Česká zemědělská univerzita v Praze

Fakulta lesnická a dřevařská

Katedra dřevěných výrobků a konstrukcí

Disertační práce

Zhodnocení vlivu vazby lignocelulózový materiál/adhesivum na vlastnosti materiálů na bázi ligninu a celulózy a hodnocení parametrů ovlivňujících kvalitu lepeného spoje u těchto materiálů

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2018 ČZU v Praze

ČESKÁ ZEMĚDĚLSKÁ UNIVERZITA V PRAZE

Fakulta lesnická a dřevařská

ZADÁNÍ DISERTAČNÍ PRÁCE

Ing. et Ing. Štěpán Hýsek

Zpracování dřeva a technika v lesním hospodářství

Název práce

Zhodnocení vlivu vazby lignocelulózový materiál/adhesivum na vlastnosti materiálů na bázi ligninu a celulózy a hodnocení parametrů ovlivňujících kvalitu lepeného spoje u těchto materiálů

Název anglicky

Assessment of the effect of bond between lignocellulose and adhesive on properties of cellulose and lignin-based materials and assessment of parameters influencing the quality of glued joints in these materials

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Cíle práce

-Zhodnotit vliv modifikace povrchu lignocelulózových elementů plazmou na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů.
-Zhodnotit vliv termické modifikace lignocelulózových elementů na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů.
-Zhodnotit vliv chemické modifikace povrchu lignocelulózových elementů na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů.
-Zhodnotit možnost využití posklizňových zbytků zemědělských plodin (zejména řepky), jako hlavní složky v kompozitních materiálech na bázi celulózy a ligninu.
-Optimalizace vstupních parametrů a lisovacích podmínek při výrobě modifikovaných materiálů na bázi ligninu a celulózy za účelem získání kompozitního materiálu požadovaných vlastností.
-Zhodnotit vliv adhesiva a jeho modifikace na vlastnosti vazby lignocelulózový materiál/adhesivum.

Metodika

Řešení práce je rozděleno do 3 okruhů:

-Modifikace povrchu lignocelulózových elementů

-Hodnocení fyzikálních a mechanických vlastností kompozitních materiálů vyrobených z lignocelulózových částic

-Hodnocení interakce adhesivum/lignocelulózový materiál

Modifikace povrchu lignocelulózových elementů

Pro úpravu povrchu lignocelulózových elementů bude využita studená plazma. Studená plazma nepůsobí žádné změny hlouběji v materiálu, ale ovlivňuje pouze povrchové vrstvy. Za účelem lepšího spojení s polymerem bude taktéž testována modifikace lignocelulózových částic chemicky a termicky. Chemická modifikace byla vybrána za účelem úpravy povrchu, zatímco termická modifikace za účelem úpravy vlastností v celém objemu dané modifikované částice. Změna vlastností lignocelulózových elementů bude testována především pomocí prvkové analýzy, fluorescenční mikroskopie a goniometru.

Hodnocení fyzikálních a mechanických vlastností kompozitních materiálů vyrobených z lignocelulózových částic

Adhesivum bude nanášeno na třísky laboratorní nanášečkou lepidla. Desky budou lisovány laboratorním lisem. Z vyrobených desek budou nařezány zkušební vzorky dle příslušných norem a budou hodnoceny standardní vlastnosti třískových desek: hustota dle ČSN EN 323:1994, pevnost v ohybu a modul pružnosti v ohybu dle ČSN EN 310:1995, rozlupčivost dle ČSN EN 319:1994, přídržnost povrchu dle ČSN EN 311:1994, bobtnání dle ČSN EN 317:1996, atd. Budou ale měřeny i nenormované vlastnosti třískových desek, jako je hustotní profil.

Hodnocení interakce adhesivum/lignocelulózový materiál

Pro zhodnocení rozhraní mezi adhesivem a modifikovaným lignocelulózovým materiálem bude toto rozhraní podrobeno mikroskopické analýze pomocí SEM. Budou pozorovány jak slepené a vytvrzené spoje (hodnocení rozložení adhesiva na povrchu modifikovaného materiálu), tak spoje porušené, získané ze vzorků po zkoušce rozlupčivosti. Na těchto porušených vzorcích bude stanovován charakter porušení (kohezní porušení materiálu třísky či adhezní porušení mezi adhesivem a třískou). Pro zhodnocení interakce adhesivum/lignocelulózový materiál z pohledu mechanických vlastností budou vyrobené spoje podrobeny pevnostním zkouškám.

Doporučený rozsah práce

Soubor publikovaných vědeckých článků s jednotícím komentářem v rozsahu 30-40 stran

Klíčová slova

kompozitní materiál, přírodní vlákno, lignin, celulóza, adhesivum, úprava povrchu, modifikace

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Předběžný termín

2017/18 ZS – FLD – SDZ

Vedoucí práce

doc. Ing. Martin Böhm, Ph.D.

Garantující pracoviště

Katedra dřevěných výrobků a konstrukcí

Elektronicky schváleno dne 8. 2. 2018

Ing. Kamil Trgala, Ph.D.

Vedoucí katedry

Elektronicky schváleno dne 16. 7. 2018

doc. Ing. Milan Gaff, PhD.

Předseda oborové rady

Elektronicky schváleno dne 18. 7. 2018

prof. Ing. Marek Turčáni, PhD.

Děkan

V Praze dne 18. 07. 2018

"Prohlašuji, že jsem disertační práci na téma Zhodnocení vlivu vazby lignocelulózový materiál/adhesivum na vlastnosti materiálů na bázi ligninu a celulózy a hodnocení parametrů ovlivňujících kvalitu lepeného spoje u těchto materiálů vypracoval samostatně s použitím uvedené literatury a na základě konzultací a doporučení školitele. Souhlasím se zveřejněním disertační práce dle zákona č. 111/1998 Sb. o vysokých školách v platném znění, a to bez ohledu na výsledek její obhajoby."

V Praze dne 23. července 2018 Ing. et Ing. Štěpán Hýsek

ABSTRAKT

Zhodnocení vlivu vazby lignocelulózový materiál/adhesivum na vlastnosti materiálů na bázi ligninu a celulózy a hodnocení parametrů ovlivňujících kvalitu lepeného spoje u těchto materiálů

Práce se zabývá modifikací povrchu lignocelulózových částic určených pro výrobu kompozitních materiálů. Hlavním cílem práce je prověření hypotéz o možnosti využitelnosti úprav povrchových vlastností lignocelulózových elementů pro zlepšení mechanických a fyzikálních vlastností materiálů na bázi ligninu a celulózy. Jako lignocelulózový materiál je využíváno nejen dřevo, neboť vzhledem k nedostatečné dodávce dřeva do dřevozpracujícího odvětví si práce klade za cíl zhodnotit možnost využití posklizňových zbytků zemědělských plodin (zejména řepky), které se doposud průmyslově nevyužívají, jako hlavní složky v kompozitních materiálech na bázi celulózy a ligninu. Dalším cílem je vývoj těchto modifikovaných materiálů a optimalizace vstupních parametrů a lisovacích podmínek za účelem získání kompozitního materiálu požadovaných vlastností. Práce se zaměřuje i na hodnocení interakce adhesivum/lignocelulózový materiál v podobě hodnocení vytvrzeného spoje a porušeného spoje na mikroskopické úrovni, hodnocení jeho mechanických vlastností a hodnocení kontaktního úhlu mezi adhesivy a materiálem.

Klíčová slova: kompozitní materiál, přírodní vlákno, lignin, celulóza, adhesivum, úprava povrchu, modifikace

ABSTRACT

Assessment of the effect of bond between lignocellulose a adhesive on properties of cellulose a lignin-based materials a assessment of parameters influencing the quality of glued joints in these materials

This thesis deals with the modification of the surface of lignocellulosic particles intended for the production of composite materials. The main aim of the thesis is to examine hypotheses about the applicability of the surface properties of lignocellulosic elements to improve the mechanical a physical properties of lignin a cellulose-based materials. As a lignocellulosic material not only wood is used, because due to the insufficient supply of wood to the woodworking industry, the work aims at evaluating the possibility of utilization of post-harvest crop residues (especially rape), which are not industrially used, as main components in cellulose an lignin-based composites. Another objective is to develop these modified materials a to optimize the input parameters a the pressing conditions in order to obtain the composite material of the desired properties. The work also focuses on the evaluation of adhesive / lignocellulosic material interaction in the form of evaluation of hardened joint a broken joint at microscopic level, evaluation of its mechanical properties a evaluation of contact angle between adhesives a material.

Keywords: composite material, natural fibre, lignin, cellulose, adhesive, surface treatment, modification

Obsah

Seznam obrázků

Seznam tabulek

Seznam článků

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1 Úvod

Jeden z problémů hrozící výrobě materiálů na bázi dřeva je nedostatečná dodávka dřeva způsobená stále rostoucími požadavky na objem dodávek dřeva z různých dřevozpracujících, ale i energetických odvětví (Dziurka a kol. 2015; Ye a kol. 2007). Jedním možným řešením je částečná nebo úplná substituce dřeva v kompozitních materiálech na bázi dřeva biomasou vyprodukovanou v zemědělství (Ye a kol. 2007). Tato biomasa je nevyčerpatelný zdroj nejen potravin a krmiv, ale i materiálu pro různé průmyslové zpracování (Papadopoulou a kol. 2014). V posledních letech bylo provedeno mnoho výzkumů zaměřujících se na využití biomasy jednoletých rostlin v kompozitních materiálech na bázi dřeva. Proběhly výzkumy týkající se možnosti využití obilné slámy (Halvarsson a kol. 2010), rýžové slámy (El-Kassas a Mourad 2013), stonků slunečnice (Guler et at. 2006), cukrové třtiny (Belini a kol. 2012), bambusu (Marinho a kol. 2013), rákosu (Han a kol. 2001), plev arašídů (Akgül a Tozluoğlu 2008) a lískových oříšků (Cöpür a kol. 2008), stonků čili papriček (Oh a Yoo 2011), rostlin produkujících lýková vlákna, jako je len, konopí a kenaf (Aisyah a kol. 2013; Papadopoulou a kol. 2014) atd.

Tato práce se zaměřuje především na využití posklizňových zbytků zemědělských plodin, které jsou v České republice nejvíce dostupné, a to řepka ozimá a pšenice ozimá (ČSÚ 2017). Pro výrobu kompozitních materiálů ze stonků zemědělských plodin je však nutné na rozdíl od dřevní hmoty tyto stonky povrchově upravit za účelem narušení voskové vrstvy na povrchu, která brání kvalitnímu spoji mezi třískou a adhesivem (Bekhta a kol. 2013; Částková a kol. 2018). Povrchová před-úprava může být provedena různými způsoby. Například alkalickou modifikací, která způsobí rozrušení esterových vazeb mezi vosky a ligninem a celulózou, stejně jako vosky rozpouští. Alternativou je vaření ve vodě, které je oblíbené díky své jednoduchosti (Bekhta a kol. 2013). Využitím těchto zdrojů surovin může dojít k řešení nedostatku dřevní suroviny, stejně jako ke zlepšení ekonomické situace zemědělců či k dosažení jiné kombinace vlastností kompozitních materiálů, než které nabízí dřevo. Komplexní pohled na důvody využívání těchto zdrojů je předložen v kapitole č. 5 této práce. Při výrobě bio-kompozitů však nesmíme opomíjet druhou složku kompozitních materiálů, a to je matrice. Otázka vhodnosti různých adhesiv pro lepení lignocelulózových materiálů je v této práci rovněž řešena.

Předkládaná disertační práce nejprve přináší literární rozbor zkoumaných oblastí. Jmenovitě práce začíná pojednáním o kompozitních materiálech na bázi obnovitelných surovin, kde jsou řešeny jejich vlastnosti z pohledu vstupních surovin. Následuje kapitola zabývající se slámou z řepky ozimé, neboť tento materiál byl zhodnocen jako perspektivní v daném odvětví. Další kapitola se zabývá úpravou povrchu lignocelulózových materiálů za účelem změny jejich vlastností, přičemž pozornost je věnována modifikaci chemické, termické, enzymatické a plazmatem. V následující kapitole je potom vypracována SWOT analýza výroby třískových desek z řepky ozimé, kde je tato problematika řešena komplexně, jsou hodnoceny její silné a slabé stránky, příležitosti a hrozby a argumenty jsou podloženy citacemi z odborných vědeckých zdrojů. Poslední část literární rešerše je věnována konkurenčnímu odvětví k výrobě kompozitních materiálů z posklizňových zbytků zemědělských plodin – výrobě biopaliv, jmenovitě bioetanolu. Jednou z hlavních silných stránek kompozitních materiálů z posklizňových zbytků zemědělských plodin je dostupnost suroviny – jak z hlediska ceny, tak z hlediska množství. A právě biopaliva druhé generace byla v rámci literární rešerše identifikována jako přímý konkurent k tomuto navrhovanému technologickému zpracování posklizňových zbytků. Pro možnost predikce vývoje dostupnosti posklizňových zbytků zemědělských plodin je konkurenční odvětví výroby biopaliv rovněž podrobně popsáno a analyzováno. Následuje obecná metodika experimentů, podrobný popis postupu experimentů je uveden vždy v příslušném článku. Disertační práce je složena celkem z 8 článků, k nimž je předložen jednotící komentář, nejdůležitější výsledky jsou zdůrazněny a diskutovány. V závěrečné kapitole je shrnut celkový přínos disertační práce.

2 Cíle práce

Jsou stanoveny následující cíle práce:

- Zhodnotit vliv modifikace povrchu lignocelulózových elementů plazmatem na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů.
- Zhodnotit vliv termické modifikace lignocelulózových elementů na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů.
- Zhodnotit vliv chemické modifikace povrchu lignocelulózových elementů na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů.
- Zhodnotit možnost využití posklizňových zbytků zemědělských plodin (zejména řepky), jako hlavní složky v kompozitních materiálech na bázi celulózy a ligninu.
- Optimalizace vstupních parametrů a lisovacích podmínek při výrobě modifikovaných materiálů na bázi ligninu a celulózy za účelem získání kompozitního materiálu požadovaných vlastností.
- Zhodnotit vliv adhesiva a jeho modifikace na vlastnosti vazby lignocelulózový materiál/adhesivum.

