Mendel University in Brno

Faculty of Forestry and Wood Technology

Department of Wood Science

Bio-based composites from agricultural residues and other waste materials

Doctoral Thesis

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2016

...If all you have is a hammer, everything looks like a nail...

Declaration

I declare that I have written the presented dissertation titled *"Bio-based composites from agricultural residues and other waste materials"* independently, and that I have used no other than the resources cited. I agree that my dissertation is published in compliance with § 47b of Act no. 111/1998 Coll., on universities, stored in the library of the Mendel University in Brno, and available for study purposes in compliance with the MENDELU Rector's Decree on archiving the electronic form of final studies.

Prohlášení

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Brno, 12.08.2016

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Petr Klímek

Abstract:

Klímek P. (2016) *"Bio-based composites from agricultural residues and other waste materials",* Dissertation thesis, Mendel University in Brno

The main goal of the dissertation is to suggest several types of bio-based composites, notably particleboards, made from alternative materials (bio-waste, waste, plants´ residues) as an alternative to the currently produced wooden particleboards. The thesis provides a review and synthesis of the state-of-the-art literature. In the first part the literature is summarized and basic economical and ecological aspects of wood replacements for particleboards by using alternative materials are discussed. Further, mechanical properties data of suggested alternative particleboards are compiled, to give state-of-art insights in alternative particleboards developments. In the state-of-art, the compiled literature data are analyzed through Ashby plots and give suggestions on what particleboards properties should be optimized. This evaluation have also proved that particleboards made from plants´ stalks, wood prunings and other wastes eg. waste tea leaves, peanut hulls, walnut shells could be economically viable alternative for the industry. The second part of this dissertation is concerned with designing and developing particleboards from the alternative resources available in Central Europe: (1) In total, 16 types of particleboards were produced from stalks coming from cup plants, Miscanthus, sunflower and topinambour. These particleboards are specified by standard mechanical tests and the effects of resin content and resin type were studied. Also chemical analysis were performed to determine the cellulose, hemicellulose and lignin contents. Structure of the Miscanthus particleboard were characterized by scanning electron microscopy (SEM). (2) Particleboards were also made and evaluated with different wastes. Particleboard made from BSG (Brewer´s spent grain) were characterized by their mechanical properties, chemical composition and microscopic structure (SEM). Further, polyethylene terephthalate (PET) waste was added to wooden particleboards. Here, in addition to mechanical properties also microscopic structure and bond failures were analyzed using SEM, with air-plasma treated PET particles studied by chemiluminescence and x-ray photoelectron spectroscopy (XPS) for their altered surface chemistry. The final section presents eight particleboard types made from recovered painted wood, as reclaimed from window frames. The effect of painted particles on the physical and mechanical properties were evaluated.

With respect to possible applications the most important finding is that all particleboards from plants stalks fulfilled minimal requirements of class P1 in EN 312, which is for general purposes in dry conditions. Furthermore, a three-layer particleboard with spruce surface layers, and a core-layer made from cup-plant would provide a regular appearance of the panel surfaces. Particleboards having 10 % BSG also fulfilled the P1 requirements of EN 312. The particle-particle bonding was found to be a weak point in a entire internal bonding system. To improve internal bonding experiments with plasma-treated beech wood particles bonded by PVAc was performed. Results have shown a significant improvement of internal bonding due to the plasma treatment. Consequently, the identical plasma treatment was applied to PET particles, which were mixed with wood in the particleboards. Bonding was here improved as well, with the IB higher compared to the untreated control. It was shown that plasma treatment has potential to compensate for declined IB of particleboards using alternative sources. In final part of this thesis, particleboards from reclaimed wood from painted window frames were produced. Results have shown that particleboards using painted-reclaimed wood as well as cleaned reclaimed wood deliver a performance comparable with regular wooden particleboards, as well as reduced thickness swelling.

Key words: Bio-composite, particleboard, mechanical properties, composites, waste, cleaner production, manufacturing, resource efficiency, agriculture, residues

Abstrakt:

Klímek P. (2016) *"Bio-based composites from agricultural residues and other waste materials",* Dissertation thesis, Mendel University in Brno

Hlavním cílem této dizertační práce je navrhnout několik typů dřevotřískových desek z alternativních materiálu jako jsou například bioodpady, odpady, zbytky z rostlin apod. Dizertační práce dává ucelený přehled formou literárního přehledu, který se zabývá obdobnou tématikou. V první části, literární zdroje jsou shrnuty a ekologický, rovněž pak ekonomická diskuze dat zjištěných z literárního přehledu je diskutována. Následně mechanické vlastnosti desek získané z literárního přehledu jsou shromážděny a sumarizovány tak aby daly přehled o tom, které vlastnosti mají být vylepšeny s ohledem na různé typy dřevotřískových desek. Toto objektivní srovnání, běžné pro obor vývoje materiálů, dokázalo, že především dřevotřískové desky ze stonků rostlin, větví dřeva a některých odpadů mohou při určitých podmínkách konkurovat klasickým dřevotřískovým deskám. V další části dizertační práce je uveden vlastní návrh a postup výroby dřevotřísek ze zdrojů dostupných ve střední Evropě. 16 typů dřevotřísek bylo vyvinuto rostlin: Mužáku prorostlého (*Silphium perfoliatum*), Slunečnice roční (*Helianthus annuus*), Ozdobnice čínské (*Miscanthus x gigantheus*) a Topinamburu (*Helianthus tuberosus L.*). Tyto dřevotřískové desky jsou specifikovány jejich mechanickými vlastnostmi a je pozorován především efekt množství a typu lepidla. Použitý materiál pro výrobu je pak rovněž specifikován chemickým složením a to množstvím celulózy, ligninu a hemicelulózy. Navíc je popsána mikroskopická struktura dřevotřískové desky vyrobené z Ozdobnice čínské pomocí elektronové mikroskopie. V druhé části dizertační práce jsou popsány mechanické a fyzikální vlastnosti dřevotřískových desek vyrobených z odpadů a bio-odpadů. Jako první, mechanické vlastnosti dřevotřískové desky s třískami nahrazenými mlátem (odpad pivovarů) jsou specifikovány. Rovněž v tomto případě je mláto specifikováno chemickým složením a to množstvím celulózy, hemicelulóz a ligninu. Mikroskopická struktura desky je pak popsána snímky elektronové mikroskopie. Jako další je vyrobena a zkoumána dřevotřísková deska s částicemi nahrazenými PET recyklátem. Předmětem výzkumu je především vliv plasmatické úpravy povrchu PET částic na mechanické vlastnosti desek s jejich přídavkem. V tomto výzkumu, krom standardních zkoušek mechanické specifikace desek a elektronové mikroskopie jejich struktury, rentgenová fotoelektronová spektrometrie (XPS) a chemiluminescence je použita pro měření chemické aktivity povrchu plasmaticky upravených a neupravených PET částic. Poslední publikace pak popisuje fyzikální a mechanické vlastnosti desek vyrobených z recyklovaného

dřeva získaného z okenních rámů. Je zkoumán vliv obsahu barvou kontaminovaných částic na fyzikální a mechanické vlastnosti desek.

S ohledem na praktické výsledky, jedním z nejdůležitějších výsledků je, že desky vyrobené ze stonků rostlin splnily požadavky normy EN 312 pro obecné použití v suchém prostředí. Nevýhodou těchto desek byla nižší pevnost a tuhost v ohybu. S ohledem na tyto výsledky byla vyvinuta deska, která má povrchovou vrstvu tvořenou smrkovými částicemi a jádro z částic získaných z rostliny Mužáku prorostlého (*Silphium perfoliatum*). Díky této kombinaci tato deska má vzhled povrchu jako klasická dřevotřísková deska. Rovněž dřevotřísková deska s 10ti procentní příměsí mláta splnila požadavky normy EN 312 pro obecné použití v suchých podmínkách. Zároveň výsledky elektronové mikroskopie naznačily, že pozice mlátových částic je zodpovědná za snížení vlastností desek. Elektronová mikroskopie identifikovala mikrostrukturu i u další desky vyrobené z Ozdobnice čínské, která rovněž splnila minimální standardní požadavky na mechanické vlastnosti. Pro zlepšení lepení částic v kompozitech byla navrhnuta povrchová úprava materiálu plasmou. V prvním pokusu, plasmaticky pravené bukové dřevo bylo lepeno PVAC lepidlem. Výsledky prokázaly, že plasmatická úprava výrazně zvyšuje pevnost lepení dřeva. Z tohoto důvodu, ta samá úprava byla použita na částice PET, které nahradily v určitém poměru dřevo v dřevotřískových deskách. Plasmatická aktivace napomohla zlepšit vlastnosti lepení v kompozitu, jelikož pevnost v tahu kolmo na plochu desky vyrobené z plasmaticky upravených PET částic zůstaly nezměněny. S ohledem na obě tyto publikace se můžeme domnívat, že plasmatická úprava částic, může zvýšit mechanické vlastnosti desek vyrobených z alternativních materiálů. V poslední části dizertační práce bylo dokázáno, že dřevotřísky mohou být vyrobeny z recyklovaného dřeva okenních rámů a jejich vlastnosti jsou stejné jako těch, které jsou vyrobené ze smrkového dřeva. Zajímavostí zde bylo především pak bobtnání desek, které bylo s největší pravděpodobností sníženo díky částicím pokrytých barvou. Toto bylo dokázáno formou mikro mechanického hodnocení bobtnání formou optického měření deformací (DIC).

Klíčová slova: bio-komposity, dřevotřísková deska, mechanické vlastnosti, kompozity, odpad, výroba, čistší produkce, účinné, zemědělství, zbytky rostlin

Preface

I would like to express gratitude to the Deutsche Bundesstiftung Umwelt and their stipendiemprogramm for supporting my project "Green composites for sustainable future" which helped to fund my research stay at Fraunhofer-Institut für Holzforschung - Wilhelm-Klauditz-Institut WKI. My endless gratitude belongs also to the commission of J. William Fulbright in Prague and the Fulbright-Masaryk Scholarship for providing me a necessary funding for my visit at Oregon State University and fund the project "Bonding mechanisms in bio-based composites by means of a micromechanical approach".

A big thanks belongs to my supervisor and maybe more closely in German language "doktorvater" for helping me throughout the difficulties which we have encountered during my doctoral studies. Thank you very much for being the role model and showing me by example that there is no such a thing like ultimate achievement. I would like to thank also to my two, unofficial, supervisors. Thank you Dipl.-Phys. Peter Meinlschmidt for tremendous professional and personal help, which you have provided me during my stay at Fraunhofer-Institut für Holzforschung - Wilhelm-Klauditz-Institut WKI. Last but not least thank you Dr. Lech Muszynski, for being my mentor and advisor during the Fulbright scholarship at Oregon State University.

I would like to thank my little brother Jan and my grandparents for supporting and encouraging me all the time. A big thanks belongs also to my amazing girlfriend for inspiring me for so many years and keeping my feet on the ground and reminding me by example that work should be fun, but at the end it is just work.

Content

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List of Abbreviations

ANOVA	analysis of variance
AOI	area of interest
BSG	brewer´s spent grain
CL	chemiluminescence
CP	cup plant
DCSBD	diffuse coplanar surface barrier discharge
DIC	digital image correlation
dpi	dot per inch
EN	European norm
ep	epidermis
EPF	European Panel Federation
EU	European Union
FOV	field of view
IB	internal bonding strength
MDF	medium density fiberboard
MDI	methylene diphenyl diisocyanate adhesive
MOE	modulus of elasticity
MOR	modulus of rupture
MUF	melamine urea formaldehyde adhesive
PB	particleboard(s)
PET	polyethylene terephthalate
PF	phenol Formaldehyde adhesive
pMDI	polymeric MDI
PVAC	polyvinyl acetate adhesive
rpm	rounds per meter
SEM	scanning electron microscopy
SF	sunflower
SP	spruce
TP	topinambour
TS	thickness swelling
TZ	transition zone
UF	urea formaldehyde adhesive

VDP	vertical density profile
WA	water absorption
XPS	x-ray photoelectron spectroscopy

1. Introduction

Wood-based particleboards have a more than 120 year tradition, starting from 1887 (Hubbard 1887). Particleboards were initially developed to accommodate wastes coming from sawmills and other wood processing sites, as a low-cost alternative to a blockboard (wood-core plywood, "Tischlerplatte") and plywood. Since, particleboards have grown in popularity and they hold nowadays the strongest position on the wood-based panel market, representing over 60 % of the entire wood-based panel production in the European Union. The total volume of particleboards produced in Europe equals to 28.4 million m^3 per anno (EPF, 2014). That volume is of course not produced based just on waste wood, as the majority of the raw material for particleboards (~70 %) is low-grade virgin wood. Low-grade timber, however, is also used in variety of structural products such as cross-laminated timber or glued-laminated timber (Glulam). These circumstances, along with occasional shortages in the wood supply are contributing to increasing costs for wood chips (Eastin et al., 2012). Prices for wood chips have gone up by 30 % between 2006 and 2011. It is obvious that increased prices for wood may have a negative effect not the sustainability in particleboard production, with higher market prices for particleboards and lower competitiveness. In response to an anticipated shortage of wood, strategies to achieve a higher resource efficiency have been initiated (European Commission, 2011; Fischer-Kowalski et al., 2013). Goal is to achieve a cleaner and more environmental friendly production, and sustain the European resource utilization. Furthermore, the currently increased raw material prices may motivate companies to improve their productivity, and invest also in more resource-efficient technologies (Giljum et al., 2009). It seems that suggestions for new particleboard types made with various wastes is welcomed politico-economically, as well as industrially. In conclusion, it might be now the time to return to the initial motivations for particleboard production. Should modern and high-end particleboard production plants consider more non-wood wastes coming from agricultural sources? Would such an approach be in compliance with European resource efficiency strategies, with a viable profitability for the industry at the same time?

1.1 Aims of study

1. Suggest and develop of alternative particleboards made from agricultural residues, waste and recycled materials, and assess the feasibility for industrial production.
2. Examine physico-mechanical properties (modulus of elasticity, modulus of rupture, internal bonding strength, density and thickness swelling) of alternative particleboards

according to European standards and compare the property profiles with conventional particleboards.

3. Study structure-property relationships of alternative materials as used in particleboards.

4. Assess possible applications of alternative particleboards based on their properties and suggest options to compensate for recuced properties.

1.2 List of papers

This doctoral thesis is a summary of the following papers:

Paper I.

Klímek P., Meinlschmidt P., Plinke B., Wimmer R., Schirp A. (2016) *Utilization of cup plant (Silphium perfoliatum L.), sunflower (Helianthus annuus L.) and topinambour (Helianthus tuberosus L.) stalks as a raw material for particleboard production.* 92 (2016) 157-164. **Industrial Crops and Products.** DOI: 10.1016/j.indcrop.2016.08.004

Paper II.

Klímek P., Meinlschmidt P., Kúdela J., Wimmer R. (2016) *Study of Miscanthus (Miscanthus x gigantheus) stalks as a material for particleboard production.* (In preparation for Industrial Crops and Products)

Paper III.

Klímek P., Meinlschmidt P. Wimmer R. (2016) *Production and characterization of one layer and three layer particleboard from cup plant (Silphium perfoliatum) stalks.* (In preparation for Industrial Crops and Production)

Paper IV.

Klímek P., Kumar K, P., Wimmer R., Kúdela J. (2016) *Utilization of brewer´s spent-grains as a material for wood-based particleboard manufacturing.* Journal of Cleaner Production (under review)

Paper V.

Král P., Ráhel´ J., Stupavská M., Šrajer J., **Klímek P.,** Kumar M. P., Wimmer R. (2014) *XPS depth profile of plasma-activated surface of beech wood (Fagus sylvatica) and its impact on polyvinyl acetate tensile shear bond strength.* 49(2)319-330, **Wood Science and Technology**, DOI: 10.1007/s00226-014-0691-7

Paper VI.

Klímek P., Morávek T., Ráhel' J., Stupavská M., Děcký, D., Král P., Kúdela J., Wimmer R. (2016) *Air-plasma treated waste polyethylene terephthalate particles as a raw material for*

particleboard production. **Composites part B: Engineering**, 90(2016) 188-194, DOI: http://dx.doi.org/10.1016/j.compositesb.2015.12.019

Paper VII.

Meinlschmidt P., **Klímek P.** (2015) *Characterization of particleboards made from recovered painted wood*. European Journal of Wood and Wood Products (under review)

Paper VIII.

Klímek P., Meinlschmidt P., Wimmer R. (2015) *Microscopic swelling of wood based panels: First trials.* Proceeding: InWood2015: Innovations in wood materials and processes, 19-22.5, 2015, Brno, Czech Republic

2. Alternative raw materials for particleboards – a state of the art review

This state-of-the-art literature review in composed of four sections. (1) Availability of alternative materials based on prices and yield. (2) Alternative particleboard development overview using straw, plant stalks, prunings, other natural materials, and non-plant wastes. (3) Material selection strategies used to suggest alternative materials suited to replace wood in particleboards; mechanical properties to be optimized to achieve alternative particleboards meeting EN 312 standards.

2.1 Availability of alternative materials

Regarding prices for the materials obtained from agriculture resources, the applicability of common econometric tools is limited. Lack of data on production capacities, along with insufficient information on potential markets are both limiting the potential to estimate realistic market prices. Prices are highly dependent on the volume of local supplies, on the harvesting costs i.e. chopping, baling and on-farm hauling of crops, with baling to be considered as the most expensive step (Khachatryan et al., 2009). A central aspect that may turn higher prices to lower price ranges is seen in the level of producer participation in residue harvest (Gallagher et al., 2003). It must be kept in mind that residues in part utilized for different purposes, such as for cattle feeding, soil erosion control, or soil nutrition, with the consequence that final prices may be increasing as higher demands Price estimates for materials potentially suitable in particleboard production are listed in table 1.

Price for wood chips in Europe is currently 59–65 €/t (Icct 2014). Lesser used crop residues coming from agricultural plants such as corn stover (stalks and leaves), wheat straw, plant stalks may offer options for substantial particleboard production savings. Estimated prices for the plant residues are at least 50% below the prices for wooden chips (table 1). However, prices are valid for individual regions only, meaning they are subject to high variability, closely depending on transportation costs and the cultivated volume. In any case, however, with the assumption of long-term supply contracts, which should provide a secure financial background, price for crops residues should be not above 40 €/t (Icct 2014).

Costs for wood chips are ranked second, and they come right after the resin costs. For medium-sized particleboard plants (production < 140 000 m³/year) prices for wood chips may be as high as 4 Mio €/anno, which represent 20 % of the entire cost structure for a given

particleboard producer (including overheads). Thus, replacing wood by cheaper materials would provide substantial production cost savings.

Table 2-1. Price for the selected raw materials

Material type	Price	
Crops residues [US]	17 – 32 €/ t (Sokhansanj & Fenton 2006; Khachatryan et al. 2009)	13 – 27 €/ t (Gallagher et al., 2003)
Wheat straw [US]	24 – 35 €/ t (Perlack and Stokes, 2011)	19 €/ t (Gallagher et al., 2003)
Rice straw [US]	23 €/ t (Gallagher et al., 2003)	6 -37 €/ t (Jenkins et al. 2000)
Corn residues [US]	13 €/ t (Gallagher et al., 2003)	
Wood chips [EU]	59 – 65 €/t (Icct et al., 2014)	65 €/t (Spelter et al., 2008)

Medium-sized particleboard plant require 106 000 tons (dry mass) of wooden resources to produce 140 000 m³ of particleboards (Spelter et al., 2008). Strictly speaking, to produce 1 m³ particleboards, 0.75 t of raw materials are required as an input. The annually particleboard production in Europa of 28.4 million m³ is equaling to an approximated consumption of 21 Mio tons of wood. To convert that to forest land-use, with assuming 10 t·ha^{-1}·year^{-1} of forest biomass production (Pretzsch, 2009), 2.5 Mio ha of forest land are needed to secure the raw materials required for one year of wood-based particleboard production. If non-wood resources are seen as an option, they don't have to be necessarily cheaper, but should meet requirements such as (1) similar biomass yield, and (2) sufficient land availability.

Fortunately, the yield from agriculture plants may be similar or even higher compared to biomass production in forests (table 2). Yields with up to three times higher than forests are obtained with giant Miscanthus (*Miscanthus x giganteus*), with biomass production as high as 44 t·ha^{-1}·year^{-1} (Pyter et al., 2007), are known for Miscanthus (*Miscanthus x giganteus*) is becoming more and more popular in colder northern European climates (Monti et al., 2015; Parajuli et al., 2015) as a bioenergy crop (Ameline et al., 2015), or as a resource in chemical production (Arnoult et al., 2015; Kim et al., 2015). Higher yields than wood are also demonstrated by cup-plants (*Silphium perfolatium L.*). The yield of cup-

plants may reach 40 t·ha^{-1}·year^{-1}. This plant originates from Eastern North America (Stanford, 1990), but is now widely established across Central Europe. Although it was grown in gardens as an ornamental plant during the 18th century, it is nowadays widely cultivated for energy production (Haag et al., 2015). Aspects of cultivation and utilization of cup-plant is reviewed by Gansberger et al. (2015). The two agricultural plants are not cultivated for food purposes. New plantations may be done on lesser-used lands, with extensive pasture land not reported in agricultural statistics, with grasses and shrubs below 30 cm, herbaceous vegetation, grasses and shrubs below 30 cm. Currently, 24 Mio ha of land in Europe is unused. It can be assumed that 3 % of European unused land could be occupied by cup plant or Miscanthus, which would be sufficient to secure the raw material demand for the entire European particleboard production. In Czech republic ~1.5 Mio ha are available for additional cultivation (Keenleyside and Tucker, 2010).

Table 2-2. Yield for the selected raw materials

Material	Yield	
forest biomass	5.9 t·ha^{-1}·year^{-1} (Amaro et al., 2003)	6 - 16 t·ha^{-1}·year^{-1} (Pretzsch, 2009)
pulp wood	2 – 10 t·ha^{-1}·year^{-1} (Campinhos, 1999)	
Spruce wood	6.1 t·ha^{-1}·year^{-1} (Campinhos, 1999)	
Topinambour stalks	6 - 8 t·ha^{-1}·year^{-1} (Dix et al., 2009)	8 t·ha^{-1}·year^{-1} (Meyer, 2007)
Hemp	6 – 7 t·ha^{-1}·year^{-1} (Dix et al., 2009)	
Rapeseed stalks	6.3 t·ha^{-1}·year^{-1} (Dix et al., 2009)	
wheat straw	3 - 5.8 t·ha^{-1}·year^{-1} (Dix et al., 2009)	
Sunflower	3.9 t·ha^{-1}·year^{-1} (Dix et al., 2009)	
maize stalks	8 – 15 t·ha^{-1}·year^{-1} (Dix et al., 2009)	
cup-plant	7 – 16 t·ha^{-1}·year^{-1} (Gansberger et al., 2015)	40 t·ha^{-1}·year^{-1} (Stanford, 1990)
Miscanthus	23 - 44 t·ha^{-1}·year^{-1} (Pyter et al., 2007)	12 - 20 t·ha^{-1}·year^{-1} (Monti et al., 2015)

Plants used as alternatives in particleboards (Table 2) have biomass yields comparable with forests. An advantage of the shown residues is that they readily available and currently rarely

used. Sunflower stalks are obtained from fields intentioned for sunflower oil seed production, and the same is true for rapeseed (*Brassica napus L.*) stalks. In Europe, sunflowers are occupying 4.25 Mio ha, while rapeseed plants are cultivated on 6.6 Mio ha (Krautgartner et al., 2016). Sunflower stalks may potentially replace ~80 % of the wood used in European particleboard production, while rapeseed stalks can easily provide 41 Mio tons of stalks per year, which is double the amount needed for the entire European particleboard production. Wheat straw is grown in the EU at a three times higher amount (74 Mio tons per year) than required by particleboard industry. Wheat straw is, however, also used for the production of energy through combustion (Kretschmer et al., 2012). Topinambour stalks are produced at ~600 000 tons per year (Izsáki and Kádi, 2013), which could replace 3 % of the wood use for the European particleboards. Hemp stalks are available at amounts of ~105 000 tons (Carus et al., 2013) per year, and this material is also grown for insulation materials, polymer-based composites, non-wovens and paper industry. Maize is taking overall 15 Mio hectares, with 60 % harvested for grains, and 40 % for silage (ESA, 2016). This volume is exceeding six times the raw material demand needed for EU-produced particleboards. Availability biomass of wood and non-wood raw materials for particleboards are shown in in figure 1.
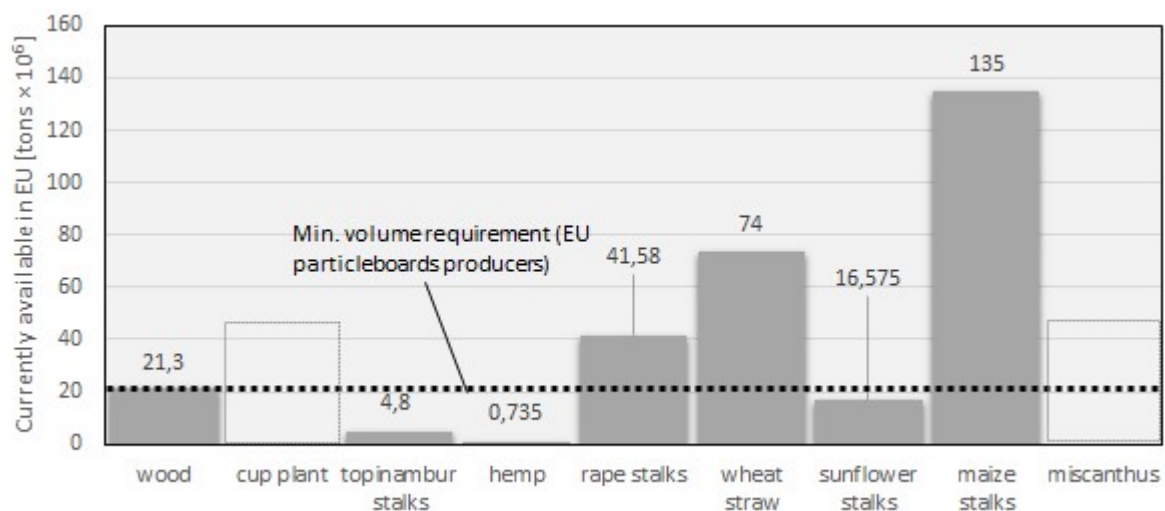
Figure 2-1. Availability of alternative materials for particleboard production. Wood represents an estimated volume of material required for European particleboard production. (Calculated from yield data in table 1 above and occupied area in EU (ha × t/ha)). Blank columns represent material cultivated as energy crops.

2.2 Particleboards produced with alternative materials

2.2.1 Straw

One of the most important food plants, feeding more than 40% of the world´s population is rice (Pathak et al. 2006; Mohdy et al. 2009). There are numerous examples for non-food utilization of the rice straw. A pilot plant study for the production of ceiling boards using rice husks was presented by Ajiwe et al. (1998). Replacements wood by rice straw at 10% have shown increases in MOR and MOE. However, MOE and MOR dropped when the wood-replacement by rice straw was above 20 % (Yang et al., 2003). Sound absorption panels using rice straw, produced from fine particles at 0.8 mm mesh size have turned to be of higher performance than plywood (Yang et al., 2003). IB of rice straw particleboards has proportionally decreased as larger-sized straw particles were used, while MOR and MOE were proportionally higher. To fulfill EN 312 requirements, particles obtained from sieving with mesh sizes between 6.35 – 12 mm were found to be ideal for the production of MDI-bonded rice straw particleboards. UF-bonded rice straw particleboards, however, did not meet the requirements for IB and MOR, irrespective from the investigated particles geometry alteration. Nevertheless, IB and MOR of rice straw UF particleboards can be increased by a pretreatment of rice straw using oxalic acid and steam, even though the average MOR was not high enough to meet EN 312 standards (Li et al., 2011). pMDI bonded rice straw particleboard mixed with coir fibers had higher IB and lower MOR and MOE (Zhang and Hu, 2014), compared to 100% rice straw particleboards. The particleboards from different parts of the rice straw particleboards without binder were suggested as well. The IB of these panels was way below the EN 312 requirements, however, results suggested that rice straw stalks were better suited for particleboards than rice leaf sheaths or leaf blades (Kurokochi and Sato, 2015). Industrially promising results are presented with low density insulation particleboards made from rice straw (density 220-360 kg/m^3), showing thermal conductivities between 0.046 – 0.060 W·m^{-1}·K^{-1} (Wei et al., 2015). These panels are competitive with low-density fiberboards made from wood.

Wheat straw was also used as a wood-replacement in particleboards. UF-bonded particleboards made from wheat straw particles met the minimal requirement of class P1 in EN 312 with a pressing time of 320 seconds, and a UF resin content of 12 – 15 % (Boquillon et al., 2004). MOR, MOE and IB of wheat straw based particleboards proportionally increased with higher UF resin content. MOR and MOE of UF-bonded wheat straw particleboards were further improved by mixing in waste veneer splinters (Azizi et al., 2011). MDI-bonded wheat straw particleboard easily meet the minimal requirement of the EN 312

as well; properties can be substantially increased by bleaching wheat straw particles prior to the particleboard production (Mo et al., 2003). Aside of UF resin and MDI resin, soybean protein resin was tried to produce wheat straw-based particleboards. Here, soybean resin-bonded particleboards did not meet the minimal requirement of P1 class in EN 312. Nevertheless, MOR, MOE and IB of soybean resin-bonded wheat straw particleboards reached similar values than those bonded with UF resin. Soybean flour-bonded wheat straw particleboard with a density of 840 kg/m^3 did meet the minimal requirements of P1 in EN 312, however, MOR was found to be weak (Cheng et al., 2004). Wheat straw was used to produce panels of lower density (Wang and Sun, 2002) for potential insulation purposes, using tannin-based adhesive (Tabarsa et al., 2011), or also a soybean protein-based adhesive (Cheng et al., 2004). Naturally PF-bonded particleboards from wheat straw fulfilled the minimal requirements by EN 312, even with 30 % of PF resin replaced by a tannin extract (Tabarsa et al., 2011).

In Poland, MDI bonded particleboards with straw coming from rapeseed (*Brassica napus* L.) stalks were suggested (Dziurka and Mirski, 2013). The particleboards from rapeseed straw were produced with densities between 350 - 550 kg/m^3. The 550 kg/m^3 panel fulfilled the requirement of P1 class in EN 312. It has to be noted that the MDI dosage was 10 %, which was almost twice the commonly used dosage in industry. The rapeseed straw particles were also mixed with polystyrene particles in a ratio of 93 %^{wood}: 7 %^{polystyrene}, and bonded with MUF (Dziurka et al., 2015). Although these panels were produced at various densities (550 – 650 kg/m^3), the MOR of the panels was not satisfying with respect to EN 312, for boards with a density below 600 kg/m^3.

2.2.2 Stalks

Grigoriou and Ntalos (2001) investigated potentials of Castor stalks (*Ricinus communis L.)* for the production of particleboards. Findings have shown reduced values for IB, MOR, MOE and the screw withdrawal capacity, when castor particles replaced wood in amounts between 25 – 100 %. The conclusion was that wood can be replaced by 50 % castor stalks and still achieve satisfying properties as defined in P1 of EN 312. Cotton (*Gossypium hirsutum* L.) stalks-based particleboards (Guler and Ozen, 2004; Khanjanzadeh et al., 2012) with density of 600 and 700 kg/m^3, also fulfilled minimal requirements of P1 class in EN 312, and these panels can be used also in furniture production (P2, EN 312). Cotton stalks-based particleboard properties proportionally declined as the density of the panels was gradually lowered. Particleboard from sunflower (*Helianthus annuus* L.) stalks (Bektas, 2005) mixed

with wood were investigated as well. Also, mechanical properties of these boards were proportionally lowerd with gradual substitutions of wood. However, particleboards with 50 % sunflower particles replacing wood can still be used for general purposes in dry conditions (P1, EN312). Low IB was found to limit limited standard applications of the PF-bonded 100%-sunflower stalks based particleboards (Khristova et al., 1996). Particleboards from sunflower stalks with densities between 150 and 200 kg/m^3 were suggested for insulation purposes (Binici et al., 2014; Mati-Baouche et al., 2014). Thermal conductivity was 0.0058 W·m^{-1}·K^{-1}, which is lower than the one measured for conventional insulation wood-based fiberboards (Troppová et al. 2014). Low density particleboards made with topinambour (*Helianthus tuberosus* L.), Miscanthus (*Miscanthus × giganteus*) and maize stalks were used in furniture production (Balducci et al., 2008; Dix et al., 2009). A wall-cabinet was produced from three layer particleboard, Miscanthus or topinambour as the core material, and spruce as the surface layers (Dix et al., 2009). As a result, alternative shelfs-fastening was suggested for the cabinet, to compensate for the reduced IB and fastening withdrawal capacity. Some stalks from lesser known plants were used as well. For instance, roselle stalks (*Hibiscus sabdariffa*) mixed with wood have met requirements of P1 in EN 312 (Ghalehno and Nazerian, 2011). Extensive research on *Sorghum* stalks (Khazaeian et al., 2015) was reported with respect to the effects of particles sizes, press temperature and pressing time on mechanical properties. Three-layer tomato (*Solanum lycopersicum* L.) stalks (Guuntekin et al., 2009) particleboards prepared with MUF or UF adhesive have shown lower MOR, which restricted their applicability according to class P1 of EN312. Particleboards from tobacco stalks (Acda and Cabangon, 2013) were produced in several alternatives with tobacco stalks gradually replacing wood. Mechanical properties were decreased as wood was gradually replaced by tobacco stalks. However, termite resistance of these particleboards significantly improved: The fully wood-based panel type has shown 100 % mass loss after 24-weeks of termite exposure, while tobacco-based (100 %) particleboards had almost no mass loss (~1.5 %). Buckwheat (*Fagopyrum esculentum*) stalks (Oh and Lee, 2012) were found suitable for particleboard manufacturing, if mixed with wood. Particleboards produced only from buckwheat stalks displayed lower MOR values, restricting their range of applications. A similar behavior was found for particleboards produced from vine (*Vitis vitifera* L. CV. *sultani*) stalks/pruning (Ntalos and Grigoriou, 2002; Yeniocak et al., 2014). Also, UF bonded particleboards from eggplant (*Solanum melongena* L.) stalks (Guntekin and Karakus, 2008) were not suitable for standard purposes due to low MOR and IB. Pepper (*Capsinum annuum*)stalks based particleboards did meet the required IB and MOE levels, however,

MOR did not pass the minimum requirements (Guntekin et al., 2008). An interesting approach for alternative particleboard was introduced by Selinger and Wimmer (2015). A novel sandwich hemp-based particleboard covered with pressed hemp-fibers nonwovens did meet the minimum requirement, although density was only 320 kg/m^3. The review by Youngquist et al. (1994) also mentioning possibilities of using cornstalks (*Zea mays* subsp. *mays* L.), mustard stalks, sugarcane (*Saccharum officinarum*), stalks cassava (*Manihot esculenta*) stalks, banana stalks, tapioca stalks or Ragweed (*Ambrosia* L.) stalks for particleboards.

2.2.3 Prunings

Various other parts of the tress, bushes, or waste materials were investigated to replace wood in particleboards. Kiwi (*Actinidia sinensis* Planch.)pruning (Nemli et al., 2003) replaced wood in particleboards and these had similar MOE and IB to the wooden particleboards, the MOR was lower. Green vine pruning (Yeniocak et al., 2014) were used to gradually replace wood in particleboards. Interestingly, if vine pruning replaced wooden particles up to 70 %, the mechanical performance remained unchanged. Nevertheless, when particleboards were prepared completely from vine prunings, all mechanical properties dropped significantly below the minimal requirements of EN 312 - P1 class. A better performance was shown using tree prunings and branches. Particleboards made from prunings of native willow (*Acacia salicina*), buttonwood (*Conocarpus erectus*), council tree (*Ficus altissima*), white leadtree (*Leuceana glauca*), manila tamarind (*Pithecellobium dulce*), saltcedar (*Tamarix aphylla*) (Nasser, 2012) were produced and their properties were similar to those made from spruce.

