen 10 und 11 und von PP bei einer Frequenz von 1 Hz.



Figure 15: Arrhenius-plots of three extruded specimens of formulation 11 (35% wood refiner fibres; 35% hemp fibres; 28.5% PP fibres; 1.5% lubricant).

Abb. 15 Arrhenius-Plots von drei extrudierten Proben der Formulierung 11 (35% Holz-Refinerfasern; 35% Hanffasern; 28,5% PP-Fasern; 1,5% Gleitmittel).

Table 1: Composition of WPC compounds. Values represent weight percentages.

Tabelle 1 Zusammensetzung der WPC-Compounds. Werte stellen Gewich	ntsprozente dar.
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Formulation number	Wood refiner fibres	Hemp fibres	Wood flour	PP-fibres (Asota)	PP-fibres (Belgian Fibres)	MAPP	Lubricant
1	70	0	0	25.5	0	3	1.5
2	52.5	17.5	0	25.5	0	3	1.5
3	35	35	0	25.5	0	3	1.5
4	17.5	52.5	0	25.5	0	3	1.5
5	0	70	0	25.5	0	3	1.5
6	70	0	0	28.5	0	0	1.5
7	0	70	0	28.5	0	0	1.5
8	0	0	70	25.5	0	3	1.5
9	0	0	70	28.5	0	0	1.5
10	35	35	0	0	25.5	3	1.5

 11	35	35	0	0	28.5	0	