3 Rozbor problematiky

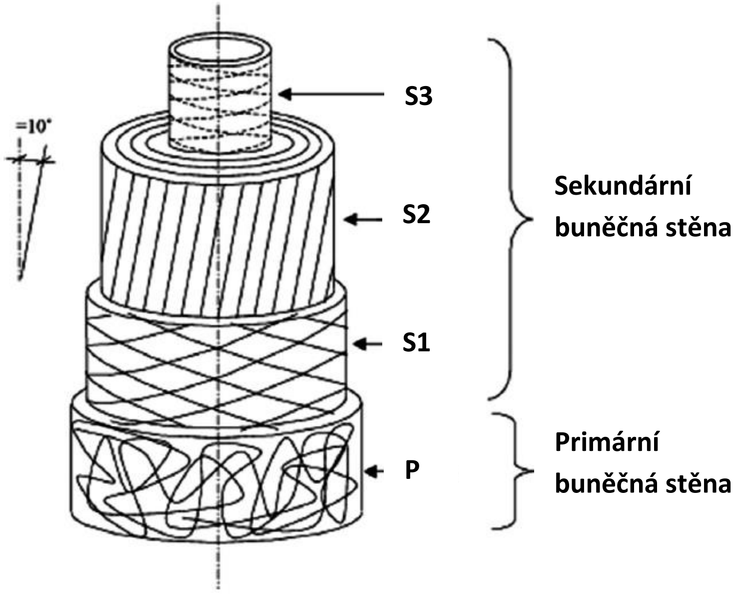
3.1 Kompozitní materiály na bázi obnovitelných surovin

Kompozitní materiály na bázi obnovitelných surovin, neboli bio-kompozity, můžeme definovat jako kompozitní materiály, které sestávají z jedné nebo více fází, která je původem z obnovitelných surovin. V případě výztužných prvků se může jednat o vlákna a částice rostlin, recyklovaného papíru nebo vedlejších produktů zemědělských plodin. Tuto definici rovněž splňují i vlákna z regenerované celulózy nebo další nanofibrily na bázi obnovitelných zdrojů, či chitin (Fowler a kol. 2006). Oproti konvenčním výztužným prvkům disponují tyto přírodní materiály výhodou v podobě nízké ceny, nízké hustoty, vysoké tuhosti, přijatelných pevnostních charakteristik, snížení opotřebení ostří, nižší dráždivosti pro lidský organismus, dobrých tepelně-izolačních vlastností, jednoduchosti produkce, široké dostupnosti, jednoduché úpravě povrchu a biodegradabilitě (Huda a kol. 2006; Mohanty a kol. 2000). Matrice může být polymer, ideálně odvozený z obnovitelných zdrojů. Případně může být použit syntetický polymer na ropné bázi, a to buď původní nebo recyklovaný termoplast nebo původní termoset. Výhody matricí z bio-plastů jsou uvedeny níže (Fowler a kol. 2006; Bledzki a kol. 2005; La Mantia a Morreale 2011).

Předpokládá se, že materiály z obnovitelných surovin nahradí v kompozitních materiálech nejen výztužné prvky, ale i plastické pojivo, zvané matrice (Fowler a kol. 2006). Můžeme jmenovat mnoho výhod využití polymerů založených na neropné bázi, jako je možnost výroby z obnovitelných zdrojů surovin (Lim a kol. 2008), ochrana klimatu prostřednictvím dočasného vázání oxidu uhličitého (Mohanty a kol. 2000), či úspora energie. Bio-plasty mohou být dále recyklovatelné, rozložitelné a kompostovatelné, mohou zlepšit ekonomickou situaci zemědělců a jejich fyzikální a mechanické vlastnosti mohou být upravovány pro daný účel použití prostřednictvím uspořádání polymerů (Mukherjee a Kao 2011). Bio-plasty musí splňovat alespoň jednu ze dvou podmínek: musí být bio-degradovatelné nebo založené na bázi obnovitelných surovin (Scott 2000). A mohou být zpracovávány stejně jako plasty na ropné bázi, ať už extruzí, zvlákňováním z taveniny, vstřikováním, thermoformingem či v pevném skupenství (Mukherjee a Kao 2011).

3.1.1 Struktura a složení přírodních vláken

Přírodní vlákna sestávají z celulózových fibril, které jsou rozmístěny v matrici z hemicelulóz a ligninu. Tyto celulózové mikrofibrily se spirálovitě vážou okolo amorfní ligninové matrice. Mikrofibrily mají průměr 10 – 30 nm a každá se skládá z 30 – 100 celulózových molekul. Lignin poskytuje ochranu a působí jako výztuha stonku, zatímco hemicelulózy jsou spojovacím materiálem mezi celulózou a ligninem. Buněčná stěna není homogenní, každé vlákno má komplexní strukturu sestávající z vrstev. Úhel odklonu celulózových mikrofibril od podélné osy vlákna se liší v jednotlivých buněčných stěnách a rovněž je rozdílný napříč různými rostlinnými druhy (Bhatia a kol. 2016; Yan a kol. 2014). Struktura přírodního vlákna se schematicky znázorněnými mikrofibrilami celulózy je zobrazena na obrázku 1.



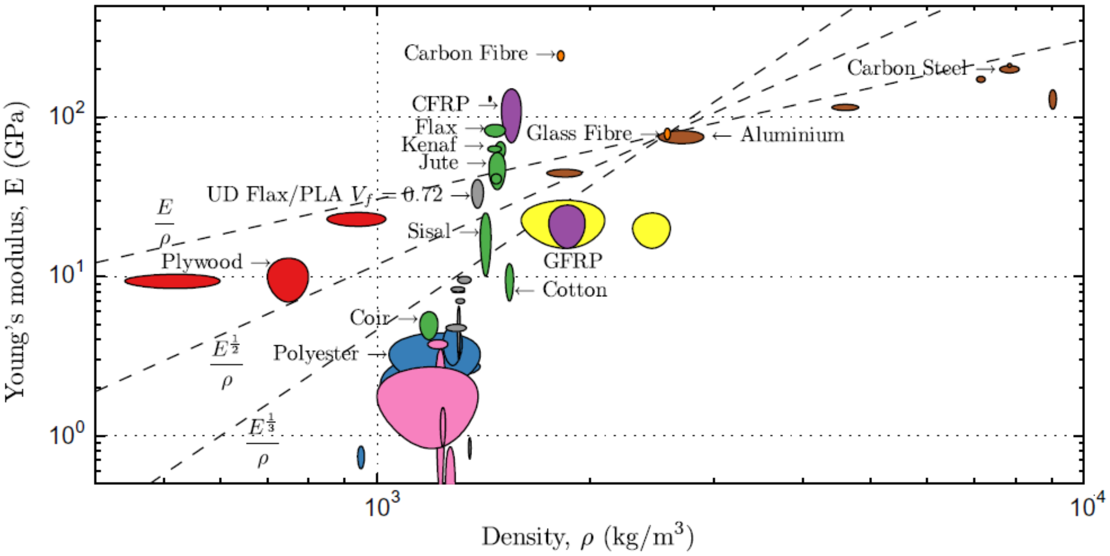
Obrázek 1 Mikrostruktura buňky lnu, Yan a kol. 2014

Celulóza sestává z dlouhých nerozvětvených řetězců β-D-glukopyranózy spojených β-1,4-glykosidickou vazbou. C-4, C-2, C-3 a C-6 hydroxylové skupiny na glukózových jednotkách jsou aktivními místy, která určují krystalické a fyzikální vlastnosti celulózy. Hydroxylové skupiny tvoří vodíkové můstky, které zapříčiňují uspořádání řetězce do vysoce uspořádané struktury. Avšak tyto vysoce uspořádané krystalické úseky mezi sebou mají i méně uspořádané místa, amorfní oblast celulózy. Stupeň polymerace řetězce celulózy se pohybuje kolem 10 000. Krystalické oblasti zapříčiňují vysokou pevnost vláken, zatímco amorfní oblasti jsou odpovědné za hygroskopicitu přírodních vláken. Hemicelulózy jsou polysacharidy složené z různých hexóz a pentóz, jsou to rozvětvené polymery s nižším stupněm polymerace (100-200) a nejsou krystalické. Jedná se o hydrofilní složku přírodních vláken a rovněž citlivou vůči kyselinám a zásadám. Lignin je pravděpodobně třírozměrný komplex kopolymerů obsahujících alifatické i aromatické složky s vysokou molekulovou hmotností. Je termoplastický a obsahuje hydroxylové, methoxylové a karbonylové skupiny. Dále je odolný vůči působení kyselin, avšak je rozpustný v zásadách při vyšších teplotách. Rostlinná vlákna dále obsahují pektiny, které poskytují vláknu pružnost a skládají se z různých polysacharidů. Další složkou vláken jsou vosky, které se skládají z různých alkoholů a zajišťují vláknům především hydrofobicitu. Vlastnosti vláken jsou ovlivněny jejich strukturou, chemickým složením, rozměry buněk a úhlem odklonu mikrofibril. Jejich složení závisí na rostlinném druhu a geografických podmínkách (Bhatia a kol. 2016).

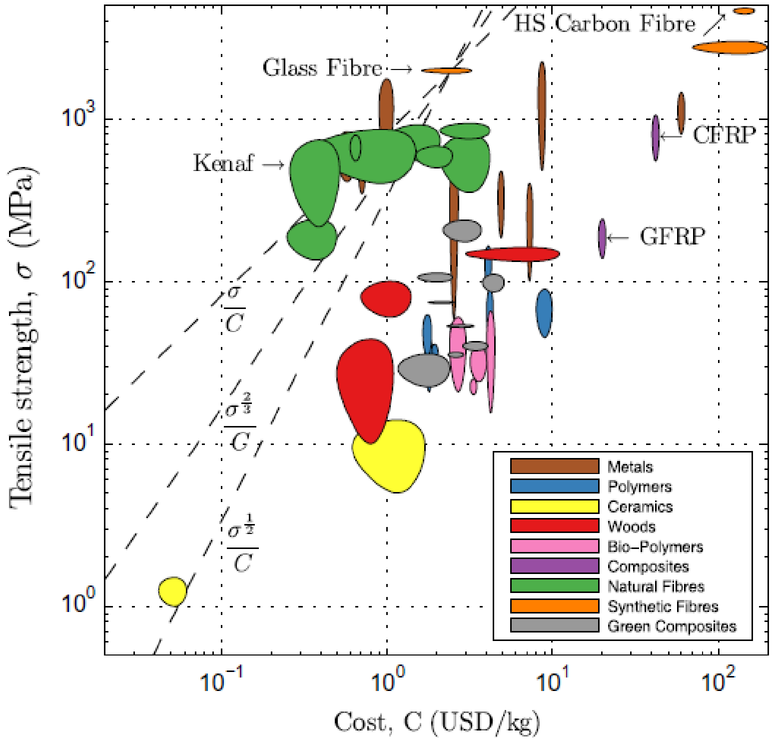
3.1.2 Vlastnosti přírodních vláken

Přírodní vlákna na bázi ligninu a celulózy mají potenciál, aby nahradila např. vlákna skelná a další konvenční materiály. Tato vlákna mají mnoho vlastností, které je činí atraktivními alternativami tradičních materiálů. Mnohé vlastnosti již byly zmíněny v textu dříve, v této kapitole je podán ucelený výčet s podrobným vysvětlením. Jejich silnou stránkou z pohledu mechanických vlastností jsou vysoké specifické vlastnosti jako tuhost, dále rázová houževnatost, pružnost a modul pružnosti. Porovnání vybraných přírodních a syntetických materiálů z hlediska hustoty a modulu pružnosti v tahu je uvedeno pomocí Ashbyho diagramu na obrázku 2. Přírodní vlákna jsou dostupná ve velkých množstvích a jsou obnovitelná, biodegradovatelná a dostupná za nízkou cenu. V porovnání s tradičními materiály jsou při zpracovávání dalšími výhodnými vlastnostmi nízká hustota, nižší opotřebení ostří obráběcích nástrojů, tlumení vibrací a nižší spotřeba energie na jejich zpracování. Z pohledu vlivu na lidský organismus jsou přírodní vlákna netoxická a méně dráždivá. V neposlední řadě využíváním těchto vláken dochází k dočasnému vázání oxidu uhličitého. Obrázek 3 znázorňuje produkční náklady výroby vybraných materiálů ve vztahu k jejich pevnosti v tahu (Dicker a kol. 2014; Sgriccia a kol. 2008).

Mezi hlavní nevýhody přírodních vláken řadíme degradaci při nižších teplotách, což zabraňuje jejich kombinaci s termosety, které mají vytvrzovací teplotu vyšší než 200 °C. Dále mají přírodní vlákna vyšší variabilitu mechanických vlastností, nežli vlákna konvenční, nižší maximální pevnost v tahu, nižší relativní prodloužení a nízkou odolnost proti přírodním vlivům. Problémy při výrobě kompozitních materiálů z přírodních vláken představuje i obsah vody volné a vázané, zejména v podobě uvolňující se páry při extruzi či lisování (Anajiwala a Blouw 2007; Sgriccia a kol. 2008).



Obrázek 2 Ashbyho diagram modulu pružnosti v tahu proti hustotě vybraných materiálů, Dicker a kol 2014



Obrázek 3 Ashbyho diagram pevnosti v tahu proti ceně vybraných materiálů, Dicker a kol 2014

3.1.3 Tvorba spoje

Obecně se vyžaduje, aby spoj dvou částí byl silnější, než spojovaný materiál, a aby k porušení došlo ve spojovaném materiálu – substrátu. Při vytváření kvalitního spoje můžeme rozeznat tři hlavní kroky. V prvním kroku se jedná o přípravu povrchu, tak aby mohla být zajištěna interakce mezi adhesivem a substrátem. Je používána většinou mechanická či chemická úprava povrchu, někdy obojí. Druhý krok je charakterizován vazbou adhesiva na povrch substrátu. Jelikož jsou vyžadovány vazby na molekulární úrovni, mělo by být adhesivum v kapalném skupenství, aby byl dosažen potřebný kontakt obou látek. Třetí krok je sestavování spoje, který zahrnuje vytvrzování adhesiva (Frihart 2005).

Pevnost lepeného spoje je mechanická vlastnost, která je determinovaná pevností adhesiva, pevností dřeva a pevností mezifáze dřevo/adhesivum. Přičemž mezifáze je definovaná jako oblast určitých rozměrů začínající v substrátu v bodě, kde se jeho vlastnosti (chemické, fyzikální, mechanické a morfologické) začínají odlišovat od vlastností surového substrátu a končící v adhesivu v bodě, kde již jsou opět lokální vlastnosti adhesiva stejné jako vlastnosti v celém adhesivu (Bergland a Rowell 2005). Jelikož má dřevo podobnou stavbu a složení jako ostatní rostlinné materiály na bázi celulózy a ligninu, můžeme tyto poznatky generalizovat i na ně. Faktory ovlivňující vlastnosti lepeného spoje jsou uvedeny v tabulce 1.

Tabulka 1 Faktory ovlivňující vlastnosti lepeného spoje, Frihart 2005

Adhesivum	Dřevo	Technologie lepení
• druh adhesiva • viskozita • rozdělení molekulových hmotností polymerů • molární poměr reaktantů • obsah sušiny • katalyzátor • způsob výroby • plniva • druh rozpouštědla • stáří • pH • pufrovací systém	• druh • hustota • vlhkost • rovina řezu • jádro/běl • juvenilní/vyzrálé dřevo • jarní/letní dřevo • přítomnost reakčního dřeva • sklon vláken • porozita • drsnost povrchu • vady způsobené sušením • vady vzniklé při opracování • špína a kontaminace • extraktiva • pH • pufrovací kapacita • chemické složení	• nános/množství adhesiva • rovnoměrnost distribuce • vlhkost vzduchu • teplota • otevřený čas lepidla • uzavřený čas lepidla • lisovací tlak • penetrace adhesiva • únik plynů • lisovací čas • předúprava • úprava po vytvrzení • teplota substrátu

3.2 Řepka ozimá

3.2.1 Statistické údaje

Brukev řepka (*Brassica napus*), jednoletá nebo dvouletá rostlina, je celosvětově jednou z nejdůležitějších olejnin. Řepka se pěstuje pro potravinářský průmysl, krmivářský průmysl a v posledních letech zejména pro účely výroby biopaliv. Dle Českého statistického úřadu se produkce řepky v České republice od roku 1990 do roku 2017 více než ztrojnásobila. V roce 2017 bylo v ČR oseto řepkou celkem 407 tis ha půdy, což je 16,5% z celkové osevní plochy v ČR (ČSÚ 2017). Světová produkce řepky rovněž rychle sloupá, dle FAO jsou celosvětově největšími producenty řepky Kanada, Čína, Indie, Německo a Francie (FAOSTAT 2015). Průměrný hektarový výnos semene řepky ozimé se celosvětově pohybuje okolo 1,9 t/ha, v Evropě potom 3 – 4 t/ha (Tofanica a kol. 2011). Hektarový výnos stonků v Evropě činí 3 – 10 t/ha, což znamená, že v roce 2014 bylo v Evropské unii vyprodukováno zhruba 42 milionů tun stonků (Eurostat 2016).