2.2.4 Natural by-products and wastes

Various by-products obtained from food-industry were investigated as a replacement of wood in particleboards. Gradual replacement of wood by poppy husks (*Papaver somniferum*) proportionally decreased mechanical properties of the particleboards (Keskin et al., 2015). Particleboards with a poppy husks content higher than 25 % did not meet the requirements for class P1 in EN 312. Particleboards from rice husks (Ajiwe et al., 1998; Ciannamea et al., 2010; Suleiman et al., 2013) showed low IB, which also limited their application according to P1 class in EN 312. Rice husks were bonded by (Ayrilmis et al., 2012) UF and PF in amount of 6, 10 and 12 %, but IB generally did not cross minimal requirements (P1, EN 312), even when mixed with higher amounts of wood (75 %^{wood}:25 %$^{rice\ husks}$). However, when rice husks underwent an alkali treatment or bleaching, the properties substantially increased above requirements of P1 in EN 312 (Ciannamea et al., 2010). Çöpür et al. (2007) prepared hazelnut

husk based particleboards with density 600 and 700 kg/m^3. Both types fulfilled at least the minimal requirements for particleboards used for general purposes in dry conditions (P1, EN 312). Particleboards were also produced from macadamia shell (Wechsler et al., 2013), bonded by castor oil based adhesive. Their properties did not fulfill the requirement according P1 in EN 312. As a benefit, macadamia-shell particleboards displayed significantly lower thickness swelling than those made from wood. Particleboards made from almond and walnut shells then displayed lower thickness swelling, reduced water absorption and also lower formaldehyde emissions, compared to the wood-made boards (Pirayesh and Khazaeian, 2012; Pirayesh et al., 2013). The almond and walnut shell-made panels did meet requirements for particleboards used for interior fitments (P2, EN 312). In the Middle East, particleboards from date palm biomass were produced. Palm's Trunk and rachis particles were bonded with MUF and PF adhesive (Amirou et al., 2013) and physical and mechanical properties of particleboards made from palm trunks were higher compared to those made from palms' rachis. At the same time, PF bonded rachis particleboards along with both types of palm trunk particleboards fulfilled requirements of class P1 in EN 312, while MUF bonded rachis particleboard did not cross minimal requirements for MOR.

2.3 Comparison of selected alternative particleboards

In following section, the mechanical properties of particleboards produced from alternative resources were compared based on their density. The comparison provided specific insights of particleboards made from alternative bio-materials, and this make it easier to visually compare mechanical properties of various types of particleboards mentioned before.

MOR of particleboards from agriculture residues did not display known trends such higher MORs with increasing densities. Strictly speaking, alternative particleboards produced at higher panels densities did not necessarily result in a satisfactory MOR. For instance, MOR of high-density (~900 kg/m^3) particleboards from oil palm leaves (R. Hashim et al., 2010) or particleboards from tissue paper mixed with corn peel (Lertsutthiwong et al., 2008) did not reach required value of class P1 in EN 312. Particleboards are compared based on their densities (Figures 3 and 4).
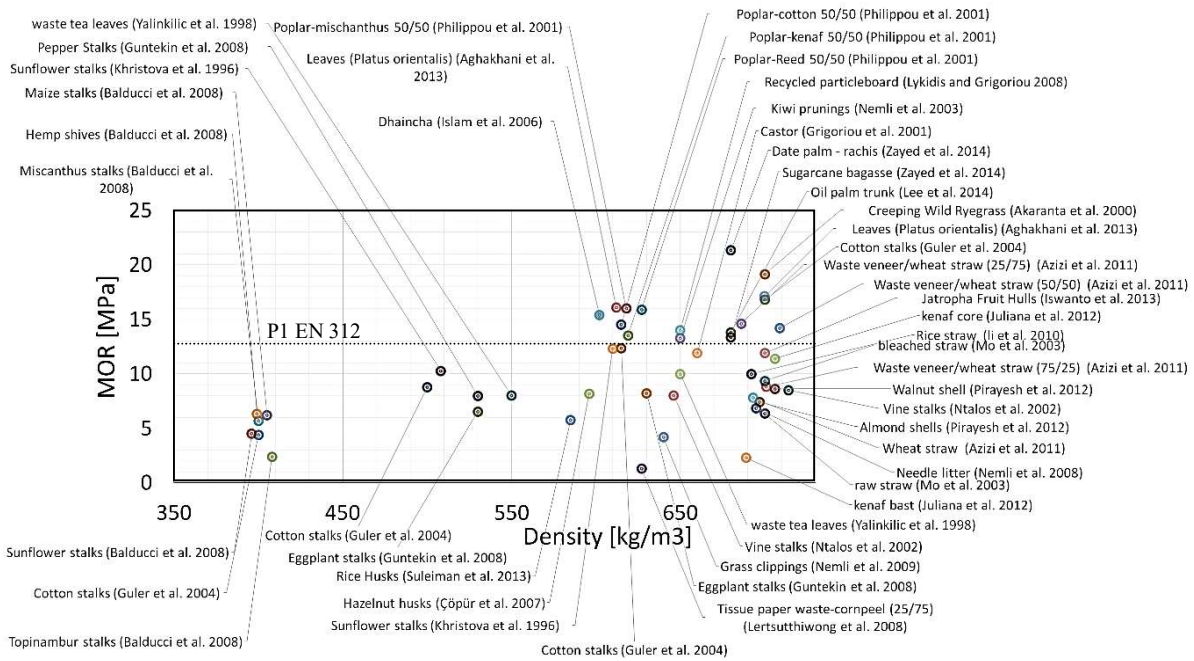
Figure 2-2. MOR – panel density chart for particleboards made with alternative raw materials
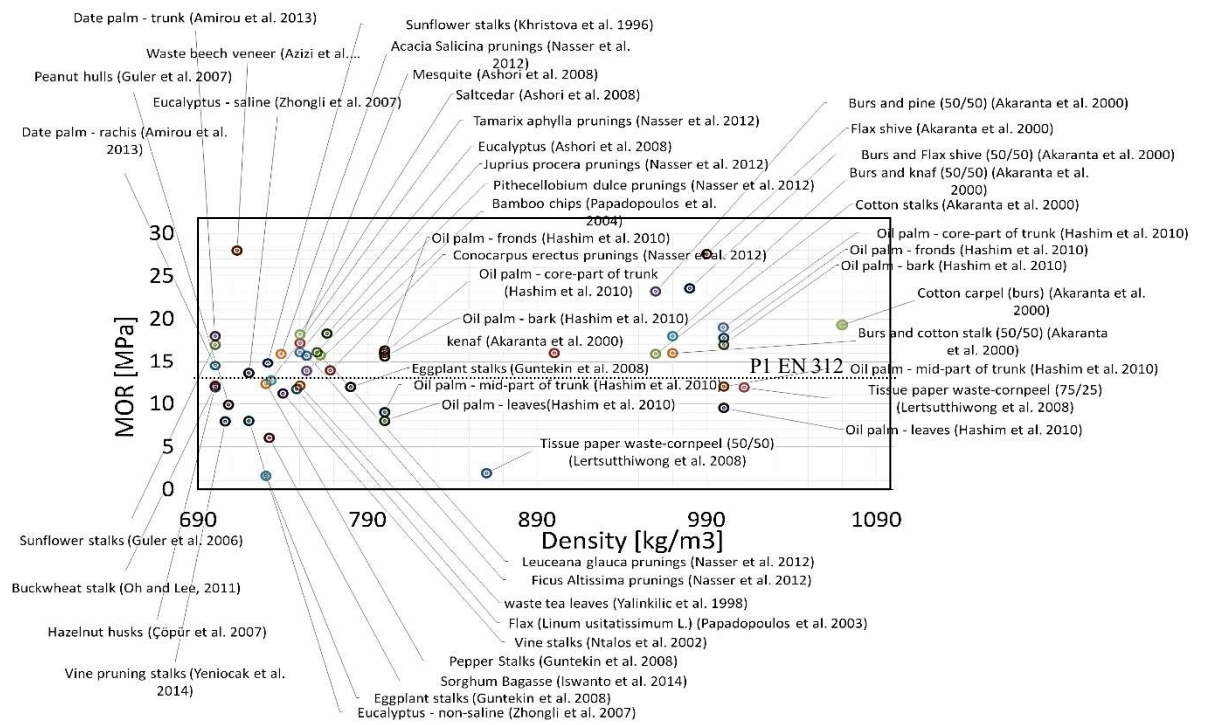
Figure 2-3. MOR – panel density chart for particleboards made with alternative raw materials

In addition, MOE values (range 1000 – 3000 MPa) for particleboards made from alternative materials were plotted along with the related density of the produced panels (Figure 4 and 5).
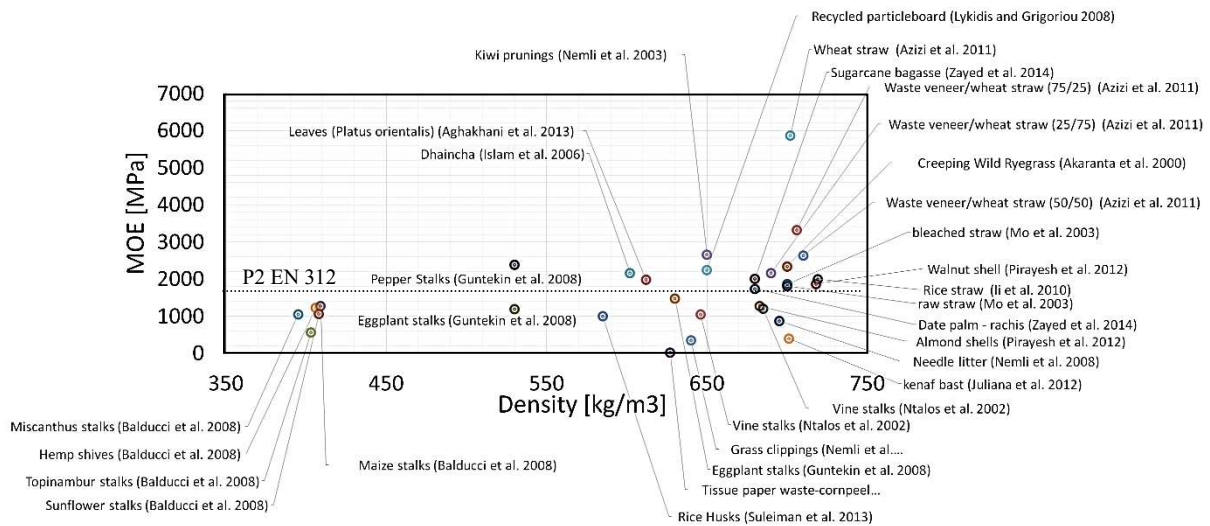
Figure 2-4. MOE – panel density chart for particleboards made with alternative raw materials
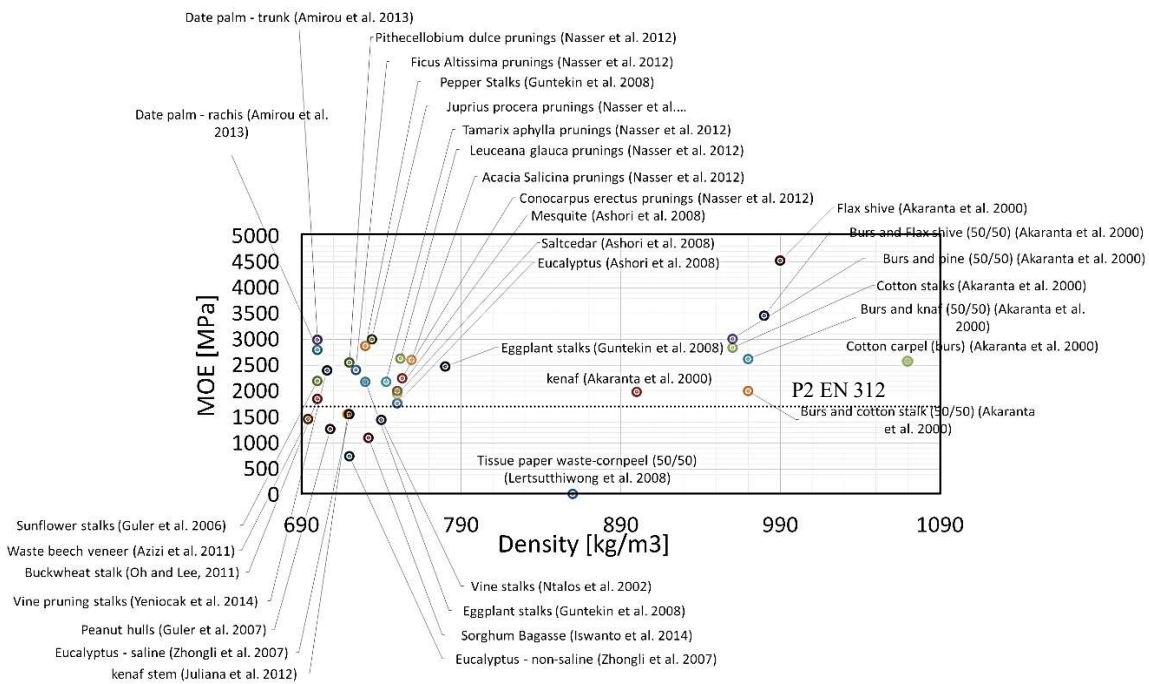
Figure 2-5. MOE – panel density chart for particleboards made with alternative raw materials

On one hand, visually IB turned out to be proportionally increased as the density of the particleboards raises (figure 6 and 7). On the other hand, IB in range 550 – 690 kg/m^3 range had ~50 % of particleboards made from alternative resources, which is below the minimum requirements of P1 in EN 312. For densities above 700 kg/m^3 the IB for ~15 % of the particleboards was insuficcient.

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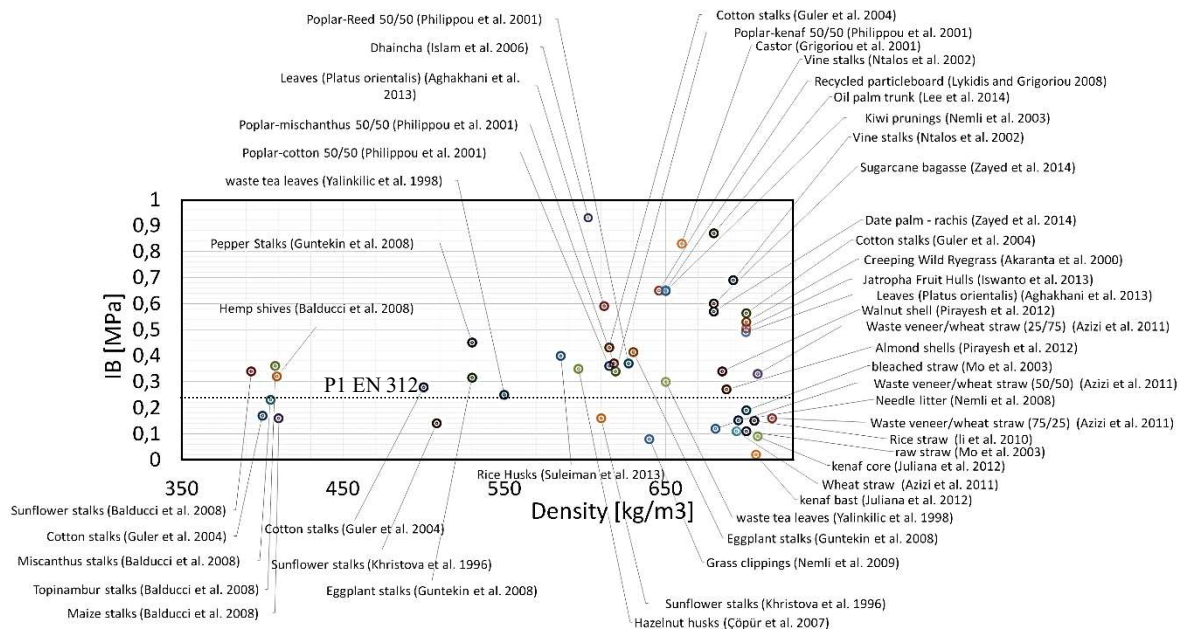
Figure 2-6. IB – panel density chart for particleboards made with alternative raw materials
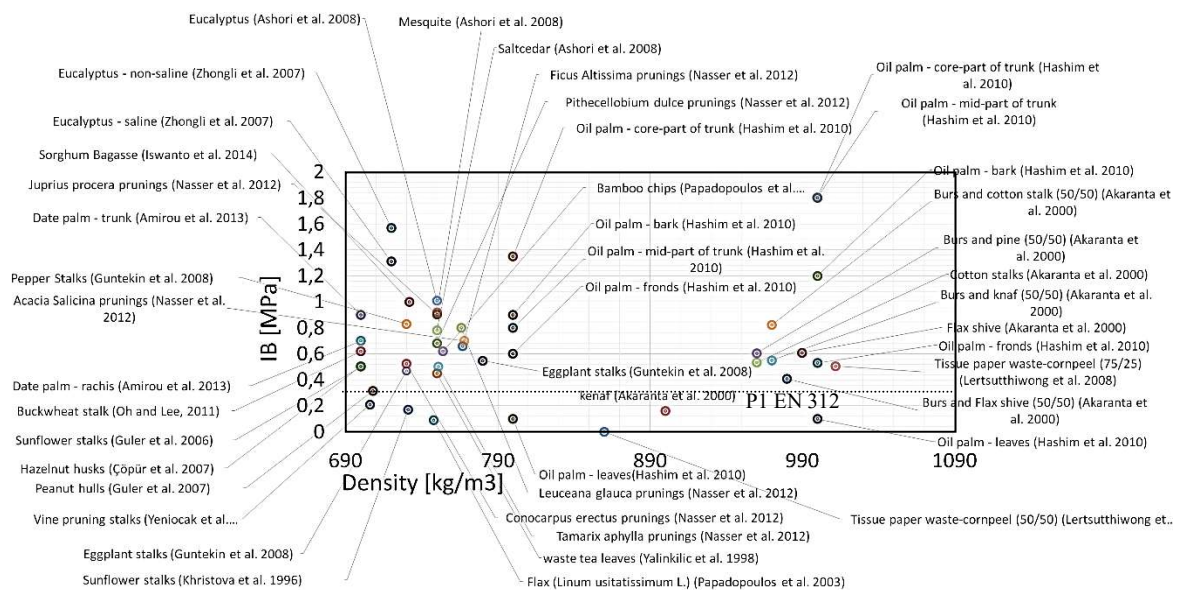
Figure 2-7. IB – panel density chart for particleboards made with alternative raw materials

2.4 Material selection strategy

The starting point for material selection is (1) the identification of function of purpose of the produced particleboard. (2) Definition of constrains obtained from available databases of the used materials. For the identification of the function, EN 312 provides minimal requirements through standardized classifications of particleboards that producers usually

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follow. In this research, general purpose particleboards to be uses in dry conditions (class P1) are in the main focus (table 3).

Table 2-3. Requirements for general purpose particleboards used in dry conditions (P1, EN 312)

Property	Test method	Thickness range [mm]						
		3 to 6	>6 to 13	>13 to 20	>20 to 25	>25 to 32	>32 to 40	>40
Bending strength [MPa]	EN 310	14	12.5	11.5	10	8.5	7	5.5
Internal bond strength [MPa]	EN 319	0.31	0.28	0.24	0.2	0.17	0.14	0.14

As soon the purpose of a particleboard is determined, the objective is to assess the alternative materials (stalks, straw, waste, pruning, husk and hulls), with the goal to meet the requirements for P1 in EN 312. The further objective is to indicate properties that need to be optimized, also to meet similar property levels than wood-made particleboards.

Constrains to create databases of assessed materials are: (1) Assessed particleboards are bonded with the UF adhesive and specific resin dosage (UF 8-12 %). (2) Particleboards are produced by methods similar to the industrial production, means without special tools and techniques. (3) MOR, MOE, IB and density of the particleboards are specified according to European standards.

For free variables are considered: (1) used particles size in particleboard production, (2) pressing schedule of particleboards, (3) material´s chemical content and material´s geographic origin, (4) thickness of particleboards.

2.4.1 Ranking by Ashby plots

To produce Ashby plots all compiled particleboard data were divided in four material classes: (1) Particleboards from plant´s stalks, (2) wood, (3) wood prunings, (4) straw and leaves. Data analyzed in following chapter were obtained from the aforementioned literature (chapter 1.2).

MOR in the "Ashby" graph (figure 8) showed that groups of particleboards from wood, wood prunings, plant stalks and waste leaves are overlapping. This means that these alternative particleboards could be produced with similar MOR like wooden ones. Concurrently, isolated groups of straw based particleboards and husks and hulls based particleboards indicated that MOR of these particleboard types need to be raised.
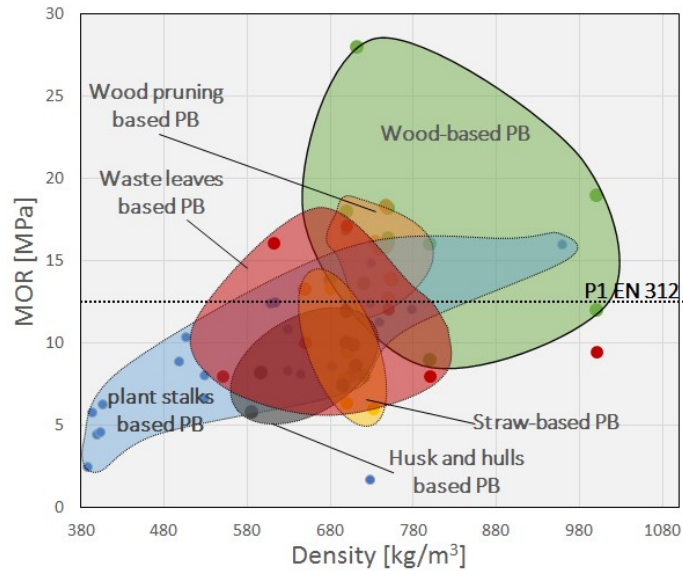
Figure 2-8. Ashby plot of alternative particleboard, showing MOR along with the panel density

MOE of stalks-based particleboards could be similar to wood-based ones, as these two groups are overlapping. The same is true for wood prunings-based particleboards. The isolated group refer to husks based particleboards, their MOE needs to be increased.
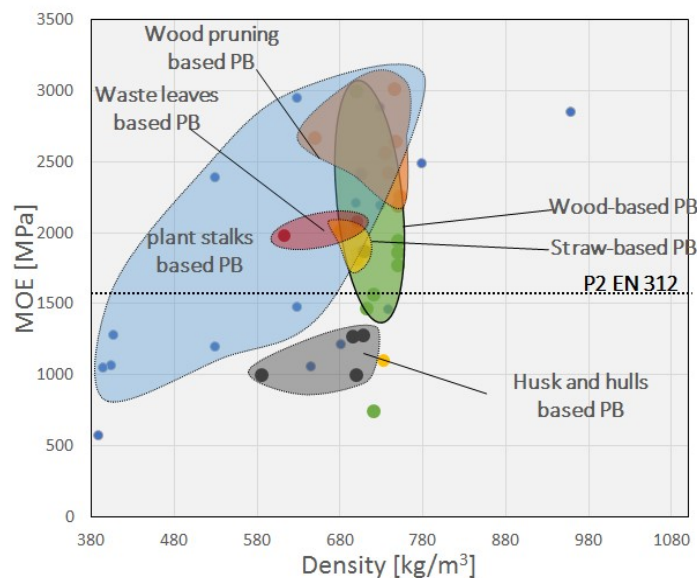
Figure 2-9. Ashby plot of alternative particleboard´s MOE ranked by density

Particleboards made from wood prunings and plant stalks may reach a similar IB than wood-based particleboards. IB of particleboards made from husks and hulls, waste tea leaves and straw needs to be improved. Nevertheless, to assess of the boards meets the requirements of

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the class P1 of EN 312 MOR and IB must be evaluated together. As depicted (Figure 10), particleboards from wood prunings, stalks and waste leaves could be produced with minimal required mechanical performance of P1 class in EN 312. Particleboards from husks and hulls or straw are for now out of region with minimal required values.
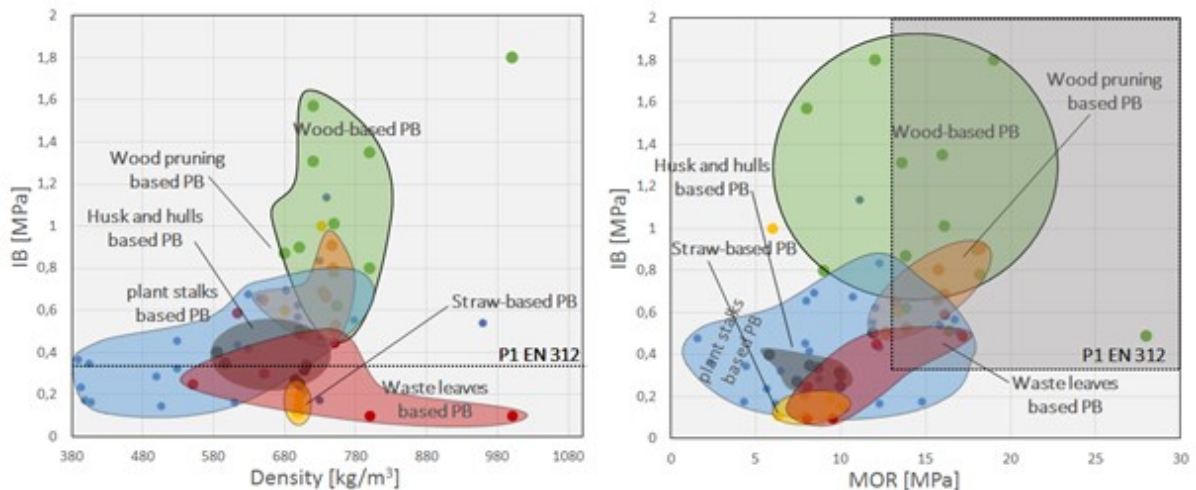
Figure 2-10. Ashby plot of alternative particleboard´s IB ranked by density and MOR

2.4.2 Monetary ranking with respect to properties

The important fact for viable replacement is the question of a lower price. In other words, if comparable properties with wood-based particleboards are achievable, are boards made residual materials cheaper? Here, an evaluation of prices is shown per unit of mechanical properties.

Such an assessment indicate the costs to be paid in order to achieve one unit of specific mechanical property. Practically, the price for the mass of wood may be twice as high than that for the same mass of an alternative material. However, if a wood-based particleboard has e.g. the double level in mechanical properties, then a production of particleboards made from alternative materials may not be feasable. In the shown scenario, the price per unit of particleboard property is set to be the same for wood and alternative materials. EQ1 was calculated with particleboard data that meet the minimum requirements of P1 in EN312.

$$P_€=\frac{€·\rho}{Prop} \quad [€·kg/m^3·MPa^{-1}] \quad\quad\quad\quad EQ\ 1.$$

$P_€$ is the price per unit of mechanical property, € is price per 1 kg of raw material used for the production of particleboards, ρ is the particleboard density in kg/m^3, and Prop are either MOR, MOE or IB.

The price per unit of MOE and MOR of wooden particleboards is significantly higher compared to those made from leaves, wood pruning and stalks. This means, that particleboards made from alternative materials and reaching minimal mechanical properties (P1 according to EN312) demonstrate a significantly lower price, as compared with wood-made boards (see figure 11). The price per unit of IB in wood-based particleboards was comparable with particleboards made from stalks only. Including the standard deviation of price per IB, also pruning and leave-based particleboards are close to those made from wood. This suggests that increased IB in stalks-based particleboards could make alternative material-based panels economically more attractive. However, in general, our analysis proved that satisfying mechanical performance of particleboards can be achieved at significantly lower prices level with alternative materials compared to wood.
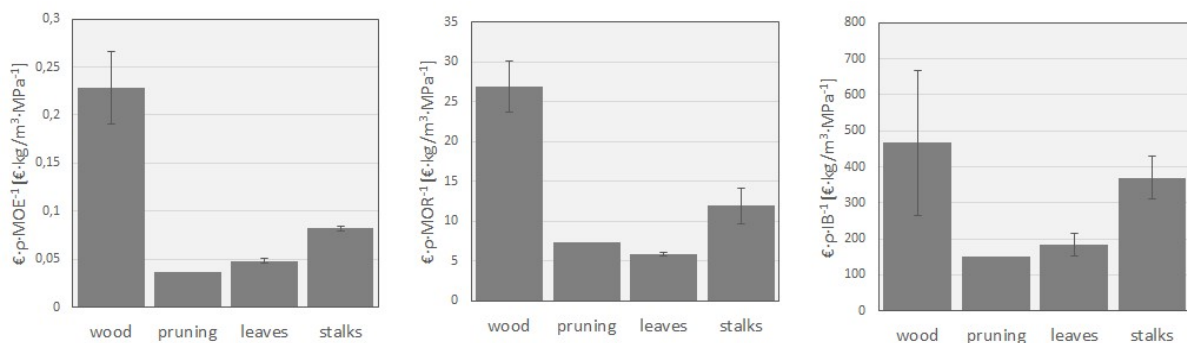
Figure 2-11. Prices per unit of mechanical property of particleboards. Price per unit of mechanical property of particleboards. Calculated as $€·\rho/p$, $€$ is being price per 1 kg (chapter 2.1), ρ is density of particleboard in kg/m^3 and p is being MOR, MOE and IB.

In conclusion, this assessment has shown the following: (1) Selected alternative materials are available in similar volume and have in some cases even higher yields than wood. (2) Alternative materials may be significantly cheaper than wood. (3) Particleboards made from alternative materials may have additional benefits such as termite resistance, or lower swelling, however, mechanical properties are ususally lower compared to wood-based particleboards. (4) Particleboards made from plant stalks and prunings may have similar mechanical performance as wood-based ones. (5) Particleboards from alternative materials may have satisfying mechanical performance at lower prices, compared to those made from wood. Prices per unit of mechanical properties in alterantive-material particleboards turned out to be significantly lower that the wood-based comprison.

3. Materials and Methods

3.1 Preparation of particles for particleboards

Raw materials (wood, plant's stalks) were chipped with a Klöckner 120X400H2W.T (Klöckner Maschinenfabrik, Lauenburg, Germany), at a cutting speed of 725 rpm; at a feeding speed of 1 m/s. The obtained chips were subsequently milled in a Condux-Werk HS 350 (Condux Maschinenbau GmbH & Co. KG, Hanau – Wolfgang, Germany) hammer mill. The produced particles were screened in an Allgaier D7336 (Allgaier-Werke GmbH, Uhingen, Germany). Sieves with mesh sizes openings 5.0 mm, 3.15 mm, 1.24 mm and 0.60 mm were used. Two particle size classes were build, a first one a with mesh size > 1.24 mm, and a second one with a mesh size < 5 mm. Particles from these two classes were manually mixed at a weight ratio of 50:50. Particles mixtures were then oven-dried in 70°C for 5 days to achieve final moisture contents between 5 to 7%.
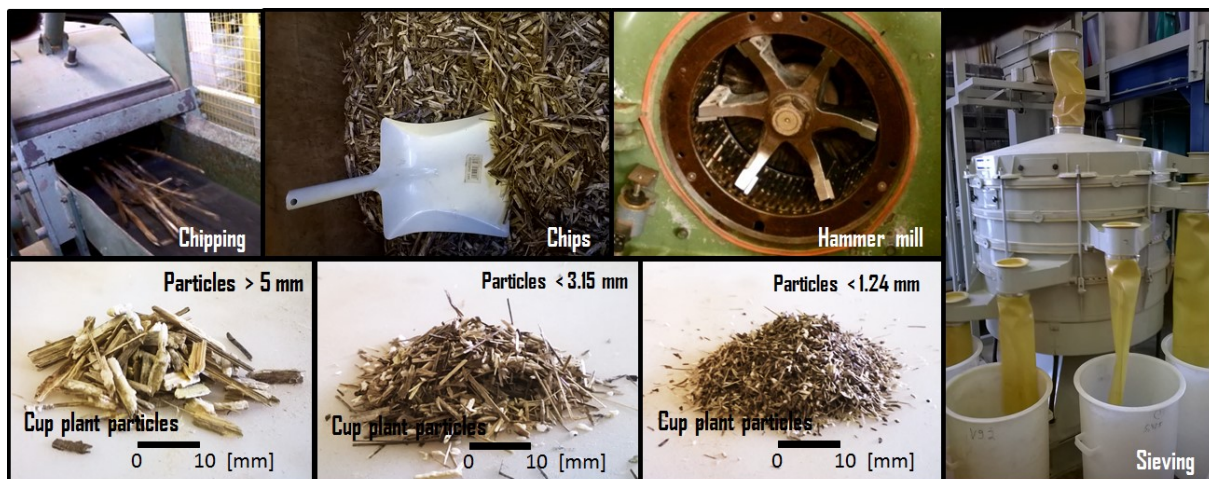
Figure 3-1. Production flow of the particles used in particleboard production

3.2 Preparation of particleboards

Particleboards were made with the target density and a target-thickness. Two adhesive types were used: 1) Methylene diphenyl diisocyanate (MDI) (Huntsman I-BOND® PM4390, Huntsman GmbH, Hamburg, Germany), and 2) urea formaldehyde (UF) (BASF Kaurit® 350, BASF Se, Ludwigshafen, Germany). Resins were applied to the particles in a drum blender for 5 minutes using a spraying nozzle. Resinated particles were manually placed and evenly distributed in a wooden forming box (550×550 mm^2) and pre-pressed. Then, mats were hot-pressed at 200 °C and 3.2 MPa for specific time (10s/mm of board´s thickness) in a hydraulic Siempelkamp® press (Siempelkamp Maschinen und Anlagenbau GmbH, Krefeld, Germany).

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Figure 3-2. Production flow of the particleboard

3.3 Testing of particleboard´s properties

Mechanical properties testing was carried out on a Zwick® 1474 (Zwick GmbH & Co. KG, Ulm, Germany) universal testing machine using testXpert II software (Zwick GmbH & Co. KG, Ulm, Germany).

3.3.1 Three-point bending

A three-point bending test (EN 310) was employed to determine the modulus of rupture (MOR), as well as the modulus of elasticity (MOE). The samples (for instance 11×50×270 mm^3) were subjected to a loading rate of 7 mm·min^{-1} until the failure was reached.

3.3.2 Internal bonding strength

Internal bonding (IB) strength according to EN 319 was measured on squared samples (for instance 11 × 50 × 50 mm^3). Prior to testing the samples were sanded and then glued onto stainless steel blocks. Blocks were positioned in gimbal-mounted holders and pre-loaded in tension by 5 N. Subsequently, a loading rate of 1 mm/min was applied until failure.

3.3.3 Thickness swelling

Thickness swelling (EN 317) was measured with samples (for instance 11 × 50 × 50 mm^3) fully immersed in 20°C distilled water. Thickness swelling was measured after 2 hours and 24 hours, respectively. As soon immersion time has elapsed the samples were taken out from the water bath with excess water removed with paper tissues. Thickness swelling was measured in the mid of the sample by a caliper.

3.3.4 Vertical density profile

Vertical density profiles (VDP) were determined with the GreCon RG44® 33KV/1mA (GreCon, Germany) x-ray density analyzer. The obtained data were analyzed using Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software.

3.3.5 Particle size measurement

For particle size measurement particles were dispersed evenly with a sieve on a transparent foil in a way that less than 5 % of the total area was covered. Then the transparent foil sized 297×420 mm^2 was scanned. The scanner was operated at 1200 dpi resolution. The particles were analyzed using the ImageJ software (Rasband, 1997). Major and minor length of the fitted ellipse to each of the particles were specified. Consequently, aspect ratio was calculated as a ratio of major length/ minor length of each particle. At the end surface area of particles was automatically measured in pixels^2 which were automatically converted on mm^2. Obtained data were analyzed using Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. Each measurement of particles was evaluated on the basis of range between first and third quartile and median value.
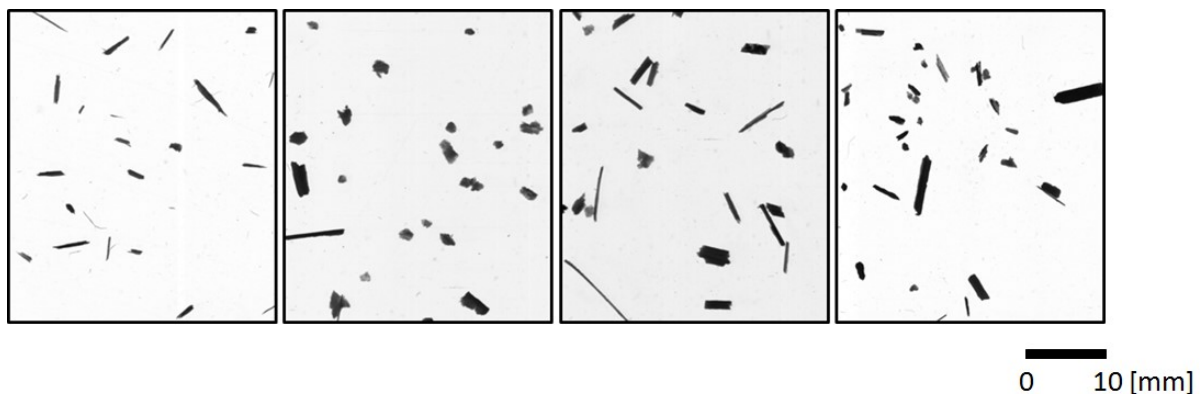
Figure 3-3. Examples of the scanned particles used in analysis for paper I.