3.2.2 Chemické složení

Rostlina řepky olejné může dosáhnout výšky až dva metry, stonek je často rozvětvený. Hustota stonků při vlhkosti 10% se pohybuje okolo 270 kg/m^3 a hustota substance 1550 kg/m^3 (Adapa a kol. 2009). Na rozdíl od dřeva, řepková vlákna jsou více heterogenní, protože rostlina obsahuje více druhů buněk. Podle Tofanica se délka vláken pohybuje v rozmezí 0,7 – 2 mm, šířka 9 – 20 μm a tloušťka buněčné stěny 1,8 – 3 μm. Stonek řepky obsahuje 41% celulózy (Kürschner–Hoffer metoda), 23,4% hemicelulóz, 21,5% ligninu, 6,8% extraktiv a 5,8% popelovin. Pokud bychom analyzovali stonek až po odstranění dřeni, procentuální zastoupení celulózy by bylo větší a popelovin menší. Chemické složení jednotlivých vláken je potom 61,3% celulózy, 13,9% hemicelulóz, 5,2% ligninu, 1,9% extraktiv a 4,8% popelovin (Tofanica a kol. 2011). Chemické složení stonků a rozměry vláken řepky jsou podobné chemickému složení dřeva listnatých dřevin a rozměrům vláken listnatých dřevin.

3.2.3 Využití

Řepkové stonky jsou zřídka sklízeny, většinou jsou po sklizni zaorávány a využívány pro obohacení půdy o minerální látky. Někteří zemědělci produkují řepkovou slámu či pelety z řepkové slámy pro energetické účely, avšak průmyslové využití v produktech s vyšší přidanou hodnotou řepková sláma dosud nenašla. Posklizňové zbytky řepky mají přitom potenciál být využívány pro výrobu kompozitních materiálů a materiálů pro konstrukční účely, dále pak v papírenském průmyslu a chemickém průmyslu.

V minulosti proběhlo několik výzkumů orientovaných na využití třísek z řepkových stonků pro výrobu třískových desek. Dziurka a Mirski zkoumali možnost vylehčení dřevotřískových desek. Prokázali, že třísky z řepky jsou vhodnou alternativou dřevěných třísek, vyrobené desky splňovaly normované požadavky pro třískové desky pro použití v suchém prostředí P2. Dále vyvinuli sendvičové desky se střední vrstvou z řepkových třísek a oboustranně odýhované bukovou dýhou o tloušťce 1,7 mm. Sendvičové panely z řepkových třísek měly lepší mechanické vlastnosti, nežli odpovídající (se stejnou hustotou) sendvičové panely z dřevěných třísek (Dziurka a Mirski 2013). Zlepšení mechanických vlastností bylo dosaženo tím, že při nižší hustotě řepky je možné do desky zalisovat větší množství třísek. V další studii Dziurka a kol. vylehčovali dřevotřískové desky substitucí dřevěných třísek ve středové vrstvě řepkovými třískami a přídavkem polystyrenu. Vyprodukované desky opět splňovaly normované požadavky na desky pro použití na vnitřní vybavení (Dziurka a kol. 2015).

Další výzkum, v kterém byly vyráběny dřevotřískové desky s příměsí řepkových třísek v různých hmotnostních poměrech, ukázal, že rozlupčivost, pevnost v ohybu a odolnost proti vytažení vrutů s rostoucím obsahem řepkových třísek klesají. Na druhou stranu vyprodukované desky splňovaly normované požadavky a s rostoucím obsahem řepkových třísek se zlepšovala rozměrová stabilita (Oh a Jmaludin 2015).

Cílem výzkumu prováděného v Íránu bylo zlepšení vlastností dřevotřískových desek pojených močovinoformaldehydovým lepidlem pomocí přídavku řepkových třísek a recyklovaného polyetylenu. Výsledky ukázaly, že rostoucí podíl řepkových třísek má negativní vliv na rozlupčivost, nasáklivost a bobtnání, ale pozitivní vliv na modul pružnosti v tahu a ohybu. Dále bylo prokázáno, že s rostoucím obsahem recyklovaného polyetylenu lze snižovat obsah UF (močovinoformaldehydového) lepidla (Rangavar a kol. 2016).

V Německu byly v laboratorních podmínkách vyrobeny třívrstvé dřevotřískové desky, kdy vrchní vrstvy byly z dřevěných třísek a byly lepeny směsí UF lepidla a lepidla na bázi pšeničných bílkovin (poměr 50/50). Ve středové vrstvě byla použita směs dřevěných třísek a jednoletých rostlin (cukrová třtina, řepka a konopí). Třísky ve středové vrstvě byly lepeny pouze UF lepidlem. Bylo dosaženo snížení emise formaldehydu, vyrobené desky splňovaly normované požadavky, avšak pokud stoupl obsah řepkových třísek ve středové vrstvě nad 50%, docházelo k výraznému poklesu rozlupčivosti (Nikvash a kol. 2012).

Výzkumné aktivity jsou patrny i u produktů s vyšší přidanou hodnotou, než mají třískové desky. Byla vyrobena tvrdá vláknitá deska mokrým způsobem, bez lepidla, pouze z vláken z řepkových stonků. Vyrobený materiál dosahoval hustoty 950 – 1120 kg/m^3 dle lisovacího tlaku a splňoval všechny normované požadavky (Huang a kol. 2016).

V Íránu byly prováděny pokusy týkající se výroby vláknité desky se střední hustotou (MDF) z řepkových vláken. Vlákna byla vyrobena podobným způsobem jako při výrobě MDF ze dřeva. Stonky řepky byly nejprve rozštěpkovány, štěpky byly jednu hodinu máčeny a dále napařovány při teplotě 170 °C a tlaku 8 barů. Čas paření byl proměnný (2, 5 a 8 minut). Uvařené štěpky byly rozvlákněny v laboratorním atmosférickém refineru. Vlákna byla vysušena na vlhkost 2% – 3% a v rotační nanášečce lepidla na ně bylo naneseno močovinoformaldehydové lepidlo v množství 9% a 11%. Další proměnnou byl lisovací čas. Byly vyrobeny MDF desky z řepkových vláken o jmenovité hustotě 700 kg/m^3. Fyzikální a mechanické vlastnosti desek byly srovnatelné s vlastnostmi MDF desek vyrobených z jiných jednoletých rostlin a byly blízké minimálním normovaným hodnotám (Yousefi 2009).

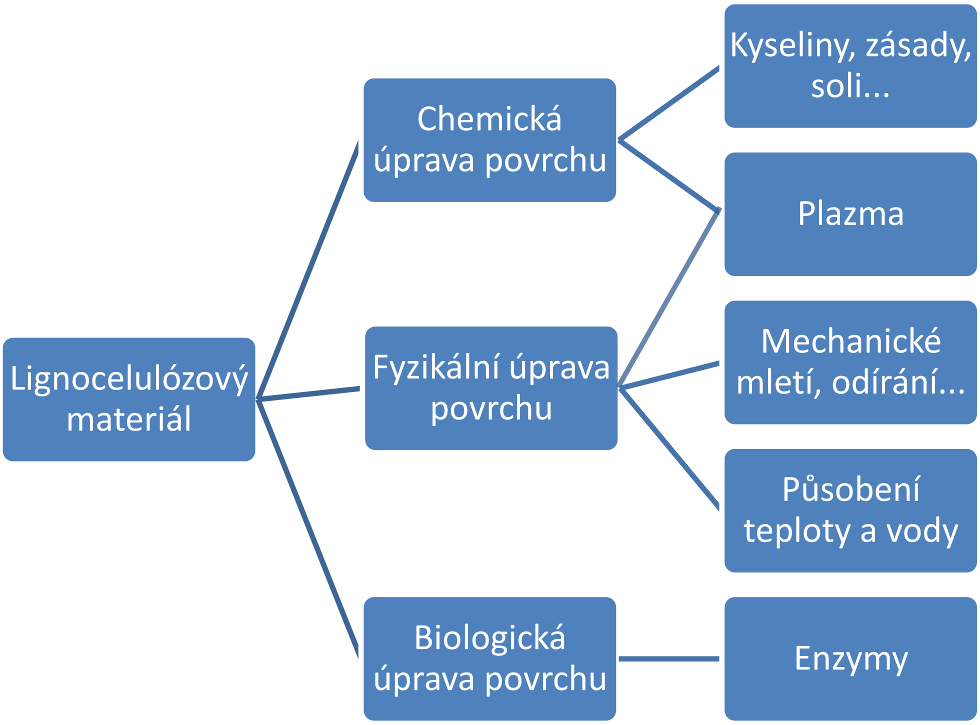
Dalším příkladem materiálu s vysokou přidanou hodnotou je dřevoplastový kompozitní materiál vyrobený lisováním z polyetylenu s nízkou hustotou a plnidla ve formě prášku z řepkových stonků. Byly zkoumány různé poměry řepka/plast. Zatímco pevnost v ohybu klesala s rostoucím obsahem řepkového prášku, modul pružnosti v ohybu stoupal. S rostoucím obsahem plnidla dále stoupala i nasáklivost a bobtnání (Zabihzadeh 2011).

Kromě fyzikálních a mechanických vlastností jsou u nově vyvíjených materiálů hodnoceny i jevy vyskytující se na rozhraní částice/adhesivum. Klímek a kol. (2016) k hodnocení rozhraní tříska/adhesivum použili SEM analýzu. Pomocí elektronového mikroskopu pozorovali rozložení adhesiva na třískách jednotlivých materiálů a druh porušení spoje (adhezní/kohezní) po provedení zkoušky rozlupčivosti (Klímek a kol. 2016). Jiní autoři kromě SEM analýzy používaly k hodnocení rozhraní tříska/adhesivum i goniometr k měření kontaktního úhlu mezi třískami a tekutinami (Liu a kol. 2010; Zhang a Hu 2014).

Řepková vlákna obsahují velký podíl celulózy, z které lze vyrobit celulózová nanovlákna. Ve dvou výzkumech (Yousefi a kol. 2011; Yousefi a kol. 2013) byla nanovlákna vyrobena mechanickým způsobem. Řepková vlákna byla nejdřív rozštěpkována a ze štěpek byla odstraněna dřeň. Štěpky byly rozvlákněny chemickou cestou pomocí NaOH a antrachinonu. Vlákna byla následně třístupňově bělena (pro odstranění ligninu) pomocí ClO_2, NaOH a H_2O_2 a pomocí KOH byly odstraněny hemicelulózy. Z takto připravené celulózy byly mletím vyrobena nanovlákna. Ve výzkumu (Yousefi a kol. 2011) byl z nanovláken následně vyroben nanopapír a pomocí částečného rozpuštění těchto vláken byl vyroben celo-celulózový kompozitní materiál.

3.3 Modifikace povrchu lignocelulózových materiálů

Rostlinné materiály na bázi celulózy a ligninu jsou často využívány v kompozitních materiálech, kde plní úlohu plnidla a vyztužovacího materiálu. Vždy je nutné zajistit důkladné spojení rostlinné částice a polymeru. Základním předpokladem pevného spojení částice a polymeru je přítomnost reaktivních skupin na rozhraní obou materiálů, které zajistí vysokou povrchovou energii. V kompozitech zpevněnými rostlinnými materiály se přitom setkáváme většinou s opačným jevem, kdy se pevné spojení mezi polární celulózou a nepolárním polymerem nevytváří snadno. Smáčení přírodního vlákna či částice polymerem ještě více zhoršují voskové substance, které přírodní vlákna často obsahují. Také přítomnost vody a volných hydroxylových skupin, především v amorfních částech, snižují možnost tvorby pevného spojení mezi rostlinnými materiály a většinou lepidel. Dále vysoká navlhavost a nasáklivost způsobuje rozměrové změny rostlinných vláken, což implikuje snižování mechanických a fyzikálních vlastností kompozitního materiálu (Mwaikambo a Ansell 2002). Na obrázku 4 je zachyceno schéma, které znázorňuje možné způsoby modifikace lignocelulózových materiálů.



Obrázek 4 Způsoby úpravy povrchu lignocelulózových materiálů (Vanneste a kol. 2017; vlastní zpracování)

3.3.1 Chemická modifikace dřeva

Chemickou modifikaci dřeva provádíme především za účelem eliminace jeho přirozených vlastností. Jedná se o rozměrovou nestabilitu a degradaci povětrnostními vlivy, ohněm a biotickými činiteli. Tyto degradační procesy jsou procesy, které rozkládají dřevo zpět na oxid uhličitý a vodu, z kterých dřevo vzniklo, a začínají prakticky ihned po těžbě. Za účelem výroby kompozitních materiálů na bázi dřeva s dlouhou životností je nutné tyto přírodní degradační procesy potlačit. Přírodní degradační procesy jsou uvedeny v tabulce 2 (Rowell 2005). Chemickou modifikací vlákna můžeme docílit nejen zlepšení adheze mezi povrchem vlána a polymeru, ale i zvýšit pevnost vlákna, snížit absorpci vody kompozitem a zlepšit mechanické vlastnosti celého kompozitního materiálu (Li a kol. 2007).

Tabulka 2 Druhy přírodních degradačních procesů, Rowell 2005

Degradační procesy	**Činitel a degradační způsoby**
Biologická degradace • enzymatické reakce • chemické reakce • mechanické poškození	Houby, bakterie, hmyz, termiti • oxidace, hydrolýza, redukce • oxidace, hydrolýza, redukce • tvorba požerků
Degradace ohněm • pyrolýza	Blesky, slunce • dehydratace, hydrolýza, oxidace
Degradace vodou • interakce vody a dřeva	Déšť, moře, led, kyselý déšť, rosa • bobtnání, sesychání, zamrznutí, praskání
Degradace povětrnostními vlivy • chemické reakce • mechanické poškození	UV záření, voda, teplo, vítr • oxidace, hydrolýza • eroze
Chemická degradace • chemické reakce	Kyseliny, zásady, soli • oxidace, redukce, dehydratace, hydrolýza
Mechanická degradace • mechanické poškození	Prach, vítr, krupobití, sníh, písek • namáhání, praskání, lámání, abraze

Vzhledem k tomu, že jsou vlastnosti dřeva ovlivněny složením buněčných stěn dřeva, mohou být změněny právě modifikací chemického složení polymerů vyskytujících se v buněčných stěnách. Pokud bychom například chtěli dosáhnout nižší nasáklivosti, pak bychom měli redukovat hydrofilní povahu buněčné stěny v podobě navázání hydrofobních skupin. Pokud by cílem modifikace bylo zvýšení rozměrové stability, pak řešením může být zesíťování buněčných polymerů, aby bylo zamezeno expanzi buněčné stěny, nebo na buněčné polymery mohou být navázány skupiny, které zamezují tvorbě vodíkových můstků, či zvyšují hydrofobicitu. V případě zvýšení odolnosti proti ohni se může jednat o navázání skupin obsahující retardéry hoření a v případě zajištění odolnosti proti UV záření lze na lignin navázat UV absorbéry (Rowell 2005).