3.3.6 Statistical analysis

All data obtained from mechanical tests were pretested for normality using Shapiro-Wilk test approving that datasets followed normal distribution. For hypotheses testing an analysis of variance (ANOVA) was employed, followed by Scheffé post-hoc tests. A significance level of 0.05 was chosen.

3.3.7 Chemical analysis

For the chemical composition (cellulose, hemicelluloses and lignin) around 200 mg were pre-hydrolyzed with 2mL of 72 H_2SO_4 (30 °C, 1h). The reaction mixture was diluted with 56 ml ultra-pure water, and post-hydrolysis was performed in an autoclave at 120 °C, and 1.2 bar for 30 min. For the high-performance liquid chromatography borate analysis, wood sugars were separated in a 5.6 mm column, 115 mm long (Omnifit®, Diba Industries, Inc., Danbury, North America) filled with strong anion exchange resin 114 MCL gel CA08F (Mitsubishi Chemical Corporation, Tokyo, Japan) at 60 °C. The mobile phase (0.7 mL/min) consisted of solution A, 0.3 M potassium borate buffer with pH 9.2, and solution B, 0.9 M potassium borate buffer with pH 9.5. After sample injection chromatographic separation started with 90 % (A) and 10 % (B), with the run lasting 35 min. Data acquisition was ceased after 50 min. For quantification a post-column derivatization of monosaccharides with Cu-bichinconinate (0.35 ml min^{-1}) was applied. The reaction was performed at 105 °C in a 30 m crocheted Teflon coil of 0.3 mm inner diameter. This enabled the subsequent detection of sugars at 560 nm (Sinner et al. 1975, Sinner and Puls 1978). Data were processed using dionex® chromeleon software (Thermo Fischer Scientific Inc., Sunnyvale, United States).

3.4 Microscopic optical deformation measurement (DIC)

The 2D optical measurement (DIC) was used to capture images of the sample using camera Dino lite (AnMo Electronic Corporation, Taipei office, Taiwan) which was focused on 4.5 × 4.5 mm^2 Field of view (FOV). The images were captured with resolution 1280×1024. A default LED light of the camera was used to illuminate the AOI. Camera was connected with software Dino Capture 2.0 version 1.5.10 where focusing was manually adjusted to obtain maximal sharpness of the captured images. Prior to focusing the AOI was in software 4 × magnified using implemented "zoom-in" function. The DIC itself was produced using software Davis 8.1.3 software (LaVision GmbH, Goettingen) and strain and displacement were calculated. The calibration of optical measurements was performed prior to test using 1 mm gridded paper. One image of the paper was captured and the size of the image was calculated and it was 3.9 µm/pixels. Five images of the sample were captured afterwards and mean value of displacement in horizontal and vertical direction was calculated and identified as error of measurement.
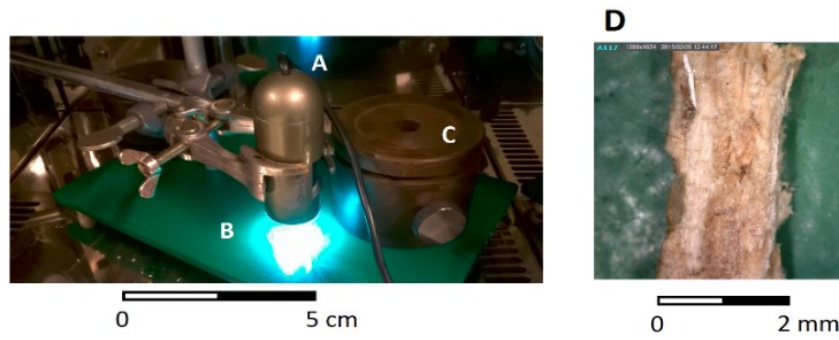
Figure 3-4. DIC Setup, where A is digital microscope, B metal base; C – weight; D – AOI, sample captured with magnification 50 ×

4. Paper I.

Using sunflower (*Helianthus annuus* L.), topinambour (*Helianthus tuberosus* L.) and cup-plant (*Silphium perfoliatum L.*), stalks as alternative raw materials for particleboards

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Peter Meinlschmidt

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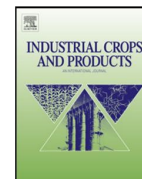
Using sunflower (*Helianthus annuus* L.), topinambour (*Helianthus tuberosus* L.) and cup-plant (*Silphium perfoliatum* L.) stalks as alternative raw materials for particleboards

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ABSTRACT

In this research the feasibility of agricultural crop residues used as alternative raw materials for particleboards was investigated. Germany-grown cup-plant (*Silphium perfoliatum* L.), sunflower *(Helianthus annuus* L.) and topinambour *(Helianthus tuberosus* L.) were used as raw materials for particleboards produced at a conventional density of 600 kg/m³. Particleboards were glued with two different adhesives, with methylene diphenyl diisocyanate (MDI) as well and urea formaldehyde (UF) resins. The physical and mechanical properties of prepared panels were measured according to standards. The raw materials were analyzed for their chemical composition; particle geometry was carefully monitored. It is shown that the obtained particleboards have acceptable performances, though properties were below those obtained from conventional spruce particleboards. Modulus of rupture of the alternative material particleboards were found to be lower than the spruce particleboards. Likewise, thickness swelling and water absorption of the agricultural residues made particleboards were higher than the compared spruce-made particleboards. The finding relevant for industrial applications was that the agricultural residue-produced particleboards bonded with MDI resins fully comply with the European standard EN 312 class P1 (use in dry conditions). This means that non-wood particleboards are suitable to be used in furniture production.

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1. Introduction

The first wooden material composed of particles dates back to 1887, where sawdust bonded with a blood-albumin adhesive were pressed to a "Holzmasseplatte" (Hubbard, 1887). The initial purpose was to utilize waste chips, sawdust or waste-wood, as regularly obtained from sawmills. Since the first particleboard factory started to operate in Germany in the year 1941, particleboards are still holding the strongest position on the European wood-based panel market. Particleboards are produced at an annual volume of 28.4 million m³ (EPF, 2014), which represents over 60% of the entire European wood-based panels production (Eastin et al., 2012).

Wood as the primary raw material to produce particleboards has been globally facing an increasing demand, which is also accompanied by higher prices (International Energy Agency, 2014). In response to an anticipated shortage of wood, strategies to achieve a higher resource efficiency in future have been initiated (Fischer-kowalski et al., 2013; European Commission, 2011). Increased raw material prices may motivate companies to improve their productivity and invest also more in resource-efficient technologies (Giljum et al., 2009). Simultaneously, a more efficient and responsible use of raw materials should not only improve productivity, but would also raise environmental standards (Jänicke, 2009).

To tackle the aforementioned issues, finding alternatives for the relatively slow growing forest trees is critical. Abundantly available plants cultivated in agriculture might be good candidates, showing also anatomical and chemical structures suitable to produce panels (Balducci et al., 2008; Wu et al., 2010; Mati-Baouche et al., 2014; Papadopoulou et al., 2015). Research pertaining

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agriculture residues used in particleboard manufacturing has been shown before. A number of plant materials with respect to particleboard production were studied, including stalks from sunflower (*Helianthus annuus* L.) (Khristova et al., 1996; Bektas, 2005; Guler et al., 2006; Binici et al., 2014), castor (*Ricinus communis* L.) (Grigoriou et al., 2001), pepper (*Capsicum annuum* L.) (Guntekin et al., 2008), vine (*Vitis vinifera* L. (cv. *sultani*)) (Ntalos et al., 2002; Yeniocak et al., 2014), cotton (*Gossypium hirsutum* L.) (Guler and Ozen, 2004), eggplant (*Solanum melongena* L.) (Guntekin and Karakus, 2008), or from kenaf (*Hibiscus cannabinus* L.) (Kalaycıoglu and Nemli, 2006). Non-wood particleboards from renewable resources are common in countries that have a low forest land cover. Another motivation for non-wood particleboards using for instance agricultural waste is the desire to achieve added-value products (Youngquist et al., 1993), rather than using the biomass just for biogas or ethanol production, combustion, or simply leave it on the field (Marechal and Rigal, 1999; Scholz and Ellerbrock, 2002; Gansberger et al., 2015).

Topinambour *(Helianthus tuberosus* L.) is cultivated widely across the temperate zone for its tuber, and has an annual biomass gain over 6–8 t/ha. Sunflower (*Helianthus annuus* L.) as another Asteraceae grows in biomass at 4 t/ha (Dix et al., 2009). Topinambour stalks have been utilized as a particleboard raw material (Balducci et al., 2008; Dix et al., 2009); and low-density panels were produced with both plants, as shown by Balducci et al. (2008), Binici et al. (2014), and Mati-Baouche et al. (2014). Cup-plant (*Silphium perfoliatum* L.) originates in Eastern North America (Stanford, 1990), but is now also established in Central Europe. Although it was grown in gardens as an ornamental plant during the 18th century, it is nowadays widely cultivated for energy production (Haag et al., 2015). Cup-plant characteristics, including aspects of cultivation and utilization was reviewed by Gansberger et al. (2015). No reported results were found for cup-plant-based particleboards. With a dry mass yield ranging between 11 t/ha and 20 t/ha per harvest, cup-plants may be a viable alternative for wood-based particleboards.

In this research, Germany-grown cup-plant, sunflower and topinambour were used as raw materials for particleboards at a conventional density of 600 kg/m^3 as e.g. used for furniture. The following is hypothesized: (1) Geometry of particles from wood and agricultural wastes vary even with consistently applied preparation and sieving procedures. (2) Non-wood particleboards can be produced showing property profiles suitable for standard applications. (3) Obtained property profiles are closely interacting with resin type as well as the amount of resin.

2. Materials and methods

Raw materials were collected and processed to particleboards as followed: (1) Sunflower *(Helianthus annuus* L.) stalks, as well as (2) Topinambour (*Helianthus tuberosus* L.) stalks, both grown and obtained in Northern Germany and (3) Dry cup-plant (*Silphium perfoliatum* L.) stalks, cultivated at the Johann-Heinrich-Thünen-Institut, Braunschweig, Germany; harvested plant stalks were 1.0–1.5 m long and had cross-sectional diameters between 10 mm and 30 mm. As the control, bark-free spruce wood (*Picea abies*

L. [*Karst*]) was used. Materials were chipped with a Klöckner 120X400H2W.T (Klöckner Maschinenfabrik, Lauenburg, Germany), at a cutting speed 725 rpm; and at a feeding speed of 1 m/s. The obtained chips were milled in a Condux-Werk HS 350 (Condux Maschinenbau GmbH & Co. KG, Hanau—Wolfgang, Germany) hammer mill. The produced particles were screened in an Allgaier D7336 (Allgaier-Werke GmbH, Uhingen, Germany). Sieves with mesh sizes openings 5.0 mm, 3.15 mm, 1.24 mm and 0.60 mm were used. Two particle size classes were build, a first one a with mesh size >1.24 mm, and a second one with a mesh size 5 mm. Particles from these two classes were manually mixed at a weight ratio of 50:50. Particles mixtures were then oven-dried at 70 °C for 5 days to achieve final moisture contents between 5–7%.

Particleboards (Fig. 1) were made with the target density of 600 kg/m^3, and a thickness of 11 mm. Two adhesive types were used: (1) Methylene diphenyl diisocyanate (MDI) (Huntsman I-BOND$^®$ PM4390, Huntsman GmbH, Hamburg, Germany), applied at amounts of 4% (MDI4) and 6% (MDI6), and (2) urea formaldehyde (UF) (BASF Kaurit$^®$ 350, Basf Se, Ludwigshafen, Germany), applied at amounts of 8% (UF8) and 12% (UF12), respectively. Resins were applied to the particles in a drum blender for 5 min using a spraying nozzle. Resinated particles were manually placed and evenly distributed in a wooden forming box (550 × 550 mm^2) and pre-pressed. Then, mats were hot-pressed at 200 °C and 3.2 MPa for 100 s in a hydraulic Siempelkamp$^®$ press (Siempelkamp Maschinen und Anlagenbau GmbH, Krefeld, Germany). The final thickness of the panels was 11 ± 0.1 mm, and in total 16 particleboards, four per each type, were prepared.

Mechanical properties testing was carried out on a Zwick$^®$ 1474 (Zwick GmbH & Co. KG, Ulm, Germany) universal testing machine using testXpert II software (Zwick GmbH & Co. KG, Ulm, Germany). A three-point bending test (EN 310) was employed to determine the modulus of rupture (MOR), as well as the modulus of elasticity (MOE). The samples (11 × 50 × 270 mm^3) were subjected to a loading rate of 7 mm min^{-1} until failure was reached. Internal bonding (IB) strength according to EN 319 was measured on squared samples (11 × 50 × 50 mm^3). Prior to testing the samples were sanded and then glued onto stainless steel blocks. Blocks were positioned in gimbal-mounted holders and pre-loaded in tension by 5 N. A loading rate of 1 mm/min was applied until failure.

Thickness swelling (EN 317) was measured with samples (11 × 50 × 50 mm^3) fully immersed in 20 °C distilled water. Thickness swelling and water absorption was measured after 2 h and 24 h, respectively. As soon immersion time has elapsed the samples were taken out from the water bath with excess water removed with paper tissues. Thickness swelling was measured in the mid of the sample by a caliper. The water absorption was determined by weighing using a scale Radwag mac 210 (Radwag USA L.L.C., Florida, United States of America) with the precision of 1 mg. The sample weight was recorded and consequently used for calculation of water soaking in percent.

Vertical density profiles (VDP) were determined with the Gre-Con RG44$^®$ 33KV/1 mA (GreCon, Germany) x-ray density analyzer. The obtained data were analyzed using Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. Data were checked for normality using Shapiro-Wilk test. For hypotheses testing an analysis of variance
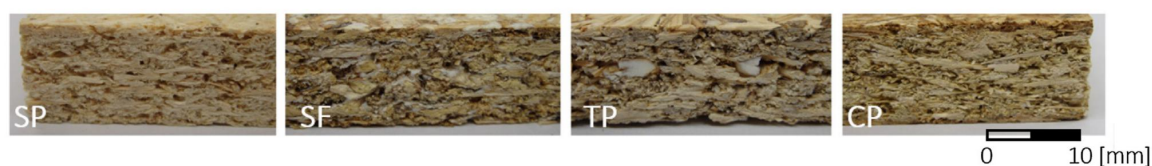

Fig. 1. Cross sectional images of the produced particleboards, using spruce wood (SP), sunflower stalks (SF), topinambour stalks (TP), and cup-plant stalks (CP).
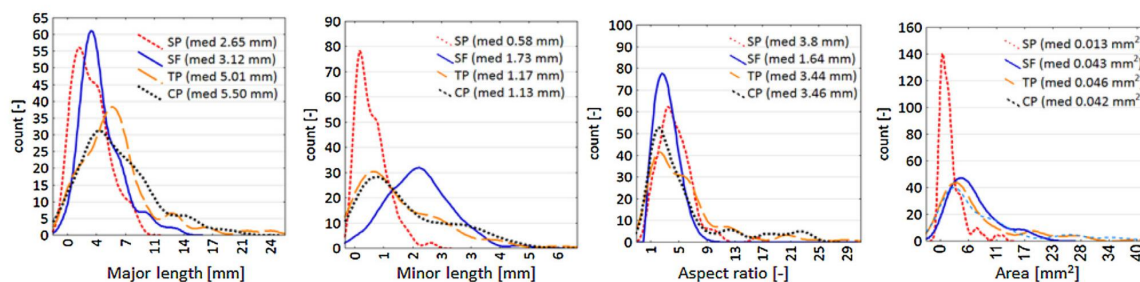
Fig. 2. Distribution of length, width, surface area and aspect ratio measured for particles produced from SP-spruce, SF-sunflower, TP-topinambour, CP-cup-plant stalks (n = 120), med.–median value.

(ANOVA) was employed, followed by Scheffé post-hoc tests. A significance level of 0.05 was chosen.

For particle size measurement the particles were dispersed evenly with a sieve on a transparent foil in a way that less than 5% of the total area was covered. Then one scan of a foil sized 297×420 mm^2 per each particleís type was captured. The scanner was operated at 1200 dpi resolution. The particles were analyzed using the ImageJ software (Rasband, 1997). Major and minor length of the fitted ellipse to each of the particles were specified. Consequently, aspect ratio was calculated as the ratio of major length/minor length of each particle. At the end surface area of particles was automatically measured in pixels^2, which were automatically converted on mm^2. Obtained data were analyzed using Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. Each measurement of particles was evaluated on the basis of interquartile range, and the median.

For the chemical analysis one sample of 200 mg per material type was prepared. These samples were then pre-hydrolyzed with 2 mL of 72 H2SO4 (30 °C, 1 h). The reaction mixture was diluted with 56 mL ultra-pure water, and post-hydrolysis was performed in an autoclave at 120 °C, and 1.2 MPa pressure for 30 min. For the high-performance liquid chromatography borate analysis, wood sugars were separated in a 5.6 mm column, 115 mm long (Omnifit®, Diba Industries, Inc., Danbury, North America) filled with strong anion exchange resin 114 MCL gel CA08F (Mitsubishi Chemical Corporation, Tokyo, Japan) at 60 °C. The mobile phase (0.7 mL/min) consisted of solution A, 0.3 M potassium borate buffer with pH 9.2, and solution B, 0.9 M potassium borate buffer with pH 9.5. After sample injection chromatographic separation started with 90% (A) and 10% (B), with the run lasting 35 min. Data acquisition was ceased after 50 min. For quantification a post-column derivatization of monosaccharides with Cu-bichinconinate (0.35 mL min^{-1}) was applied. The reaction was performed at 105 °C in a 30 m crocheted Teflon coil of 0.3 mm inner diameter. This enabled the subsequent detection of sugars at 560 nm (Sinner et al., 1975; Sinner and Puls 1978). Data were processed using dionex® chromeleon software (Thermo Fischer Scientific Inc., Sunnyvale, United States). The detected glucose was taken as an equivalent for the cellulose content, since this long-chain polysaccharide is made up of glucose monomer units (Gibson, 2012). The sum of detected mannose, galactose, arabinose, rhamnose and xylose was taken equal to the hemicellulose content, while the insoluble substrate that remained after hydrolysis was considered to be the lignin content (Weiss et al., 2013).

3. Results and discussion

3.1. Particle size measurement

The used lignocellulosic materials delivered different particles sizes, which are important to document. The sunflower particles

had a major particle length of 3.12 mm, while spruce had 2.65 mm. The values ranged for the sunflower particles between 2 and 5 mm, while for spruce particles the range was between 1 mm and 4 mm (Fig. 2). While sunflower and spruce particles were similar in their major length, the major particle length of topinambour and cup-plant particles turned out to be higher. Major length of topinambour particles was 5 mm, while cup-plant had 5.5 mm. Particle length ranges for topinambour and cup-plant were both shifted towards higher values.

Minor lengths (Fig. 2) of the spruce particles were under those of the agricultural residues (spruce 0.58 mm, sunflower 1.73 mm, topinambour 1.17 mm, cup-plant 1.13 mm). Values ranged between 0.36 mm and 1 mm for spruce, between 0.72 mm and 1.8 mm for topinambour, 0.7 mm and 2.25 mm for cup-plant particles, and between 1.25 mm and 2.23 mm for the sunflower particles. The fact that particles produced from agriculture residues had higher minor as well as higher major lengths, this resulted also in higher surface areas.

With respect to the aspect ratios, the most significant difference was observed between spruce and sunflower particles. While spruce particles had an aspect ratio of 3.8, sunflower particles showed an aspect ratio of 1.64. Topinambour particles had 3.44, while cup-plant particles had 3.46. The ranges for aspect ratios were quite consistent across the used material types.

The particle sizes have significant effects on particleboard properties. Even with particle widths (minor length) and thicknesses being constant, higher particle lengths were found to have a lowering effect on the IB, while MOR and MOE were increasing (Miyamoto et al., 2002). A general finding is, that more "cubic" particles (lower aspect ratios) have a positive effect on IB, while MOE and MOR are more profiting from more elongated particles higher aspect ratios (Miyamoto et al., 2002; Arabi et al., 2011). As in the own research particle production from wood and the agriculture residues underwent the same preparation and sieving processes, particle sizes were anticipated to be consistent in size. However, data revealed fairly different particle sizes among the material types. When a raw material chip is fractured, the intrinsic material properties such as normal and shear stresses developed during cutting are crucial (Hellström, 2008). Therefore, it can be concluded that even with a consistently applied preparation processes the particle geometries will vary with the used material, a fact needed to be considered in production processes. This also approves the first stated hypothesis. However, this might not be the most relevant reason why particleboards made from alternative materials perform lower than wood-made panels. Juliana et al. (2012) found that even with aspect ratio and particle shapes being constant, IB, MOR and MOE of kenaf shive-made particleboards were under the performance of regular wood-based particleboards.

Table 1
Chemical composition of used raw materials for particleboard production, the values in brackets are obtained from literature.

	Spruce wood (Stelte et al., 2011)		Sunflower stalks (Jung et al., 2013; Khristova et al., 1996)		Topinambour stalks (Gunnarsson et al., 2014)		Cup plant stalks (Trischler and Sandberg, 2014)	
Cellulose [%]	45.4 (43)		40.9 (38–41)		30.9 (25–31)		38.6 (36)	
Mannose [%]	12		1.7		1.5		2.1	
Galactose [%]	2.1		1		1.3		1	
Arabinose [%]	1.1	$\sum$ 20.9 (23)	0.7	$\sum$ 19.4 (16–19)	1	$\sum$ 17.1 (13–21)	0.7	$\sum$ 20.6 (12)
Rhamnose [%]	0.2		0.5		0.7		0.5	
Xylose [%]	5.5		15.5		12.6		16.3	
lignin [%]	28.2 (25)		21.6 (12)		16.3 (11–17)		21.4 (18)	

3.2. Chemical analysis of particles

Chemical compositions (Table 1) of the agricultural residues were different from the one measured for spruce. Compared to spruce hemicellulose content of sunflower stalks were similar, while lignin and cellulose were reduced. Topinambour contained lower amount of cellulose and almost half the lignin of spruce. The cup-plant particles were lower in cellulose and lignin, but similar in hemicelluloses, relative to spruce. Chemical compositions of annual plants vary with the time of harvest, resulting in differences of chemical composition values reported in the literature (Gunnarsson et al., 2014). Sample preparation and the used analytical method also might have contributed to found differences.

As cellulose and hemicelluloses contain a large number of hydroxyl groups (Pirayesh and Khazaeian, 2012), they are predominantly responsible for the bonding to with polar adhesive polymers (Ayrilmis et al., 2009). The lower holocellulose content (cellulose and hemicellulose) of the agricultural residues might be a reason why bonding among these particles is restricted, with the consequence of reduced the mechanical properties. Likewise, water uptake is proportional to the abundancy of free hydroxyl groups (Gwon et al., 2010; Nourbakhsh et al., 2011), meaning that the reduced holocellulose content in the agriculture residues may have resulted in lower water absorption.

Lignin as an amorphous polymer constituent in the cell walls is more hydrophobic, making plants less accessible to water (Achyuthan et al., 2010). Lower lignin content as found with the agricultural residue particles is most likely causing a higher water uptake (Nourbakhsh et al., 2011). In addition, further variables such as the amount of extractives are also possibly interfering with the final properties of particleboards. For instance, thickness swelling and water absorption of particleboards made from wood is proportionally decreased with the higher extractive content (Nasser, 2012). To summarize, chemical composition of particles is playing a role in the physical and mechanical performance of particle-

boards. The various characteristics of particleboards are complex and intercorrelated, and isolating a single effect as a pivotal point is difficult (Weigl et al., 2007). These complex relationships between e.g. chemical composition (i.e. cellulose, lignin) and other particleboards properties are therefore not yet fully understood.

3.3. Bending properties

Fig. 3 is showing MOR results for the four particleboard types, along with the two adhesives and the two adhesive dosages. Overall, the spruce particleboards have shown higher MOR values, with the 6%-MDI bonded particleboard having the highest MOR (16 MPa). The lowest MOR was found for the UF-bonded sunflower particleboard (8 MPa). Although non-significant, the boards with higher resin content showed also higher MOR values. The cup-plant particleboard had higher average MOR values, compared to the other alterative particleboards. Assessing the particleboards specification according to EN 312 standard, both MDI-bonded cup plant particleboards and all alternative particleboards with higher MDI dosage were suitable for general purposes in dry conditions. While the spruce particleboard bonded with the lower UF dosage also fulfilled class P1 of EN 312, none of the UF alternative boards did meet the P1 standard.

MOE results were similar to those for MOR (Fig. 4). MOE was highest for the spruce MDI-bonded particleboards, with the MOE values being 10% above the UF-bonded particleboard of spruce. The MDI-bonded alternative particleboards (SF, TP, CP) performed similar to the spruce UF-bonded particleboard. The 6% MDI sunflower particleboards (SF) delivered MOE values not significantly different from the MDI bonded spruce particleboard (p > 0.05). Also, both types of MDI-bonded Topinambour (TP) and the cup plant (CP) particleboards showed similar (p > 0.05) MOE, also like the MDI-bonded spruce particleboards (SP). MOE of sunflower and cup-plant made particleboards showed similar (n.s. p > 0.05) MOE as the UF-bonded spruce particleboards. The MDI-bonded spruce
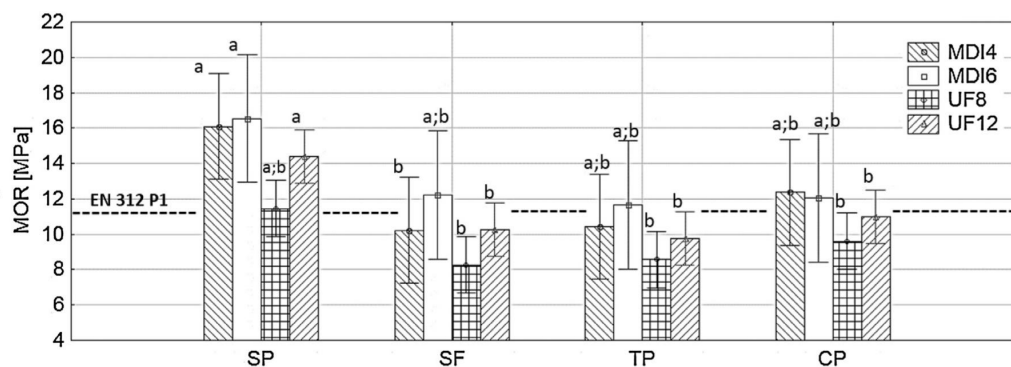
Fig. 3. Modulus of rupture (MOR) of the produced particleboards. Each column represents six measurements; errorbars indicate 95% confidence level); SP-spruce particleboards, SF-sunflower particleboard, TP-topinambour particleboard, CP–cup-plant particleboard. a;b–columns with same letters are not significantly different (p > 0.05), MDI4–4% Methylene diphenyl diisocyanate (MDI), MDI6–6% Methylene diphenyl diisocyanate, UF8–8% urea formaldehyde, UF12–12% urea formaldehyde.
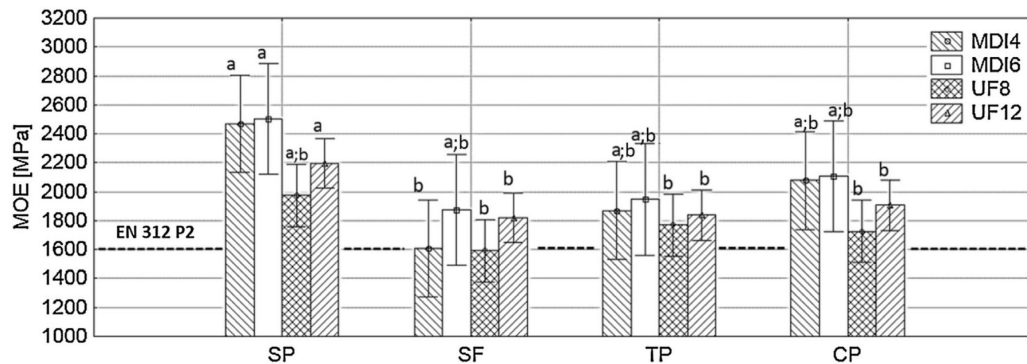
Fig. 4. Modulus of elasticity (MOE) of produced particleboard (each column represents data obtained from 6 measurements; errorbars indicated 95% confidence level); SP–spruce particleboards, SF–sunflower particleobard, TP–topinambour particleboard, CP–cup-plant particleboard. a;b–columns with the same letter are not significantly different (ANOVA;p > 0.05).

particleboards were in coherence with the EN 312 class P4 standard, which is on load-bearing boards used in dry conditions. Our particleboards from alternative resources complied with class P2 (boards for interior fitment, including furniture, for use in dry conditions) of the EN 312 standard. This approves hypotheses 2 and 3, suggesting that non-wood particleboards can demonstrate property profiles suitable for standard applications; and that the property profiles are closely interacting with resin type and with the amount of resin as well. As mentioned, particleboards can be made from various alternative resources. Examples are particleboards made from tea leaves as reported by Yalinkilic et al. (1998), from rice straw as shown by Li et al. (2010), from wheat straw with waste veneer (Azizi et al., 2011), from walnut shells (Pirayesh et al., 2012), or from almond shells (Pirayesh and Khazaeian, 2012). The obtained MOR from particleboards made of sunflower stalks did meet the MOR of sunflower-made particleboards made by Guler et al. (2006).

As discussed, the lower MOE and MOR performance of the alternative material particleboards may have various reasons. Mati-Baouche et al. (2014) argued with differences in anatomical structure, also Wu et al. (2010) referred to the intrinsic structural properties of the used raw material. Particleboards from agricultural residues seemingly contain particles that exhibit a structural composition different from wood. An excessive presence of parenchymatic pith tissue in agricultural plant materials was noted by (Balducci et al., 2008), which was proven to have an reducing effect of MOE and MOR.

3.4. Internal bonding

Internal bonding (Fig. 5.) was linked with the amount of applied resin, as well as resin type. The MDI-bonded spruce particleboards have shown significantly higher values (+50%) than all the other particleboard types. No significant difference (p > 0.05) was found for IB between the UF-bonded spruce particleboards, and the MDI-bonded alternative particleboards. The higher UF resination resulted in higher IB across all particleboard types. The most pronounced effect was observed for the spruce particleboards (+20%), while the lowest effect was seen with the cup-plant particleboards (+8%).

IB of the 8%-UF bonded spruce particleboard was similar to the sunflower one, but lower than the topinambour and cup-plant 4% MDI-produced particleboards. Likewise, the IB of the 12% UF-spruce particleboards turned out to be similar to the particleboards made from sunflower, topinambour as well as cup-plant particleboards, the latter all bonded with 6% MDI. All panels met P1 class of EN 312. The drawback of the reduced IB of the alternative material particleboards could be partly compensated by different approaches. One option would be to use finer particles (Arabi et al., 2011), which further improves IB. Particleboards of a higher density (Wong, 1999), or lower boardís thicknesses (Hunt et al., 2008) have also delivered higher IB values.

Fig. 5. Internal bonding strength (IB) of the produced particleboards with each column representing 12 measurements; errorbars indicate 95% confidence level); SP–spruce particleboards, SF–sunflower particleobard, TP–topinambour particleboard, CP–cup-plant particleboard. a;b;c;e–columns with the same letter are not significantly different (p > 0.05).

Fig. 6. The density profile of produced panels; SP–spruce particleboards, SF–sunflower particle board, TP–topinambour particleboard, CP–cup-plant particleboard.

3.5. Vertical density profile

Vertical density profiles (VDP) of the particleboards produced from agricultural residues were not different from the spruce particleboards (Fig. 6.). This means that VDP of all produced particleboards were consistent with the classical distribution mentioned in literature (Wong et al., 1998; Wong, 1999). It is therefore assumed that the density profiles did not play dominant role for the observed differences in the physical and mechanical performance.

3.6. Thickness swelling and water absorption

The MDI-bonded particleboards showed significantly lower thickness swelling after 2 h of immersion (TS2h), compared to the UF bonded particleboards (Fig. 7). For the MDI-bonded particleboards the lowest swelling was found for the spruce particleboards, while the highest thickness swelling was found for the sunflower particleboards. All UF-bonded particleboards had similar swelling values, with exception for the cup-plant particleboards, which was showing significantly higher thickness swell (20%, sig. p < 0.05). Higher MDI dosages did not reduce TS2h for the particleboards made from spruce and sunflower. However, the higher MDI dosage significantly (sig. p < 0.05) reduced TS2h of the particleboards made with cup-plant particles. In contrast, the higher UF resin dosage significantly reduced thickness swelling of the spruce and cup-plant particleboards. The Higher UF dosage did not change TS2h of sunflower and topinambour particleboards.

The TS24h of MDI4-bonded sunflower particleboards were close to those bonded with UF (Fig. 8). Further, the higher MDI dosage resulted in a significantly reduced TS24h for the sunflower particleboard. Reduced TS24h was also seen for the particleboards made from spruce and cup-plant, respectively, all bonded with the higher MDI dosage. For UF-bonded particleboards the higher resin content significantly reduced TS24h of spruce as well as cup-plant particleboard. The TS24h of topinambour and sunflower particleboards did not show significant differences when the higher dosage of UF resin was used.

The significantly reduced thickness swell of the particleboards bonded with MDI can be explained by the strong bonding between MDI and wood. MDI isocyanate groups are building irreversible urethane covalent bonds, which are of higher resistance against moisture (Pizzi and Mittal, 2003). In contrast, the higher swelling of particleboards bonded with UF resins can be assigned to the reversibility of the aminomethylene bridges that are created during curing, which are also known to result in a lower resistance to the water (Pizzi and Mittal, 2003).

An improved resistance of UF-bonded particleboards against water uptake can be achieved through increasing the molar ratio between urea and formaldehyde. Our data have shown that the swelling of sunflower particleboards were close to those reported by Bektas (2005) as well as Guler et al. (2006). Khristova et al. (1996) reported a lower thickness swelling coefficient, compared to our data. These authors have used phenol-formaldehyde adhesive, which is known to improve water resistance. Balducci et al.

Fig. 7. Thickness swelling (TS) and water absorption (WA) after 2 h of produced particleboard (each column represents data obtained from 12 measurements; errorbars indicated 95% confidence level); SP–spruce particleboards, SF–sunflower particleobard, TP-topinambour particleboard, CP–cup-plant particleboard. a;b;c;e;f;g;h–columns with the same letter are not significantly different (ANOVA;p > 0.05).
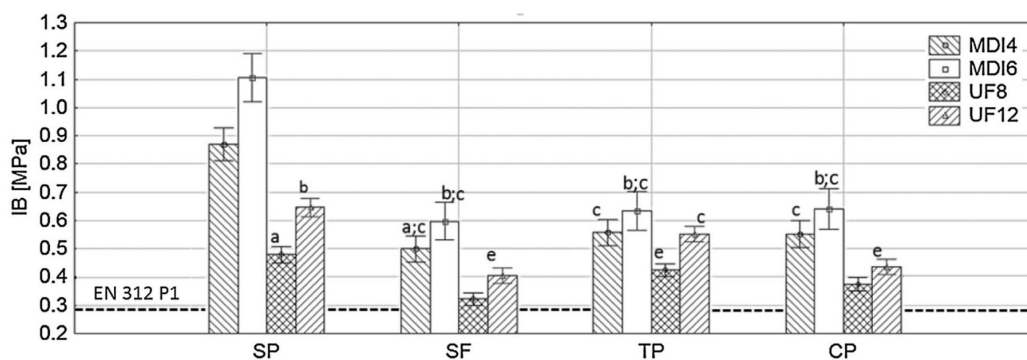
Fig. 8. Thickness swelling (TS) and water absorption (WA) after 24 h of produced particleboard (each column represents data obtained from 12 measurements; errorbars indicated 95% confidence level); SP–spruce particleboards, SF–sunflower particleboard, TP–topinambour particleboard, CP–cup-plant particleboard. a;b;c;e;f;g;h–columns with the same letter are not significantly different (ANOVA; p > 0.05).

(2008) produced particleboards from agricultural residues at much lower densities, thus thickness swelling of these boards were lower. The own thickness swelling data are seen as relatively high, which can be attributed to the fact that no wax or other hydrophobic substances were added. In general, the addition of paraffin (Papadopoulos, 2006) or the use of phenolic resins (Khristova et al., 1996; Pizzi and Mittal, 2003) would decrease water uptake and thickness swelling of particleboards.

4. Conclusions

This research successfully shows that particleboards can be produced from agricultural residues at acceptable properties. Especially the MDI-bonded particleboard types made with agricultural residues were found to be a viable alternative to classical UF-bonded particleboards made from spruce. While higher MDI dosages did not significantly improve the bending properties, it did improve the internal bonding for all tested particleboard types. The mechanical properties of the tested alternative particleboards were found to be significantly lower, when compared with spruce particleboards. A future challenge is to understand the mechanisms that lead to altered property profiles in particleboards. One way here is to identify resin vs. material failure through e.g. shear blocks tests. Another way might be a micromechanical approach, by identifying critical strain situations in the wood particles and the wood-adhesive interphases. Through this, strain maxima can be identified as the "weak points", leading to mechanical failure. These identified strain maxima would be relevant triggers for improving properties of particleboards made with any type of raw material. Although the particleboards made from agriculture residues demonstrated generally lower mechanical and physical properties, with exception of the UF-bonded sunflower and cup-plant particleboard, the requirements for general purpose particleboards used in dry conditions (EN 312) were met.

Acknowledgements

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Further reading

EN 317 Particleboards and fiberboards—determination of swelling in thickness after immersion in water. 1993.

EN 310 Wood-based panels—determination of modulus of elasticity in bending and of bending strength. 1993.

EN 319 Particleboards and fiberboards—determination of tensile strength perpendicular to the plane of the board. 1993.

EN 312 Particleboards—Specifications. 2010.

5. Paper II.

Study of Miscanthus (*Miscanthus x gigantheus*) stalks as a material for particleboard production

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Title: Study of Miscanthus (*Miscanthus x gigantheus*) stalks as a material for particleboard production

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Key words: Particleboard, Miscanthus, alternative material, chemical composition, anatomical structure, swelling, modulus of rupture, modulus of elasticity

Abstract:

In the paper Miscanthus (*Miscanthus x gigantheus*) stalks are studied as a possible replacement of the wood in particleboard panels. Firstly, Miscanthus particles were chemically studied and content of cellulose, hemicellulose and lignin was compared with spruce wood. Secondly, the microscopic structure of Miscanthus stalk was identified using scanning electron microscopy. The Miscanthus particles are used to fully replace wood in the production of particleboards. Particleboards from Miscanthus and Spruce were produced on two levels of MDI resin dosage (4 % and 6 %). The standard mechanical properties: Modulus of rupture (MOR), modulus of elasticity (MOE) and internal bonding strength (IB) were measured as well as thickness swelling of particleboards. The mechanical properties of Miscanthus particleboards are lower compared to wood, however Miscanthus particleboards are still suitable for general purposes in dry conditions according to EN 312. Furthermore, lower swelling at higher levels of water absorption was measured for Miscanthus particleboards compared to spruce. At the same time, no evident effect of higher MDI resin dosage on MOE, MOR or IB was observed for Miscanthus particleboard. Aside of physical and mechanical performance of the particleboards, SEM study outlined possible weak links in the ruptured samples of the Miscanthus particleboards.

Introduction

Wood is traditional raw material for particleboards production for many decades, and not by accident particleboards nowadays occupy the most of the wood based panel market. Beside of medium density fiberboards and oriented strand boards, more than 28 million m^3 of particleboard panels is produced per year (EPF, 2014) in Europe. Considering the relatively high production volumes and the decline of natural resources (Giljum et al., 2009), a critical shortage of wood could be a matter of time. The idea how to face this challenge in Europe may follow concepts developed in countries with little forested areas. Here alternative natural materials are utilized in particleboard-like product. Residues obtained from abundantly available agriculture plants are used for particleboards production. The advantage of this concept is in ecologically and economically efficient material utilization. While some parts of the plant are used for food, chemical, or biogas production (Mast et al., 2014), other, unutilized parts, may be processed in particleboards production. Common current practice is that residues such as stalks, husks, or straw are left on field or sometimes even burned. Obviously transformation of so called agricultural waste in a particleboard may mean economic profits for the particleboards producers, as the expenses for waste material are in general lower than for wood. At the same time, utilization of the waste material in industrial production cuts environmental burdens.

Naturally, some research addressing particleboard production from plants residues was already conducted. Particleboards from rice straw (Gerardi et al., 1998; Li et al., 2010; Yasin et al., 2010), wheat straw (Mo et al., 2003), sunflower stalks (Bektas, 2005; Guler et al., 2006; Khristova et al., 1996; Mati-Baouche et al., 2014) or cotton stalks (Guler and Ozen, 2004) were already produced. Balducci *et al*. (2008) and Dix *et al*. (2009) introduced residues of several central European agricultural plants as a raw material for low density particleboards and Selinger and Wimmer (2015) recently introduced light sandwich particleboards from woven and nonwoven hemp shives and fibers. It is obvious that agriculture could provide materials to replace wood in particleboards. While various agriculture residues were recognized viable in the production of the particle based panels, there has been a very limited research concerning utilization of the Miscanthus (*Sinensis giganteus*) plant. Balducci *et al*. (2008) and Dix *et al*. (2009) introduced a light weight Miscanthus particleboard, which due to low density was not suitable for any engineering purposes. Miscanthus was also used in production of fiberboard panels (Salvadó et al., 2003).

Miscanthus genus comprises perennial, woody, rhizomatous, bamboo-like grasses native to tropical and subtropical regions of Asia and Southeast Africa. They are generally 1.5–4 m high with stem diameter from 1–2 cm. Some of the species such as *M. floridulus* and *M. lutarioparius* can reach height 6–7 m. Due to tolerance to varied ecological conditions, Miscanthus is becoming popular in the colder European climate (Monti et al., 2015; Parajuli et al., 2015). Miscanthus is commonly used as a bioenergy crop (Ameline et al., 2015) or resource for chemical production (Arnoult et al., 2015; Kim et al., 2015). Nevertheless, we assume that Miscanthus due to its structure, thick nodal woody stem, large plantation area in Europe estimated 38.300 ha (Xue et al., 2015) and dry mass yield up to 40 t/ha (Lewandowski et al., 2003; Monti et al., 2015) may be attractive for particleboard production. The presented knowledge motivated us to state following goals: (1) Design of miscanthus particleboard which can be used for general purposes according to EN 312. (2) Compare the properties of the miscanthus particleboard with spruce particleboard. (3) Observe an effect of increased adhesive amount on the bending, internal bonding and thickness swelling properties of the particleboards. (3) Microscopically evaluate the differences in a structure between miscanthus and spruce particleboard.

Materials and methods

In the experiment Miscanthus (*Sinensis gigantheus*) stalks obtained from fields in northern Germany were used. The Miscanthus stalks were approximately 1.7 m long, with a cross-sectional diameter between 15-30 mm. As a control, virgin spruce (*Picea abies L. karst*) wood without bark was used.

 Preparation of the particles

Firstly the raw material was chipped in a chipper Klöckner 120X400H2W.T (Klöckner Maschinenfabrik, Lauenburg, Germany) using a cutting speed of 725 rpm and a feeding of speed 1 m/s. The obtained chips of approximate dimensions of $20 \times 10 \times 5$ mm^3 were subsequently milled in a hammer mill Condux-Werk HS 350 (Condux Maschinenbau GmbH & Co. KG, Hanau – Wolfgang, Germany). The produced particles of different size were screened afterwards in a cascade vertical screener Allgaier D7336 (Allgaier-Werke GmbH, Uhingen, Germany). The screener's sieve with mesh size openings of 5.0 mm; 3.15 mm; 1.24 mm and 0.60 mm sorted the particles to different fractions. The particles of mesh > 1.24 and < 5 mm were taken and manually mixed together at a weight ratio 50:50. Consequently, the

particles mixture was oven-dried at 74°C for 4 days, the final moisture content was from 5 to 7 %. The samples of the particles used are in figure 1.

Figure 5-1 Spruce and Miscanthus particles used in production of a particleboard panel

Preparation of panels

Particleboards with target density 600 kg/m^3 and thickness of 11 mm were produced from spruce and Miscanthus (Figure 2), using a methylene diphenyl diiosacyanate (MDI) resin (Huntsman I-BOND® PM4390, Huntsman GmbH, Hamburg, Germany). Two levels of resin dosage were used. MDI was applied in amounts of 4% (MDI4) and 6% (MDI6). The resin was applied to the particles in a drum blender for 5 minutes, using a pneumatic spraying nozzle. The resinated particles were manually distributed in a wooden forming box (550×550 mm^2) and manually pre-pressed. After pre-pressing, the formed mat was hot-pressed at 200 °C and 3.2 MPa for 100 sec in a hydraulic press Siempelkamp (Siempelkamp Maschinen und Anlagenbau GmbH, Krefeld, Germany). After production, the panel target thickness was controlled at several randomly selected spots. The final thickness of the panels was 11±0.1 mm. In total, 4 particleboard types were manufactured.
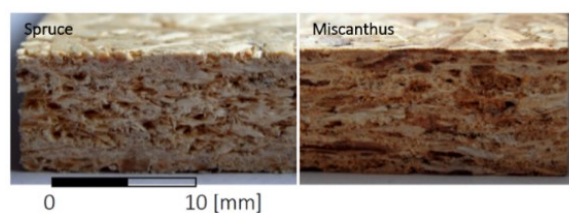
Figure 5-2 Cross section of the spruce and Miscanthus particleboards

Material properties and data evaluation

The mechanical testing was carried out on a Zwick® 1474 universal testing machine using testXpert II software (Zwick GmbH & Co. kg, Ulm, Germany).

A three point bending test (EN 310) was employed to determine the bending properties. The samples ($12 \times 50 \times 290$ mm^3) were subjected to a loading rate of 7 mm·min^{-1} until the failure was reached.

The internal bonding (IB) strength according to EN 319 was measured on square samples (50×50 mm^2). Prior to testing, the samples were sanded and then glued between stainless steel blocks. The blocks were positioned in gimbal-mounted holders and pre-loaded in tension by 5 N. Subsequently, a loading rate of 1 mm/min was applied until the failure was reached.

Thickness swelling was determined according to EN 317. Conditioned samples of size $12 \times 50 \times 50$ mm^2 were fully immersed in 20 °C distillated water. The thickness swelling was measured at two time intervals, after 2 and 24 hours. After the immersion time had elapsed, the test samples were taken out of the water and the excess water was removed using a paper cloth. Then the thickness swelling was measured manually, using a thickness gauge, in the center of the samples.

Vertical density profile (VDP) was measured using an x-ray density analyzer GreCon RG44® 33KV/1mA (GreCon, Germany). The equipment analyzed five samples of $12 \times 50 \times 50$ mm^2 dimensions.

The obtained data were analyzed using Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. The normality of the data distribution was confirmed by the Shapiro-Wilk test. The significance differences (level 0.05) among the results was tested using the analysis of variance (ANOVA) and Scheffé post-hoc test.

Scanning electron microscopy

The surface morphology of the particle boards was investigated using a scanning electron microscope Tescan Vega Ts5310 (Tescan Brno, s.r.o., Brno, Czech Republic). The morphology of the used Miscanthus stalks was studied as well as the interactions between the particles in both particleboard types were inspected. Specimens obtained from the ruptured region of IB sample were coated with gold in a vacuum sputter coater. The SEM accelerating voltage was 16.7 kV.

Chemical analysis

For the chemical composition (cellulose, hemicelluloses and lignin) around 200 mg were pre-hydrolyzed with 2mL of 72 H2SO4 (30 °C, 1h). The reaction mixture was diluted with 56 mL ultra-pure water, and post-hydrolysis was performed in an autoclave at 120 °C, and 1.2 bar for 30 min. For the high-performance liquid chromatography borate analysis, wood sugars were separated in a 5.6 mm column, 115 mm long (Omnifit®, Diba Industries, Inc., Danbury, North America) filled with a strong anion exchange resin 114 MCL gel CA08F (Mitsubishi Chemical Corporation, Tokyo, Japan) at 60 °C. The mobile phase (0.7 mL/min) consisted of solution A, 0.3 M potassium borate buffer with pH 9.2, and solution B, 0.9 M potassium borate buffer with pH 9.5. After sample injection chromatographic separation started with 90 % (A) and 10 % (B), with the run lasting 35 min. The data acquisition was ceased after 50 min. For quantification a post-column derivatization of monosaccharides with Cu-bichinconinate (0.35 ml min^{-1}) was applied. The reaction was performed at 105 °C in a 30 m crocheted Teflon coil of 0.3 mm inner diameter. This enabled the subsequent detection of sugars at 560 nm (Sinner et al. 1975, Sinner and Puls 1978). Data were processed using dionex® chromeleon software (Thermo Fischer Scientific Inc., Sunnyvale, United States).

Results and discussion

Chemical composition

The chemical composition of Miscanthus particles was different from the spruce wood (Table 1-). The miscanthus particles contained by 7 % less cellulose and by 9 % less lignin than spruce particles. The measured data meets well those obtained from the literature (Kim et al., 2012; Salvadó et al., 2003; Stelte et al., 2011; Tro et al., 1998). There is hypothesized that lower lignin content may cause higher water absorption of material, due to lignin inherent hydrophobicity (Achyuthan et al., 2010). In the same time, other authors (Nasser, 2012; Nemli et al., 2003) suggested that reduced amount of cellulose in raw material may decline particleboards mechanical properties.

Table 5-1 Chemical composition of the Miscanthus particles and spruce particles

| | Miscanthus particles | | | Spruce particles | | |
	measured	(Kim et al., 2012)	(Salvadó et al., 2003)	measured	(Stelte et al., 2011)	(Tro et al., 1998)
Cellulose	38 %	36-38 %	42 %	45 %	43 %	42 %
Hemicelluloses	21 %	18-26 %	21 %	21 %	23 %	24 %
Lignin	17 %	13-18 %	21 %	28 %	25 %	28 %

Scanning electron microscopy

As is evident from the Figure 3, the microscopic structure of the Miscanthus is considerably different from the wood. The Miscanthus stalks cross-section in transversal (Figure 3. D) and cross-section in longitudinal (Figure 3. A, B, C) direction is represented. The figure shows particular components of stalk structure. From the outside, the stalk is consists of epidermis (ep) and an outer layer. The core is filled with soft parenchyma cells. The most important to our study is the stalk outer layer providing wood-akin material for particleboard production. Our observations are consistent with (Kaack et al., 2003; Xue et al., 2013).
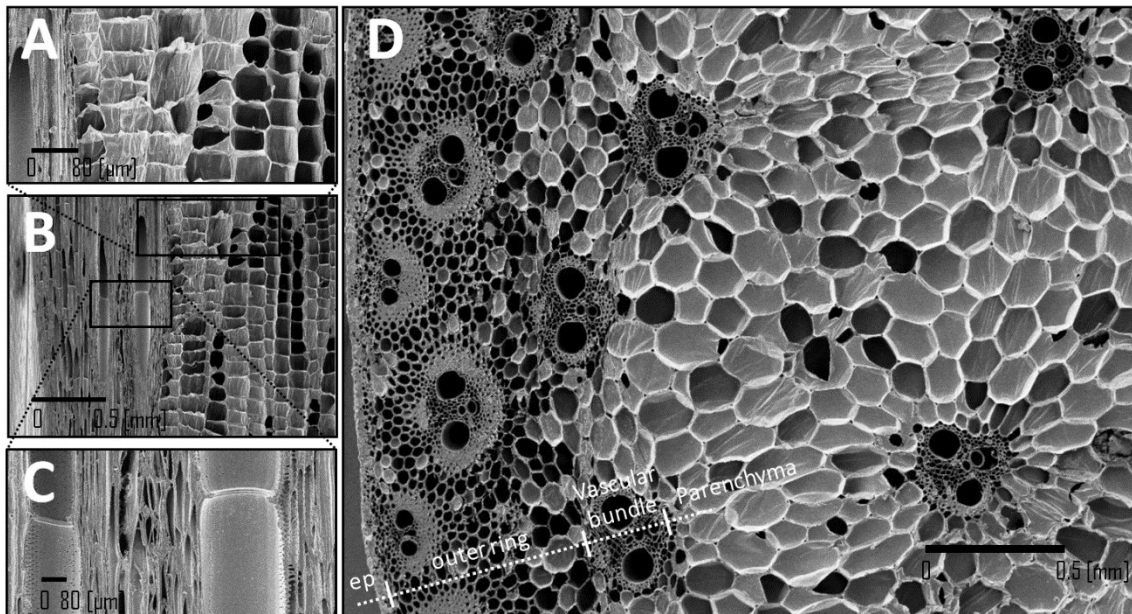
Figure 5-3. Microscopic structure of Miscanthus stalks. The longitudinal (A, B, C) and transverse cross-section (D). ep – epidermis

Figure 4 demonstrates the microscopic structure of ruptured IBs in samples of Miscanthus (Figure 4. A,B,C) and spruce (Figure 4. D,E,F). It is evident that the particles from the outer layer of the Miscanthus stalk are similar to the spruce particles (Figure 4. A, D). Nevertheless, soft parenchyma cells are present on the ruptured surface of the Miscanthus particleboard (Figure 4. B,C), which indicate that these soft components may cause rupture of the Miscanthus particleboard. In fact, very little adhesive coverage was visible on the surface of Miscanthus particleboard compared to the spruce particleboard (Figure 4. E). This suggests

that Miscanthus particleboards had ruptures in the soft parenchyma cells, while the spruce particleboard showed traces of structural i.e. wood failure.

This finding may be important for further development of Miscanthus particleboards. On the ground of the observed failures, we can hypothesize that sorting out the parenchyma cells before the pressing of particleboard may improve Miscanthus particleboards mechanical properties.
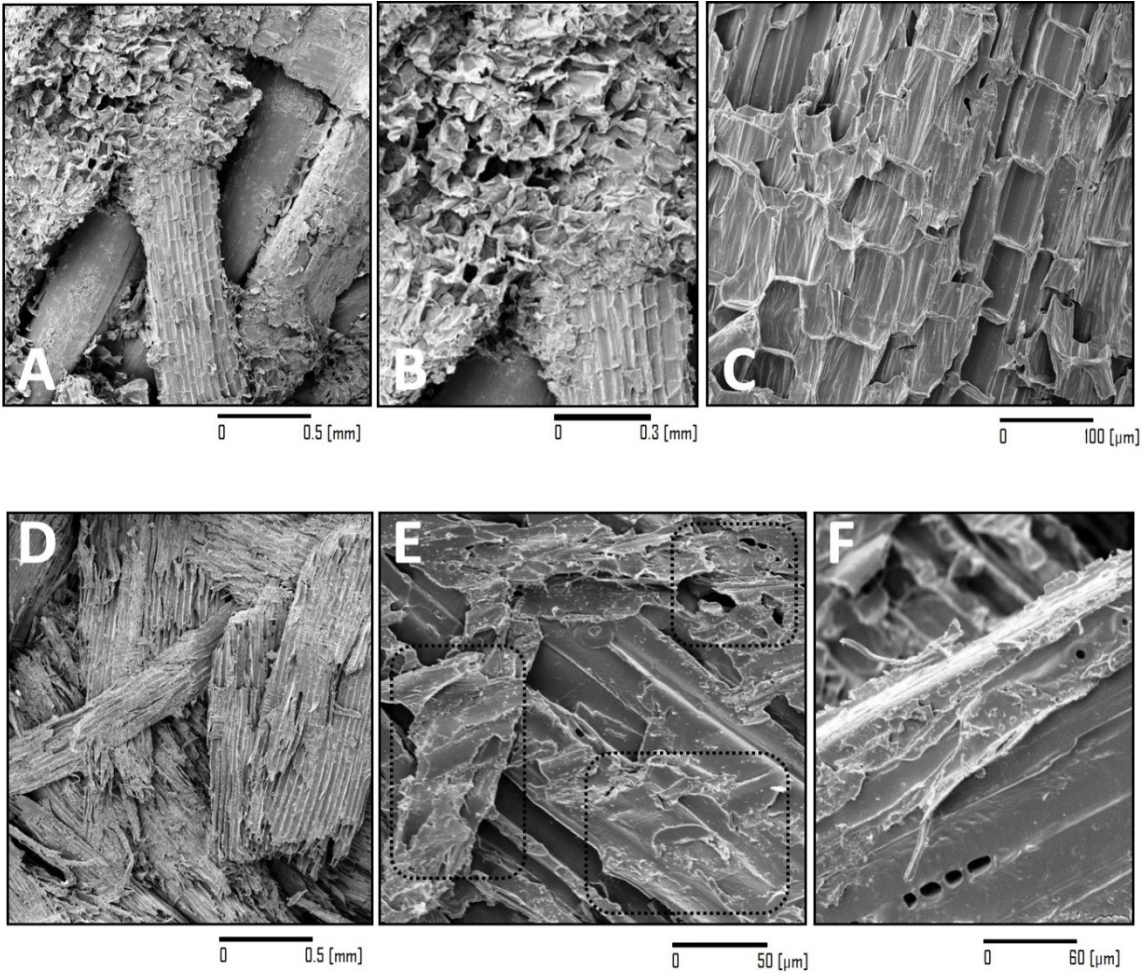
Figure 5-4. Microscopic structure of the ruptured Miscanthus (A,B,C) and Spruce (D,E,F) particleboards. Marked areas (E) indicate structural failure of the spruce particleboard.

The bending properties

The average modulus of rupture (MOR) of the spruce particleboards was by 20 % higher than MOR of the Miscanthus particleboards (Figure 3.). On the other hand, ANOVA proved significant differences in MOR between the of spruce and Miscanthus particleboards in case

when the particleboards were bonded by higher dosage of MDI resin. At the same time, no effect of the increased resin dosage on the MOR was proven either for the Miscanthus or the spruce particleboards. The modulus of elasticity (MOE) showed similar trends as MOR. The average MOE of the Miscanthus particleboards was by 31 % lower. At the same time, higher dosage of the MDI resin did not seem to increase MOE of the boards. Our particleboards displayed MOR and MOE similar to some of the fiberboard types mentioned in (Salvadó et al., 2003). Our particleboards had significantly lower density than the fiberboards produced by (Salvadó et al., 2003); on the other hand, our design used a resin for the particles bonding, while the mentioned fiberboards were manufactured as a binder-less composites. In comparison with low density Miscanthus particleboards of other authors (Balducci et al., 2008; Dix et al., 2009), the MOR and MOE of our Miscanthus particleboards were twofold better. The higher MOR and MOE were probably due to the increased density of the manufactured Miscanthus panels. On the other hand, the MOR and MOE were similar to the three layer Miscanthus urea-formaldehyde-bonded particleboard of (Balducci et al., 2008). The MOR of our particleboards was ~~than~~ similar to the boards produced from other plants. The bending properties of boards produced from cotton stalks (Guler and Ozen, 2004), sunflower stalks (Khristova et al., 1996) or cotton, kenaf and reed mixed with poplar (Philippou and Karastergiou, 2001) were similar.

Assessing the viability of Miscanthus particleboards according to the Standard, it was found that average MOR and MOE met the requirement of EN 312 P1 class. The MOR of both panel types shows that these panels are suitable for general purposes in dry conditions. The P1 class according to EN312 Standard has no requirements concerning MOE, however the average values of both particleboards fulfilled even the requirement for the EN 312 P2 class.
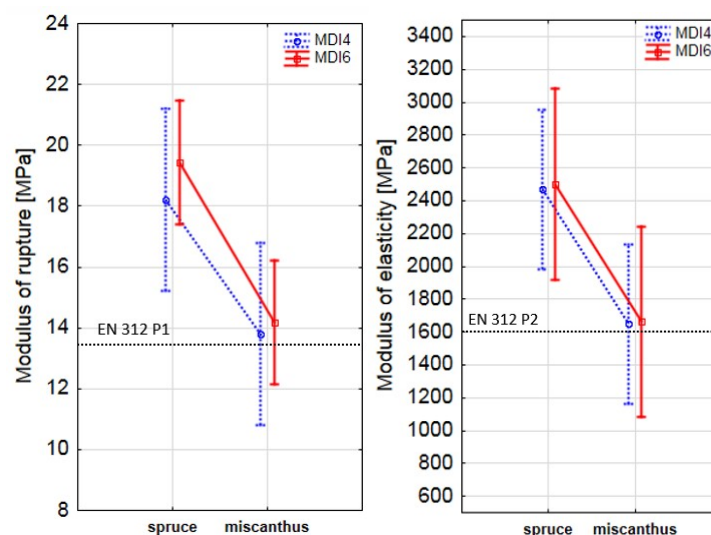
Figure 5-5. Modulus of rupture (MOR) and modulus of elasticity (MOE) of the spruce and Miscanthus particleboards; MDI4 – particleboards are bonded with 4 % weight amount of the MDI resin; MDI 6 - particleboards are bonded with 6 % amount of the MDI resin

Figure 4 shows that Miscanthus particleboards had significantly lower IB than common spruce particleboards. In our opinion, the different anatomical structure of Miscanthus compared to spruce considerably affects the IB strength of miscanthus particleboards. For instance, the presence of the soft pith particles in the Miscanthus particleboards, may cause weak bonding linkage throughout the composite. The similar IB was also measured by (Balducci et al., 2008) for Miscanthus particleboard. Not by accident, particleboards from alternative materials often display lower IB strength compared to wooden particleboards. For example, IB values of particleboards manufactured from cotton stalks (Guler and Ozen, 2004), vine stalks (Yeniocak et al., 2014), tree leaves (Aghakhani et al., 2013), hazelnut husks (Çöpür et al., 2007) or rice husks (Suleiman et al., 2013) were similar to our Miscanthus particleboards. A surprising finding was that the higher dosage of MDI resin did not increase IB strength of Miscanthus particleboards, while IB strength of spruce increased significantly. The internal bonding strength of the Miscanthus particleboards was significantly lower than IB of the conventional spruce particleboard, nevertheless, it was beyond the minimal value of 0.28 MPa. This allows Miscanthus particleboards to use for general purposes in dry conditions according to EN 312.

Figure 5-6. Internal bonding strength (IB) of the spruce and Miscanthus particleboards; MDI4 – particleboards are bonded with 4 % weight amount of the MDI resin; MDI 6 - particleboards are bonded with 6 % amount of the MDI resin

The thickness swelling after 2 hours (TS 2h) showed that both Miscanthus particleboards swelled less (-30 %) than the spruce particleboards. Both MDI bonded Miscanthus particleboards showed significantly lower swelling than spruce particleboards bonded by lower MDI dosage. While the higher MDI dosage reduced the swelling of the spruce particleboard, there was not observed a similar effect for the Miscanthus particleboard. The interesting outcome is that the thickness swelling of the Miscanthus particleboards was generally lower than of spruce particleboards, while the water uptake was significantly higher than in the spruce particleboards.

The swelling after 24 hours was similar. The Miscanthus particleboards manifested significantly lower swelling after 24 hours than the control spruce samples. However, the effect of higher resin amount was more pronounced than in TS 2h. In case of the board manufactured with a higher dosage of the resin, the TS 24h was reduced significantly. The spruce particleboards bonded by the higher dose of MDI showed the same thickness swelling as the Miscanthus particleboards bonded by the lower dose of MDI resin. The water absorption remained higher for Miscanthus particleboards compared to spruce particleboard. The thickness swelling values of the boards are in Figure 5.

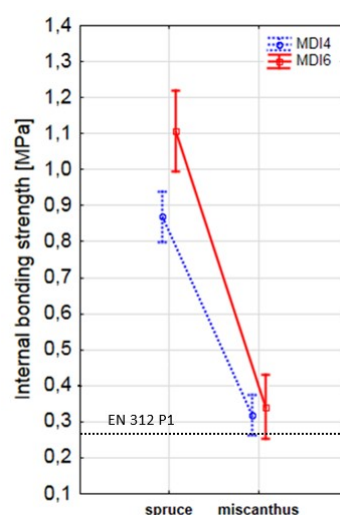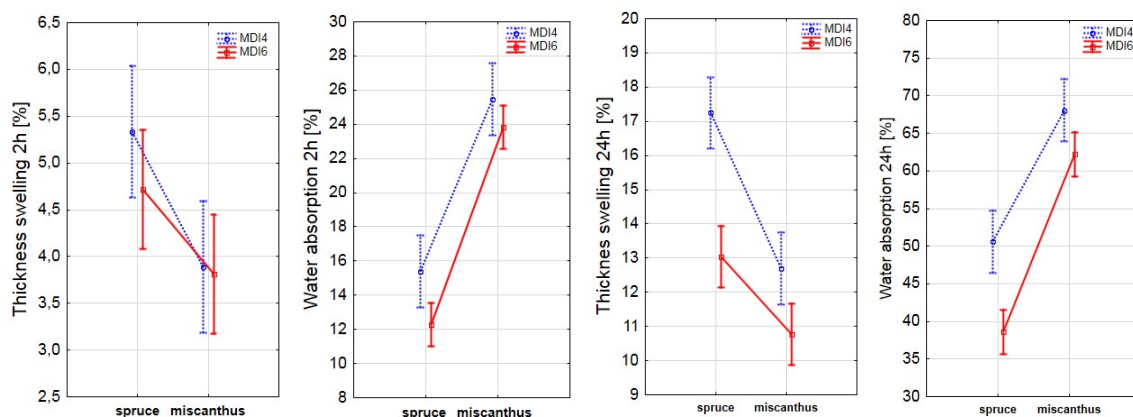Figure 5-7. Thickness swelling and water absorption after 2 and 24 hours of the spruce and Miscanthus particleboards; MDI4 – particleboards are bonded with 4 % weight amount of the MDI resin; MDI 6 - particleboards are bonded with 6 % amount of the MDI resin

The interesting outcome concerning the swelling properties is that Miscanthus displayed lower swelling compared to the spruce particleboards, while the Miscanthus water uptake was significantly higher than in the spruce particleboards. We assume that this could be due to the high abundant pith particles in the Miscanthus particleboard. The Miscanthus pith is composed of soft, spongy parenchyma cells, storing and transporting nutrients throughout the plant during the plant growth. The dry pith particles in the Miscanthus particleboards may perform like sponges, absorbing water without swelling. The water absorption and thickness swelling of our boards meets well the results obtained for a low density Miscanthus particleboard (Balducci et al., 2008). The water absorption and thickness swelling are also similar to some types of the Miscanthus fiberboards manufactured by (Salvadó et al., 2003). Our relatively high swelling values may also be attributed to the fact that no wax or other hydrophobic substances were used. In general, adding water-repellent chemicals such as paraffin (Papadopoulos, 2006), using phenolic resin for particles gluing (Khristova et al., 1996; Pizzi and Mittal, 2003) or surface finishing with an overlay such as veneer (Král et al., 2013; Nemli et al., 2005) can improve water repellency of the panel.

Density profile

The vertical density profile (Figure 6) of particleboards manufactured from Miscanthus was not different compared to the density profile of spruce particleboards. The conventional shape of the density profile (Wong, 1999; Wong et al., 1998), with density peaks i.e. highest density near to the surface layer of the boards was observed for both particleboard types. This finding allows us to declare that the density profile was not responsible for the differences in physical and mechanical performance between spruce and Miscanthus particleboards.
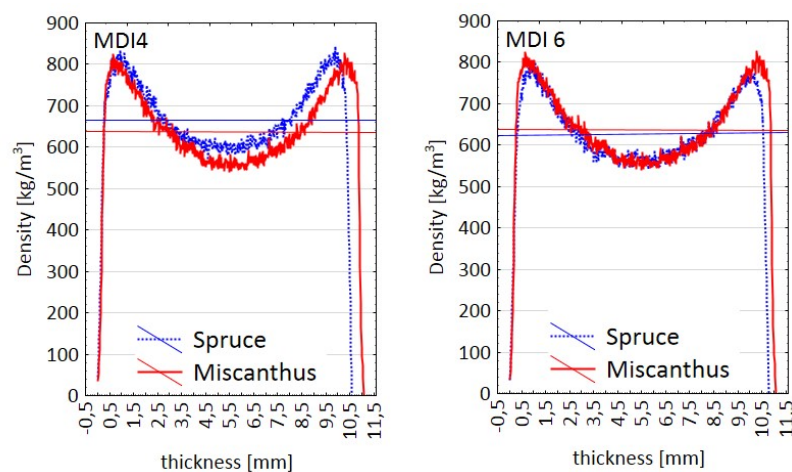
Figure 5-8. Vertical density profiles of the spruce and Miscanthus particleboards, MDI 4 – particleboards are bonded with 4 % amount of the MDI resin; MDI 6 - particleboards are bonded with 6 % amount of the MDI resin

Conclusions

In this research, the wood in particleboards was successfully substituted by particles obtained from Miscanthus stalks. Despite the fact that the mechanical properties observed for particleboards manufactured from Miscanthus stalks are lower than those of spruce particleboards, the Miscanthus particleboard still meet the minimal requirements for general usage in dry conditions according to EN 312. The microscopic evaluation of the Miscanthus and spruce particleboards indicated that soft parenchyma cells may trigger failures and compromise mechanical properties of Miscanthus particleboards. Simultaneously, we hypothesize that parenchyma cells, due to their structure, are responsible for higher water uptake of Miscanthus particleboards. The effect of parenchyma cells in the particleboards requires further research. The interesting aspect of the research was also the thickness swelling of Miscanthus particleboards, with relatively low thickness swelling but high water absorption   observed.

6. Paper III.

Production and characterization of one layer and three layer particleboard from cup plant (*Silphium perfoliatum*) stalks

In preparation for Industrial Crops and Products

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Title: Production and characterization of one layer and three layer particleboard from cup plant (*Silphium perfoliatum*) stalks

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Abstract:

In this research the feasibility of using agricultural crop residues for particleboards was investigated. Crop residues are materials left in an agricultural field or orchard after harvest. Here, we used three plant stalks of cup-plant (*Silphium perfoliatum L).* Particleboards were produced in two types, one layer cup plant particleboard and three layer cup plant particleboard, where core of particleboard made from cup plant particles is covered with spruce furnish. The particleboards were glued with methylene diphenyl diisocyanate (MDI) and the physical and mechanical properties of prepared panels were measured according to standards. It is shown that the obtained particleboards perform well, even properties were below those from control, conventional spruce (*Picea abies L. (Karst)*) particleboards. Especially the modulus of rupture of the cup plant particleboard was the major weakness. Likewise, thickness swelling of the boards made from cup plant stalks was higher than the one for the spruce particleboards. On the other hand it was proven that three layer cup plant particleboard has higher MOR and MOE and lower thickness swelling than its one layer counterpart. The important finding relevant for industrial applications was that the three-layer particleboard made from cup plant stalks were fulfilling the European standard EN 312 class P1 (used in dry conditions). At the same time, furnish on the cup plant particleboard made from spruce particles gives a comparable look of the surface between three-layer cup plant particleboard and three layer spruce particleboard.

Introduction

Wood is traditional raw material for particleboards production since 1887, and even nowdays wood is the most common material for particleboard production. Particleboards, beside of medium density fiberboards and oriented strand boards, are produced in volume exceeding more than 28 million m^3 per year (EPF, 2014) in Europe. Considering the relatively high production volumes and the decline of natural resources (Giljum et al., 2009), a critical shortage of wood could be a matter of time. The idea how to face this challenge in Europe may follow concepts developed in countries with little forested areas. There alternative natural materials are utilized in particleboard-like product. The advantage of this concept is in ecologically and economically efficient material utilization. While some parts of the plant are used for food, chemical, or biogas production (Mast et al., 2014), other, unutilized parts, may be processed in particleboards production. Common current practice is that residues such as stalks, husks, or straw are left on field or sometimes even burned. Obviously transformation of so called agricultural waste in a particleboard may mean economic profits for the particleboards producers, as the expenses for waste material are in general lower than for wood. At the same time, utilization of the waste material in industrial production cuts environmental burdens.

Particleboards from rice straw (Gerardi et al., 1998; Li et al., 2010; Yasin et al., 2010), wheat straw (Mo et al., 2003), sunflower stalks (Bektas, 2005; Guler et al., 2006; Khristova et al., 1996; Mati-Baouche et al., 2014) or cotton stalks (Guler and Ozen, 2004) were already produced. Balducci *et al.* (2008) and Dix *et al.* (2009) introduced residues of several central European agricultural plants as a raw material for low density particleboards and Selinger and Wimmer (2015) recently introduced light sandwich particleboards from woven and nonwoven hemp shives and fibers. It is obvious that agriculture could provide materials to replace wood in particleboards.

No reported results were found for cup-plant-based particleboards where high dry mass yield ranging between 11 t/ha and 20 t/ha per harvest. This yield can easily compete with yield of forest biomass which can reach ~16 t/ha per harvest (Pretzsch, 2009). Cup-plant (*Silphium perfoliatum L.)* originates in Eastern North America (Stanford, 1990), but is now also established in Central Europe. Although it was grown in gardens as an ornamental plant during the 18th century, it is nowadays widely cultivated for energy production (Haag et al., 2015). Cup-plant characteristics, including aspects of cultivation and utilization was reviewed by Gansberger et al. (2015).

The presented knowledge motivated us to state hypotheses: (1) The mechanical properties of particleboards made from cup plant are high enough to fulfill requirements of EN 312. (2) The three layer particleboard made from cup plant in core layer and with spruce particles in the surface layer will perform better than its one layer counterpart

Materials and methods

In the experiment, two types of raw materials were used for particleboard production. As a control, particles from virgin spruce (*Picea abies L. karst*) wood without bark were used. As an alternative material, cup plant (*Silphium perfoliatum*) stalks obtained from Thünnen institute, Braunschweig were processed. Cup plant stalks were approximately 1.8 m long with squared cross-section approximately 25×25 mm^2.