Acetylace

K acetylaci dřeva se používá anhydrid kyseliny octové. Jedná se o esterifikaci volných hydroxylových skupin, kdy do reakce vstupuje anhydrid kyseliny octové a dřevo s volnými hydroxylovými skupinami a vystupuje kyselina octová a acetylované dřevo, kde na místo -OH skupin jsou -O-C(=O)-CH_3 skupiny (Rowell 2005). Tímto způsobem lze modifikovat vlákna, třísky, ploché třísky, štěpky, dýhy, i dřevo o různých rozměrech stejně tak jako jiné materiály na bázi ligninu a celulózy. Esterifikace anhydridem kyseliny octové způsobí plastifikaci celulózových vláken. Hydroxylové skupiny v buněčných stěnách vláken jsou nahrazeny acetylovými skupinami, což způsobí hydrofobizaci vláken. Jako vedlejší produkt vzniká při acetylaci kyselina octová, která musí být z vláken vymyta. Zvýšení hydrofobicity vlákna má za následek menší rozměrové změny kompozitního materiálu (Li a kol. 2007).

Ostatní anhydridy

K esterifikaci volných -OH skupin lze použít i jiné anhydridy. V minulosti byly použity například anhydridy kyseliny ftalové, máselné, propionové, jantarové či maleinové. Pomocí anhydridů kyseliny jantarové a maleinové lze modifikovat vlákna na vlákna termoplastická, s možnou následnou výrobou kompozitu s vysokou hustotou. Pomocí ftalanhydridu lze docílit velmi vysokou rozměrovou stabilitu dřeva, nicméně úprava je pouze dočasného charakteru, neboť navázané skupiny podléhají ve vodě hydrolýze (Rowell 2005).

Izokyanáty

Pro dosažení kvalitnějšího spojení vlákna a polymeru lze použít modifikaci vláken izokyanáty. Izokyanátové skupiny velmi dobře reagují s hydroxylovými skupinami vláken a vytváří silné kovalentní vazby, které následně zlepšují kompatibilitu vláken a pojiva (Mohanty a kol. 2001). Při modifikaci izokyanáty se jedná o navázání skupiny -C(=O)-NH-R v místech hydroxylových skupin. Touto modifikací lze docílit zvýšení rozměrové stability, mechanických vlastností a zvýšení odolnosti proti hnilobě (Rowell 2005).

Izokyanáty jsou široce užívány i v adhesivech pro lepení dřeva, především kvůli jejich reaktivitě již za pokojové teploty se skupinami, které obsahují reaktivní vodíkové skupiny, jako jsou aminové a alkoholové. Jsou využívány v různých druzích adhesiv pro lepení dřeva, zejména díky tomu, že mohou reagovat s mnoha jinými monomery nebo mohou polymerizovat sami. Nejvíce jsou však používány pro výrobu polyuretanů (Frihart 2005). Vysoká reaktivita izokyanátů je jejich výhodou, ale i nevýhodou. Výhoda spočívá především ve velmi rychlé polymerizaci a vysoké konverzi monomerů. Nevýhodou je, že izokyanáty velmi rychle reagují rovněž s vodou, která je ve dřevě obsažena. Reakce s vodou může zapříčinit snížení efektivní molekulové hmotnosti. Nevýhodou je rovněž jejich toxicita pro živé organismy (Frihart 2005).

Silytace

Úprava silany představuje navázání $–Si(OH)_3$ skupin na –OH skupiny vlákna a výrazně zvyšuje chemické propojení mezi adhesivem a vláknem, což má za následek zlepšení adhese. Ještě vyšší účinnosti silytace lze docílit předúpravou hydroxidem sodným (Bhatia a kol. 2016).

Mercerizace

Úprava vláken v alkalickém prostředí je nejrozšířenější metodou úpravy jejich vlastností a nazývá se mercerizace. Její podstata spočívá v rozrušení vodíkových můstků mezi biopolymery, čímž se zvýší drsnost povrchu vlákna. Touto modifikací se z vlákna odstraní určité množství ligninu, vosků a olejů, které se nachází na povrchu buněčných stěn, depolymerizuje se celulóza a obnaží se krátké krystaly celulózy (Mohanty a kol. 2001). Mercerizace zlepšuje navázání adhesiva na povrch vlákna, zmenšuje průměr vláken a zvyšuje aspect ratio (poměr stran), což je důležitý ukazatel zejména při výrobě kompozitních materiálů z vláken. Prokázalo se, že mercerizace snižuje mechanické vlastnosti samotných vláken, avšak zvyšuje mechanické vlastnosti výsledného kompozitního materiálu. Tato úprava rovněž zvyšuje amorfní povahu lignocelulózových materiálů (Xue a Hub 2013; Lee a kol. 2003; Bhatia a kol. 2016). Jako nejvýhodnější metoda alkalické modifikace vláken se ukázala modifikace v 5-10% roztoku NaOH (Modibbo a kol. 2009).

Další možností zvýšení hydrofobicity vlákna a zlepšení jeho smáčení polymerem je benzoylace vláken benzoylchloridem v alkalickém prostředí (Li a kol. 2007). Existuje však nepřeberné množství chemických látek, kterými lze vlákna modifikovat, mezi další často používané způsoby můžeme řadit akrylaci, peroxidaci, modifikaci permangany a další (Li a kol. 2007).

3.3.2 Modifikace plazmatem

Nevýhodou tradičních metod chemické modifikace povrchu je produkce nebezpečných látek, které mohou ohrožovat životní prostředí a lidské zdraví. Z tohoto pohledu je vůči životnímu prostředí více vlídná metoda úpravy povrchu plazmatem. Plazma je ionizovaný plyn obsahující ionty, elektrony, neutrální a excitované molekuly a fotony (Baltazar-y-Jimenez a kol. 2008). Interakce plazmatu s pevným povrchem vede k různým změnám povrchových vlastností v závislosti na druhu použitého plynu. Může dojít ke zvýšení nebo snížení povrchové energie, k zesíťování celulózy v povrchové vrstvě či naopak k vytvoření volných reaktivních skupin (Baltazar-y-Jimenez a kol. 2008; Podgorski 2000). Pro modifikaci povrchu lignocelulózových materiálů za účelem lepšího spojení s polymerem jsou používány především následující plyny: kyslík (Mahlberg a kol. 1999), vzduch (Baltazar-y-Jimenez a kol. 2008), argon (Zanini a kol. 2005).

Podle teploty můžeme rozlišit dva základní druhy plazmatu – vysokoteplotní a nízkoteplotní plazma. Vysokoteplotní plazma je charakterizováno elektrony s velmi vysokými teplotami a těžkými částicemi, přičemž obojí mohou být nabité nebo neutrální a jsou blízko maximálnímu stupni ionizace (100%). Nízkoteplotní plazma se skládá z nízkoteplotních částic (nabité a neutrální molekul a atomy) a relativně vysokoteplotních elektronů, které mají nízký stupeň ionizace (do 10%). Vysokoteplotní plazma může být generováno například v elektrickém oblouku, raketových motorech, plazmových tryskách či při termonukleárních reakcích. Nízkoteplotní plazma lze vytvořit katodovými, koronovým či radiofrekvenčními výboji nebo ve fluorescentních trubicích (Denes a kol. 2005).

Při modifikaci povrchů rozlišujeme následující tři druhy plazmatu (Sun 2016):

- Chemicky nereaktivní plazma – většinou ho tvoří pouze jeden inertní prvek (např. Ar-plazma, které ionizuje ostatní molekuly, avšak argon není spotřebováván v chemických reakcích)
- Chemicky reaktivní plazma – je tvořeno anorganickými či organickými molekulami, které jsou chemicky reaktivní (O_2, N_2, CF_4), avšak na ošetřeném povrchu nevytváří vrstvu polymeru

- Polymery-formující plazma – toto plazma je reaktivní a na povrchu ošetřovaného materiálu formuje vrstvu polymeru, tvoří ho páry různých organických a anorganických sloučenin

Výhody plazmatické úpravy povrchu (Sun 2016; Chu a kol. 2002):

- Suchý proces modifikace, není nutné následné sušení materiálu
- Modifikuje pouze povrch, neovlivňuje vlastnosti hlouběji v materiálu
- Spolehlivý, rychlý a bezpečný způsob modifikace
- Nízká spotřeba chemikálií, žádná produkce odpadu
- Modifikace i povrchů, které jsou odolné vůči jiným metodám

Parametry plazmatu

Plazma může být charakterizováno vnějšími a vnitřními parametry. Vnější parametry zahrnují materiál, tvar a rozměry generátoru a elektrod, složení plynu, průtok plynu, celkový a parciální tlak a elektrickou energii, která nabíjí elektrody. Vnitřní parametry zahrnují hustotu nabitých a neutrálních částic, druh volných radikálů, atomů a molekul a průměrnou energii a rozdělní energie všech druhů částic. Tyto parametry potom přímo ovlivňují základní vlastnosti plazmatu, jako je např. stupeň ionizace (Denes a kol. 2005).

Nízkoteplotní plazma generované za atmosférického tlaku

Dále rozlišujeme dva základní způsoby plazmatické úpravy povrchu, za atmosférického a za sníženého tlaku. Při prvním zmiňovaném způsobu se jedná o působení plazmatu v otevřeném prostoru při atmosférickém tlaku, zatímco druhý způsob je charakterizován působením plazmatu na povrch v uzavřeném prostoru se sníženým tlakem (Sun 2016). Ošetřování povrchu plazmatem při atmosférickém tlaku je méně náročné na přístrojové vybavení a je v posledních letech progresivní metodou (Cheng a kol. 2010). Studené plazma nezpůsobí žádné změny hlouběji v materiálu, ale pouze ovlivňuje povrchové vrstvy (Mahlberg a kol. 1999), přičemž nejdůležitější parametry při ošetřování povrchu touto metodou jsou doba kontaktu plazmatu s povrchem, vzdálenost mezi tryskou a povrchem a velikost proudu (Baltazar-y-Jimenez a kol. 2008).

Modifikace lignocelulózových částí se neprovádí pouze za účelem úpravy povrchu pro lepší adhesi adhesiva, nicméně i za účelem aktivace povrchu pro efektivnější průběh chemických reakcí při výrobě biopaliv (Vanneste a kol. 2017; Schultz-Jensen a kol. 2010).

3.3.3 Enzymatická modifikace

Laccázy a peroxidázy jsou enzymy produkované houbami (především ligninovorními), některými rostlinami, bakteriemi a zvířaty, které oxidují fenol. Tyto enzymy jsou schopné rozložit všechny hlavní komponenty lignocelulózových materiálů. Zatímco laccázy katalyzují oxidaci fenolických látek za přítomnosti kyslíku, peroxidázy vyžadují jako substrát peroxid vodíku (Widsten a Kaelbauer 2008). Během procesu vysokoteplotního rozvlákňování dochází k postupnému měknutí ligninu ve střední lamele a při teplotě kolem teploty skelného přechodu ligninu dojde k oddělení vláken. Po vychladnutí na pokojovou teplotu lignin opět ztuhne a na povrchu vlákna vytvoří krustu, která redukuje účinky jakéhokoli lepidla (Kharazipour a kol. 1997). Vysokoteplotní rozvlákňování má za následek depolymerizaci ligninu prostřednictvím rozštěpení etherických vazeb mezi jeho fenylpropanovými jednotkami. Depolymerizovaný, vodou extrahovatelný, lignin má velký obsah fenolických hydroxylových skupin a je zásadní pro oxidaci působením enzymů v podobě oxidace fenolických hydroxylových skupin na fenoxylové radikály (Widsten a Kaelbauer 2008). Pomocí katalytického působení oxydoreduktáz dochází pak k polymerizaci ligninu prostřednictvím zesíťování fenoxylových radikálů. Této reakce se dá využít zejména při lepení částic na bázi celulózy a ligninu (Felby a kol. 2002). Enzymatické působení na štěpky před procesem rozvlákňování má za následek jednak snížení energie potřebné k jejich rozvláknění, ale i snížení množství lepící směsi (Kharazipour a kol. 1997). Enzymatického působení bylo využito při výrobě vláknitých desek ze smrku, borovice a buku (Felby a kol. 2002; Kharazipour a kol. 1997). Existuje i možnost využití enzymatického působení na lignin při výrobě třískových desek. Technický lignin, vyprodukovaný jako vedlejší produkt při výrobě celulózy, lze za přítomnosti enzymů oxidovat za účelem jeho následného použití jako lepidla. Po radikalizaci ligninu a nanesení na třísky dochází během lisování k jeho zesíťování a tvorbě pevného spojení mezi třískami (Widsten a Kaelbauer 2008).

3.4 SWOT analýza výroby třískových desek z řepky

3.4.1 Silné stránky

- **Nízké nákupní náklady (nevyužívaný odpad)** - Řepkové stonky v současné době nejsou využívány, při sklizni jsou rozštěpkovány a ponechány na poli nebo nanejvýše využívány pro energetické účely (Karaosmanoğlu 1999; Díaz a kol. 2009; Zabanitou a kol. 2007). Jelikož se jedná o nevyužité posklizňové zbytky, lze předpokládat nízké nákupní náklady.

- **Dostupný materiál a ve velkém množství** - V roce 2017 bylo v ČR oseto řepkou celkem 407 tis ha půdy, což je 16,5% z celkové osevní plochy v ČR (ČSÚ 2017). Hektarový výnos stonků v Evropě činí 3 – 10 t/ha, což znamená, že v roce 2014 bylo v Evropské unii vyprodukováno zhruba 42 milionů tun stonků (Eurostat 2016).

- **Obnovitelný zdroj** – Jedná se o obnovitelný zdroj, který lze každoročně sklízet za účele získání ligninu a celulózy (Karaosmanoğlu 1999).

- **Politika EU a ČR** – Politika Evropské unie přispívá k velkým osevním plochám řepky ozimé, pro zemědělce je tato plodina velmi finančně výhodná. Evropská unie si stanovila cíl (Nařízení 2009/28/EC Evropského parlamentu a Rady) snížit emise skleníkových plynů o 20% v porovnání s hodnotami v roce 1990. Dále k tomuto byla přijata směrnice 98/70/ES (Nařízení 98/70/EC Evropského parlamentu a Rady) o jakosti paliv, která ukládá dodavatelům pohonných hmot snížit do 2020 intenzitu emisí skleníkových plynů v palivové směsi o 6% v porovnání s rokem 2010, které představuje pobídku pro rozsáhlejší užití nízkouhlíkových paliv v dopravě. Většina z těchto 6% je z velké většiny tvořeno řepkou, proto je předpoklad vysoké spotřeby řepky (Zpráva Komise Evropskému parlamentu a Radě v souvislosti s článkem 9 Nařízení 98/70/EC, ze dne 31. 5. 2017). Tato problematika je nadále upravována i na národní úrovni, povinný obsah minerálního oleje je upraven zákonem č. 353/2003 Sb., o spotřebních daních, kde je určeno, že směsi středních olejů a těžkých plynových olejů musí obsahovat alespoň 30% metylesteru řepkového oleje (§45 odst. 2 písm. c).