Firstly material was chipped in chipper Klöckner 120X400H2W.T (Klöckner Maschinenfabrik, Lauenburg, Germany) using cutting speed 725 rpm and feeding speed 1 m/s. Obtained chips of approximate dimension $20 \times 10 \times 5$ mm^3 were milled in hammer mill Condux-Werk HS 350 (Condux Maschinenbau GmbH & Co. KG, Hanau – Wolfgang, Germany). The particles of different size were screened afterwards in cascade vertical drum screener Allgaier D7336 (Allgaier-Werke GmbH, Uhingen, Germany). The screeners sieve with mesh size openings of 5.0 mm; 3.15 mm; 1.24 mm and 0.60 mm sorted the particles to different fractions respectively. Particles utilized in particleboards manufacturing were taken from sieves with openings > 3.15 and < 5 mm and manually mixed in weight ratio 50:50. Afterwards, the particles were oven-dried in 74°C for 4 days obtaining moisture content from 5 to 7 %. For production of three layer particleboards, the spruce particles with dimensions <1.24 mm were used in surface layers. The shelling ratio, which is the ratio of the face layer thickness to the total thickness of the panels, equaled 0.3.

The particleboards from spruce and cup plant (Figure 1) with target density 600 kg/m^3 and thickness of 11 mm were produced using methylene diphenyl diiosacyanate (MDI) resin (Huntsman I-BOND® PM4390, Huntsman GmbH, Hamburg, Germany). Two resin dosage were used. MDI was applied in amounts of 4% (MDI4) and 6% (MDI6). The resin was applied on the particles in a drum blender for 5 minutes using a pneumatic spraying nozzle. Consequently the particles with applied resin were manually distributed in a wooden forming

box (550×550 mm^2) and manually pre-pressed. After pre-pressing, the formed mat was hot-pressed at 200 °C and 3.2 MPa for 100 sec in a hydraulic press Siempelkamp (Siempelkamp Maschinen und Anlagenbau GmbH, Krefeld, Germany). The panel target thickness was controlled after production in random places on the board and was 12 ± 0.1 mm. In total, one particleboard per each type was manufactured.

Figure 6-1. Cross-section of produced particleboards. 3LCP – three layer cup plant particleboard, 3LSP – three layer spruce particleboard, 1LCP – one layer cup plant particleboard, 1LSP – one layer spruce particleboard.

Mechanical testing was carried out on a Zwick® 1474 universal testing machine using testXpert II software (Zwick GmbH & Co. kg, Ulm, Germany).

A three point bending test (EN 310) was employed to determine the bending properties. The samples ($12 \times 50 \times 290$ mm^3) were subjected to a loading rate of 7 mm·min^{-1} until the failure was reached.

The internal bonding (IB) strength according to EN 319 was measured on square samples (50×50 mm^2). Prior to testing, the samples were sanded and then glued between stainless steel blocks. Blocks were positioned in gimbal-mounted holders and pre-loaded in tension by 5 N. Subsequently, a loading rate of 1 mm/min was applied until the failure was reached.

Thickness swelling was determined according to EN 317. Conditioned samples of size $12 \times 50 \times 50$ mm^2 were fully immersed in 20 °C distillated water. The thickness swelling was measured at two time intervals, after 2 and 24 hours. After the immersion time had elapsed, the test samples were taken out of the water and excess water was removed using a paper cloth. Then the thickness swelling was measured manually, using a thickness gauge, in the center of the samples.

Vertical density profile (VDP) was measured using the x-ray density analyzer GreCon RG44® 33KV/1mA (GreCon, Germany). The equipment analyzed five samples of $12 \times 50 \times 50$ mm^2 dimension.

The obtained data were analyzed using Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. The normality of the data distribution was confirmed by the Shapiro-Wilk test. The significance differences (level 0.05) among the results was tested using the analysis of variance (ANOVA) and Scheffé post-hoc test.

Results and discussion

It was found that the average MOR of the cup plant particleboards is lower than MOR of spruce particleboards. Although three layer particleboard from cup plant showed higher average MOR than one layer cup plant particleboard, no significant difference in MOR between one and three layer cup plant particleboards was proven. The positive aspect of the spruce face layer in cup plant three layer particleboard was proven. MOR of three layer cup plant particleboard was not significantly different (ANOVA, $p>0.05$) to one layer spruce particleboard. As is presented in figure 2. Both spruce particleboard as well as three layer cup plant particleboard types are suitable, according to EN312, for general usage in dry conditions – class P1. On the other hand average MOR of the one layer cup plant particleboard did not fulfilled requirement of the MOR according to EN 312 for any class.

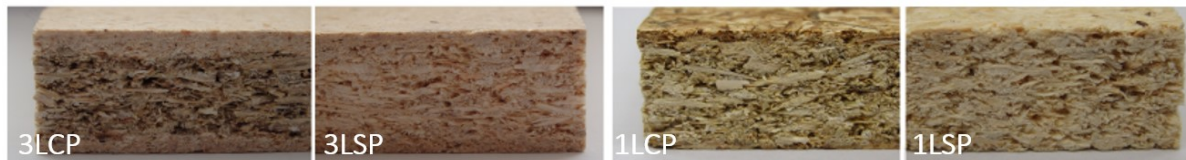Figure 6-2. Modulus of rupture (MOR) of measured particleboards. 3LCP – three layer cup plant particleboard, 3LSP – three layer spruce particleboard, 1LCP – one layer cup plant particleboard, 1LSP – one layer spruce particleboard.

There was observed that the MOE of both cup plant particleboards types are similar (ANOVA, $p>0.05$) to one layer spruce particleboard. Also MOE of both cup plant particleboards is significantly (ANOVA, $p<0.05$) lower than MOE of three layer spruce

particleboard. At the same time, there is found no significant difference between MOE of three layer and one layer cup plant particleboard. Although average MOE of the particleboards is varying with panel´s type (figure 3), novel cup plant particleboards are classified according to EN 312 as P2 (particleboards used in dry conditions for interior fitments, including furniture).

Figure 6-3. Modulus of elasticity (MOE) of measured particleboards. 3LCP – three layer cup plant particleboard, 3LSP – three layer spruce particleboard, 1LCP – one layer cup plant particleboard, 1LSP – one layer spruce particleboard.

Mechanical properties

The measured MOR and MOE of one layer spruce particleboard and three layer spruce particleboard is consistent with data reported by (Rofii et al., 2011). There was also reported by (Geimer and Lehmann, 1975) that MOE and MOR of three layer particleboard is higher than for one layer particleboard. However the MOE and MOR is affected by particles alignment, face layer density as well as used raw material (Nasser, 2012). We assume that mentioned factors may be responsible for the lower MOR and MOE of novel cup plant particleboard compared to three layer spruce particleboard. Cup plant as a raw material has different morphology (Gansberger et al., 2015) and particles size than spruce wood, these differences are naturally projected to the properties of the particleboard. It was proven that three layer cup plant particleboard has higher MOR and MOE than one layer cup plant particleboard. The same MOE and MOR relation, using Miscanthus core layer, was reported by (Balducci et al., 2008). Also (Juliana et al., 2012) successfully increased MOE and MOR

of particleboard made from Kenaf stalk core covered by Rubberwood face layers. Similar MOR and MOE as cup one layer particleboard was found for particleboards made from waste tea leaves (Yalinkilic et al., 1998), bleached straw (Mo et al., 2003), eggplant stalks (Guntekin and Karakus, 2008) or rice straw (Li et al., 2010).

Novel cup plant particleboards showed lower IB compared to spruce particleboard. One layer cup plant particleboard showed average IB of 0.30 MPa and three layer cup plant particleboard showed average IB 0.34 MPa. There was not proven significant difference between three layer and one layer cup plant particleboard. As is seen in figure 4. Both particleboards made from cup plant are suitable for general usage in dry conditions according to EN 312. It is known that core layer is mainly responsible for the internal bonding strength characteristics. Thus similar IB of three layer particleboard and one layer particleboard is natural. (Rofii et al., 2011) reported that characteristics of surface layer has not significant effect on the IB. Also (Balducci et al., 2008) measured that face layer of three layer Miscanthus particleboard has not effect on IB. Reduced internal bonding in similar manner as for cup plant particleboards was found for particleboards produced from rice husks (Suleiman et al., 2013), hazelnut husk (Çöpür et al., 2007) or waste tea leaves (Yalinkilic et al., 1998). On the other hand it is not exceptional that internal bonding strength of the particleboards produced from alternative materials is found even lower than measured by us for cup plant stalks. Internal bonding strength under the 0.2 MPa was measured for instance for rice straw (Li et al., 2010) or grass (Nemli et al., 2009) particleboards.

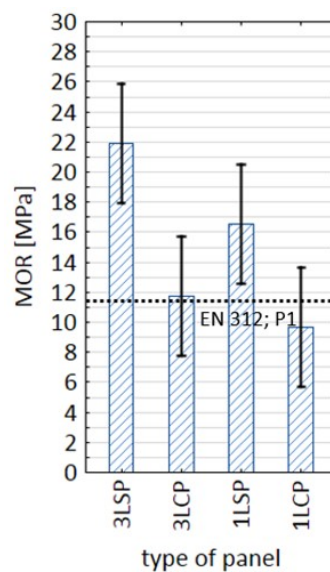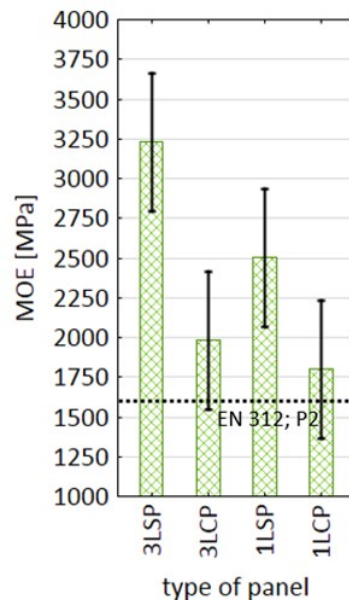Figure 6-4. Internal bonding strength (IB) of measured particleboards. 3LCP – three layer cup plant particleboard, 3LSP – three layer spruce particleboard, 1LCP – one layer cup plant particleboard, 1LSP – one layer spruce particleboard.

Physical properties

Three layers particleboard made from cup plant showed similar thickness swelling after 2 hours (TS2h) as three layer spruce particleboard. It is evident that using spruce particles in surface layer significantly decreased TS2h of novel cup plant particleboard. TS2h of one layer cup plant particleboard is over 100 % higher than TS2h of three layer cup plant particleboard.

Thickness swelling after 24 hours (TS24h) was different. It is measured that TS24h of both cup plant particleboards is significantly higher than one measured for their spruce counterparts. However it must be noted, that surface layer composed from spruce particles has positive effect on the TS24 o cup plant particleboard. TS24 of three layer cup plant particleboard was lower (ANOVA,p<0.05) than one measured for one layer cup plant particleboard.

As an important outcome is that TS2h and TS24h is significantly reduced when cup plant stalks are used in core layer of three layer particleboard compared to one layer cup plant particleboard. The lower TS of three layer particleboard than one layer particleboard was also measured by (Balducci et al., 2008) where Miscanthus or topinambour stalks were utilized in core layer of three layer particleboard.
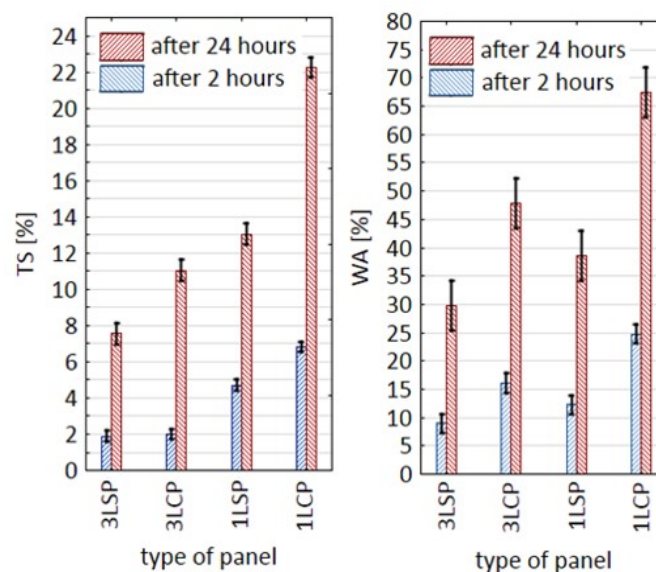
Figure 6-5. Thickness swelling (TS) and water absorption (WA) of produced particleboards. 3LCP – three layer cup plant particleboard, 3LSP – three layer spruce particleboard, 1LCP – one layer cup plant particleboard, 1LSP – one layer spruce particleboard.

Vertical density profile

As is seen in figure 6, vertical density profile of the cup plant particleboard is different to one measured for spruce particleboard. One layer cup plant particleboard showed flat density profile without peaks close to the surface layers, as measured for spruce particleboard. When spruce particles were present in the surface layers of the cup plant particleboard, the density profile was also altered. It was found that density in the core layer of the three layer cup plant particleboard was higher than the density in the surface layers of the particleboard. It is evident that density profile may alter the mechanical performance of the cup plant particleboards. Being said also in (Wong et al., 2003), the density profile similar to one measured for spruce particleboards is beneficial to MOE and MOR of the particleboards. At the same time flat density profile measured for one layer cup plant particleboard is commonly connected with reduced bending properties of the particleboards, which is proven also in our research. On the other hand three layer cup plant particleboard is having higher density in core layer; that at first glance should provide better IB of the three layer cup plant particleboard. Interestingly it is not shown in our results. It must be noted that commonly not only the central layer, but transition zone (TZ) between surface and core layer is more prone to fail during the internal bonding testing (Schulte and Frühwald, 1996). And as shown in figure 6. The three layer cup plant particleboard´s transition zone has similar density as core layer of one layer cup plant particleboard. Thus internal bonding strength remained on the same level.
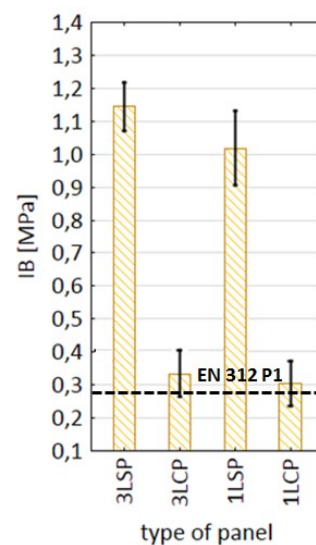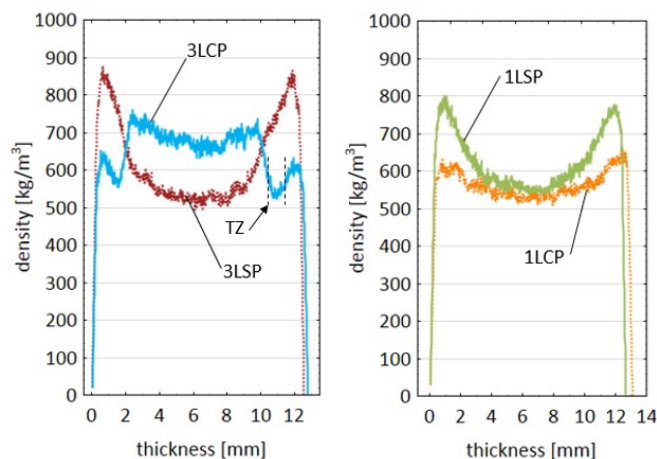
Figure 6-6. Vertical density profile of produced particleboards. 3LCP – three layer cup plant particleboard, 3LSP – three layer spruce particleboard, 1LCP – one layer cup plant particleboard, 1LSP – one layer spruce particleboard; TZ – transition zone between surface and core layer.

Conclusions

In this research, we successfully produced one layer and three layer cup plant particleboards. Their mechanical and physical properties are compared with control panels made from spruce. The IB of the cup plant three-layer particleboard was similar to the cup plant one layer particleboard. At the same time, three-layer cup plant particleboard has delivered better MOE and MOR than one layer cup plant particleboard. This suggest further steps, spruce furnish could increase MOR and MOE of particleboards from alternative materials. In the same time, the density profile of the three-layer cup plant particleboard was also altered, as the density of core layer was higher compared to surface, which is highly unusual and needs further research.

7. Paper IV.

Utilization of brewer´s spent-grains as a material for wood-based particleboard manufacturing

Journal of Cleaner Production (under review)

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Title: Utilization of brewer's spent-grains as a raw material for wood-based particleboard manufacturing

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Abstract: In this study we investigate suitability of bio-waste, brewer's spent grains (BSG), in production of particle boards. Firstly, chemical composition of BSG is analyzed for cellulose, lignin and hemicelluloses content. Then, BSG replace 10, 20, 30 and 50 % of wood in particleboards laboratory production. These four types of BSG-based particleboards with density of 620 kg/m^3 bonded by UF resin were tested for their modulus of rupture, modulus of elasticity, internal bond and thickness swelling. Along with it, scanning electron microscopy was used to study inner morphology of BSG-based particleboards. Generally the mechanical properties of particleboards with BSG particles were lower compared to control wood-based particleboards. Also thickness swelling of BSG-based particleboards was higher compared to control wood-based particleboard. Results of SEM suggested that smaller fraction of BSG can cover wooden particles which may potentially restrict bonding in particleboard composite. As promising was identified particleboard with 10 % of BSG particles, which showed similar performance as control wood-based particleboard and can be used as a particleboard for general purposes in dry conditions according to EN 312.

Key words: particleboard, Brewer's spent grains, particleboard, composite, bioresource

1. Introduction

Brewer´s spent grains (BSG) are a major by-product of the beer industry, representing around 85% of the entire by-products produced (Mussatto et al., 2006; Thiago et al., 2014). BSG can

be classified as a bio-waste, identified as a compostable waste from food processing plants, according to the Directive 2008/98/EC on waste (Lorenz et al., 2013). (; . In the European Union BSG is generated at amounts of 3.4 million tons per anno; (Stojceska et al., 2008), and in the US over 4.5 million tons (Buffington, 2014). In the Czech Republic, over 184.000 tons of BSG are annually generated (Basářová, 2010). This high amount of bio-waste is reason to explore innovative added-value utilizations.

BSG have been used as animal feed (Mussatto et al., 2006; Pérez-Bibbins et al., 2015), and was also suggested as a human food supplement (Gupta et al., 2013; Prentice and D'Appolonia, 1977; Stojceska et al., 2008). BSG as a bio-waste may be utilized for energy and biogas production BSG (Kafle and Kim, 2013). Chemical procedures allowed the production of protein concentrates, and also obtaining fermentation products such as ethanol, gums, antibiotics, enzymes or oil extracts (Mussatto et al., 2006; Thiago et al., 2014). The fibrous structure of BSG has led to work using BSG as a pulp replacement to produce printing paper, paper towels and business cards (Ishiwaki et al., 2000). BSG particles replaced sawdust in building bricks, that resulted in increased water capacity and minor improvement of flexural properties of the bricks (Russ et al., 2005).. Is was also shown that BSG can be used as a functional filler in polypropylene matrices (Revert et al., 2015). In summary, BSG have shown utility to be used in the food and chemical industry, as well as in certain ways for engineered materials.

In a recent review (Sheets et al., 2015) particleboards are mentioned as material that could potentially contribute to utilize fibrous and particulate wastes, including bio-based waste materials. Various types of wastes have already been used with particleboards. These materials include waste grass clippings (*Lolium perenne L.*) (Nemli et al., 2009), paper sludges (Taramian et al., 2007), waste paper assortments (Fuwape et al., 2007; Lertsutthiwong et al., 2008), sawdust (Hrázský and Král, 2003; Luciane Simal et al., 2014), polymer wastes such as polyethylene terephthalate (Klímek et al., 2016; Rahman et al., 2013), cardboards (Ayrilmis et al., 2008), tire rubber (Terzi et al., 2009), and of course recycled wood-wastes (Azizi et al., 2011; Colak et al., 2010; Lykidis and Grigoriou, 2008; Wang et al., 2008). The particleboard industry demands relatively clean raw materials, consistent in quality, available at low cost, and with minimal economic and environmental burdens (Kofoworola and Gheewala, 2009). Considering the aforementioned conditions BSG seem to fulfill most of these conditions. Dry BSG can be used in form of flakes and particles, similar like wooden particles. BSG is generated throughout the year in the brewing process,

does not carry any chemical additives or other potential pollutants, making BSG a clean and environmentally friendly renewable raw material (Thiago et al., 2014). BSG is produced at 3.4 million tons per year in the European Union). Particleboards are produced at a total volume of 35.5 million m^3 per year in the EU (Unece & Fao, 2014), and with the 3.4 million tons BSG per year the potential replacement of wood with BSG can be estimated at 10 %. Replacing up to 10% of wood through BSG would certainly deliver economic benefits to the manufacturers, since wood prices have grown by about 30 % between 2006 – 2011 (Eastin et al., 2012).

In this research BSG obtained from the microbrewery at Mendel University in Brno (Czech Republic) were used as a gradual replacement (up to 50 %) of wood in particleboards with a targeted density of 620 kg/m^3. The following four hypotheses are stated: H1: Chemical composition of BSG originating from a Czech microbrewery is comparable with other findings (1) Particleboards produced from with mixed wood - BSG particle furnishes deliver properties suitable for furniture according to EN312. (2) Engineering properties of particleboards will interact with gradual replacement of wood by BSG. (3) Morphological study of ruptured samples will help to explain effect of the BSG on the properties of particleboards.

2. Materials and methods

The raw material utilized in this research consisted of wooden particles with an average width of 1.7 mm, and an average length 7.5 mm. Commercial UF adhesive Prefere 4170 (Dynea[TM], Lillestrom, Norway) with hardener Kronoadd HL 100 (Dukol Ostrava s.r.o, Ostrava, Czech Republic) were used in an amount of 8 % solid content of resin relative to the particle dry mass. BSG were obtained from the microbrewery operated by the Department of Food Science of the Mendel University in Brno, Czech Republic. BSG were rinsed with distilled water and then stored at -5 $^\circ$C prior to use. The stored material was dried at 50 ± 5 ^{0}C for 24 h until 10% moisture content was reached. The dried material was stored in a closed container at -5 $^\circ$C to avoid microbial growth (Figure 1).
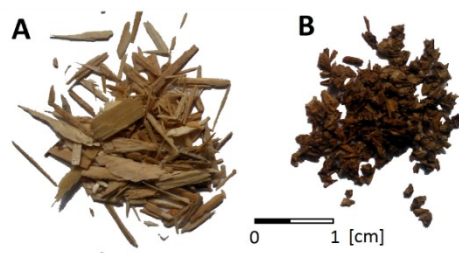
Figure 7-1. Wooden particles (A) and BSG particles (B), as used for the production of particleboards

In the production of particleboards wood particles were mixed with BSG particles according to the experiment design outlined in table 1. The particle furnish with a moisture content of 5 % was mixed with Urea formaldehyde adhesive Prefere 4170 (Dynea^{TM}, Lillestrom, Norway), and with the hardener Kronoadd HL 100 (Dukol Ostrava s.r.o, Ostrava, Czech Republic), all blended in a resinating drum for 10 minutes. Distillated water was added to adjust the moisture content of the batch at 11 %. The furnish was manually placed into a forming box, 650×750 mm^2 in dimension, and positioned on a 3 mm thick stainless steel plate. After pre-pressing squared-metal rods (15 mm side length) were placed on both sides along the pre-formed mat. The mat was covered by a stainless steel plate before hot-pressing in Strozatech HL400 laboratory press (Strozatech s.r.o, Brno, Czech Republic), for 180 sec at a specific pressure of 3.2 MPa. The temperature of 190°C was kept for entire pressing time. After pressing the boards were cooled and conditioned for two weeks in a 65 % relative humidity and 24°C climatized room. Boards were then trimmed to a final dimension of 600×700 mm^2. Production parameters are summarized in table 2.

Table 7-1. Experimental design

Board type	Raw material	
	BSG [%]	Wood [%]
control	0	100
B	10	90
C	20	80
D	30	70
E	50	50

Table 7-2 Production parameters of particleboards

Parameter	Value
Press temperature	190 °C
Pressing time	3 min
Thickness	15 mm
Dimensions	650×750 mm^2
target density	620 kg/m^3
Hardener content	2 %
Resination ([g] solid to [g] dry wood particles)	8 %

Hardener ([g] solid to [g] solid resin)	1.5 %
Targeted moisture content of particles	11 %

For the chemical composition (cellulose, hemicelluloses and lignin) around 200 mg were pre-hydrolyzed with 2mL of 72 % H_2SO_4 (30 °C, 1h). The reaction mixture was diluted with 56 ml ultra-pure water, and post-hydrolysis was performed in an autoclave at 120 °C, and 1.2 bar, for 30 min. For the high-performance liquid chromatography borate analysis, wood sugars were separated in a 5.6 mm column, 115 mm long (Omnifit®, Diba Industries, Inc., Danbury, North America) filled with strong anion exchange resin 114 MCL gel CA08F (Mitsubishi Chemical Corporation, Tokyo, Japan) at 60 °C. The mobile phase (0.7 ml/min) consisted of solution A, which was a 0.3 M potassium borate buffer with pH 9.2, and solution B, being a 0.9 M potassium borate buffer with pH 9.5. After sample injection chromatographic separation started with 90 % (A) and 10 % (B), with the run lasting 35 min. Data acquisition was ceased after 50 min. For quantification a post-column derivatization of monosaccharides with Cu-bichinconinate (0.35 ml min^{-1}) was applied. The reaction was performed at 105 °C in a 30 m crocheted Teflon coil of 0.3 mm inner diameter. This enabled the subsequent detection of sugars at 560 nm (Sinner et al. 1975, Sinner and Puls 1978). Data were processed using dionex® chromeleon software (Thermo Fischer Scientific Inc., Sunnyvale, United States).

Scanning electron microscopy (SEM) Tescan Vega TS5130 (Tescan Brno, s.r.o., Brno, Czech Republic) was used to observe the surface morphology of the particle boards with and without BSG. Morphology and interaction between BSG particles and wood particles was observed. Samples were coated with gold in vacuum sputter coater. The accelerating voltage was 16.7 kV. Mechanical testing was carried out on a Zwick®Z050 universal testing machine with the 50 kN loading cell. The experimental procedures were controlled by a testXpert v11.02 software (Zwick GmbH & Co., Ulm, Germany).

For the bending properties the three point bending test following EN 310 was employed. The samples were loaded at a rate of 8 mm·min^{-1} until failure (between 60 to 90 s). A clip-on deflectometer (Zwick GmbH & Co. kg, Ulm, Germany) was used. Internal bond (IB) strength was measured according to EN 319 on squared samples (50 × 50 mm^2). Prior to testing of the samples were sanded and glued between the stainless steel blocks with approximately 1 g of hot-melt adhesive Siga®N-40 (Siga a.s., Zlín, Czech Republic), and conditioned for one week. Blocks were positioned in gimbal-mounted block holder and pre-

loaded in tension with 5 N. A loading rate of 1 mm/min was applied until failure, which reached between 60 to 90 s.

Thickness swelling was determined according to EN 317 with the 50×50 mm^2 samples fully immersed in 20 °C distillated water. Thickness swelling and water absorption were measured after 2 hours, as well as after 24 hours of immersion. As soon the immersion time has elapsed the test samples were taken out and the water removed. Thickness swelling was manually using a caliper (Neiko 01409A). Water absorption was determined by weighing using a regular laboratory balance with an accuracy of 1 mg. Samples weights before and after water immersion were noted for calculation of the water absorption percentages.

The obtained data were analyzed with Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. Firstly, descriptive statistics was done, including test for normality of the data employing the Shapiro-Wilk test. Mean differences across among the results was tested using the analysis of variance (ANOVA) and Scheffe post-hoc test.

3. Results and discussion

3.1 Chemical composition of BSG

Out data show that BSG contain 24.5% cellulose, 23.8% hemicelluloses and 15.8% lignin. Cellulose content of our BSG was similar to reported data (see table 3), and higher than contents found by Mussatto and Roberto (2005). Reported lignin contents are more variable. While Mussatto et al. (2006) reported similar lignin contents, our numbers were considerably lower than those shown by Buffington (2014), and also Mussatto and Roberto (2005). Our found hemicellulose contents was higher than those reported by Buffington (2014), but lower than measured by Mussatto and Roberto (2005) and Russ et al. (2005). As chemical compositions of BSG seemingly show high variability, it is anticipated that these differences may be related to the type of malting barley used, the malting process and the employed brewing conditions. Sample preparation and the used analytical method also might have contributed to found differences. Due to the high variability present with the own as well as the reported data, hypotheses 1 could not be approved. However, it can be concluded that BSG contain even-balanced contents of cellulose, lignin and hemicelluloses, at about 20% each (table 3).

Table 7-3. Chemical composition of BSG as compared with literature (n.d. no data)

Components	own data	(Buffington, 2014)	(Russ et al., 2005)	(Mussatto et al., 2006)	(Mussatto and Roberto, 2005)
Cellulose	24.5 %	22.2 %	23-25 %	25.4 %	16.8 %
Lignin	15.8 %	26.8 %	7.0-8.0 %	11.9 %	27.8 %
hemicellulose	23.8 %	14.1 %	30-35 %	n.d.	28.4 %

3.2 Mechanical properties

MOR results of the particleboards were proportionally reduced with increasing ratios of BSG. No significant differences were found for control and type B (10% BSG, $p>0.05$) only. For the other BSG-types (C, D, E, Table 1) MOR values were significantly lower than the control (wood only). MOR of the C and D type was 30 % under the control. MOR of the E type (50% wood, 50% BSG) was down by 47% relative to the control. MOE results delivered a similar trend, meaning the higher the BSG content, the lower the obtained MOE values. The same MOE was measured for particleboard B (10% BSG) as well as the control. The negative effect of BSG on MOE was less pronounced than for MOR. The average MOE of board C (20% BSG) and D (30% BSG) was by 18% lower than the control. MOE of the particleboard type E (40% BSG) was down by 35 % compared to the control. The spherical BSG particles are smaller than wood particles, and also the aspect ratio is reduced, with the found reductions in MOR and MOE (Arabi et al., 2011). Furthermore, the discernible brittleness of the BSG flakes might also have a negative effect on MOR and MOE of the particleboard. An equal mechanical performance was reported for particleboards using various bio-wastes (Nemli et al., 2009, 2008; Pirayesh and Khazaeian, 2012; Pirayesh et al., 2012). To compensate for reduced MOR and MOE sandwich constructions using veneer overlays (Ayrilmis et al., 2008), higher UF resin contents (Boquillon et al., 2004) or the use of methylene diphenyl diioscyanate (PMDI) instead of UF resins (Li et al., 2010) might be reasonable strategies

Internal bonding (IB) was significantly reduced when BSG was added. Even with the 10 % substitution of wooden particles (type B), IB was alreardy decreased by 35 %. However, not significant IB differences were found among the B, C and D (20-40% BSG) particleboards. The IB of type E (50% BSG) particleboards were 70 % lower than the control. The reasons for the strong reduction in IB may be again related to the fact that BSG particles show very different morphology, compared to wood.

BSG can be described as a fibrous tissue (S.I. Mussatto et al., 2006) different to the porous cell structure of wood (see chapter 3.3). It is assumed that the fibrous BSG is lacking thick cell walls, which could be responsible for the found reduction in strength properties. Revert et al. (2015) also found reduced tensile strength properties when BSG was utilized with a polypropylene matrix. A decreased IB was reported when wood was replaced by fiber-like waste grass clippings (Nemli et al., 2009), or by the fibrous structure of waste-paper (Grigoriou, 2003). To achieve a better IB, a higher dosage of adhesives (Boquillon et al., 2004), or a different resin type should be implemented (Li et al., 2010).

The results of mechanical properties proven both previously stated hypothesis. The mechanical properties of particleboards are interacting with gradual replacement of wooden particles by BSG. The results showed, that MOR, MOE and IB are proportionally decreased with substitution of wooden particles above 10 %.

Second hypothesis that particleboard with utilized BSG is also proven since particleboard type B fulfilled minimal requirement according to EN 312 and can be used for interior fitments in dry conditions. Particleboards C, D fulfilled values of IB, however MOR is below required value of EN 312.

Table 7-4. The mechanical properties of boards made from BSG and wood particles and the test results of ANOVA and Duncan´s mean separation tests.

Mechanical properties	Board type	Mean	Std. Deviation	xmin	xmax	p
MOR [N·mm^{-2}]	control^{Y}	11.9	2.97	6.09	15.63	
	B^{Y}	9.14	2.12	5.11	11.52	
	C^{x}	7.51	0.94	6.47	8.89	•
	D^{x,w}	7.28	1.68	4.69	9.11	•
	E^{w}	5.77	2.68	3.40	12.11	•
MOE [N·mm^{-2}]	control^{Y}	2374	428	1466	2945	
	B^{y}	2425	355	1847	2777	
	C^{x}	1926	143	1673	2064	•
	D^{x,w}	1866	497	1214	2470	•
	E^{w}	1537	445	1055	2473	•
IB [N·mm^{-2}]	control	0.49	0.03	0.45	0.55	
	B^{x}	0.30	0.02	0.27	0.32	•
	C^{x}	0.24	0.02	0.20	0.25	•
	D^{x}	0.26	0.04	0.21	0.34	•
	E	0.15	0.02	0.12	0.16	•

• Values are different to the control (ANOVA, $p < 0.05$)

[W,X,Y] Values having the same letter are not significantly different (Duncan test)

3.3 Morphological evaluation

The microscopic evaluation of the different particleboard types (Figure 2.) was done to find structural evidence for the found property differences. Findings show that BSG particles are filling voids and pores of the particleboards (Figure 2. B and E), while a smaller BSG particles covering surface of the wooden particles (Figure 2. C and D). We assume, that BSG particles covering the surface of the wooden particles, may also restrict particle-particle bonding, explaining the reduced IB. At the same time BSG particles are located in pores and may consume adhesives and restrict a proper contact among the wooden particles, again reducing IB.
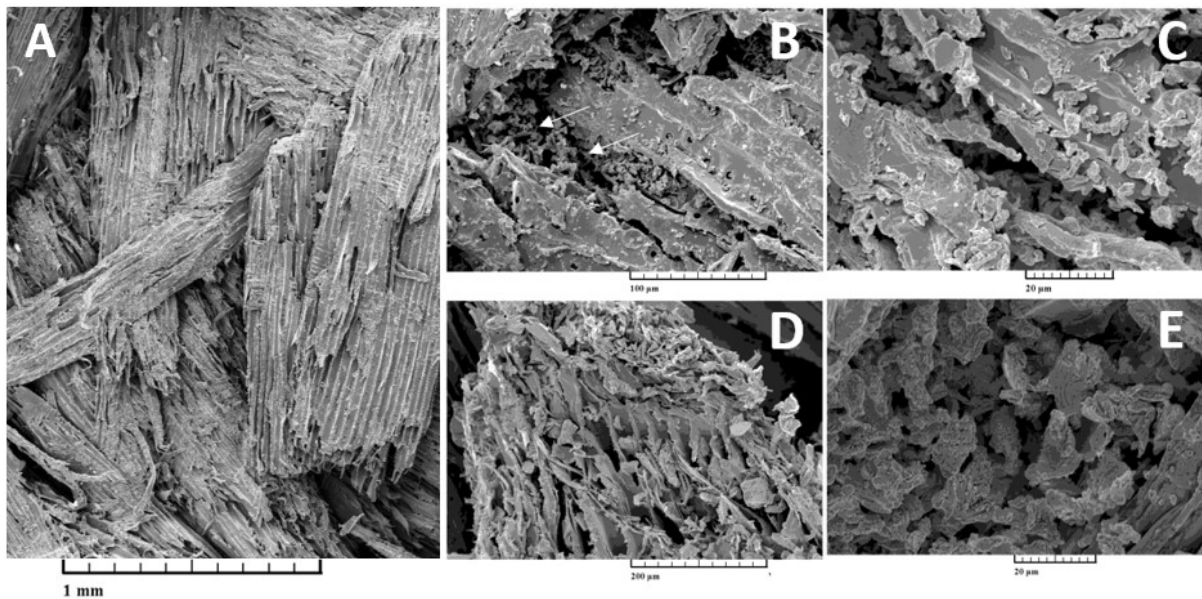
Figure 7-2. Particleboard without (A) and with 30 % of BSG particles (B;C.D.E). larger BSG particles filling present void structures (B, marked); smaller BSG particles located on wooden particle surfaces (C and D), BSG particles filling voids (E)

3.4 Thickness swelling and water absorption of the boards

The thickness swelling after 2 hours (table 5) of the particleboards with 20 %, 30 % and 50 % BSG was significantly ($p < 0.05$) higher than the control. At the same time the difference in thickness swelling between control and particleboard with 10 % BSG is statistically insignificant. Also TS2h was similar ($p > 0.05$) for particleboards with 20 %, 30 % and 50 % BSG. Water absorption after 2 hours (WA2h) has shown that the water uptake of the particleboards with 20 %, 30 % and 50 % BSG was higher ($p < 0.05$) than the control (ANOVA; $p < 0.05$), while no difference was found for particleboard with 10 % BSG and the control ($p > 0.05$).

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TS after 24 hours (TS24h) showed similar interaction as TS2h. Control and particleboard with 10 % had similar (p>0.05) TS24h ~22 %. Particleboards with 20 %, 30 % and 50 % was significantly higher than control (p<0.05). At the same time no difference in water absorption after 24h was found among the control and BSG-based panels.

The higher WA2h of BSG was found also by Russ et al. (2005), who have added BSG into clay bricks. The inverse trends found for WA24h and TS24h in BSG-based particleboards may be explained by the structural differences between BSG and wooden cell wall structures (Mussatto et al., 2006). While BSG filling voids in particleboards may adsorb and retain some water, the absence of thick wooden cell-wall in BSG may cause disproportional swelling reaction. At the same time, small BSG particles are covering surface of the wooden particles, which probably cause insufficient contact between wooden particles. The fact, that particles are not tightly bonded may have created additional spaces for swelling of wood. Relatively high swelling and water uptake is also due to the fact that no wax or other hydrophobic substances were added. Generally, adding water repellents such as paraffin (Papadopoulos, 2006), or using of phenolic resin (Khristova et al., 1996; Pizzi and Mittal, 2003), will improve water repellency of particleboards.

Table 7-5. The physical properties of boards made from BSG and wood particles and the test results of ANOVA and Duncan´s mean separation tests.

Physical properties	Board type	Mean	Std. Deviation	xmin	xmax	p
Swelling after 2 hours [%]	control	17	0.75	15.98	17.91	
	B^X	18	1.28	15.99	19.09	
	C^X	19	1.55	17.31	20.44	•
	D^X	21	1.62	18.54	22.44	•
	E	24	0.75	23.04	24.76	•
Swelling after 24 hours [%]	control	22	2.27	19.65	24.59	
	B^X	25	3.50	21.17	29.03	
	C^X	27	1.87	24.41	29.23	•
	D^X	24	1.16	21.18	24.43	•
	E^X	27	1.19	25.82	28.68	•
Water absorption after 2 hours [%]	control	92	7.83	96.26	105.71	
	B	89	3.89	83.11	93.61	
	C^x	97	6.36	85.03	101.89	•
	D^x	98	3.30	93.76	102.43	•
	E^x	100	5.30	83.23	96.30	•
Water absorption after 24 hours [%]	$control^W$	108	4.37	103.99	114.04	
	B^W	98	5.27	82.33	106.67	
	C^W	99	2.04	96.66	102.34	

D^W	100	3.74	95.67	105.66
E^W	98	4.46	92.01	104.40

• Values are different to the control (ANOVA, $p < 0.05$)

$^{X\,Y\,Z\,W}$ Values having the same letter are not significantly different (Duncan test)

4. Conclusions

This research has successfully shown that particleboards can be produced with 10 % of BSG with acceptable properties. While 10 % substitution of wooden particles by BSG particles did not changed properties of particleboard, the higher content of BSG particles in particleboard reduced MOR, MOE, IB and increased thickness swelling of particleboards. This fact can be attributed to the inner structure which was investigated by SEM. BSG-based particleboard indicated that smaller fractions of BSG particles covered the surface, while some occupied voids between the wooden particles. The fact that smaller fraction of BSG particles are covering the wooden particle´s surface may restrict proper bonding between wooden particles and thus reduce the mechanical properties. Voids occupied by BSG particles on the other hand may retain water and cause higher swelling. A future challenge is to increase mechanical properties of the particleboards with higher addition of BSG. One of the ways is to investigate BSG-based particleboards bonded with various resin types or higher resin dosage. Although BSG based particleboards has generally lower mechanical and physical properties, the particleboards with 10 % of BSG has met requirements for general purpose particleboards used in dry conditions (EN 312).

8. Paper V.

XPS depth profile of plasma-activated surface of beech wood (Fagus sylvatica) and its impact on polyvinyl acetate tensile shear bond strength

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ORIGINAL

XPS depth profile of plasma-activated surface of beech wood (*Fagus sylvatica*) and its impact on polyvinyl acetate tensile shear bond strength

Pavel Král · Jozef Ráhel' · Monika Stupavská · Jan Šrajer · Petr Klímek · Pawan Kumar Mishra · Rupert Wimmer

Abstract   High surface selectivity of atmospheric pressure plasma treatment was demonstrated experimentally by XPS depth profile measurement of plasma-activated beech wood. Wood surface activated by diffuse coplanar surface barrier discharge was sequentially sputtered by Ar^+ ion beam followed by immediate XPS analysis of freshly uncovered surface. According to the assessment, less than 330 nm of sputtered material was sufficient for complete removal of all plasma-formed functional groups. For the sake of practical implications of minimal vertical extent of plasma-mediated changes, the character of tensile shear bond strength improvement of polyvinyl acetate adhesive was examined with respect to its specific mass. A constant additive character of plasma activation to the bond strength was observed within the examined range of adhesive-specific mass.

Introduction

The growing popularity of polyvinyl acetate-based adhesives to bond indoor products is driven mainly by concerns about the health and environmental hazards associated with formaldehyde and volatile organic compounds (VOC) emission of competing adhesive formulations. Nevertheless, since polyvinyl acetate is a water-based adhesive, its use for bonding of generally nonpolar and hence non-wetting wooden surfaces suffers from inadequate contact of adhesive and adherent on atomic level. Only weak van der Walls interactions (such as London forces) instead of desired hydrogen bonds with wood fractions are formed. The situation is

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commonly addressed by improved formulations of adhesives and/or by employing the cold press to overcome the potential barrier of repulsive forces.

An alternative approach, which is nowadays routinely used in polymer printing industry, is the use of nonthermal plasma pretreatment (activation). High-voltage or high-frequency electromagnetic field is used to heat the ambient electrons above the ionizing energy of the surrounding gas. When some appropriate measures are taken to prevent an extensive heat transfer from the high-energy electrons to surrounding gas (such as placing a dielectric barrier between the power electrodes to constrain the lifetime of single plasma channel into the tens of ns), it is possible to design a plasma reactor operating close to room temperature that facilitates a considerable flux of gas-phase atomic and molecular radicals toward the solid surface to provide its desired chemical functionalization. The benefits of using the nonthermal plasma activation lay mainly in its applicability to heat sensitive materials and no need for additional drying steps, but also the possibility to avoid the complex formulation of polyvinyl acetate adhesives and even to affect positively the polyvinyl acetate curing kinetics (Avramidis et al. 2011a) and finally its generally straightforward implementation into the production line.

The work of several research teams within the last two decades demonstrates convincingly the plasma-assisted improvement of wood surface wettability. For plasma treatment done at atmospheric pressure (which offers far better technical feasibility and economy compared to that of low-pressure systems), three distinct types of plasma system configurations were mainly studied: volume dielectric barrier discharge (DBD), surface DBD and plasma jets. Plasma jets offer an excellent efficiency requiring plasma treatment times of only units of seconds (Busnel et al. 2010; Potocnáková et al. 2013). The jet systems suffer from limited cross-section diameter of plasma plume, which makes the treatment of large size areas time-consuming. Volume DBD, sometimes incorrectly called industrial corona, is a standard electrode configuration employed for decades to improve the surface wettability in polymer printing industry. Consequently, this configuration was the first to be tested for activating the wood surfaces. Material is either fed through the discharge gap formed by a pair of plane parallel electrodes (Podgorski et al. 2000; Avramidis et al. 2011b) or the material itself works as a return electrode for pulsed discharge current (Rehn et al. 2003). Treatment times of units of seconds are needed to achieve complete wettability over substantially wider areas compared to plasma jets. For sufficiently flat material surfaces, it is possible to address the intrinsic shortcomings of volume DBD, which are an excessively high-voltage requirement and resistive power losses in material bulk, by employing the configuration of surface DBD. Here, both polarity electrodes are placed underneath the dielectric panel in a way that allows formation of nonthermal plasma on its opposite side. Dielectric panel covered by thin (<0.5 mm) plasma sheath is consequently brought into contact with treated wood surface. There are virtually no limits to the thickness or electrical conductivity of the wood piece. The work by Odrášková et al. (2008) on so-called diffuse coplanar surface barrier discharge (DCSBD), which is a particular type of surface DBD being developed by the authors' team and which will be further discussed in this paper, showed almost a threefold improvement in energy efficiency compared to the volume DBD. A more recent study by Lux et al. (2013) on local

temperature increase in 1 mm depth below the plasma-treated beech wood surface reports only 10 °C increase upon 9 s plasma treatment and 14 °C increase upon 18 s treatment. Pair comparison between the lateral spreading of sessile droplet and the water absorption to the wooden body reveals a pronounced effect of DCSBD plasma treatment on the former, but almost none (i.e., below a statistical significance) on the latter. This observation supports the hypothesis that the plasma-affected material is located mostly on uppermost wood surfaces. Further supporting evidence for this hypothesis can be drawn from the pair comparison of ATR–FTIR spectra of treated and untreated surfaces by Lux et al. (2013). Only minute spectroscopic changes were recorded, despite the fact of dramatic macroscopic differences of both surfaces. This may be explained by substantially lower volume occupied by plasma-modified material compared to that of evanescence field extending from the infrared beam ATR crystal (i.e., 0.5–5 μm). In this work, X-ray photoelectron spectroscopy (XPS) data of chemical depth profile of plasma-activated beech wood (*Fagus sylvatica*) are presented to provide direct experimental proof of the above-stated hypothesis of low depth of plasma modification.

Besides a pure scientific interest on the mechanism of plasma–wood surface interactions, the proven low extent of plasma-affected volume might have some interesting cost-saving implications for the wood adhesive bonding. The failure of adhesive joints is caused either by rupture within the adhesive itself or at the adhesive–wood interface or within the bulk of wood (cohesive failure). Standard methods of chemical or mechanical surface pretreatment result in the formation of a so-called weak boundary layer (WBL) that contributes to cohesion failure (Stehr and Johansson 2000). At the same time, thermoplastic adhesives (such as polyvinyl acetate) exposed to shear load are able to compensate to some extent the imposed external stress by their elastic deformation. As a consequence, joints prepared with larger amounts of adhesive exhibit higher tensile shear bond strength. To counteract the effect of WBL formation, larger amounts of adhesive must be used. The introduction of atmospheric pressure plasma activation of wood surfaces is reported to improve the bondability or paint adhesion by up to 30 % (Sakata et al. 1993; Rehn et al. 2003; Wolkenhauer et al. 2008; Busnel et al. 2010; Acda et al. 2012). This improvement is generally attributed to the enhanced interactions on adhesive–wood interface. With plasma activation resulting in a minimized formation of WBL, the adhesion strength improvement may be directly converted to the lesser amount of adhesive needed, since less elastic deformation of adhesive is needed to compensate for the weakened cohesive strength of WBL.

To validate this cost-saving hypothesis, tensile shear bond strength of polyvinyl acetate adhesive of various amounts was measured on plasma-activated surfaces.

Materials and methods

Substrate and adhesive

Twelve beech wood (*F. sylvatica*) straight-grained boards of $86 \times 7 \times 800$ mm^3 with a moisture content of 10 ± 1 % were used for testing of bond shear strength.

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Specimens were stored under conditions of 24 °C and 65 % relative humidity in the conditioning chamber Sanyo MTH 2400. Not more than 24 h before the treatment, board surfaces were sanded with 100-grit sandpaper and all dust was carefully removed by air blast. For XPS measurements, specimens were cut to $10 \times 7 \times 10$ mm^3. Polyvinyl acetate adhesive Duvilax LS 50 (Duslo a.s. Slovakia) of durability class D2 (according to EN 204:1991) was used for evaluation of tensile shear strength.

Plasma treatment

Plasma activation was done at atmospheric pressure air on in-house build DCSBD equipped with driving pulley to facilitate the movement of wooden boards at adjustable speed in close contact with the layer of generated plasma (Fig. 1). The DCSBD electrode element consisted of 16 equidistantly spaced conductive electrode strips of alternating polarity, screen-printed on one side of 96 % Al$_2$O$_3$ dielectric plate of $228 \times 92 \times 0.6$ mm^3 size. The width of a single conductive strip was 3 mm, and mutual distance of adjacent strips was 1.5 mm. The width of 3 mm was found to provide better treatment uniformity to that of 1.5 mm width used in the past (Odrášková et al. 2008). The screen-printed side of electrode was electrically insulated by circulating transformer oil, which also acted as a cooling medium to dissipate the plasma-generated heat. The system was powered by sinusoidal voltage of 10 kV$_{RMS}$ at 15 kHz and 450 W input power, supplied by Lifetech VF1500 power generator. The speed of the driving pulley was adjusted to a plasma treatment time of 30 s. The choice of this particular treatment time came from previous results of contact angle measurements. It is the double of the time needed to achieve complete wetting by water sessile droplet. In practice, such estimated treatment time is used as a starting point for further treatment time optimization procedure. Small specimens for XPS were treated manually for 30 s. Plasma layer generated above the free ceramic surface takes the form of numerous microfilaments of sub-millimeter diameter and 3 mm in length that are rapidly moving, which gives an illusion of diffuse plasma appearance to the naked eye. Bringing the electrically nonconductive wood specimen into close contact with the ceramic surface converts the shape of plasma microfilaments into plasma strips of real spatial uniformity
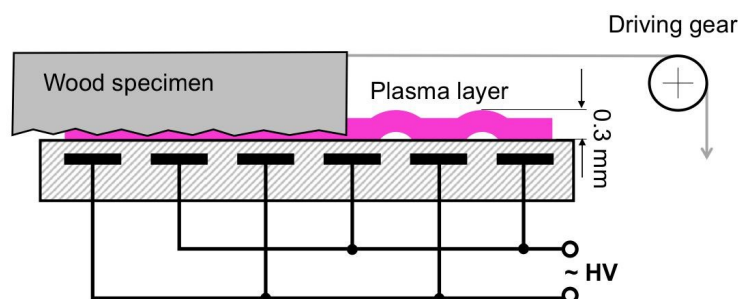
Fig. 1 Schematic of DCSBD plasma treatment reactor (not to scale). Intrinsic roughness of wood surface provides sufficient space for discharge plasma to be formed

following the pattern of power feed electrodes. The visual appearance of the phenomenon can be observed when treating transparent materials such as glass (Homola et al. 2013).

Contact angle measurement

Screening of free surface energy γ_s of initial and plasma-activated wood surface was done by means of the sessile drop technique using the SEE System E (Advex Instruments) device. Surface contact angle of 15 droplets of 2 µl volume was measured for each testing liquid, i.e., water, glycerol and diiodomethane. Assessment of dispersive and polar components of free surface energy was done by regressive Owens–Wendt method—OWRK (Owens and Wendt 1969) using the SEE System software library.

X-ray photoelectron spectroscopy

XPS measurements were done on the ESCALAB 250Xi (ThermoFisher Scientific). The system is equipped with 500 mm Rowland circle monochromator with microfocused Al Kα X-ray source. An X-ray beam with 200 W power and 650 µm spot size diameter was used. This X-ray spot size was found to be sufficient to compensate the natural chemical structure inhomogeneity of wooden surface, so that the signal from various sites of the investigated surface was the same within the statistical error. Positive charge accumulated on the surface was neutralized by electron flood gun. The survey spectra were acquired with pass energy of 50 eV and resolution of 1 eV. High-resolution scans were acquired with pass energy of 20 eV and resolution of 0.05 eV. In order to obtain depth profile, a series of 10 s bursts of Ar^+ ion beam of 200 eV energy were scanned over an area of 3.25×3.25 mm^2. Spectra were referenced to the hydrocarbon type C 1s component set at a binding energy of 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software.

Tensile shear strength measurement

Tensile shear strength was determined according to EN 205:2003. The adhesive of known mass (80, 110 and 160 g/m^2) was applied to single-bonded surface within the 3 min from plasma activation and brought immediately into contact with the other plasma-activated board. Similar to that, reference specimens without plasma activation were prepared. Afterward, specimens were pressed in ITALPRESSE SCF/6-S for 24 h under 0.5 MPa at a temperature of 25 °C. After curing, specimens were conditioned at 24 °C and 65 % relative humidity for 6 weeks.

Actual tensile shear strength measurements were done on test specimens of $20 \times 14 \times 100$ mm^3 cut from bonded boards (14 from each board) on which pair of grooves separated by 10 mm was made in compliance with EN 205:2003. Universal tensile strength testing machine ZDM 10/90 (VEB TIW Rauenstein) equipped with Mini MFA 2 (MF GmbH) extensometers was employed. A loading speed of 5 mm/min resulted in bond rupture within the time range of 30–50 s. The

tensile shear strength was determined as a ratio between the maximum applied force and 400 mm^2 area of bonded surface.

Results and discussion

Contact angle measurement

Results are summarized in Table 1. Untreated beech wood exhibits poor water wettability with a sessile droplet contact angle of $(70 \pm 4)°$. Calculation from OWRK model suggests that this is due to the small polar component of free surface energy, which is only 8 mJ/m^2. Plasma activation lasting 30 s was able to achieve complete wettability of beech surface by water, i.e., below the contact angle measurement detection limit. The calculation from remaining two test liquids resulted in a value of 21 mJ/m^2 of polar component of surface free energy, which is almost a threefold increase of the initial state. The total free surface energy increased by 24 mJ/m^2.

X-ray photoelectron spectroscopy

Figure 2 shows typical XPS spectra for untreated (A) and plasma-activated (B) beech wood specimens. Corresponding calculated O/C ratios are listed in the first column of Table 2. The C and O occurring at 285.2 and 532.9 eV, respectively, are the predominant species. Each specimen contains traces of same impurities, arising most probably from contamination during specimen preparation. The O/C ratio was found to be 0.29 for untreated specimen. This value is in good agreement with that estimated from the literature data (Inari et al. 2011). Exposure to plasma resulted in more than twofold increase of O/C ratio. The increase of oxygen containing groups is in good agreement with similar XPS studies done on wood (Tóth et al. 2007; Avramidis et al. 2012) as well as with above-presented data on increased polar part of free surface energy. To specify the changes in more detail, peak fitting routines were done. High-resolution scans of C 1s peaks were decomposed into four components for all specimens: C–C/C–H at 285 eV, C–O at 286.6 eV, C=O/O–C–O at 287.9 eV and O–C=O at 289.2 eV. Differences in peak areas indicating the surface changes are shown in Fig. 3 and in the remaining columns of Table 2.

Table 1 Contact angle and free surface energy of specimens

Specimen	Water	Glycerol	Diiodomethane	γ_s (mJ/m^2)	$\gamma_s^{disperse}$ (mJ/m^2)	γ_s^{polar} (mJ/m^2)
Untreated	$(70 \pm 4)°$	$(80 \pm 4)°$	$(51 \pm 8)°$	36 ± 3	28	8
Plasma-treated (30 s)	–	$(22 \pm 3)°$	$(41 \pm 5)°$	60 ± 3	39	21

Free surface energies of liquids used in calculation (mJ/m^2)—water: $\gamma = 72.8$, $\gamma^d = 21.8$, $\gamma^p = 51.0$; glycerol: $\gamma = 64.0$, $\gamma^d = 34.0$, $\gamma^p = 30.0$; diiodomethane: $\gamma = 50.8$, $\gamma^d = 50.8$, $\gamma^p = 0.0$

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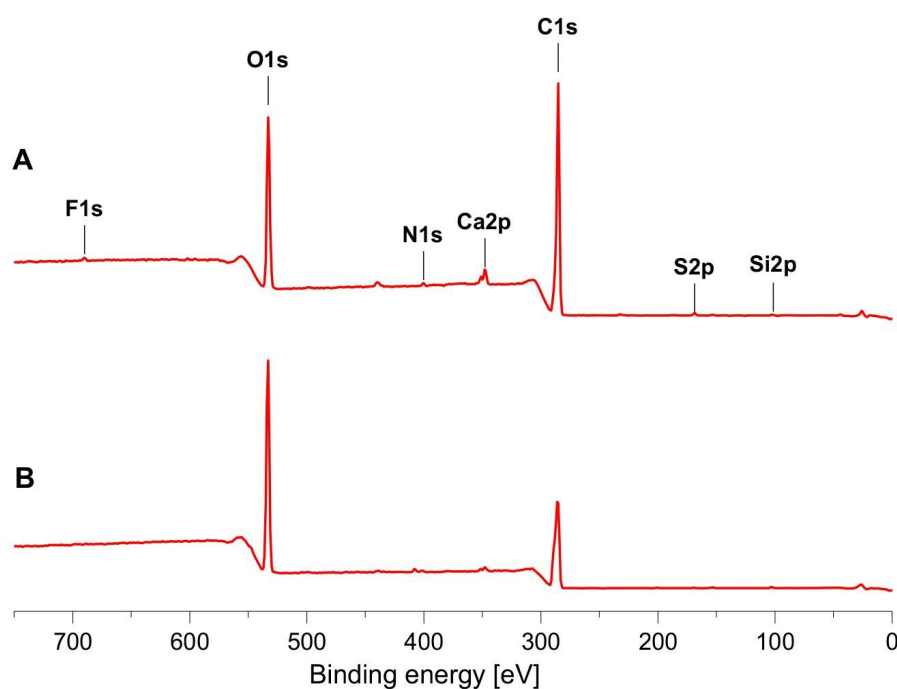
Fig. 2 XPS survey spectra of **a** control specimen; **b** plasma-treated specimen—*uppermost layer*

Table 2 Analysis of XPS spectra

Specimen	Atomic ratio	Relative area of chemical bonds (%)			
	O/C	C–C/C–H	C–O	C=O	O–C=O
Untreated					
Top layer	0.29	68	24	5	3
Plasma-treated specimen					
Top layer	0.62	42	32	19	7
Last (30th) layer	0.29	65	26	5	4

The most significant changes in beech wood resulting from plasma treatment are the decrease of C–C/C–H component and increase of O–C=O chemical bond. For these components, relative areas are changed by a factor of 1.6 and 2, respectively. For C=O only component, the effect of enhancement becomes even stronger: a plasma-treated process enhanced relative area of C=O by nearly a factor of four. The component C–O at 286.6 eV is assumed to be derived mainly from cellulose because of its high stability. The relative area corresponding to this component is practically resistant to plasma treatment. All of these functional groups represent polar bonds which correspond very well with the observed improved wettability by polar liquids such as water.

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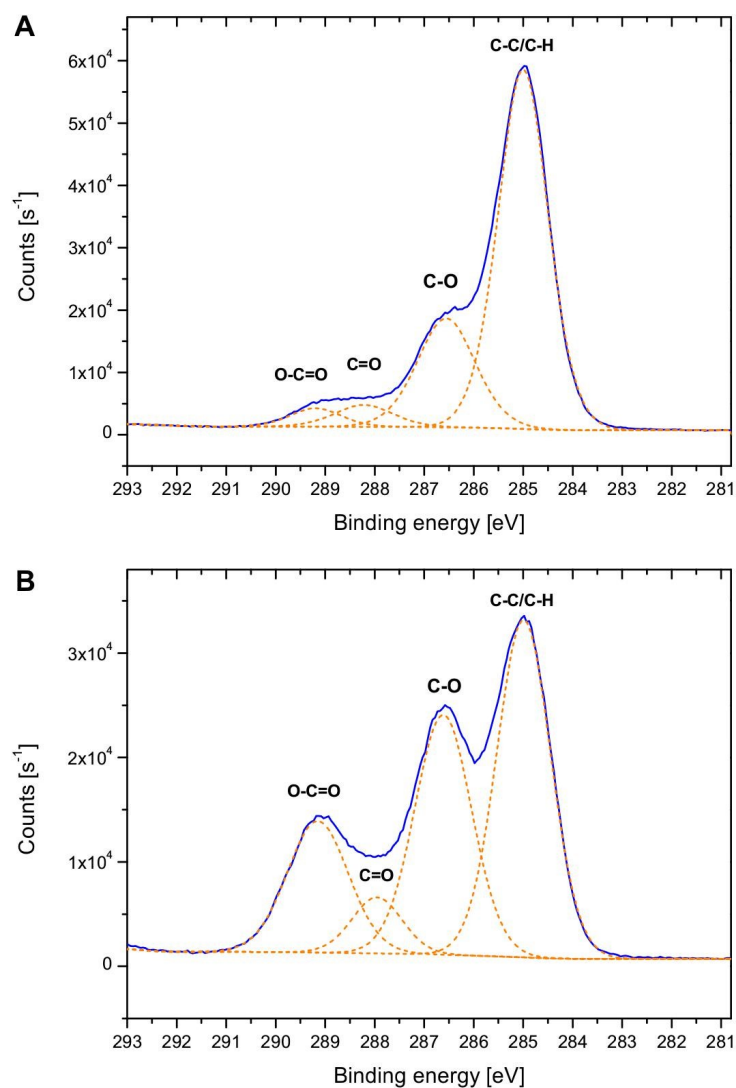
Fig. 3 Deconvoluted C 1s peaks for **a** control specimen; **b** plasma-treated specimen—*uppermost layer*

For depth profile analysis, an Ar^+ ion beam integrated into the present XPS system was employed for serial sputtering steps gently removing already XPS analyzed uppermost wood surface layers to allow an XPS scan of the layer underneath. It was important to choose carefully the ion gun operating parameters, especially the ion beam energy. It has to be as low as possible to minimize the wood internal changes induced by ion collisions cascade, but high enough to provide a reasonable sputtering yield. After 30 sputtering steps, the XPS signal converged to that of plasma untreated (reference) specimen, see Table 2. Further sputtering led to no significant changes in spectrum. The changes in the gradual depth profile of principal chemical bonds are shown by deconvoluted C 1s peak in Fig. 4.

The plot shows that progressive number of sputtering steps results in surface with higher C–C/C–H bond and decay of O–C=O and C=O bond coverage. The concentration of C–O remained virtually unchanged. For the sake of evaluating the effect of ion beam itself on wood compounds' chemical structure stability, the same sputtering experiment was made on plasma untreated specimens. No significant changes in depth profile spectra were observed. The changes in all C 1s components were within the range of ±2 %. In particular, the preferential sputtering of oxygen atoms led to the reduction of C=O component (the most pronounced indicator of plasma activation) from 5 to 3 % after 30 sputtering steps. Hence, ion beam does not interfere with the presented measurement via creating C=O functional groups of its own.

Attempts to determine the depth of sputtered crater by direct experimental observation failed, chiefly due to the intrinsic high surface roughness of wood material, but also due to the intentionally low sputtering yield of Ar$^+$ ion bombardment. Neither by confocal optical microscopy nor by scanning electron, it was possible to extract unambiguous information on topographic changes from the background surface roughness. Nevertheless, some rough estimation of maximum sputtered depth can be made from below trivial formula for vertical sputtering rate [m/s]:

$$\frac{z}{t} = \frac{M}{\rho N_A e} YIS \qquad (1)$$

where M and ρ stand for molar mass and density of sputtered substance, respectively, N_A for Avogadro constant, I for ion current, S for sputtered area, Y for sputtering yield and e for elementary charge.

According to literature (Yu et al. 2002), sputtering yield of cellulose bombarded by 30 keV Ar$^+$ beam is $Y = 9.7$ atoms/ion. This relatively high number is mainly
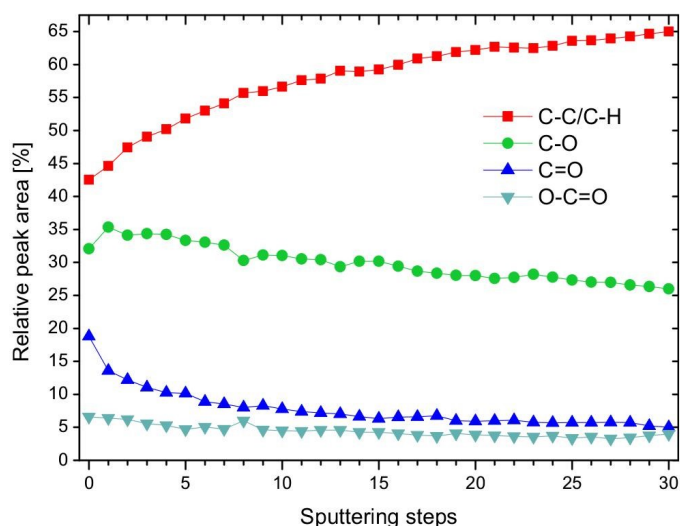
Fig. 4 XPS chemical depth profile of carbon components for plasma-treated beech wood

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Table 3 Tensile shear bond strength of polyvinyl acetate joint

	160 g/m^2		110 g/m^2		80 g/m^2	
	Untreated	Plasma	Untreated	Plasma	Untreated	Plasma
Shear bond strength (N/mm^2)	8.2 ± 2.3	9.3 ± 1.1	5.8 ± 2.4	7.0 ± 2.2	2.9 ± 1.3	3.7 ± 1.5
Difference (N/mm^2)	+1.1		+1.2		+0.8	
p value	0.067		0.056		0.32	
Number of valid specimens	19	13	31	26	7	9

due to the high sputtering yield of oxygen atoms with low surface binding energy of 0.075 eV, which are therefore sputtered preferentially. To the authors' knowledge, there are no experimental data on sputtering yield of cellulose for lower energy ions (i.e., 200 eV in this experiment), but in general it should be lower. The magnitude of this reduction can be estimated from the known data of polyethylene terephthalate (which has a close stoichiometry to cellulose) to be at least of factor five (Kormunda and Pavlik 2010). Inserting values of $Y = 2$, $I = 5$ mA, $\rho = 1.6$ g/cm^3 for cellulose $M = 16$ g/mol for oxygen into formula (1) gives the vertical sputtering rate of 1.1 nm/s that corresponds to 330-nm-deep crater after the whole sputtering sequence. It should be emphasized however that this estimation should be used only as an upper limit value. In reality, owing to the intrinsically high wood surface roughness, the depth sputtered profile must be lower owing to the differences in local angels of incidence. In addition to this, low-energy ion fluence would be affected by deposited electrical charge on nonconductive wood surface, and finally, the sputtering yield would become continuously lower as oxygen atoms are being depleted from the surface. Nevertheless, this upper boundary estimation of 330 nm is smaller than the cell wall thickness of *F. sylvatica* wood (Koch and Kleist 2001). The authors therefore dare to conclude that the effect of plasma activation is indeed localized only on the uppermost layer of wood surface structure.

Tensile shear bond strength measurement

Measurement data of tensile shear bond strength are summarized in Table 3. In line with expectations, higher quantity of adhesive resulted in higher value of shear bond strength. Plasma activation in all three investigated cases increased the average shear bond strength by a surprisingly constant additive value of 1 N/mm^2. Since all collected experimental data were of normal distribution, it was possible to calculate the p value of Student's t test to validate the statistical significance of observed difference. For adhesive quantities of 160 and 110 g/m^2, it may be said that at a significance level of 0.1, the plasma activation improves the strength of adhesive joint. A hypothesis that the low penetration depth obtained by the current XPS study is caused by an insufficient plasma activation dose can be rejected at this very same significance level, since in the opposite case this would fail to provide an adhesion improvement. In terms of process economy, the shear bond strength increase of 1 N/mm^2 corresponds roughly to adhesive saving of 20 g/m^2.

Owing to the large dispersion of measured data, the difference is not of statistical significance for specimens of 80 g/m^2. It should be noted, however, that the quantity of 80 g/m^2 is substantially below the minimum quantity of 120 g/m^2 recommended by adhesive manufacturer. Insufficient quantity of adhesive results in only partial filling of interfacial voids and hence, in substantial uncertainty of actual surface bonding area. An interesting consequence comes from the constant additive character of plasma activation effect. An eager researcher wanting to maximize the relative improvement in tensile shear strength test is advised to evaluate adhesive joints prepared by minimum amount of adhesive given by the manufacturer specification sheet.

Conclusion

This XPS study confirms the formation of polar functional groups on the wood surface exposed to atmospheric pressure plasma. The result provides an elucidative microscopic insight into the observed macroscopic effect of improved wettability of plasma-activated surface. Sputtering experiment with low-energy Ar$^+$ ions revealed that the plasma activation is a highly surface-specific phenomenon, which for given operation conditions forms a negligible WBL. The absence of a WBL was cross-checked with the precise measurements of tensile shear bond strength of polyvinyl acetate adhesive. Observed increase of bond strength proves a constructive role of XPS-identified functional groups, despite its high surface-specific occurrence. These results suggest a constant addition character of plasma activation to the bond strength. Although the presented results are obtained only for DCSBD plasma source at atmospheric pressure air, for other geometry variants of DBD or nonthermal plasma jet, similar results should be expected, providing that a similar temperature of working gas is kept, so that the effect of thermal degradation of wood material can be neglected.

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9. Paper VI.

Air-plasma treated waste polyethylene terephthalate particles as a raw material for particleboard production

Composites part B: Engineering

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Utilization of air-plasma treated waste polyethylene terephthalate particles as a raw material for particleboard production

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ARTICLE INFO

ABSTRACT

Wood-plastic composite boards involving up to 30 wt. % of polyethylene terephthalate (PET) flakes were evaluated for its physical and mechanical properties — internal bonding strength, modulus of rupture and thickness swelling. It was found that the problem of the decline of mechanical properties can be successfully mitigated by air plasma pretreatment of PET flakes. The samples with 30 wt. % of plasma treated PET exhibited the same internal bonding strength as the control pure wood sample; samples with 15 wt. % of plasma treated PET exhibited the same modulus of rupture. The role of plasma treatment is to generate chemically active functional groups to PET flakes surface. This was verified by measuring the thermal chemiluminescence of plasma treated flakes.

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1. Introduction

Polyethylene terephthalate (PET) has become the most favorable material for water and soft drinks bottles across the globe. Due to increased production in the last decades, the recycling of PET is of major concern [1]. The recycling is usually performed by a thermochemical procedure in which flakes are used as the input material [2]. In plastic industry, recycling is a common approach. For example, recycled low density polyethylene and aluminum of Tetra Pak were successfully used in manufacturing composite rigid boards, using a hot press [3]. This type of boards has found market niches in building industry [4,5] which may motivate utilization of PET plastic in a similar way. PET was utilized in particleboards in which PET flakes partially substituted wood in form of flakes [6] or dust [7]. Although this approach restricted the swelling of boards, the bending and internal bonding properties declined obviously. Internal bonding strength is a major quality criterion in boards [8], e.g. it determines the screw withdrawal strength [9]. Plasma treatment of composite components may help to improve the

composite cohesive properties. In the case of wood composites plasma treatment increased the PVA-adhesion of particleboards and fiberboards [10]. This was followed by research of [11,12] where plasma treatment increased the quality of fibrous-plastic materials. Plastic components treated with plasma were successfully used for composites production [13,14].

In addition, plasma treatment of plastic fractions of composites was demonstrated profitable in more branches of material development. For instance, jute composite [15,16] or cement composites [17] were improved in this way. With respect to PET, the work [27] showed that oxygen containing plasma of both high and low pressure had positive effects on the surface wettability of PET films. This effect was due to the incorporation of polar functional groups of C–O and O–C=O to the film surface. A similar improvement of wettability of PET in its particulate form (i.e. chips, flakes) may be supposed; providing that a suitable plasma generator is chosen to facilitate an adequate contact between the plasma and complex-shape PET flakes. Our work on this issue consisted of the following tasks: (1) production of particle boards with various PET admixtures by employing common particleboard production technologies in the laboratory; (2) utilization of the plasma treated PET flakes in particleboards in proportions of 15 and 30% of overall

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weight; (3) comparison of the properties of particleboards between untreated PET flakes and air plasma treated PET flakes.

2. Materials and methods

The research consisted of five phases: (1) preparation of PET particles by plasma activation by non-thermal plasma, (2) chemiluminescence and XPS analysis of PET flakes (3) preparation of particleboards with different replacement of wood particles by PET and (4) physical and mechanical evaluation of the particleboards according to Standards EN 310, EN 317 and EN 319, (5) scanning electron microscopy (SEM) evaluation of samples with PET particles and microscopic evaluation of ruptures in cohesive zones of PET flakes and wood particles.

2.1. Plasma treatment of particles

Plasma activation was done at atmospheric air pressure, using a Diffuse Coplanar Surface Barrier Discharge -DCSBD (Fig. 1). The DCSBD generates a thin layer (less than 0.3 mm) of non-thermal plasma over a flat dielectric plate made of 96% Al_2O_3, with the dimensions of 230×95 mm. Plasma was ignited by 16 pairs of equidistantly spaced strip electrodes located at an opposite alumina plate, where the circulating transformer oil provided the electrical insulation and dissipation of heat originated in plasma. The width of an individual conductive strip was 1 mm, the distance between the strips was 1.5 mm. The system was powered by sinusoidal voltage of 10 kV_{RMS} at 15 kHz and 400 Watt input power, supplied by Lifetech VF700 power generator.