- **Dobré mechanické a fyzikální vlastnosti** – Chemické složení stonků a rozměry vláken řepky jsou podobné chemickému složení dřeva listnatých dřevin a rozměrům vláken listnatých dřevin (Adapa a kol. 2009; Tofanica a kol. 2011). Kompozitní materiály vyrobené z této suroviny mají vlastnosti srovnatelné s komerčně vyráběnými produkty na bázi dřeva (Huang a kol. 2016; Nikvash a kol. 2012; Dziurka a kol. 2015; Dukarska a kol. 2017).

- **Lze využít stávající technologii výroby třískových a vláknitých desek** – Vzhledem k podobnému složení řepkových vláken a třísek, jako vláken a třísek dřeva, předpokládáme, že bude možné po úpravách využít stávající technologii výroby desek.

- **Pro uskladnění lze stonky zkomprimovat** – Stonky jednoletých a dvouletých rostlin obsahují dřeň, díky které je stonky možné pro účely převozu, manipulace či skladování zkomprimovat do skladných balíků.

- **Jednoletý cyklus pěstování řepky** – Jednoletý cyklus pěstování řepky ozimé (Su a kol. 2014), a tedy i produkce stonků, přináší významnou výhodu v podobě možnosti rychlé reakce na změny na trhu.

- **Nízká energetická náročnost výroby** – Hustota stonků řepky při vlhkosti 10% se pohybuje okolo 270 kg/m^3 a hustota substance 1550 kg/m^3 (Adapa a kol. 2009). Oproti dřevu, které má výrazně vyšší hustotu, je desintegrace stonků snadnější, energeticky méně náročná (Zhu a Pan 2010).

- **Redukce emisí CO_2** – Na rozdíl od spálení stonků v tuhém stavu či výroby biopaliv, výrobou desek dojde k vázání CO_2 v produktu na několik desítek let (Schlamadinger a Marla 1995).

3.4.2 Slabé stránky

- **Variabilita vlastností** – Přírodní materiály vykazují oproti uměle vytvořeným materiálům vyšší variabilitu vlastností (Hýsek a kol. 2016; Anajiwala a Blouw 2007; Das a kol. 2012).

- **Nasáklivost a navlhavost** – Díky volným hydroxylovým skupinám obsaženým ve vláknech celulózy mají řepková vlákna schopnost absorbovat molekuly vody jak ze vzduchu, tak z vody kapalné (Hofstetter a kol. 2006), což následně ovlivňuje i nasáklivost a navlhavost materiálů vyrobených z těchto vláken. V kompozitních materiálech však lze nasáklivost a navlhavost do značné míry omezit vhodným adhesivem a aditivem (Dukarska a kol. 2017).

- **Technologie sbírání slámy z pole není zcela vyvinuta** – V současné době jsou stonky řepky ozimé při sklizni rozštěpkovány a ponechány na poli. Pro sběr stonků by bylo vhodné použití sběracího a balícího agregátu, které jsou již využívány při sběru posklizňových zbytků jiných plodin (Tang a kol. 2017; Carvalho a kol. 2017).

- **Technologie výroby není zcela vyvinuta** – Desky z třísek řepky se doposud komerčně nevyrábí, v současné době probíhá výzkum, který si klade za cíl i vývoj technologie výroby desek (Hýsek a kol. 2018c).

- **Stále nízká poptávka po environmentally-friendly products** – Poptávka po environmentally-friendly products roste, avšak pouze čtvrtina obyvatel (26%) EU si tyto produkty často kupuje (Flash Eurobarometer 2013).

- **Odběr živin z půdy** - Při porovnání se zaoráváním stonků do půdy dochází k odebírání živin z půdy, což má za následek nutnost hnojení anorganickými hnojivy (Su a kol. 2014). Nicméně pro vstřebání živin do půdy je nutné slámu zaorávat. V dnes široce rozšířeném případě, kdy se pole po sklizni pouze podmítá a neoře, množství vstřebaných živin se podstatně snižuje (Su a kol. 2015; Zhu a kol. 2016).

- **Objemnost suroviny** – Dřeň zastupuje ve stonku podstatnou část a díky ní je hustota stonků při vlhkosti 10% cca 270 kg/m^3, což znamená vyšší objemnost v porovnání se dřevem (Adapa a kol. 2009).

- **Degradace biotickými činiteli** – Tak jako každý přírodní ligno-celulózový materiál, i stonky řepky mohou v případě nevhodného skladování degradovat působením biotických činitelů (Anajiwala a Blouw 2007; Das a kol. 2012).

- **Sezónnost sklizně** – Díky sezónnosti sklizně (Tofanica a kol. 2011) je nutné materiál naskladňovat ve velkém množství, což implikuje i s tím spojené náklady na uskladnění.

3.4.3 Příležitosti

- **Velký trh s velkoplošnými kompozitními materiály pro konstrukční a nábytkářské účely** – V Evropské unii bylo v roce 2015 vyprodukováno 53,8 milionů m^3 velkoplošných kompozitních materiálů na bázi dřeva (EPF 2017).

- **Zlepšení ekonomické situace zemědělců** – Zpeněžení vedlejšího produktu z pěstování řepky ozimé, její slámy, přinese zemědělcům významný peněžní příjem.

- **Řeší situaci nedostatku dřevní suroviny** – Částečná náhrada dřeva v kompozitních materiálech na bázi ligninu a celulózy řepkou ozimou může výrazně přispět k řešení nedostatku dřeva v různých dřevozpracujících, ale i energetických odvětvích (Dziurka a kol. 2015; Ye a kol. 2007). A tím i k ochraně neméně důležitých mimoprodukčních funkcí lesa, což je velmi důležitou pozitivní externalitou.

- **Legislativní podpora ekologicky šetrných produktů** – Podpora ekologicky šetrných řešení ze strany národních vlád se do budoucna předpokládá a může napomoci jejich většímu rozšiřování oproti produktům z neobnovitelných zdrojů.

- **Nízká spotřeba energie pro výrobu** – Energetická náročnost výroby finálního výrobku z kompozitů na bázi dřeva je výrazně nižší, než u výrobků z betonu, oceli či skla. Předpokládá se, že výroba desek z řepky bude ještě méně energeticky náročná, než výroba desek ze dřeva.

- **Expanze i do jiných odvětví než jen nábytkářský a stavební průmysl** – Hlavními odvětvími pro uplatnění výrobků ze stonků řepky se předpokládá nábytkářský a stavební průmysl (v podobě velkoplošných materiálů). Nicméně kompozitní materiály ze stonků řepky, například kompozity z vláken či tvarové výlisky, mohou najít uplatnění i v automobilovém, lodním a jiném průmyslu.

- **Využití i stonků jiných rostlin** – Ve vyráběných kompozitních materiálech nemusí být zastoupena pouze vlákna či třísky řepky ozimé, účelově je lze kombinovat i s jinými přírodními vlákny či třískami (Oh a Jmaludin 2015; Nikvash a kol. 2012).

3.4.4 Hrozby

- **Konkurence kompozitních materiálů z jiných obnovitelných surovin** – Probíhají výzkumy zaměřené na využití i jiných materiálů z obnovitelných surovin. Jako perspektivní se jeví například bambus (Marinho a kol. 2013), či cukrová třtina (Belini a kol. 2012), rákos (Han a kol. 2001), len, konopí a kenaf (Aisyah a kol. 2013; Papadopoulou a kol. 2014).

- **Betonová lobby** – Lobby ze strany konvenčních stavařských firem může rozšiřování materiálů na bázi dřeva a jiných přírodních zdrojů výrazně zpomalit, v současné době se jedná například a legislativní znevýhodňování a limity, které jsou na dřevostavby aplikovány.

- **Nízká informovanost spotřebitelů** – Obecně většímu růstu výroby produktů z obnovitelných surovin v Evropě může bránit nízká informovanost spotřebitelů, zejména v zemích východních Evropy stále převládají spotřebitelé, kteří upřednostňují levnější variantu z neobnovitelných zdrojů před variantou z obnovitelných zdrojů

- **Škůdci** – U jakékoli monokultury, i u řepkového pole, je nebezpečí velkých škod způsobených škůdci. S rostoucí plochou monokultury se toto nebezpečí zvyšuje a je nutné přijímat agronomická opatření. V případě řepky ozimé se jedná např. o šlechtění, správné agronomické postupy, ošetření porostu proti škůdcům, atd. (Zegeda-Lizarazu a Monti 2010).

- **Konkurence biopaliv** – Alternativní využití posklizňových zbytků zemědělských plodin k produkci kompozitních materiálů je výroba biopaliv, zejm. bioetanolu. Na surovinu pro výrobu biopaliv navíc nejsou kladeny tak vysoké kvalitativní požadavky jako pro materiál určený k výrobě kompozitních materiálů (Haq a kol. 2016; Taha a kol. 2016).

- **Snížení objemu produkce řepky** – Nezanedbatelnou hrozbou je snížení produkce řepky ozimé, ať už kvůli změně politiky, která zapříčiňuje vyšší produkci řepky oproti jiným surovinám, tak či kvůli jiným faktorům, např. snížení poptávky po řepkovém oleji. Evropská komise nenavrhuje prodlužovat snížení emisí skleníkových plynů prostřednictvím paliv, dle Nařízení 98/70/ES o jakosti paliv po roce 2020 (Zpráva Komise Evropskému parlamentu a Radě v souvislosti s čl. 9 Nařízení 98/70/EC)

3.5 Konkurenční odvětví k výrobě kompozitních materiálů z posklizňových zbytků zemědělských plodin

Biopaliva jsou považována za jedno z perspektivních řešení energetické krize, oproti fosilním palivům způsobují nižší emise skleníkových plynů a surovinu pro jejich výrobu lze získávat a transportovat velmi jednoduše. V neposlední řadě vlastnosti biopaliv přispívají ke zvýšení efektivity motoru. Výhodou je i schopnost bioetanolu rozložit se v přírodě (Jambo a kol. 2016). S produkcí bioetanolu jsou však spojeny i problémy a kontroverze. Závažnost a druh těchto problémů se různí v závislosti na surovině, z které je bioetanol vyráběn.

3.5.1 Produkce bioetanolu

Z hlediska technologie výroby lze vylišit tři generace bioetanolu. Bioetanol první generace je vyráběn z potravinářských plodin (respektive plodin u kterých existuje i potravinářské využití). Bioetanol druhé generace se vyrábí z lesní štěpky či posklizňových zbytků zemědělských plodin, tedy nepotravinářské biomasy a třetí generace bioetanolu se vyznačuje výrobou z řas (Jambo a kol. 2016).

Bioetanol první generace se vyrábí fermentací glukózy obsažené v plodinách s vysokým obsahem cukrů. Tento technologický proces výroby je jednoduchý a levný, nicméně výroba tohoto druhu bioetanolu je kritizována kvůli neetičnosti využívání potravinových zdrojů tímto způsobem v době, kdy miliony lidí po celém světě trpí hladem a podvyživením. Kromě neetičnosti může výroba bioetanolu první generace vést k růstu cen potravin či nedostatku potravin (Gupta a Verma 2014; Jambo a kol. 2016).

Tuto nevýhodu odstraňují biopaliva druhé generace, kdy je vstupní surovinou biomasa na bázi celulózy, jejíž dostupnost je také velmi dobrá a produkce nenáročná, ale potravinám nekonkuruje. Biomasa na bázi celulózy, jako je dřevo, posklizňové zbytky zemědělských plodin, tráva a odpadní materiály jsou atraktivní suroviny pro produkci bioetanolu díky jejich dostupnosti ve vyšších množstvích a nižší ceně. Produkci bioetanolu druhé generace ve větším měřítku však brání některé technologické postupy, které snižují výtěž. Problémem je lignin, jakožto nedílná součást biomasy, která zaujímá ve stoncích rostlin až 40% sušiny. Komplikace způsobuje i samotná celulóza, která je chemicky velmi odolná a její štěpení je náročné (Haq a kol. 2016; Jambo a kol. 2016).

Z výše uvedených důvodů je nyní celosvětově velkou výzvou vývoj technologie výroby bioetanolu z mořských řas, který se označuje jako bioetanol třetí generace. Mořské řasy jsou snadno pěstovatelné v různých podmínkách, potřeba plochy na produkci jednotky biomasy je nízká, váží oxid uhličitý a nekonkurují potravinám. Nadějí pro úspěch této generace je i nízký obsah ligninu v řasách, nicméně výzkum produkce bioetanolu z tohoto zdroje je teprve v počátcích a dosud neexistuje průmyslově aplikovatelná technologie (Aditiya a kol. 2016; Balat a Balat 2009; Jambo a kol. 2016; Limayem a Ricke 2011).

3.5.2 Analýza výroby a produkce bioetanolu

V současnosti je bioetanol vyráběn prakticky pouze z obilovin a cukrové třtiny. Tato výroba biopaliv ze zemědělských plodin příznivě působí na rozvoj venkovských oblastí tvorbou pracovních míst a zvýšením příjmů obyvatel. Nicméně z důvodu konkurence této vstupní suroviny potravinám, čelí tato technologie výroby kritice kvůli snižování zdrojů pro produkci potravin a zvyšování cen zemědělských plodin. Výroba bioetanolu z kukuřice má také negativní vliv na životní prostředí v podobě uvolňování těkavých organických látek do ovzduší, snižování biodiverzity a eroze půdy. Z těchto všech důvodů je celosvětově hledáno řešení produkce bioetanolu bez uvedených negativních efektů (Mussatto a kol. 2010). Následující SWOT analýza představuje silné a slabé stránky, příležitosti a hrozby produkce a využití bioetanolu, působící faktory jsou zpracovány dle Chanthawonga a Dhakal 2016; Jambo a kol. 2016; Hasibuan a Naziri 2017.

Silné stránky

- Půda pro pěstování biomasy je široce dostupná
- Již existuje vyvinutá technologie a technika pro produkci biomasy (bioetanol 1. a 2. generace)
- Výrobu bioetanolu lze integrovat do stávajících zemědělských podniků

- Využití biomasy pro tyto účel přispívá k energetické bezpečnosti

Slabé stránky

- Cena vstupní biomasy fluktuuje
- Výrobní náklady v porovnání s fosilními palivy jsou vyšší
- Nevyvinutá technologie výroby bioetanolu 3. generace
- Legislativní překážky a slabý marketing v některých zemích
- Nízká výtěžnost (při současné technologii)

Příležitosti

- Substituce fosilních paliv
- Zvyšující se poptávka po biopalivech
- Hospodářskopolitická podpora
- Řešení globálního oteplování, nedostatku energie a fosilních paliv a znečišťování životního prostředí
- Zlepšení ekonomické situace obyvatel ve venkovských oblastech

Hrozby

- Konkurence potravinářským plodinám (1. a 2. generace)
- Ropná lobby
- Diskontinuální dodávka biomasy
- Legislativní a administrativní překážky
- Bioetanol se využívá pouze jako biopalivo

Vzhledem k tomu, že bioetanol první generace se pravděpodobně do budoucna nebude vyrábět kvůli etickým důvodům, a technologie výroby bioetanolu třetí generace ještě není zcela dořešena, tak se jako nejpravděpodobnější následující vývoj jeví růst produkce bioetanolu druhé generace. Tato výroba je konkurenční k výrobě kompozitních materiálů z posklizňových zbytků zemědělských plodin a vzájemně by si tedy tato dvě odvětví mohla zdražovat a odčerpávat vstupní surovinu.