PET flakes batches of 5 g were spread over the DCSBD electrode surface and activated for 60 s, until the sufficient volume of material was obtained. The mass of 5 g allowed to spread flakes into a single layer to ensure good contact with the plasma generated for each individual PET flake (Fig. 2.). During the treatment, the flakes were slowly stirred with a flat paint brush to improve their overall contact with plasma. Routine check of wettability improvement was done by a floating test on water level. Owing to the surface tension around the flakes circumference, untreated PET flakes floated on the water surface. Plasma exposure lasting for 60 s was sufficient to lower surface tension to such extend that treated PET flakes sank to the bottom of the water beaker.

The extent of plasma created surface radicals was measured by thermally induced chemiluminescence of 50 mg PET flakes, using the "LUMIPOL 3" chemiluminometer [28] operated in inert N_2 atmosphere under the isothermal regime of 80 °C. The method is a well-established tool for assessing oxidative degradation of polymers induced e. g. thermally or by UV radiation [32]. We have used this method to monitor ongoing oxidative changes resulting from preceding plasma treatment. The measurement was used also for evaluating the plasma treatment aging effect.
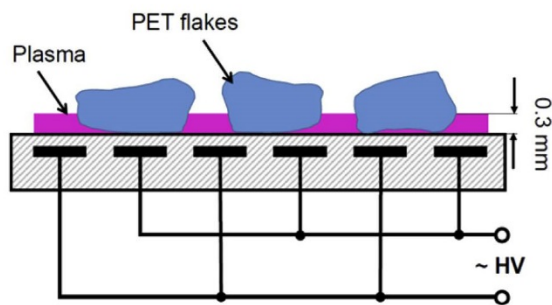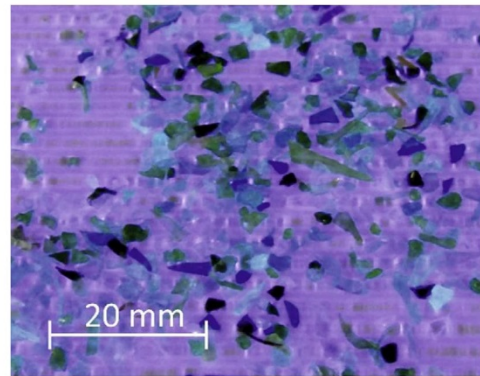

Fig. 2. Plane view on PET flakes in contact with DCSBD plasma.

The chemical nature of surface changes was evaluated by ESCALAB 250Xi (Thermo Scientific) X-ray photoelectron spectrometer (XPS), equipped with microfocused Al Kα monochromated x-ray source (1486.6 eV). The X-ray beam of 200 W with the diameter of 650 μm was used. This X-ray spot size was found to be sufficient to compensate the natural chemical structure inhomogeneity of PET flake surface, so that the signal from various sites of the investigated surface was the same within the statistical error. Positive charge accumulated on the surface was neutralized by electron flood gun. High-resolution scans were acquired with pass energy of 50 eV and resolution of 0.05 eV. Spectra were referenced to the hydrocarbon type C 1s component set at a binding energy of 284.8 eV. The spectra calibration, processing and fitting routines were done using Avantage software.

2.2. Particleboards production

The tested particleboards were manufactured of spruce wooden particles supplied by a local particleboard producer. The average particle width was 2.25 mm, and the average length was 17.7 mm. The wood particle batches were supplemented with milled polyethylene terephthalate flakes (PET) of 1.6 mm average size. The wood particle moisture content was 5.24%, determined using a drying scale "Radwag Mac210".

PET was used in two variants: (1) untreated PET particles and (2) PET treated by air plasma (PLAS-PET). Urea formaldehyde adhesive "Prefere 4170" and hardener "Kronoadd HL 100" were used as a resin mixture. Firstly the wooden particles were mixed with resin, hardener and portion of distilled water to homogenise moisture content of wood particles batches on 11%. The mixing was done in a resinating drum for 10 min. Thereafter, the particles of PET were mixed separately for 10 min with the resin and hardener to ensure coating 8% (solid content) of weight. Finally particles of wood and PET were mixed in specified proportions (Table 1).

The prepared particle mixture was poured into boxes with bottom dimensions of 500×500 mm^2 posed on the stainless steel

Table 1
Experimental design.

Board type	Raw material		
	PET (%)	PLAS-PET (%)	Wood (%)
C	0	0	100
C15	15	0	85
C30	30	0	70
P15	0	15	85
P30	0	30	70

Fig. 1. Scheme of plasma treatment set-up.

plates, and the particle mats were pre-pressed manually. The final thickness of the pressed boards – 5 mm was determined by metal stoppers fixed on the margins of the plate bottom. The moulded piece was covered with the second plate and pressed in the laboratory press (Strozatech, HL400) for 50 s at a specific pressure of 3.2 MPa and temperature of 190 °C. After pressing, the boards were cooled and conditioned at 65% relative humidity and 24 °C temperature for two weeks, and afterwards trimmed to the final size of 400 × 400 mm². There were produced 5 boards in total. The production parameters are in Table 2.

2.3. Material properties and data evaluation

Mechanical testing was carried out on a Zwick®Z050 universal testing machine with a 50 kN loading cell. The experimental procedures were optioned and controlled by a testXpert v11.02 software (Zwick GmbH & Co. kg, Ulm, Germany).

The three point bending test (EN 310) [18] was employed for assessing the bending properties. The samples were loaded with a loading rate of 5 mm min^{-1} until the failure was reached (between 60 and 90 s). A clip-on deflectometer (Zwick GmbH & Co. kg, Ulm, Germany) was employed.

The internal bonding (IB) strength according to EN 319 [19] was measured on the square samples (50 × 50 mm²). Prior to the testing, the samples were sanded and glued between stainless steel blocks with approximately 1 g of a hot-melt adhesive (Siga®N-40) and conditioned for one week. The conditioned blocks were positioned in a gimbal-mounted block holder and pre-loaded in tension by 5 N. Subsequently, loading rate of 1 mm/min was applied until the failure was reached (between 60 and 90 s).

Thickness swelling was determined according to EN 317 [29]. Conditioned samples sized 50 × 50 mm² were fully immersed in distilled water with a temperature of 20 °C. The thickness swelling and water absorption were measured two times: after 2 and 24 h. After the immersion time had elapsed, the test samples were taken off from the water and the excess water was removed. Then the thickness swelling was measured manually, using a caliper (Neiko 01409A), in the centers of the samples. The water absorption was determined by weighing using a scale (Radwag mac 210) with precision of 1 mg. The sample weight immediately taking off from water was recorded and consequently used for calculation of water soaking in percent.

The density of each panel was determined according to EN 323 [30]. Firstly the length, width and thickness of the samples were measured using a caliper (Neiko 01409A). Subsequently the weight of the samples (50 × 50 mm²) was measured using a scale (Radwag mac 210). The density was than calculated as a weight per volume of the sample. Ten samples per board were measured.

The obtained data were analyzed by a Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. Firstly, descriptive statistics was produced and next the normality of the data distribution was verified by the Shapiro–Wilk test. The significance of differences

among the results was tested using the analysis of variance (ANOVA) and Scheffe post-hoc test.
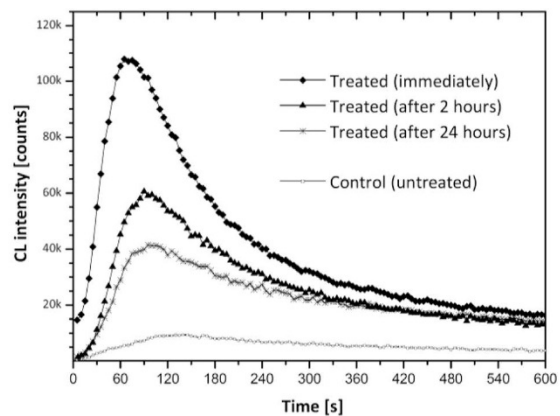
2.4. Scanning electron microscopy

The surface morphology of the particle boards was investigated using a scanning electron microscope Vega TS5130 (Tescan Brno, s.r.o., the Czech Republic). Morphology and interaction between the PET particles and wood chips were inspected. Specimens obtained from the ruptured region of IB sample were coated with gold in a vacuum sputter coater. The SEM accelerating voltage was 16.7 kV. The regions of ruptures between wood particles and PET flakes were identified and scanned. SEM was proposed to study adhesive failure mechanism also by Refs. [6] and [31].

3. Results and discussion

The intensity of chemiluminescence (CL) emission is shown in Fig. 3. Immediately after the treatment, the plasma treated PET flakes exhibited more than 10 times higher CL peak intensity than the untreated flakes. According to the model described e.g. in Refs. [28,32] free radicals on the polymer surface, created either by direct plasma exposure or by subsequent auto-oxidation processes, react rapidly with ambient O_2 to form peroxy radicals ROO$^\bullet$ and hydroperoxides ROOH. These are known to be precursors for CL emission forming ketone functional group R–C=O. Hence the number of detected photon counts in Fig. 3 represents a good lower estimate of hydroperoxides and/or peroxy radicals available for subsequent chemical bonding with resin. It also represents a source for creating polar ketone –C=O groups, which would explain the observed wettability improvement by our water level PET flakes floating test.

The CL aging effect manifested itself as a gradual reduction to 6 and 4 fold improvement against the reference signal (untreated flakes) for samples aged for 2 h and 24 h respectively. This gradual reduction can be attributed to ongoing auto-oxidation processes occurring at slower rate at the room temperature. Still, the measurement indicates that even 24 h after being exposed to air plasma the PET flakes surface is still chemically active.

XPS analysis shown in Table 3 confirms the expected increase of oxygen functional groups on plasma treated surface. The O/C ratio was increased from 0.20 to 0.94. To specify the changes in more detail, high-resolution scan of C 1s peaks was deconvoluted into three components: C–C/C–H at 284.8 eV, C–O at 286.6 eV, and

Table 2
Production parameters of particleboards.

Parameter	Value
Press temperature (°C)	190
Pressing time (sec.)	50
Thickness (mm)	5
Dimensions (mm)	500 × 500
Target density (kg/m³)	600
Hardener content (%)	2
Resination ([g] solid to [g] dry wood particles) (%)	8
Hardener ([g] solid to [g] solid resin) (%)	150
Target moisture content of particles (%)	11

Fig. 3. Thermal chemiluminescence emission of PET flakes at 80 °C.

Table 3
Analysis of XPS spectra.

PET flake	Atomic ratio O/C	Relative area of chemical bonds [%]		
		C–C/C–H	O–C=O	C–O
Untreated	0.20	83	7	10
Plasma-treated	0.94	62	20	18

O–C=O at 288.9 eV (Fig. 4). The most significant change resulting from plasma treatment is the increase of O–C=O chemical state at the expense of C–C/C–H component. The chemical state of C–O is increased as well, although not as much as in the case of O–C=O. These results do not contradict our earlier CL measurements indicating the presence of novel C–O and C=O groups. It is also in agreement with the known formation of carboxyl O=C–OH end-groups which accompanies the oxidative degradation of PET [33]. We conclude our chemical analysis with the note, that while XPS measurement represents an ultimate tool to resolving the chemical nature of surface changes, method of CL represents faster and more affordable option for routine quality monitoring of plasma treatment.

The variability in the board density was not significant among the panels: C 554 ± 42 kg/m^3; C15,568 ± 38 kg/m^3, C30,541 ± 31 kg/m^3, P15,558 ± 42 kg/m^3 and P30,556 ± 33 kg/m^3. The density variation between the produced particleboards was not considered to have an effect on the physical and mechanical properties of the particleboards.

The internal bonding (IB) of the control sample reached the value of 0.8 N/mm^2. Addition of untreated PET flakes resulted in significant decrease of IB value: for C15 samples (ANOVA, p < 0.05) by 20%; for C30 samples up to 45% of IB decrease (ANOVA, p < 0.05) was observed. These findings are similar to those of [6].

For plasma treated PET flakes, the IB did not decrease (Table 4). The P15 reached a value of 0.7 ± 0.1 N/mm^2 which does not give a statistically significant difference (ANOVA, p > 0.05) compared to the C reference sample. The same was true for P30 with IB of 0.72 N/mm^2, i.e. without a statistically significant difference between C and P30. These results can be fully assigned to the plasma treatment effects on the surface wettability of the PET particles with urea formaldehyde adhesive, as well as the

interphase bonding strength guaranteed by plasma created functional groups.

A similar trend was observed in the modulus of rupture (MOR, Table 4). The MOR value of sample C was 11.8 N/mm^2, the C15 exhibited a decrease by 58% in comparison to C; C30 even by 74%. The boards with addition of plasma treated PET behaved differently. The MOR of P15 fell down by 34% and P30 by 50%; also MOE of C15, C30 as well as P30 was lower by 50%. On the other hand, P15 exhibited (ANOVA p < 0.05) MOE similar to C. This can be assigned to different PET particles size affecting the board's bending properties [20,21]. On the other hand, our plasma treatment had a beneficial effect on MOE of the C15, even though not such pronounced as for IB. It should be noted, however, that the bending properties are attribute of the outer layers [22]. These outer layers are commonly covered by other materials supplementing decorative outlook [23] and also ensuring higher bending performance [24]. A similar approach is reported in Ref. [5] for board made from beverage carton covered by beech veneer to increase the board bending characteristics.

The swelling of particleboards was lowered by utilizing PET as a material in the particleboard (Table 5.). The control sample reached swelling rates of 20% after 2 h and 25% after 24 h. This corresponds well to traditional particleboard swelling reported in the literature [26]. The swelling of boards with wooden particles substituted with PET flakes shows decrease of thickness swelling by 50%. We did not find (ANOVA; p > 0.05) differences between the boards dependent on different PET admixture. The water absorption course was similar. Particleboards with PET admixture absorbed by 20% less water than the classical spruce particleboard. The descriptive statistics is in Table 6.

The results of thickness swelling and water absorption well correspond to the results of [6] and are similar to [7]. The lower swelling is explained by the presence of PET, swelling negligibly of its own and compensating the relatively high swelling of wooden particles [25]. From the aspect of plasma treatment, an important outcome of this experiment is the observation according to which the plasma-induced conversion of hydrophobic PET surface into hydrophilic did not contribute to the increased swelling of the final board.

3.1. Morphology and evaluation of bonding failure

The SEM images of 30% wt. PET particleboard were used to visually characterize the resin distribution and failure type between PET flakes and wood particles. The plasma treated P30 samples clearly showed that resin is equally distributed over the surfaces of PET flakes as well as over wood particles. At microscopic level, two distinct types of failure were present in P30 samples. The adhesion failed either on the wood (Fig. 5Aand B) or in the cohesive zone of the bonding line (Fig. 5C). Both failure types are commonly considered as a result of effective materials bonding [26]. SEM images of C30 sample show (Fig. 5 D and E) that the resin distribution was significantly different to those of the plasma treated samples. Without previous plasma treatment of PET flakes, the resin distribution on the PET flake surface was rather poor (Fig. 5E). When the sample was thoroughly inspected under a high magnification (Fig. 5D), small droplets were found on small areas of PET flakes. Assessing the shape and size of the droplets, we conclude that the resin was not successfully distributed on the surface of the PET particles. Furthermore, these droplets do not indicate any rupture, we assume that these isolated regions did not act in the bonding with wood particles at all.

Different failure mechanisms may have several explanations. Failure in wood may be explained by the nature of UF adhesive
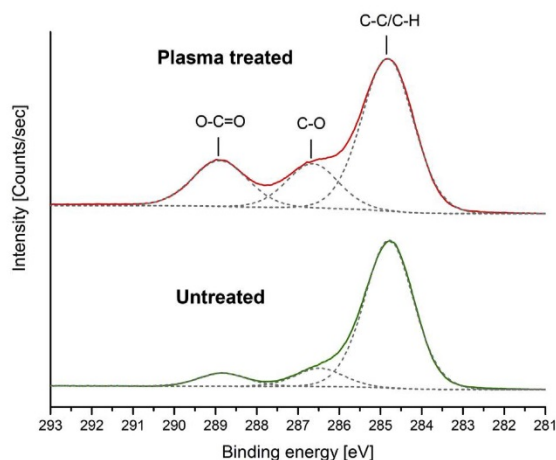
Fig. 4. Deconvoluted highly resolved C1s peak for plasma-treated and control specimen of PET flake.

Table 4
The mechanical properties of particleboards made from PET and wood particles and the test results of ANOVA and Scheffé post-hoc test.

Mechanical properties	Board type	Mean	Std. Deviation	x_{min}	x_{max}	p Value
MOR (N/mm^{-2}); n = 4	C[Y]	11.8	1.9	5.5	13.4	–
	C15[X]	5.7	2.1	2.3	7.1	0.0001
	C30[X]	2.4	0.5	1.9	2.9	0.0001
	P15[Y]	7.4	2.0	4.1	8.5	0.0160
	P30[X;Y]	5.5	0.7	4.7	6.4	0.0003
MOE (N/mm^{-2}); n = 4	C[Z]	1048.2	109.5	936.3	1155.2	–
	C15	541.8	88.0	427.2	708.9	0.0027
	C30	528.4	14.5	518.1	538.7	0.0049
	P15[Z]	800.5	96.0	737.4	911.0	0.1413
	P30	522.4	48.9	465.9	551.5	0.0021
IB (N/mm^{-2}); n = 10	C[C]	0.78	0.10	0.69	0.95	–
	C15[A;B]	0.63	0.10	0.48	0.81	0.4834
	C30[B]	0.45	0.06	0.35	0.52	0.0055
	P15[C]	0.72	0.13	0.50	0.97	0.9999
	P30[A;C]	0.72	0.11	0.60	0.87	0.9725

p Value: compared to control sample (C) (Scheffe post-hoc test).
Significance level of 0.05 (for ANOVA).
[A;B;C;X;Y;Z] Board Types having the same letter are not significantly different (Scheffé post-hoc test).

because this adhesive is known for its saturation and penetration depth into the wood cells [26]. The failure in wood is a typical result of the common shear tensile strength test for UF adhesives used in bonding of wood. The second type – cohesive failure, indicates that the transition zone between the material and resin is not the weakest link of the system. Ruptures occurred in the resin alone without partial failures in the bonded material. The adhesive was visible on the surface of PET flakes, so we may deduce that the resin was chemically bonded on the PET surface. This was most probably caused by chemical activation of the surface, where the number of peroxyradicals and hydroperoxides significantly increased. Aside of chemical bonding, the plasma treated surface of PET particles may be more suitable for better bonding since lower contact angle with liquids [11]. Our findings of the resin distribution on PET particles without plasma treatment meet the results of [6] where a SEM analysis of common PET flakes bonded in a particleboard composite was carried out.

The common industrial adhesive discussed in this work was effectively distributed and fixed onto the surface of the air plasma treated PET flakes. Our approach seems to give promises for alternative PET flakes utilization replacing recycling. This approach is also beneficial in terms of the properties of the wood composite itself. The PET flakes substitution up to 30% of wood mass provided benefits to the final composite: significantly lower swelling without compromising the composite's overall mechanical performance.

4. Conclusions

In our research we found that the decline of mechanical properties of composite boards with PET admixture can be considerably mitigated by PET plasma treatment. The samples containing 30 wt. % of plasma treated PET exhibited the same internal bonding strength as the control sample without PET admixture, while an almost 50% reduction of internal bonding was observed for analogous samples with PET untreated. A similar trend was observed for the modulus of rupture of 15 wt. % composites. The role of plasma activation is to provide sufficient new bonding sites for urea formaldehyde resin. The chemical nature of these sites, revealed by combined XPS and thermal chemiluminescence (CL) measurements, involves mostly oxygen-containing functional groups of carboxyls and hydroperoxydes. Thermal chemiluminescence measurements of aged samples confirmed the presence of surface radicals even 24 h after the plasma treatment. This is a quite practical technological feature,

Table 5
The swelling properties of particleboards made from PET and wood particles and the test results of ANOVA and Scheffé post-hoc test.

Board type	Mean	x_{min}	x_{max}	Std. deviation	p Value
Thickness swelling (2 h) [%]					
C	16.5	8.0	22.1	6.3	–
C15[X]	9.8	8.9	10.8	1.3	0.00395
C30[X]	10.3	8.0	14.8	2.5	0.00057
P15[X]	10.3	9.9	10.6	0.5	0.00214
P30[X]	10.6	8.3	12.7	2.0	0.00539
Thickness swelling (24 h) [%]					
C	20.8	13.0	26.6	6.2	–
C15[Y]	10.2	9.9	10.6	0.5	0.00470
C30[Y]	10.3	8.0	14.8	2.5	0.00272
P15[Y]	13.0	11.7	15.0	1.6	0.00721
P30[Y]	10.8	10.6	11.0	0.3	0.00661

p Value: compared to control sample (C) (Scheffe post-hoc test); n = 5.
Significance level of 0.05 (for ANOVA).
[X;Y] Board Types having the same letter are not significantly different (Scheffé post-hoc test).

Table 6
The water absorption properties of particleboards made from PET and wood particles and the test results of ANOVA and Scheffé post-hoc test.

Board type	Mean	x_{min}	x_{max}	Std. deviation	p value
Water absorption (2 h) [%]					
C	97.46	94.19	100.00	2.98	–
C15[X]	79.15	75.16	82.16	3.60	0.0056
C30[X]	78.55	75.98	83.68	4.44	0.0064
P15[X]	77.18	76.19	78.19	1.00	0.0038
P30[X]	74.55	72.03	77.08	3.57	0.0039
Water absorption (24 h) [%]					
C	107.16	100.12	112.19	3.28	–
C15[Y]	92.64	90.63	95.16	2.31	0.024
C30[Y]	90.49	87.16	93.18	3.06	0.011
P15[Y]	91.64	89.16	94.12	3.51	0.030
P30[Y]	83.14	82.16	84.12	2.39	0.002

p Value: compared to control sample (C) (Scheffe post-hoc test); n = 5.
Significance level of 0.05 (for ANOVA).
[X;Y] Board Types having the same letter are not significantly different (Scheffé post-hoc test).
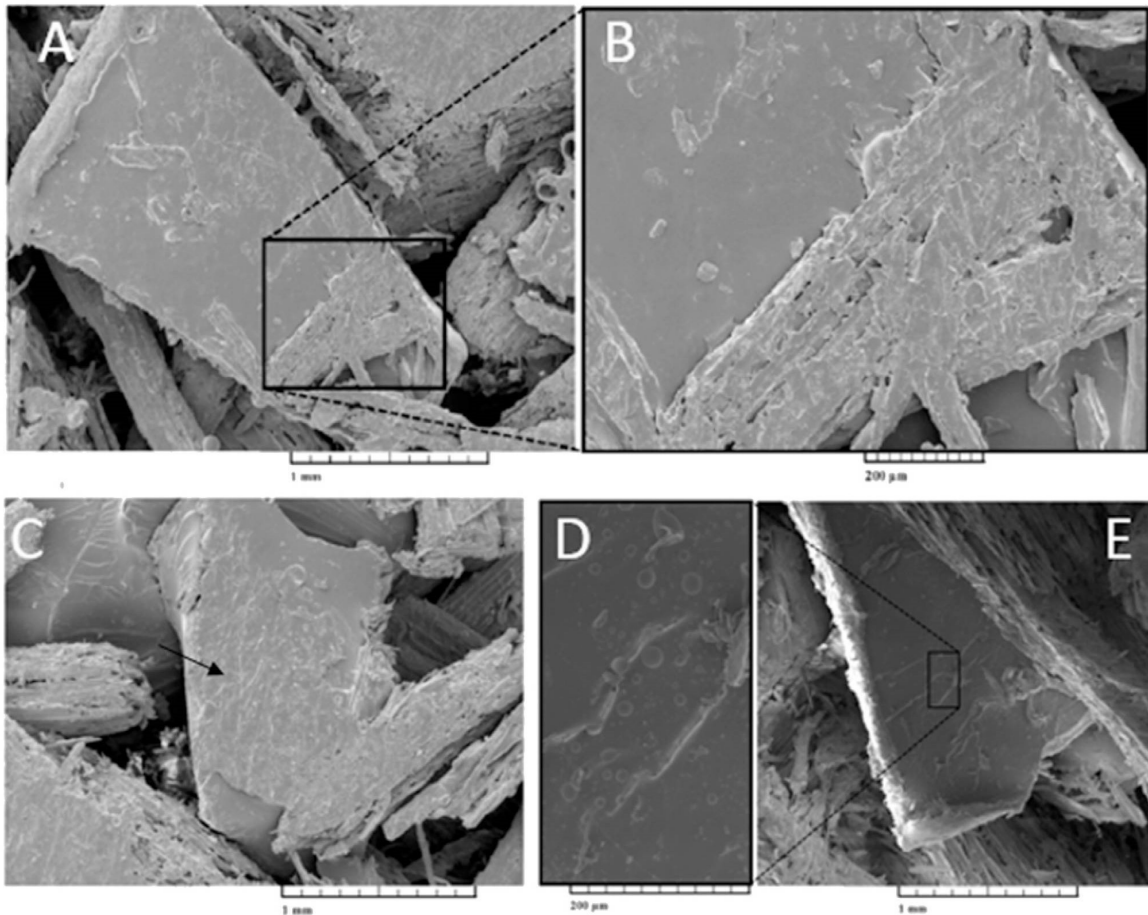
Fig. 5. SEM images of the surface of ruptured P30 and C30 internal bonding sample: (A, B) wood failure on P30; (C) P30 cohesive failure of the bonding region; (D, E) insufficient resin distribution on the sample C30. The region with cohesive failure is marked by arrow.

which places less stringent time constraints on the actual process of plasma assisted wood-plastic particleboard production.

Acknowledgment

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10. Paper VI.

Characterization of particleboards made from recovered painted wood

European Journal of Wood and Wood Products (under review)

Peter Meinlschmidt

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Title: Characterization of particleboards made from recovered painted wood

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Abstract:

The major objective of our research is to utilize recovered wood of window frames in particleboard production. Nowadays, recovered window frames according to German ordinance can be used only for energy production, although potential for particleboard production is severe. In our research painted (contaminated) or surface milled (cleaned) recovered wood is utilized in laboratory particleboard production. The standard (EN 312) mechanical and physical properties of boards are measured as well as vertical density profile. There was found that contamination of windows by paint has a negative effect on the MOR, MOE and IB properties, on the other hand all particleboards are still viable at least for non-load bearing applications. There was found that the painted particles may affect also vertical density profile of the particleboard. The particleboard from cleaned particles delivered same performance as conventional spruce particleboard and as an advantage offered lower thickness swelling. Our research successfully presented sustainable production of the particleboards from material which is nowadays for energy use in large-scale combustion facilities.

Keywords: Particleboard, recycling, recovered wood, waste wood, window frame, demolition waste

1. Introduction

Traditional particleboards are exhibiting an over 120 year tradition and today still holding the strongest position on the market among all wood-based panels and comprise the largest part of all wood based panels produced in Europe (EPF 2015). Shortcomings of virgin softwood (Mantau 2012) and increasing prices for raw materials (International Energy Agency, 2014)

challenge researches to find alternative raw materials for particleboard production. The industrially efficient and responsible use of raw materials should not only assist in increasing productivity but also in environmental protection (Jänicke, 2009). The reasonable way is presented by a cascade utilization of wood (Höglmeier et al., 2013). Here a particleboard is almost at the end of the cascade process and there are many products which outlived their usefulness e.g. windows, doors, furniture etc. suitable for particleboard production. Wood recycling can significantly decrease environmental burdens trough the reduction of input materials, water, and energy used in production process (Zhong et al., 2010). The wood recycling became of higher importance in the last few decades with decreasing virgin wood and increasing raw material costs. Although some countries already successfully implemented usage of recovered wood of about more than 50 % (i.e. Italy ~95% and UK ~51%) of total material input into the particleboard production (EPF 2015), however the situation differs across the European countries. In some countries the recovered wood is not even considered for particleboard production, these regions are mostly well forested and wood recycling strategy will probably appear later. The recovered wood can be easily obtained from wood waste of old wooden buildings (Höglmeier et al., 2013), including furniture which reached it end of usefulness. Since these products consist of at least 90% wood, the recovery and recycling into particleboards can be very beneficial. Various researchers have dealt with the challenge of recycling of wood in particleboard panels (Kharazipour and Roffael, 1997; Wang et al., 2008, 2007; Yang et al., 2007). The investigations included also formaldehyde emission from particleboards made from recovered particleboard panels (Marutzky 1989, Himmel et al. 2014a). In addition recycled wood could be naturally used also for fiberboards (Athanassiadou et al., 2005; Dix et al., 1997; Hashim et al., 2005; Mantanis et al., 2004) and other usage branches e.g. Animal husbandry, mushroom production or wood flour products (Ernst and Militz, 2004). Plastic composites (Ashori and Nourbakhsh, 2009; Kazemi Najafi, 2013) or building materials (Poon and Chan, 2007) presenting viable processes of material recycling as well. However in applied research mainly challenge to utilize not cleaned material without any pre-treatment is stressed. It is known that wood is fully natural substance, however recovered wood is contaminated by paint, lauqer etc. which were needed previously to establish durable and custom made product. Contaminations such as paint, lacquer, wood preservatives etc. are not always of natural origin (Gann et al., 2005). Since in our research we are focusing on the utilization of recovered wood from window frames, mostly paints of unknown origin are of major concern. The motivation of using a recovered window frames could be seen in a face

that window frames in Germany currently fell in class AIV i.e. material for energy use in large-scale combustion facilities (German Government, 2002). Currently this material is abundantly available since there exists a take-back system of old windows in case of new window installation. On the other hand replaced windows are not further used by any means. The major research objectives are: (1) Produce the particleboard from the recovered wood of window frames, suitable for standardized (EN 312) applications. (2) Observe effect of the paint contamination of the particles on the properties of particleboards.

2. Materials and methods

In the experiment three types of the raw material for the particleboard production were used. (1) Spruce wood. (2) Meranti (genus: Shorea) wood particles obtained from recovered wood of painted window frames. (3) Meranti wood particles obtained from surface milled recovered wood (Cleaned) of painted window frames. Each coated surface of a window frame was milled off by 3 mm on one side planner prior to chipping. The material before disintegration is in figure 1.
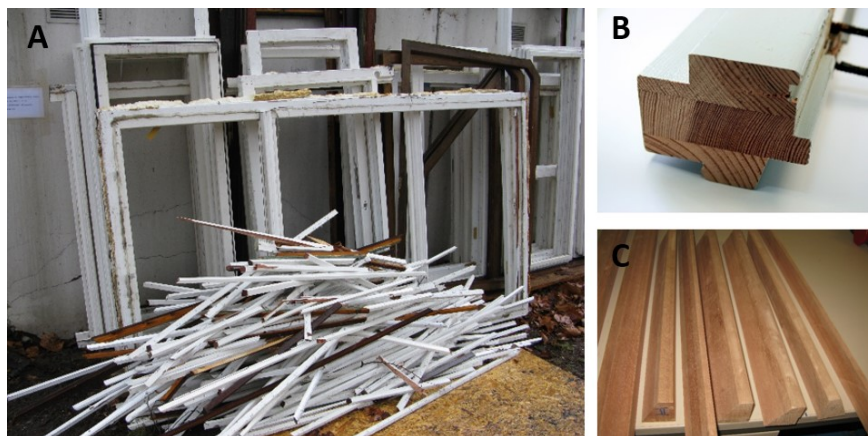
Figure 10-1. Recovered material used for production of the particles; A, recovered painted window frame, B – painted (contaminated) recovered wood of window frame C – Surface milled (cleaned) recovered wood of window frame

2.1 Preparation of the particles

Wooden particles were prepared simulating common production of particles in laboratory scale. Firstly the recovered wood pieces were chipped in a chipper Klöckner 120X400H2W.T (Klöckner Maschinenfabrik, Lauenburg, Germany) using a cutting speed 725 n/min and feeding speed approximately 1 m/s. Obtained chips of dimension $20 \times 20 \times 5$ mm^3 were then

milled in hammer mill Condux-Werk HS 350 (Condux Maschinenbau GmbH & Co. KG, Hanau – Wolfgang, Germany). Produced particles of different size were screened afterwards in cascade vertical drum screener Allgaier D7336 (Allgaier-Werke GmbH, Uhingen, Germany). The screeners sieve with a mesh size openings of 5.0 mm; 3.15 mm; 1.24 mm and 0.60 mm sorted the particles on different fractions respectively. In the production of particleboard the particles of mesh > 1.24 and < 5 mm were used. Particles separated from two sieves were manually mixed together in weight ratio 50:50. Particles were oven dried to moisture content of 9 %.

2.2 Preparation of the panels

The urea formaldehyde resin (BASF Kaurit® 350, Basf Se, Ludwigshafen, Germany) in amount of 12 % was applied to the particles in a drum blender for 5 minutes. The resin mixture contained the ammonia-based hardener in amount of 2.5 %. The paraffin in amount of 1.5 % was added separately by different spraying nozzle. The resinated particles were manually dispersed into a wooden pre-forming box (500×500 mm^2) and pre-pressed in non-heated press by 0.4 MPa in hydraulic press. Obtained formed mat was hot-pressed at 200°C and 3.2 MPa for 160 sec in hydraulic press Siempelkamp (Siempelkamp Maschinen und Anlagenbau GmbH, Krefeld, Germany) afterwards. The final thickness of 16 mm was obtained through the control software of the press. By this process, 9 types of particleboards in total were manufactured according to the research design listed in Table 1.

	Raw material [%]		
abbreviation	Spruce	Cleaned	Contaminated
Control	100	0	0
R20c	80	20	0
R20n	80	0	20
R50c	50	50	0
R50n	50	0	50
R80c	20	80	0
R80n	20	0	80
R100c	0	100	0
R100n	0	0	100

Table 10-1. Research design of produced particleboards; Spruce – spruce wood particles, cleaned – Particles from the surface milled recovered window frames, contaminated – particles from the painted recovered window frame

2.3 Material properties and data evaluation

Mechanical testing was carried out on a Zwick 1474® universal testing machine. The experimental procedures were optioned and controlled by a testXpert II software (Zwick GmbH & Co. kg, Ulm, Germany).

The three point bending test (EN 310) was employed to measure the bending properties. The samples ($18 \times 50 \times 370$ mm^3) were loaded with a loading rate of 9 mm/min until the failure was reached (between 60 to 90 s). The clip-on deflectometer (Zwick GmbH & Co. kg, Ulm, Germany) was during the measurements employed.

The internal bonding (IB) strength according to EN 319 was measured on the square samples ($16 \times 50 \times 50$ mm^3). Prior to testing of the samples were sanded and then glued between the stainless steel blocks. Blocks were positioned in gimbal-mounted block holder and pre-loaded in tension by 5 N. Subsequent loading rate of 1 mm/min was applied until the failure was reached between 60 to 90 s.

Thickness swelling was determined according to EN 317. Conditioned samples sized $16 \times 50 \times 50$ mm^3 were fully immersed in 20 °C distillated water. The thickness swelling was measured at two time intervals, after 2 and 24 hours. After the immersion time had elapsed, the test samples were taken off the water and excess water was removed by paper cloth. Then the thickness swelling was measured manually, using a thickness gauge, in the centers of the samples.

Vertical density profile was measured using the x-ray density analyzer GreCon RG44® 33KV/1mA (GreCon, Alfeld-Hannover, Germany). The equipment analyzed five samples of $16 \times 50 \times 50$ mm^3 dimension.

The obtained data were analyzed by a Statistica v.12 (StatSoft inc., Tulsa, Oklahoma) software. Firstly, descriptive statistics was produced and subsequently the normality of the data distribution was confirmed by the Shapiro-Wilk test. The significance of differences among the results was tested using the analysis of variance (ANOVA) and Scheffe post-hoc test.

3 Results and discussion

3.1 The mechanical properties

From the measurements is evident that contamination has significant effect on the MOR of the particleboards from recovered wood (figure 2). The lowest MOR of 14 MPa was measured for particleboard fully produced from contaminated particles. Generally particleboards produced from contaminated particles delivered lower average MOR than control sample. Average MOR of particleboards from contaminated particles is also lower compared to particleboards produced from cleaned particles of recovered wood. On the other hand ANOVA proves only significantly different MOR (ANOVA; $p<0.05$) between boards R50c and R50n. No other significant differences were shown among other panel types. The particleboards produced from cleaned recovered wood having similar MOR as control, close to 17 MPa. The similar results reported for particleboard made from recovered wood by (Himmel et al., 2014b). Also our MOR is similar to MDF produced from recycled wood (Athanassiadou et al., 2005) and MOR is lower than reported by (Mantanis et al., 2004). Although MOR of some particleboards types is reduced, according to EN 312 the boards R20c; R50c; R80c; R100c have fulfilled requirements given by EN 312 (ANOVA, $p<0.05$) to be sufficient for utilization as load-bearing boards for use in dry conditions (EN 312; P4). The boards R20n; R50n and R80n fulfilled requirements (ANOVA, $p<0.05$) for non load-bearing applications (EN 312; P3). The board R100n fulfilled requirement of boards for general purpose use in dry conditions (EN312; P1).
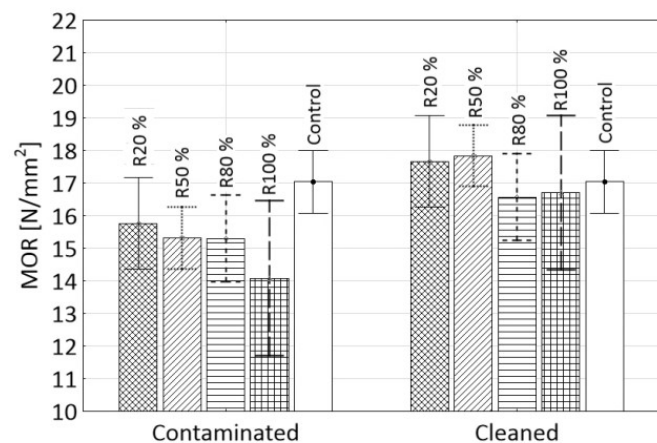

Figure 10-2. Modulus of rupture (MOR) of panels considering contamination; R20 % – 20 % wood is replaced, R50 % - 50 % wood is replaced, R80 % - 80 % wood is replaced, R100 % - 100 % wood is replaced by recovered wood. Control – Spruce particleboard (each column represents data obtained from 5 measurments; errorbars indicated 95% confidence level)

The MOE (figure 3.) of the particleboards made from recovered wood was more significantly affected by the contamination of particles than MOR. The lowest values of MOE close to 2600 MPa was measured for boards R80n and R100n. The highest MOE among the recycled panel types was presented by R20c and R50c and it was 2950 MPa which is similar to (Himmel et al., 2014b). Generally the MOE of the particleboards from recycled particles was gradually decreasing with spruce particles substitution. The decrease of MOE with higher substitution of the spruce particles was more pronounced when contaminated particles were used. The R50n, R80n and R100n presented significantly reduced MOE (ANOVA,p<0.05) compared to control. On the other hand all other types of particleboards produced from recovered wood has similar MOE to control. Although the MOE of the panels is various, all panels match the requirements of MOE for bearing boards for use in dry conditions (EN312; P4).
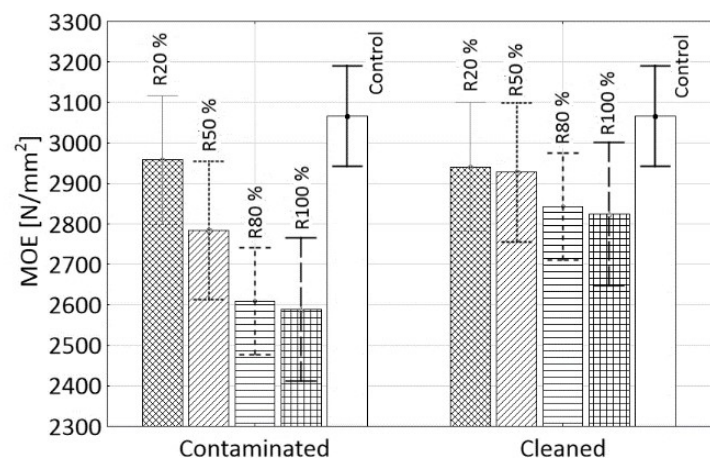

Figure 10-3. Modulus of elasticity (MOE) of panels considering contamination; R20 % – 20 % wood is replaced, R50 % - 50 % wood is replaced, R80 % - 80 % wood is replaced, R100 % - 100 % wood is replaced by recovered wood. Control – Spruce particleboard (each column represents data obtained from 5 measurments; errorbars indicated 95% confidence level)

The internal bonding strength (IB) was significantly lower for R50n and R100n compared to control. The positive fact on the other hand is, that there were found no difference between the control and particleboards produced from cleaned particles. Similar results were measured for particleboard by (Himmel et al., 2014a; Kharazipour and Roffael, 1997) and similar

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results were mentioned also for fiberboards (Athanassiadou et al., 2005; Dix et al., 1997; Mantanis et al., 2004) made from recycled wood. Interesting results of IB are observed for R80n where measured IB is actually higher than for R50n and R20n. It is evident the IB could be more affected by actual content of painted particles rather than amount of used recovered wood contained in particleboard. Although IB of boards with contaminated particles was lower, all panel types fulfilled requirements for bearing boards for use in dry conditions (EN312; P4). Results are in figure 4.
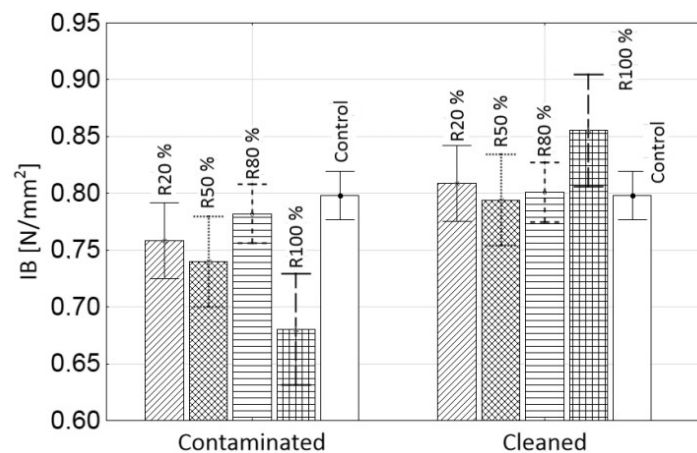

Figure 10-4. Internal bonding (IB) of panels considering contamination; R20 % – 20 % wood is replaced, R50 % - 50 % wood is replaced, R80 % - 80 % wood is replaced, R100 % - 100 % wood is replaced by recovered wood. Control – Spruce particleboard (each column represents data obtained from 12 measurments; errorbars indicated 95% confidence level)

3.2 The physical properties

It can be seen (figure 5.) that the thickness welling (TS) of boards prepared recycled wood is lower than control. Positive fact is that the particleboards from cleaned particles showed gradual decreasing of the TS2h with replacement of the spruce particles. However particleboards with contaminated particles behaves differently. Here R20n and R50n showed higher TS2h than control, while R80n and R100n presented lower swelling than control. Results indicates that TS2h is not fully related only with amount of recovered wood content. It is probably more connected with actual content of painted particles than with amount of recovered wood. Further decrease of the thickness swelling could be caused by the meranti wood itself. Meranti wood has different swelling characteristics as well as density i.e.

compaction ratio than spruce wood (Forest Product Laboratory, 1999). We assume that different wood morphology may cause decrease TS2h of particleboards from recycled wood.
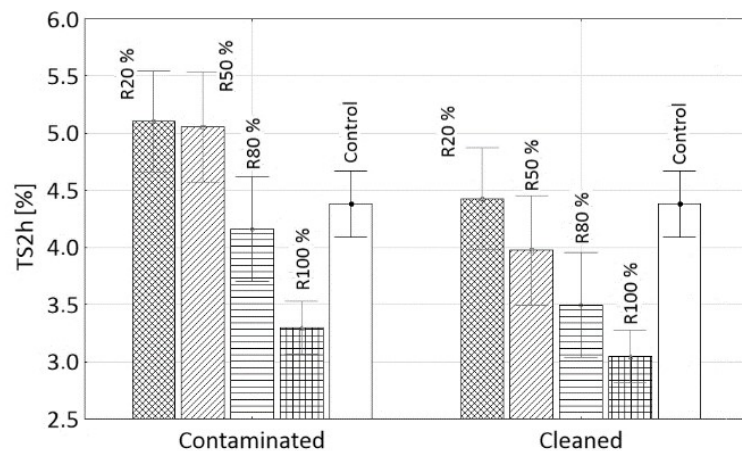

Figure 10-5. Thickness swelling of particleboards after 2 hours; R20 % – 20 % wood is replaced, R50 % - 50 % wood is replaced, R80 % - 80 % wood is replaced, R100 % - 100 % wood is replaced by recovered wood. Control – Spruce particleboard (each column represents data obtained from 8 measurments; errorbars indicated 95% confidence level)

Thickness swelling after 24h (TS24h) was different to TS2h. The highest TS24h, 16 %, was measured for R20n. Again as in case of TS2h it is obvious that the contaminated particles may cause higher swelling (Figure 6.). The board R20n, R50n and R80n presented significantly higher swelling than their counterparts produced from cleaned recovered wood. However the positive outcome is that there has been shown that full replacement of spruce particles by cleaned particles of recovered wood may deliver lower swelling than control. The results of TS24h shown that some of the boards with contaminated particles do not match the requirements of EN 312 (ANOVA, $p < 0.05$). The board type R20n, R80n and R20c do not match the requirements for P3. The results of the thickness swelling are similar to one reported by (Kharazipour and Roffael, 1997) and TS is higher than mentioned in (Mantanis et al., 2004). The differences may be caused by different amount of hydrophobic substances added in particleboards and/or different quality and origin of recycled material used for particleboard production.
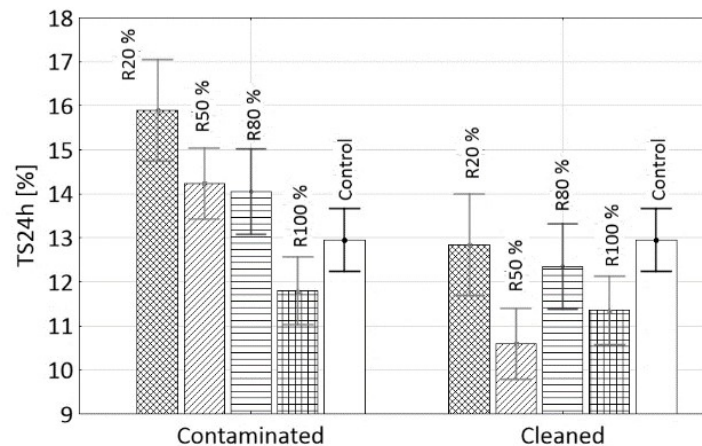
Figure 10-6. Thickness swelling of particleboards after 24 hours; ; R20 % – 20 % wood is replaced, R50 % - 50 % wood is replaced, R80 % - 80 % wood is replaced, R100 % - 100 % wood is replaced by recovered wood. Control – Spruce particleboard (each column represents data obtained from 8 measurments; errorbars indicated 95% confidence level)

3.3 Density profile

The density profile (Figure 7) was altered by using contaminated particles. Common steep profile gradient of the control sample made from spruce was changed by addition of particles of the contaminated recovered wood. Significant density profile change is obvious when higher amount of the contaminated particles was used. Particleboards from the contaminated particles showed the fluctuating tendency of the core part in density profile. Contamination caused mostly by various paints, lacquers and binders may exhibit higher densities (Šrajer et al., 2013) in density profile. For instance Titandioxid which is commonly in white lacquer contained, has many times higher density (Prasai et al., 2012) than the wood. X-ray measurements may than result in altered density profile with fluctuating tendency. Also assuming that density profile is formed by moisture transfer during the pressing (Wong et al., 1998), it is possible that density profile is formed differently in places with contaminated particles. Since profile shape is connected with the mechanical and physical properties of particleboards (Wong et al., 1999), we assume that mentioned changes can be responsible for different behavior of the panels produced from cleaned and contaminated particles.
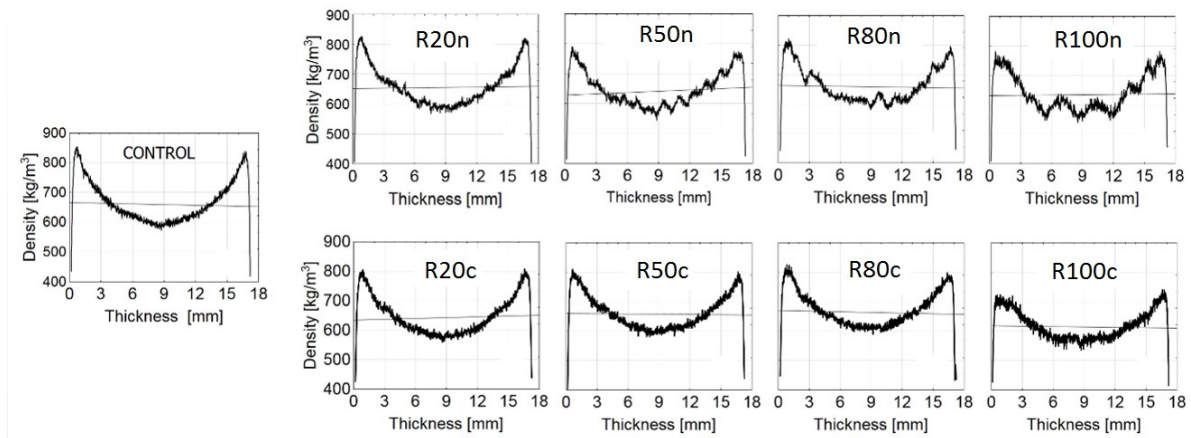
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Figure10-7. Density profile of produced boards; horizontal line indicate average density of the board, R20

In summary both our objectives were fulfilled. There were found that all types of the particleboards from cleaned recovered wood providing same mechanical performance as a common spruce particleboard. Furthermore the particleboards from cleaned recovered wood having lower swelling than conventional spruce particleboards. Considering usage of contaminated particles, the mechanical properties of the particleboards from contaminated particleboards were lower than control, and also some of the types has higher swelling than controls. On the other hand it must be noted that the significant advantage of the production from contaminated particles is no needs of additional operation prior to the particleboards production. On the other hand unknown chemical composition of the paints may result in additional VOC emissions. We recommend that the particles with paint than should be sorted out of the production process in any case. Solution of the sorting for instance by near infrared spectroscopy is already developed by (Maruschat et al., 2014a, 2014b). Than the contaminated particles can be sorted out and used for instance in energy production. The positive contribution of our research is seen in the successful introduction of particleboards from recovered wood which is nowadays directly burned and used for energy purposes (Höglmeier et al., 2013).

4. Conclusions

In our research we successfully produced particleboards from recovered wood of window frames. The recovered wood was used in two forms: (1) cleaned where surface of frames were surface milled (-3 mm) prior to chipping and (2) contaminated, where the painted

surface of window frames remained. The particleboards with different content of recovered wood was successfully produced and standard physical and mechanical behavior was reported. Moreover the density profile was measured. There were found that contamination has negative effect on the MOR, MOE and IB properties, however the boards are according to EN 312 still viable. Also density profile was altered by usage of contaminated particles. Interesting behavior was reported by thickness swelling of particleboards. The highest swelling was obtained when spruce particles were replaced by contaminated wood by 20 and 50 %. It seems that contamination has negative effect on thickness swelling, however is not connected with volume of replacement as it is connected probably with real amount or placement of painted particles in particleboard. This chapter needs some further investigation in the future. The effect of specified amount and not random amount of painted particles in particleboard should be part of one of the following research. On the other hand, in industrial production, these particles should be sorted out to avoid additional VOC or other unknown chemical   threats.

11. Paper VIII.

Microscopic swelling of wood based panels: First trials

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MICROSCOPIC SWELLING OF WOOD BASED PANELS: FIRST TRIALS

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INTRODUCTION

In last decades composite materials helped to achieve many goals of human kind. Medicine (Ciocca et al., 2014), metal (Garcia-Avila et al., 2014) and building industry (Hunt, 2004; Khedari et al., 2004), wood branches (Dalvand et al., 2014; Kelly, 1977; Mantia and Morreale, 2011; Rizvi and Semeralul, 2008) or plastic industry (Mitchell et al., 2014) using composites to create by-design materials with demanded physical and mechanical performance. In branch of renewable materials the wood composites became very popular, for their versatility in applications, high stiffness to density ratio and no less important sustainability (Mantia and Morreale, 2011). This properties generally comes from composites sub-components. Composite materials such as particleboard or fiberboard basically consist larger or/and smaller wood components bonded by various binders, where various techniques are processed in order to achieve homogenous material with consistent mechanical performance. Nevertheless mechanical performance as well as shape stability is changing in

various physical fields. One of the most common is change of wood composites thickness and shape as reaction to increased moisture (Fan et al., 1999; Heon et al., 2013), (Forest Product Laboratory, 1999). The swelling is usually tested according to standards EN 317, specified by the ratio of total thickness before and after immersion in water. This property is well described for common (Fan et al., 1999) and alternative materials (Buyuksari et al., 2010; Lertsutthiwong et al., 2008; Nemli et al., 2009) used for wood based composites. Although common macroscopic swelling is specified, during the water uptake the microscopic elements consisted in composites are interplaying with the dimensional change. It can be assumed that particles are during the production of particleboard partially compressed and thermally treated, so swelling may be similar to compressed and thermally treated woods as described Kúdela et al. 2012 (Kúdela and Rešetka, 2012). Nevertheless composite by its complex structure, consisting of microscopic polymer bonds and interphases between particles created by heat, moisture and pressure may produce complicated intrinsic swelling interactions. Although the classical thickness swelling may give sufficient information about product quality, the microscopic swelling of composites giving insight into the swelling behavior of product components is missing. We believe that this can be important for specification of input materials, since geometry of particles (Rokiah Hashim et al., 2010), used resin (Iswanto et al., 2014) or production process used, may give various microscopic swelling interactions. In our research are stating following research questions: (1) Is it possible to develop reliable method for specification of microscopic swelling in particleboard and fiberboard? (2) Is it possible to indicate swelling behavior of various particles, contained in particleboard? (3) How is the swelling of wood fibers different to swelling of wood particles?

MATERIALS AND METHODS

This research consisted of three main phases: (1) Sample preparation particleboard and fiberboard for microscopic evaluation of swelling. (2) Establishment of recording setup in climate chamber for image capturing. (3) Optical measurement using method of digital image correlation (DIC).

Sample preparation

The samples were prepared from particleboard (PB), which consisted of Spruce (*Picea abies*) particles of sizes between 1 to 3 mm width, 5 to 15 mm length and thickness of 0,75 – 1 mm. The board was produced simulating industrial production process using laboratory

equipment. The UF adhesive was used. When the board was cooled and conditioned in 24°C and 60 % relative humidity of air the sample of size 50 × 50 mm^2 was obtained. The cross-section of sample was inspected using camera Dino lite (AnMo Electronic Corporation, Taipei office, Taiwan) and area of interest (AOI) was identified. The AOI consisted of particles with different thickness and orientations. 2 mm of surface layer was obtained using laboratory hand-saw and surface was carefully sliced by razor blade to obtain smooth surface. Same approach was followed when the sample was obtained from commercial medium density fiberboard (MDF). Final samples size is in figure 1.

Figure 1. Samples prepared for digital image correlation; particleboard sample – left, MDF sample - right

Equipment used for optical measurement

To create controlled environment where swelling of sample may be captured the climate chamber Vötsch VLC 4006 (Vötsch industieltechnik GmbH) was used. The steel stand with laboratory clamp was placed in the conditioning chamber and 5 kg steel weights were placed close to AOI on the bottom plate of the stand to avoid rigid body movement caused by vibrations of the climate chamber. Then camera Dino lite was mounted in the stand vertically to captured area underneath. The specimen was carefully positioned in the center of FOV and subsequently 50 times magnified (see figure 2).

Figure 2. DIC Setup where A being camera, B monitored region; C – weight; D – sample captured with magnification 50 ×
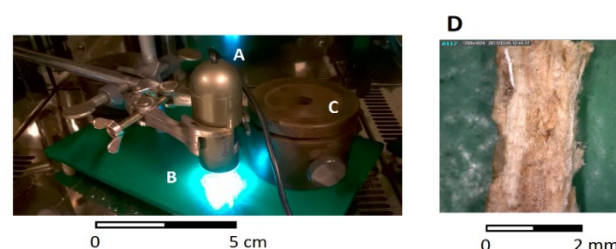

Microscopic digital image correlation

The 2D optical measurement (DIC) was used to capture images of the sample using camera Dino lite (AnMo Electronic Corporation, Taipei office, Taiwan) which was focused on 4.5 × 4.5 mm Field of view (FOV). The images were captured with resolution 1280×1024.

A default LED light of the camera was used to illuminate the AOI. Camera was connected with software Dino Capture 2.0 version 1.5.10 where focusing was manually adjusted to obtain maximal sharpness of the captured images. Prior to focusing the AOI was in software 4 × magnified using implemented "zoom-in" function. The DIC itself was produced using software Davis 8.1.3 software (LaVision GmbH, Goettingen) and strain in horizontal/thickness (εxx) direction was calculated. The calibration of optical measurements was performed prior to test using 1 mm gridded paper. One image of the paper was captured and the size of the image was calculated and it was 3.9 µm/pixels. Then the climate chamber was turned on without changing of environment, five images were captured and mean value of displacement in horizontal and vertical direction was calculated and identified as error of measurement (v_{err}). v_{err} in horizontal direction was calculated on 0.09 µm and v_{err} in vertical direction was 0.04 µm.

The images for microscopic swelling identification were taken in conditions of 80 % relative humidity and 24 °C for 240 minutes. The acquisition interval of image capture was 15 minutes. 15 images in total were correlated by integral correlation relative to first image with interrogation window size 32 × 32 and overlap 50 %. Then the values along the inspection line specified by us in DaVis software (Figure 3) in center of the sample were listed and swelling profiles of PB and MDF were produced in time intervals of 60; 120; 180 and 240 minutes. The bicubic interpolation was used to obtain final results in plots. The total swelling was calculated according to EN 317. The maximal thickness of the sample at the beginning of measurement and maximal displacement in horizontal/thickness direction after 240 min was used in calculation.

Figure 3. The samples 50 × magnified with specified inspection line (orange) and sub-inspection lines (green)
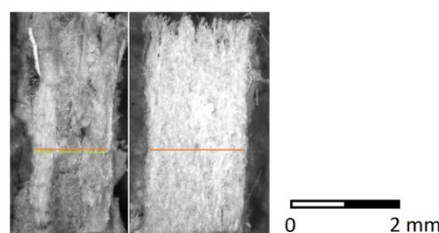

Results and discussion

Particleboard

The thickness swelling of particleboard after 240 min conditioning in 90 % RH and 24° C was calculated on 2.5 %. The microscopic swelling profile presented complex swelling interactions where highest swelling was presented by the particle placed in position 100 – 760

µm. Interestingly it seems that particle start to swell not uniformly, the data provided first insight into the behavior, further research must be performed to introduce micro-mechanism of particles swelling. The highest swelling was showed by particle with longitudinal orientation in the board. The swelling was highest due to swelling of wood in tangential direction and median value 8 % corresponding with swelling of pine wood in tangential direction. The second part of inspected region (Figure 5-2) shown fluctuated swelling since particle has different orientation and wood particle was present as a thin bundle (Figure 4A). It seems that the voids in the central region of the inspected area were filled by swelling of wood since swelling profile indicated negative ε_{xx}. The last particle showing swelling from 3 to 5 % correspond with its radial orientation perpendicularly to the thickness.

Figure 4. The strain map (µm/ µm) of the particleboard and particle-bundle (magnification 200 ×) in the central sub-inspection line
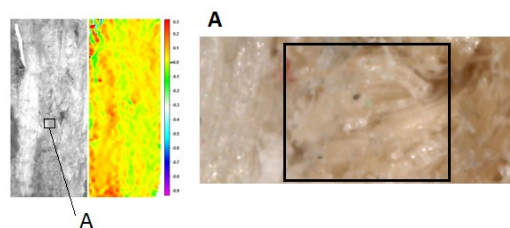
In general it seems that swelling interactions in particleboard composites depends on the orientation of the particles. The dominant swelling of particle with tangential orientation in thickness of the sample may force to swell central particle with different geometrical orientation into the voids. The orientation of the particle seems to be dominant since highest positive displacement of the sample was achieved on the right side of the sample, while minor negative on the left side. To explain interactions between dimensions, orientation and shape further research must be designed.

Figure 5. Microscopic swelling profile of the particleboard and statistical evaluation of selected sub-inspection lines
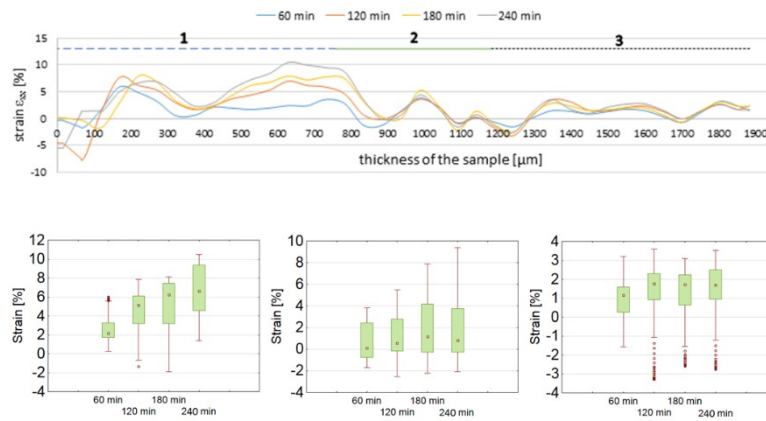
Fiberboard

The strain maps (figure 6) shown relatively uniform strain of the strain, the MDF was found to have more regular displacement which reached similar value as in particleboard. The swelling was calculated on 2.4 %. Although the strain was uniformly distributed the size of the fibers may play an important role as well. The larger fibers localized between 400 and 650 µm of the sample (figure 7) thickness shown swelling peaks in microscopic swelling profile. The fibers seem to swell and fill the voids in the board since higher presence of negative εxx is indicated. However due to low magnification we can not identify thickness swelling of separate fibers. More conclusions may be found with higher magnificantion and also when density and fibres' thickness is defined.

Figure 6. The strain map (µm/ µm) of the fiberboard and larger fibers (magnification 200 ×) in the central sub-inspection line
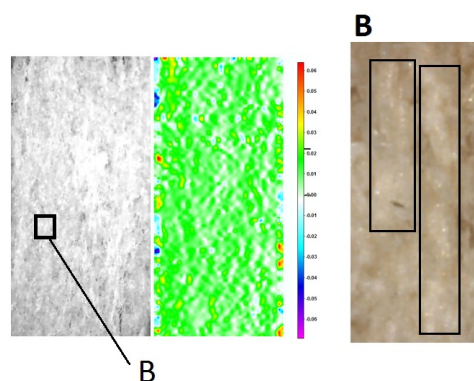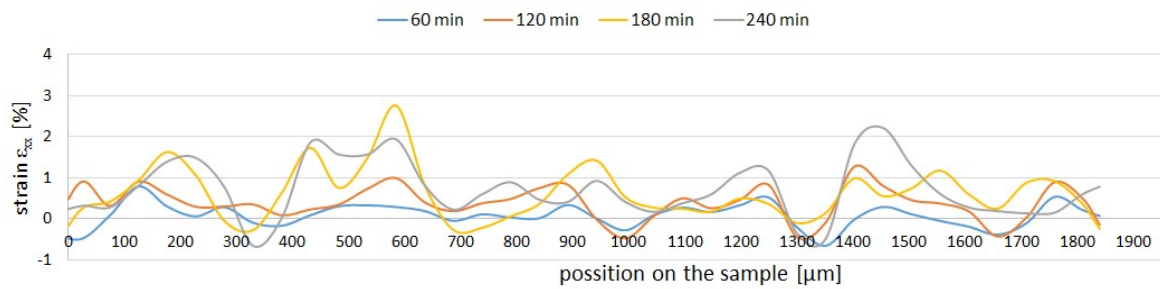


Figure 7. Microscopic swelling profile of the fiberboard

Swelling of the components

For specific evaluation, three particles were in interest (Figure 8) along with interphase of the particle (Figure 7A). After 60 minutes of humid air exposure, the swelling of the interphase and wooden particle is constant, close to ~1 %. After 120 min the average swelling of wooden particles is higher then swelling of the interphase and interestingly the opposite result is measured after 180 min. The swelling wood seems to be constant after 180 min to 240 min and is ~4%. Swelling of the interphase, on the other hand, is increased up to ~6 % after 240 min of humid air exposure.

Our results shown that swelling reaction to the humid air is different to the wooden particle and interphase. It seems that first swelling reaction is driven by the wooden particles as they react on the change of humity sooner. Later on, when center of the particles is restricted to swell any further, the interphase starts to swell and reach even higher values than the particle. This might indicate that interphase between the particles have been densified more than the particle's core. More research in this direction must be carried out.

Figure 8. Microscopic swelling of wooden particles and interphases between particles in particleboard
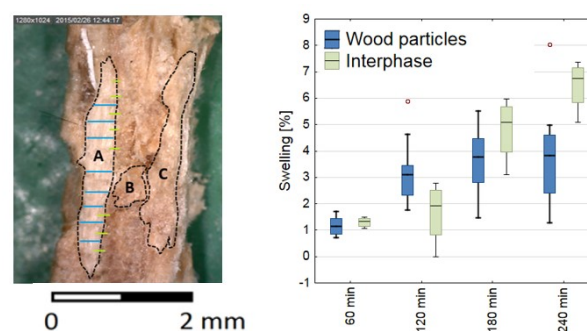
Swelling of the painted particles in recycled particleboard

Our results showed that painted particles display none swelling reaction after 120 minutes humid air exposure. Actually, results showed that part of the painted particle (Figure 9) is compressed by the swelling reaction of the surrounded particles. The thickness swelling assessment of the recycled particleboard proven our previous hypothesis (Paper VI.), that

actual content of painted particles in particleboards might affect the thickness swelling of particleboards more then content of recycled wood.

Figure 9. Microscopic swelling of recycled particleboard containing painted wood
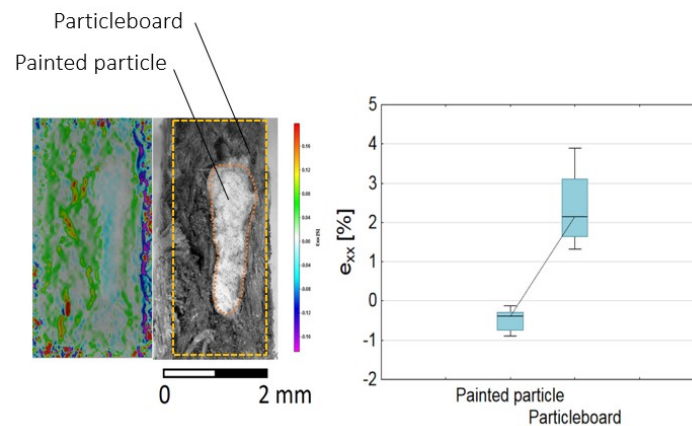
CONCLUSIONS

In our research we successfully established method for DIC evaluation of microscopic changes of wood based composites which can be directly transferred and used for evaluation of other materials. The benefits of this technique may have significant contribution in practical investigations of polymers. Also in assessment of damages caused by increased humidity for historically valuable pieces (paints, wall claddings) may be this technique interesting since only small piece (2×2 mm) for evaluation is needed. Secondly in the field of wood based composites this technique was found possible to use and further research including effect of particles size, geometrical orientation or used resin should follow. Moreover the thorough swelling profiles may explain benefits of different density distributions in the wood based panels.

ACKNOWLEDGMENT

12. Conclusions

The dissertation has proven, that selected alternative materials can be cheaper than wood and can be abundant source for particleboard production. At the same time, that some alternative materials are treated as a waste, although they can be successfully utilized in particleboard production. That means that Particleboard industry may become an important also for waste management, which is politically prioritized as European committee declared to achieve greener and more sustainable production in next decade.

In paper I. we have suggested particleboards from cup plant, sunflower and topinambour stalks. Here the effect of resin type and resin dosage on the properties of particleboards was investigated. Especially MDI bonded particleboards from agricultural plants are a viable alternative to classical UF bonded particleboards from spruce wood. Higher MDI dosage has not significant effect on the bending properties. On the other hand higher dosage of MDI resin significantly increased IB of all particleboards. Interesting outcome of our research is, that mechanical properties of the alternative particleboards is significantly lower compared to spruce particleboards, although production procedure were kept constant.

In Paper II, Particleboard from Miscanthus was suggested. In this research, the wood in particleboards was successfully substituted by particles obtained from Miscanthus stalks. Despite the fact that the mechanical properties observed for particleboards manufactured from Miscanthus stalks are lower than those for spruce particleboards, the Miscanthus particleboard still meet the minimal requirements for general usage in dry conditions according to EN 312. The microscopic evaluation of the Miscanthus and spruce particleboards by scanning electron microscopy indicated that soft parenchyma cells may contribute to the failures and compromise mechanical properties of Miscanthus particleboards. Simultaneously, we have assumed that parenchyma cells, due to their microscopic structure, are responsible for higher water uptake of Miscanthus particleboards. The effect of parenchyma cells in the particleboards requires further research. The interesting aspect of the research was also the thickness swelling of Miscanthus particleboards, with relatively low thickness swelling but high water absorption observed.

In paper III. We have suggested three layer particleboard with cup plant core and spruce furnish. This particleboard can be prioritized also for its surface appearance, which is not different to the classical three layer spruce particleboard. The IB of the cup plant three

layer particleboard was similar to the cup plant one layer particleboard. Surface layer made in three layer cup plant particleboard has delivered better MOE and MOR. Which suggest that spruce furnish could increase MOR and MOE of particleboards from alternative materials. The density profile of the three layer cup plant particleboard was also altered, as the density of core layer was higher compared to surface, which is highly unusual and needs further research.

In Paper IV we have proven that particleboards can be produced with 10 % of BSG particles and still comply the minimum requirements according to EN312. While 10 % substitution of wooden particles by BSG particles did not changed properties of particleboard, the higher content of BSG particles in particleboard reduced MOR, MOE, IB and increased thickness swelling of particleboards. This fact can be attributed to the inner structure which was investigated by SEM. BSG-based particleboard indicated that smaller fractions of BSG particles covered the surface, while some occupied voids between the wooden particles. The fact that smaller fraction of BSG particles are covering the wooden particle´s surface may restrict proper bonding between wooden particles and thus reduce the mechanical properties. Voids occupied by BSG particles on the other hand may retain water and cause higher swelling. A future challenge is to increase mechanical properties of the particleboards with higher addition of BSG. One of the ways is to investigate BSG-based particleboards bonded with various resin types or higher resin dosage.

In Paper V. we have confirmed through XPS study, that polar functional group are formed on a surface of wood exposed to atmospheric pressure plasma. The macroscopic observation also proven improved wettability of this surface. Tensile shear bond strength of PVAC adhesive confirmed improved bonding strength of plasma treated wood. These results suggested that plasma treatment can improve bonding of the wooden surfaces. These results were motivation to try the same treatment in field of composites where internal bond strength restricted their application. In Paper VI we tried this treatment on the surface of PET particles, which gradually replaced wood in particleboard up to 30 %. In our research we found that the decline of mechanical properties of composite boards with PET admixture can be considerably mitigated by PET plasma treatment. The samples containing 30 wt. % of plasma treated PET exhibited the same internal bonding strength as the control sample without PET admixture, while an almost 50% reduction of internal bonding was observed for analogous samples with untreated PET. The role of plasma activation is to provide sufficient new bonding sites for urea formaldehyde resin. The chemical nature of these sites, revealed by combined XPS and thermal chemiluminescence (CL) measurements, involves mostly

oxygen-containing functional groups of carboxyls and hydroperoxydes. Thermal chemiluminescence measurements of aged samples confirmed the presence of surface radicals even 24 hours after the plasma treatment. This is a quite practical technological feature, which places less stringent time constraints on the actual process of plasma assisted wood-plastic particleboard production.

In Paper VII we successfully produced particleboards from recovered wood of window frames. There were found that contamination by paint has negative effect on the MOR, MOE and IB properties, however the boards are according to EN 312 still viable. Interesting behavior was observed in thickness swelling of particleboards. The highest swelling was measured when spruce particles were replaced by contaminated wood by 20 and 50 %. It seems that contamination has negative effect on thickness swelling; however, this is probably not connected with an actual volume of replacement as it is with real amount of painted particles in particleboard. This chapter was further developed in paper VIII, where we have established method for DIC evaluation of microscopic changes of wood-based composites. In this paper we have presented not only swelling profile of particleboards and fiberboards, but swelling of painted particles in particleboard from recovered wood as well. In was, as hypothesized before, proven that painted particles are not swelling in a particleboard system at all. Secondly this technique could be directly transferred to the research where effect of particles size, geometrical orientation or used resin on the thickness swelling of particleboards can be investigated. Moreover the thorough swelling profiles may explain benefits of different density distributions in the wood based panels.

As we successfully introduced the microscopic optical measurement to explain different thickness swelling of recycled particleboard, further research should be focused on the way how to explain different mechanical behavior between the panels made from alternative resources. The actual failure trigger and weak spots should be identified for various particleboards. Then with identified failure triggers, the actual measures to prevent premature critical failure, for every new type of particleboards may be adapted.

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