4 Metodika

Byla zvolena forma disertační práce v podobě předložení publikovaných článků zaměřených na téma disertační práce a obsahujících její výsledky. Podrobná metodika konkrétních experimentů je uvedena vždy v příslušném článku, obecně však lze řešení práce rozdělit do třech okruhů:

- Modifikace povrchu lignocelulózových elementů
- Hodnocení fyzikálních a mechanických vlastností kompozitních materiálů vyrobených z lignocelulózových částic
- Hodnocení interakce adhesivum/lignocelulózový materiál

4.1 Modifikace povrchu lignocelulózových elementů

Pro úpravu povrchu lignocelulózových elementů bude využita studená plazma. Studená plazma nepůsobí žádné změny hlouběji v materiálu, ale ovlivňuje pouze povrchové vrstvy. Za účelem lepšího spojení s polymerem bude taktéž testována modifikace lignocelulózových částic chemicky a termicky. Chemická modifikace byla vybrána za účelem úpravy povrchu, zatímco termická modifikace za účelem úpravy vlastností v celém objemu dané modifikované částice. Změna vlastností lignocelulózových elementů bude testována především pomocí prvkové analýzy, fluorescenční mikroskopie a goniometru.

4.2 Hodnocení fyzikálních a mechanických vlastností kompozitních materiálů vyrobených z lignocelulózových částic

Adhesivum bude nanášeno na třísky laboratorní nanášečkou lepidla. Desky budou lisovány laboratorním lisem. Z vyrobených desek budou nařezány zkušební vzorky dle příslušných norem a budou hodnoceny standardní vlastnosti třískových desek: hustota dle ČSN EN 323:1994, pevnost v ohybu a modul pružnosti v ohybu dle ČSN EN 310:1995, rozlupčivost dle ČSN EN 319:1994, přídržnost povrchu dle ČSN

EN 311:1994, bobtnání dle ČSN EN 317:1996, atd. Budou ale měřeny i nenormované vlastnosti třískových desek, jako je hustotní profil.

4.3 Hodnocení interakce adhesivum/lignocelulózový materiál

Pro zhodnocení rozhraní mezi adhesivem a modifikovaným lignocelulózovým materiálem bude toto rozhraní podrobeno mikroskopické analýze pomocí SEM. Budou pozorovány jak slepené a vytvrzené spoje (hodnocení rozložení adhesiva na povrchu modifikovaného materiálu), tak spoje porušené, získané ze vzorků po zkoušce rozlupčivosti. Na těchto porušených vzorcích bude stanovován charakter porušení (kohezní porušení materiálu třísky či adhezní porušení mezi adhesivem a třískou). Pro zhodnocení interakce adhesivum/lignocelulózový materiál z pohledu mechanických vlastností budou vyrobené spoje podrobeny pevnostním zkouškám.

5 Syntéza výsledků a diskuze

Následující kapitola představuje výsledky disertační práce publikované v odborných vědeckých časopisech a spojuje je svým jednotícím komentářem do jednoho celku. Separáty článků za období doktorského studia do 23. 7. 2018 jsou uvedeny v kapitole 10.

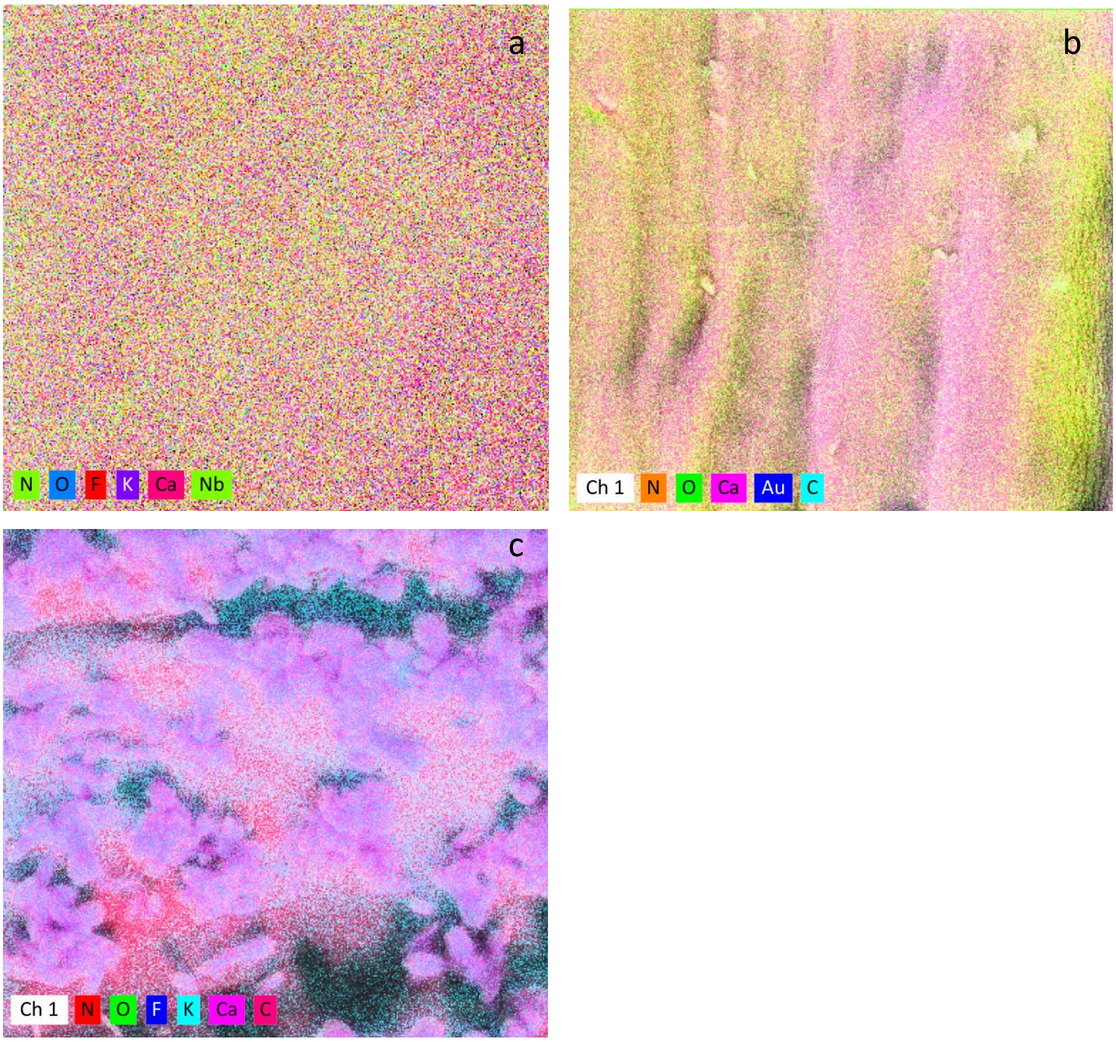
V současné době je hlavní surovinou pro výrobu dřevotřískových desek dřevo nízké kvality, jeho podíl tvoří ve výrobě dřevotřískových desek cca 70%. Avšak díky zdokonalujícím se technologiím v pilařském zpracováním dřeva se toto dřevo stále častěji uplatňuje i při výrobě lepeného lamelového dřeva či CLT panelů, kde je více zhodnoceno. Zvýšená poptávka po této surovině pak nutně zvyšuje ceny třísek. Tento nárůst cen hlavní vstupní suroviny může způsobit výpadky v dodávce či snížení konkurenceschopnosti dřevotřískových desek (Klímek a Wimmer 2017). Nedostatek kulatiny nižší kvality však není způsoben pouze výše uvedenou konkurencí, potenciální hmotu pro výrobu třísek odčerpává i papírenský, energetický a chemický průmysl. Požadavky na dodávky této dřevní hmoty jsou stále rostoucí a již vyústily v její nedostatek, který se projevuje např. snížením zisků dřevozpracujících podniků (Seintsch 2011; Lauri a kol. 2012; Sujová a kol. 2017). Přírůsty dřeva v Evropě navíc nepokrývají tuto rostoucí poptávku (Bostedt a kol. 2016). Možným řešením může být částečná náhrada dřeva jednoletými a dvouletými rostlinami, jejichž stonky tvořené rovněž celulózou a ligninem mohou být využity jak pro výrobu materiálů (Halvarsson a kol. 2010; Marinho a kol. 2013; Hýsek a kol. 2016), tak pro energetické účely (Haq a kol. 2016; Taha a kol. 2016). Jako perspektivní materiál se jeví posklizňové zbytky zemědělských plodin (Guler a kol. 2006; Belini a kol. 2012; El-Kassas and Mourad 2013; Částková a kol 2018), jejichž využití se jeví vhodné jak ekonomicky, tak politicky (Klímek a Wimmer 2017).

Mají-li být kompozitní materiály z posklizňových zbytků zemědělských plodin komercializovány, je nutné zhodnotit problematiku jejich výroby komplexněji, zohlednit všechny aspekty ovlivňující jejich výrobu, ne pouze materiálové charakteristiky, na které se doposud publikované vědecké práce především zaměřují. Komplexní posouzení tohoto problému je uvedeno v této práci v kapitole SWOT analýza výroby třískových desek z řepky a spolu s dalšími výsledky bylo publikováno v časopisu BioResources (Gajdačová a kol. 2018). Analýza identifikovala silné stránky využití třísek z řepkových stonků pro výrobu desek především v podobě dobrých mechanických vlastností desek a jednoletého cyklu pěstování řepky. Naopak variabilita vlastností, nasáklivost a navlhavost stonků byly vnímány jako slabé stránky. Domnělá slabá stránka tohoto způsobu využití posklizňových zbytků v podobě odběru živin z půdy nebyla shledána jako relevantní. Při porovnání se zaoráváním stonků do půdy sice dochází k odebírání živin z půdy, což má za následek nutnost hnojení anorganickými hnojivy (Su a kol. 2014). Nicméně pro vstřebání živin do půdy je nutné slámu zaorávat. V dnes široce rozšířeném případě, kdy se pole po sklizni pouze podmítá a neoře, se množství vstřebaných živin podstatně snižuje (Su a kol. 2015; Zhu a kol. 2016). Mezi příležitosti patří především zlepšení ekonomické situace zemědělců, neboť zpeněžení vedlejšího produktu z pěstování řepky ozimé může přinést zemědělcům významný peněžní příjem. Z hrozeb je nutné zmínit škůdce monokultur a konkurenci biopaliv.

Pro výrobu kompozitních materiálů ze stonků zemědělských plodin je však zpravidla nutné na rozdíl od dřevní hmoty tyto stonky povrchově upravit za účelem narušení voskové vrstvy na povrchu, která brání kvalitnímu spoji mezi třískou a adhesivem (Bekhta a kol. 2013; Částková a kol. 2017). V rámci prezentované disertační práce byly zvoleny jak chemické, tak fyzikální i biologické způsoby povrchové úpravy vstupního materiálu. Po úpravě posklizňových zbytků (pro tyto experimenty byla zvolena sláma řepky ozimé, sláma pšenice ozimé a plevy pšenice ozimé) byl efekt úpravy zjišťován a modifikovaný materiál charakterizován pomocí vhodných metod. Z povrchových vlastností byla hodnocena morfologie povrchu (SEM), povrchové napětí (testovacími inkousty, goniometrem), prvková analýza povrchu (EDS). Mezi pozorované objemové vlastnosti patří rovnovážná vlhkost, prvkové složení (spektroskopie), makromolekulární složení (FTIR, FLIM analýza).

Byla provedena hydrotermická a chemická (v alkalickém prostředí) modifikace třísek ze stonků řepky ozimé, přesná metodika byla již publikována v časopise BioResources (Částková a kol. 2018). Výsledky ukázaly, že prvkové složení povrchu a celkové prvkové složení třísek řepky ozimé je významně ovlivněno typem modifikace. Obrázek 5 zachybuje prvkové složení povrchu a tabulka 3 celkové prvkové složení řepkových třísek nemodifikovaných a modifikovaných hydrotermicky a chemicky.

Třísky modifikované v alkalickém prostředí vykazovaly nejvyšší pH, neboť po této modifikaci nebylo možné zbytkový hydroxid sodný z třísek zcela vymýt. Modifikací částic byla rovněž změněna povrchová energie jejich povrchu. Oba dva způsoby modifikace snížily kontaktní úhel povrchu částice s vodou, nejvyššího poklesu bylo dosaženo hydrotermickou modifikací. Naproti tomu nebyl zjištěn statisticky významný rozdíl v rovnovážné vlhkosti třísek modifikovaných a neupravených.



Obrázek 5 Prvková analýza povrchu řepkové slámy. (a) neupravený povrch, (b) hydrotermick upravený povrch, (c) chemicky upravený povrch

Tabulka 3 Celkové prvkové složení řepkových třísek

Prvek / Modifikace	**Reference**	**Hydrotermicky**	**Chemicky**
Al (mg/kg)	45,30 ± 4,1 ^{a}	59,73 ± 0,95 ^{b}	61,93 ± 8,95 ^{b}
B (mg/kg)	11,01 ± 0,52 ^{a}	7,85 ± 0,2 ^{b}	7,94 ± 0,9 ^{b}
Ca (mg/kg)	6941,9 ± 99 ^{a}	5858,5 ± 41,6 ^{b}	5705,2 ± 657,7 ^{b}

Cd (mg/kg)	0,08 ± 0,01 ^{a}	0,09 ± 0,01 ^{a}	0,09 ± 0,02 ^{a}
Cr (mg/kg)	0,23 ± 0,0 ^{a}	0,25 ± 0,02 ^{a}	0,25 ± 0,04 ^{a}
Cu (mg/kg)	1,03 ± 0,07 ^{a}	0,82 ± 0,03 ^{b}	0,67 ± 0,07 ^{c}
Fe (mg/kg)	42,67 ± 11,8 ^{a}	46,97 ± 1,39 ^{a}	50,83 ± 8,42 ^{a}
K (mg/kg)	5036,8 ± 198 ^{a}	1026,1 ± 34,5 ^{b}	732,8 ± 88,3 ^{c}
Mg (mg/kg)	998,8 ± 18,38 ^{a}	739,1 ± 11,72 ^{b}	1089,8 ± 107,9 ^{a}
Mn (mg/kg)	8,09 ± 0,3 ^{a}	6,71 ± 0,05 ^{b}	4,80 ± 0,57 ^{c}
Ni (mg/kg)	0,33 ± 0,13 ^{a}	0,10 ± 0,05 ^{b}	0,19 ± 0,1 ^{ab}
P (mg/kg)	248,9 ± 29,72 ^{a}	217,5 ± 9,3 ^{a}	210,3 ± 24,84 ^{a}
S (mg/kg)	1340 ± 45,6 ^{a}	431,5 ± 13 ^{b}	323,4 ± 27 ^{c}
Zn (mg/kg)	1,26 ± 0,08 ^{a}	1,68 ± 0,27 ^{a}	2,50 ± 0,45 ^{b}
Na (mg/kg)	245,5 ± 49,5 ^{a}	663,8 ± 29,1 ^{a}	4187,8 ± 508,5 ^{b}

Aritmetický průměr ± směrodatná odchylka (n = 3). Odlišná písmena (horní index) ve sloupcích značí statisticky významný rozdíl (Tukeyův HSD test, $P < 0,05$).

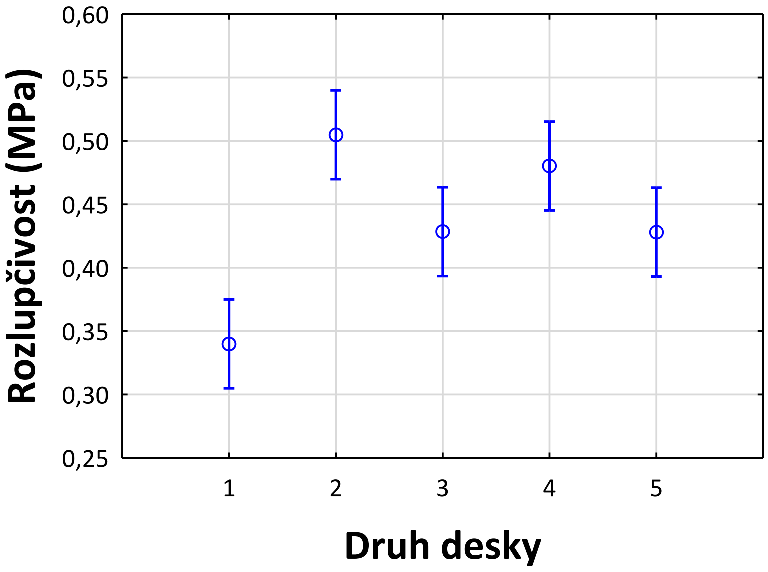
Z připravených třísek byly dále vyrobeny třískové desky. Bylo použito práškové lepidlo na bázi polyesteru a epoxidové pryskyřice DAKOTEX2600 (Dakota Coatings N.V., Belgium). Obsah lepidla byl 10%. Lepidlo bylo na třísky naneseno pomocí laboratorní nanášečky lepidla (Imal, Modena, Italy) a desky byly lisovány pomocí laboratorního lisu (Strozatech, Brno, Česká republika) při teplotě lisovacích desek 185°C po dobu 10 min. Po době 10 min byla uprostřed desek dosažena teplota 170°C. Rychlost uzavírání lisu byla 150 s. Všechny naměřené výsledky byly porovnány s hodnotami komerčně vyráběných materiálů. Pro toto porovnání byly zvoleny DTD P2 tloušťky 12 mm a OSB3 o tloušťce 12 mm. Takto vyrobené desky byly podrobeny fyzikálním a mechanickým zkouškám za účelem zjištění vlivu příslušné modifikace na jejich vlastnosti, přesná metodika experimentů je uvedena v (Hýsek a kol. 2018c).

Z výsledků je patrné, že modifikace řepkových třísek měla statisticky významný vliv jak na příjem vlhkosti, tak na tloušťkové a objemové bobtnání desek. Nejvyšší hodnoty bobtnání vykazují desky, jejichž třísky byly modifikovány v alkalickém prostředí. Naproti tomu nejnižších hodnot bobtnání dosahují desky, jejichž třísky modifikovány nebyly. Výsledky jsou uvedeny v tabulce 4. Vliv modifikace řepkových třísek na rozlupčivost byl prokázán. Desky vyrobené z třísek modifikovaných ve vroucí vodě dosáhly nejvyšších hodnot pevnosti i v porovnání s komerčně vyráběnými druhy desek (obrázek 6, statistická významnost rozdílů je uvedena v tabulce 5). Vysoké hodnoty rozlupčivosti mohou být způsobeny nestandardním vertikálním hustotním profilem. Přídržnost povrchu byla v porovnání s dřevotřískovými deskami menší, tato charakteristika byla opět ovlivněna průběhem vertikálního hustotního profilu. Modifikací třísek v alkalickém prostředí bylo dosaženo pevnějšího adhesivního spojení mezi třískou a adhesivem. Pří zkoušce rozlupčivosti vykazovaly desky z těchto třísek i kohezní porušení ve třísce (obrázek 7). Modifikací třísek tedy bylo dosaženo zvýšení mechanických vlastností desek, avšak došlo ke zhoršení fyzikálních vlastností (Hýsek a kol. 2018c).

Tabulka 4 Tloušťkové bobtnání a nevratné tloušťkové změny desek

Druh desky	Tloušťkové bobtnání (%)	Nevratné tloušťkové změny (%)
Řepková deska (reference)	54,7 (7,7)	30,5 (8,9)
Řepková deska (hydrotermická mod.)	63,1 (7,1)	37,8 (12,2)
Řepková deska (alkalická mod.)	70,7 (9,8)	29,8 (8,7)
DTD	24,8 (4,0)	8,6 (9,3)
OSB	29,4 (15,0)	12,1 (16,5)

V závorkách jsou uvedeny variační koeficienty v %

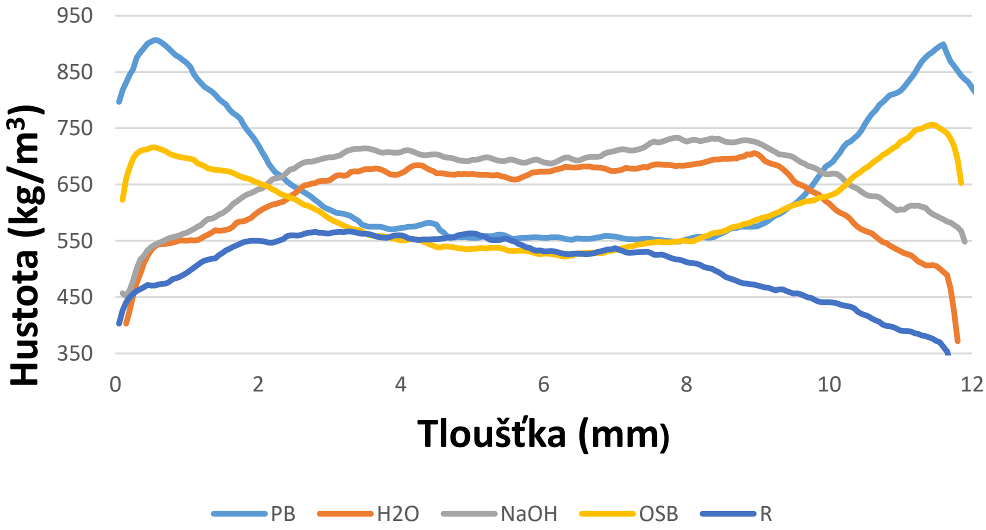


Obrázek 6 Pevnost v tahu kolmo k rovině desky: 1 – deska z neupravených třísek, 2 – deska z hydrotermicky upravených třísek, 3 – deska z alkalicky upravených třísek, 4 – dřevotřísková deska, 5 – OSB deska

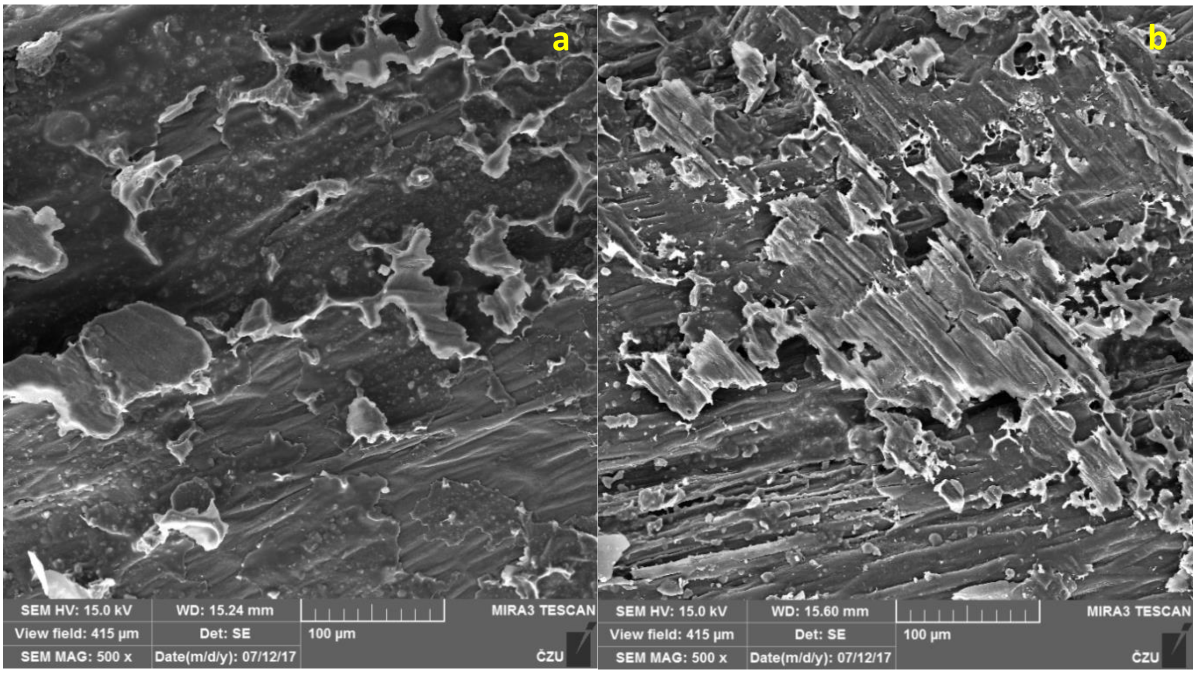
Tabulka 5 Statistická významnost rozdílů z obrázku 6 (dle Tukeyova HSD testu, α=0,05)

Druh desky	**1**	**2**	**3**	**4**	**5**
1		s.	s.	s.	s.
2	s.		s.	n.s.	s.
3	s.	s.		s.	n.s.
4	s.	n.s.	s.		n.s.
5	s.	s.	n.s.	n.s.	

s.- statisticky významný rozdíl, n.s. – statisticky nevýznamný rozdíl (1 – deska z neupravených třísek, 2 – deska z hydrotermicky upravených třísek, 3 – deska z alkalicky upravených třísek, 4 – dřevotřísková deska, 5 – OSB deska)



Obrázek 7 Vertikální hustotní profil desek (PB – dřevotřísková deska, H2O – hydrotermická modifikace, NaOH – alkalická modifikace, OSB – OSB deska, R – neupravené třísky)



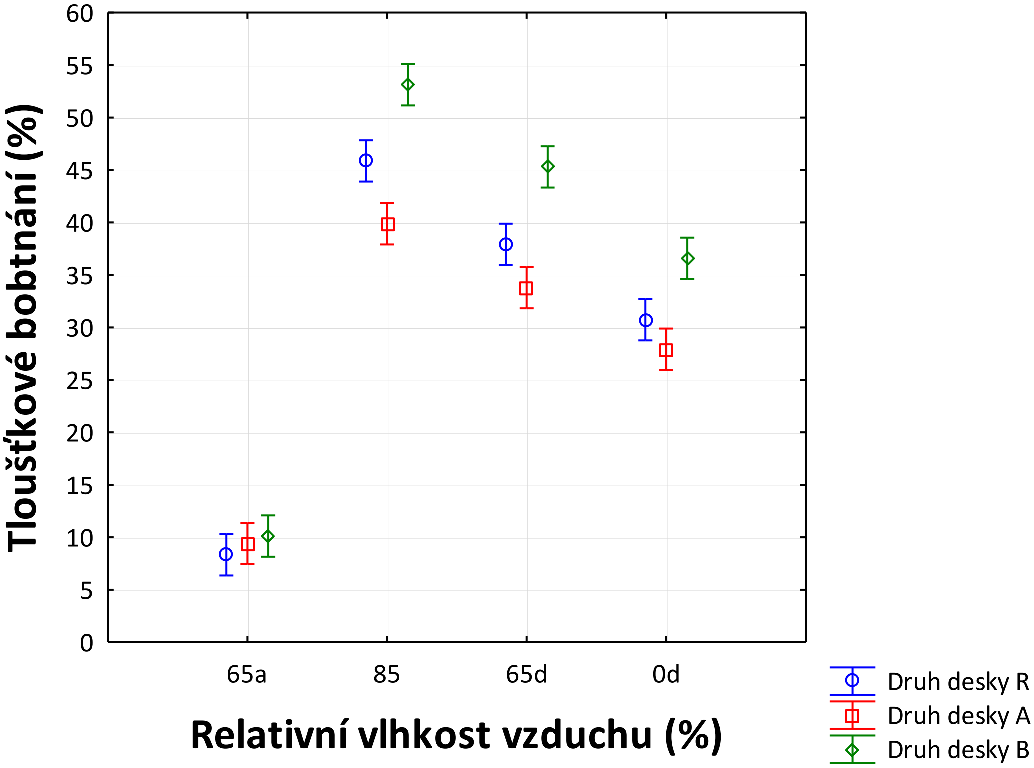
Obrázek 8 SEM mikroskopie vzorků po zkoušce rozlupčivosti, (a) neupravené třísky – chyba adheze, (b) alkalicky upravené třísky – chyba koheze částice

Hlubší analýza mechanických vlastností takto vyrobených desek ukázala, že zatímco desky vyrobené z hydrotermicky upravených třísek dosáhly vyšší pevnosti v ohybu oproti deskám vyrobeným z alkalicky upravených třísek, plastický potenciál obou materiálů byl v rámci statistické chyby srovnatelný. Referenční dřevotřísková deska, která dosáhla srovnatelné pevnosti, jako deska z hydrotermicky upravených řepkových třísek měla potom plastický potenciál statisticky významně nižší, než řepkové desky z modifikovaných třísek (Sikora a kol. 2018). Využitím modifikovaných řepkových třísek lze tedy významně navýšit absorpční kapacitu kompozitních materiálů. Této vlastnosti lze využít například v automobilovém průmyslu pro výrobu komponent absorbující energii při nárazu.

Výše uvedeným výsledkům odpovídají i výsledky z analýzy ohýbatelnosti materiálů, kdy průhyb na mezi úměrnosti byl nižší pro desky z alkalicky upravených třísek oproti deskám z hydrotermicky upravených třísek, avšak průhyb na mezi pevnosti byl srovnatelný pro oba dva typy desek. Oproti referenčním DTD a ODB deskám vykazovaly oba dva typy desek výrazně vyšší průhyby na mezi pevnosti, a tedy i lepší ohýbatelnostní charakteristiky (Gaff a kol. 2018).

Cílem disertační práce je i zhodnocení vlivu modifikace povrchu lignocelulózových elementů plazmatem na vlastnosti kompozitního materiálu vyrobeného z těchto modifikovaných elementů a optimalizace vstupních parametrů a lisovacích podmínek při výrobě modifikovaných materiálů na bázi ligninu a celulózy za účelem získání kompozitního materiálu požadovaných vlastností. Za tímto účelem byly plazmaticky upraveny třísky ze stonků pšenice ozimé a byly sledovány vlastnosti třískových desek vyrobených z takto upravených třísek. Za použití močovinoformaldehydového lepidla byly vyrobeny desky o nominální hustotě 540 kg/m^3 a tloušťce 6 mm. Byly zvoleny dva stupně plazmatické modifikace (nízkoteplotní plazma generované za studeného tlaku). V první variantě (modifikace A) byl výkon generátoru nastavený na napětí 26,9 V s proudem 6,9 A, ve druhé variantě (modifikace B) se použilo maximálního možného napětí 28,6 V s proudem 8,7 A). Lisovací cyklus byl optimalizován tak, aby bylo dosaženo vertikálního hustotního profilu ve tvaru M, tedy aby nejnižší hustota byla uprostřed desky a nejvyšší na jejím povrchu. Rovněž musel být lisovací cyklus upravený oproti lisování dřevotřískových desek tak, aby nedošlo k tvorbě prasklin uprostřed desky. Při lisování třískových desek ze slámy za použití adhesiva na bázi vody jsou díky povrchu slámy desky na praskání náchylnější, než při lisování třískových desek ze dřeva. Bližší popsání lisovacího cyklu je uvedeno v příslušné publikaci Hýsek a kol. 2018b.

Výsledky ukázaly statisticky významný vliv plazmatické předúpravy třísek na výsledné vlastnosti kompozitu. Došlo ke zvýšení mechanických vlastností desek v obou případech plazmatické modifikace, avšak došlo zároveň ke zhoršení fyzikálních vlastností. Desky vyrobené ze třísek upravených vyšším stupněm plazmatické modifikace vykazovaly výrazně vyšší rovnovážnou vlhkost a tloušťkové bobtnání, nežli desky referenční (povrchově neupravené). Tloušťkové bobtnání desek při absorpci a desorpci je zachyceno na obrázku 9. Nejvyšší tloušťkové bobtnání vykazovaly desky typu B a nejnižší desky z referenčních třísek (označení R). Výjimkou je první klimatizační stupeň (20°C/RH 65%, absorpční cyklus), kde bylo zjištěno vyšší tloušťkové bobtnání u referenčních desek, nežli u desek vyrobených z modifikovaných třísek nižším stupněm plazmatické modifikace, avšak tento rozdíl není statisticky významný (Tabulka 6).



Obrázek 9 Graf závislosti tloušťkového bobtnání na relativní vlhkosti vzduchu (a – absorpce, d – desorpce)

Tabulka 6 Statistická významnost rozdílů z obrázku 9 (dle Tukeyova HSD testu, α=0,05)

T = 20°C, RH = 65%, Absorpce			
	R	A	B
R		n.s.	s.
A	n.s.		n.s.
B	s.	n.s.	

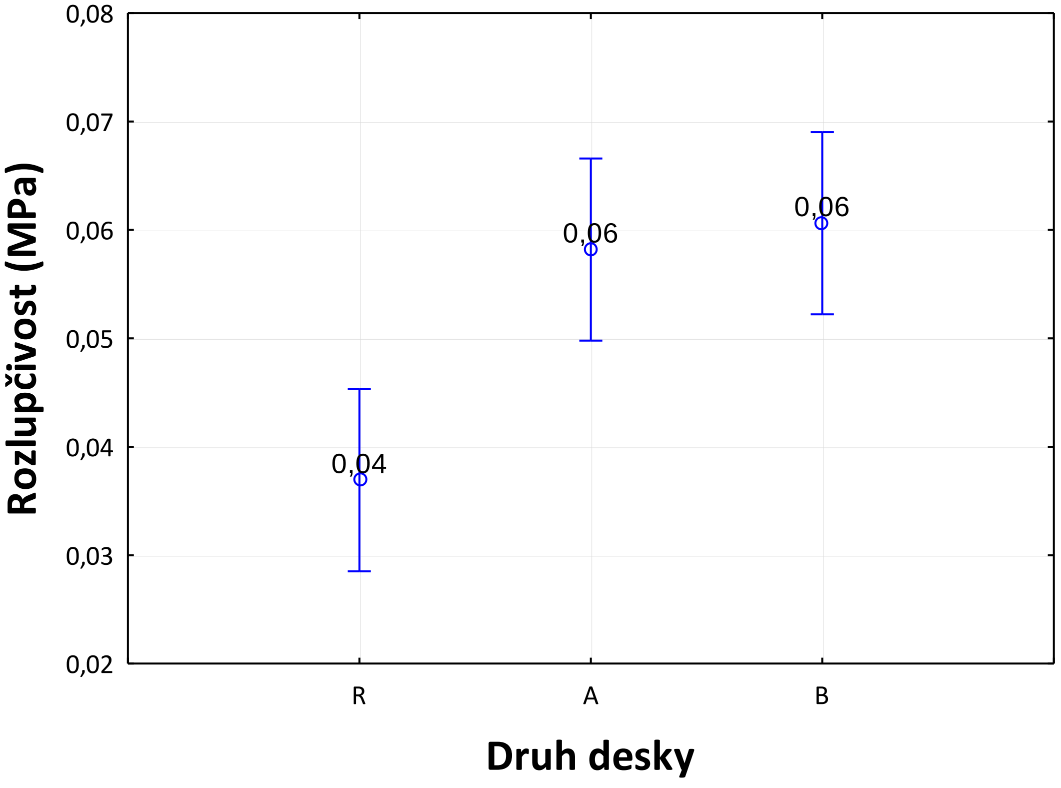
T = 20°C, RH = 85%			
	R	A	B
R		s.	s.
A	s.		s.
B	s.	s.	

T = 20°C, RH = 65%, Desorpce			
	R	A	B
R		s.	s.
A	s.		s.
B	s.	s.	

T = 103°C, Desorpce			
	R	A	B
R		n.s.	s.
A	n.s.		s.
B	s.	s.	

s.- statisticky významný rozdíl, n.s. – statisticky nevýznamný rozdíl

Obrázek 10 potom zachycuje pevnost v tahu kolmo k rovině vyrobených desek a v tabulce 7 jsou uvedeny údaje o statistické významnosti rozdílů. Z výsledků je patrné, že úprava povrchu plazmatem způsobila v obou případech statisticky významný nárůst rozlupčivosti. Neprokázal se však rozdíl mezi různými variantami plazmatické modifikace.



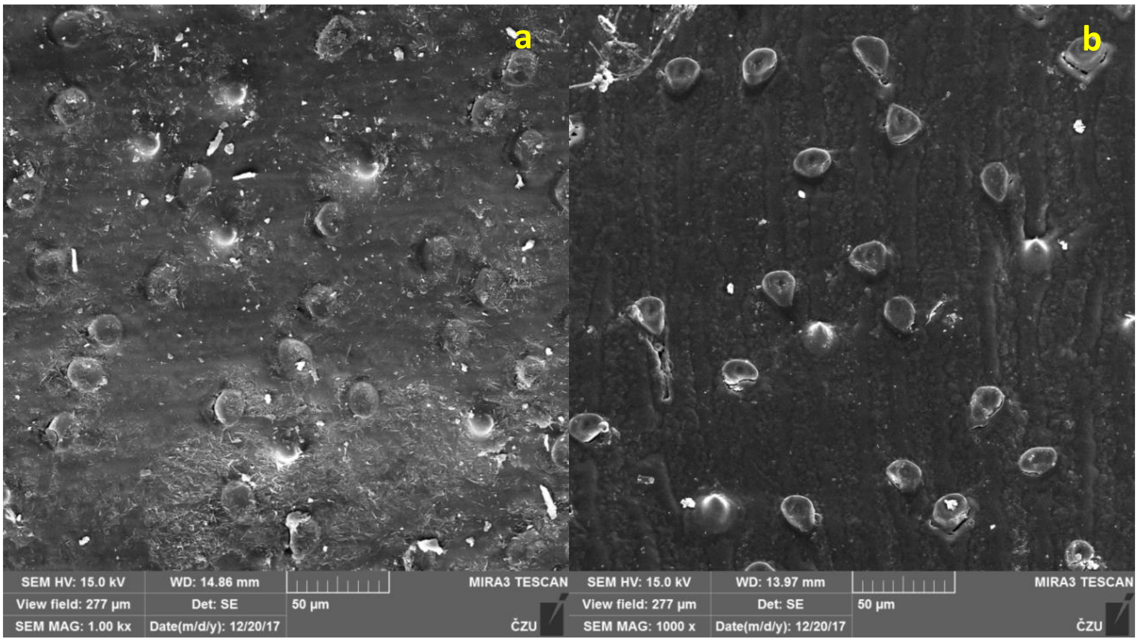
Obrázek 10 Pevnost v tahu kolmo k rovině desky v závislosti na plazmatické úpravě (desky ze stonků pšenice ozimé)

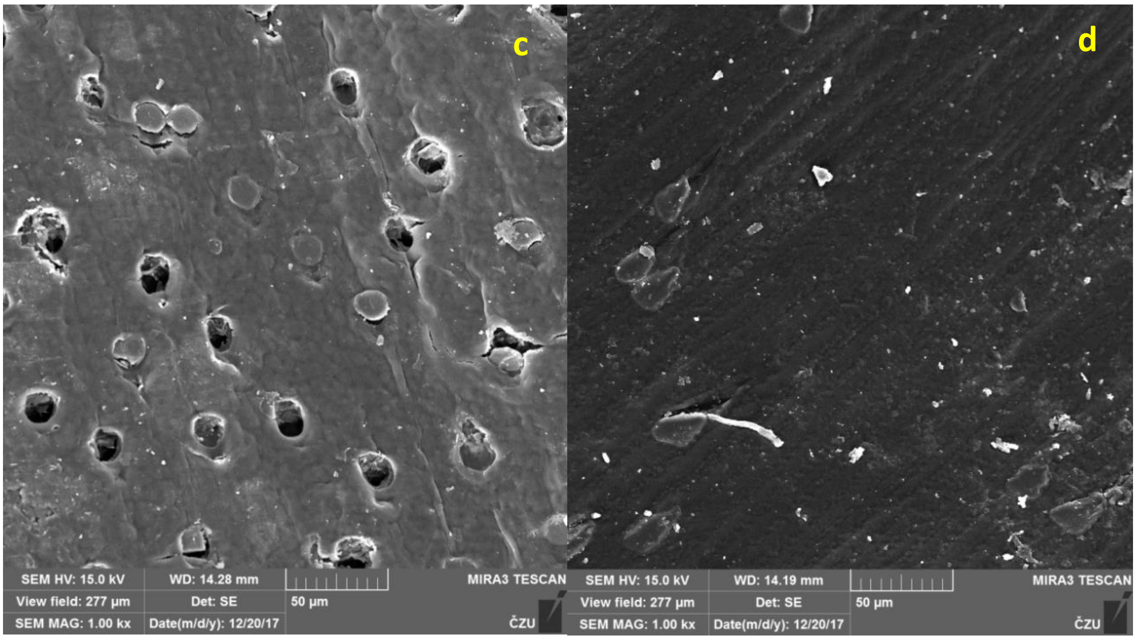
Tabulka 7 Statistická významnost rozdílů z obrázku 10 (dle Tukeyova HSD testu, α=0,05)

Druh desky	R	A	B
R		s.	s.
A	s.		n.s.
B	s.	n.s.	

s.- statisticky významný rozdíl, n.s. – statisticky nevýznamný rozdíl

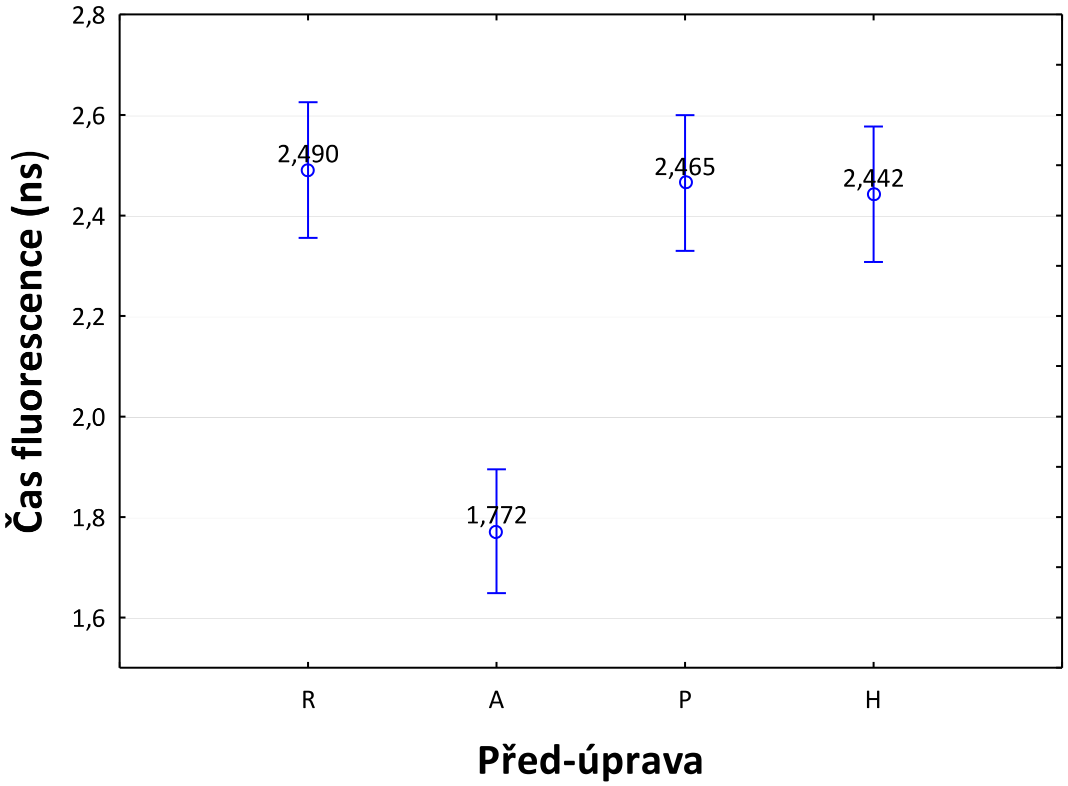
Za účelem porovnání efektu hydrotermické, chemické a plazmatické úpravy na jednom materiálu byly vybrány plevy pšenice ozimé. Plevy obilovin mají výborné tepelně-izolační vlastnosti, a aby byla tato vlastnost částečně přenesena i do lisovaných desek, byla zvolena nižší hustota desek. Za použití močovinoformaldehydového adhesiva byly vyrobeny lisované desky o nominální hustotě 450 kg/m^3. Přesná metodika experimentů je uvedena v manuskriptu Hýsek a kol. 2018a, manuskript je momentálně v recenzním řízení v časopisu Industrial Crops and Products. Elektronová mikroskopie jasně ukázala vliv modifikací na strukturu povrchu plev (obrázek 11). Z obrázku je patrné, že u referenčních plev jsou jizvy po odpadnutých trichomech v povrchové vrstvě (epidermis), zatímco u hydrotermicky upravených plev vyčnívají nad povrch, protože povrchová vrstva chybí. Alkalická modifikace dokonce způsobila rozrušení jizev. Plazma nezpůsobilo žádné viditelné porušení povrchu.





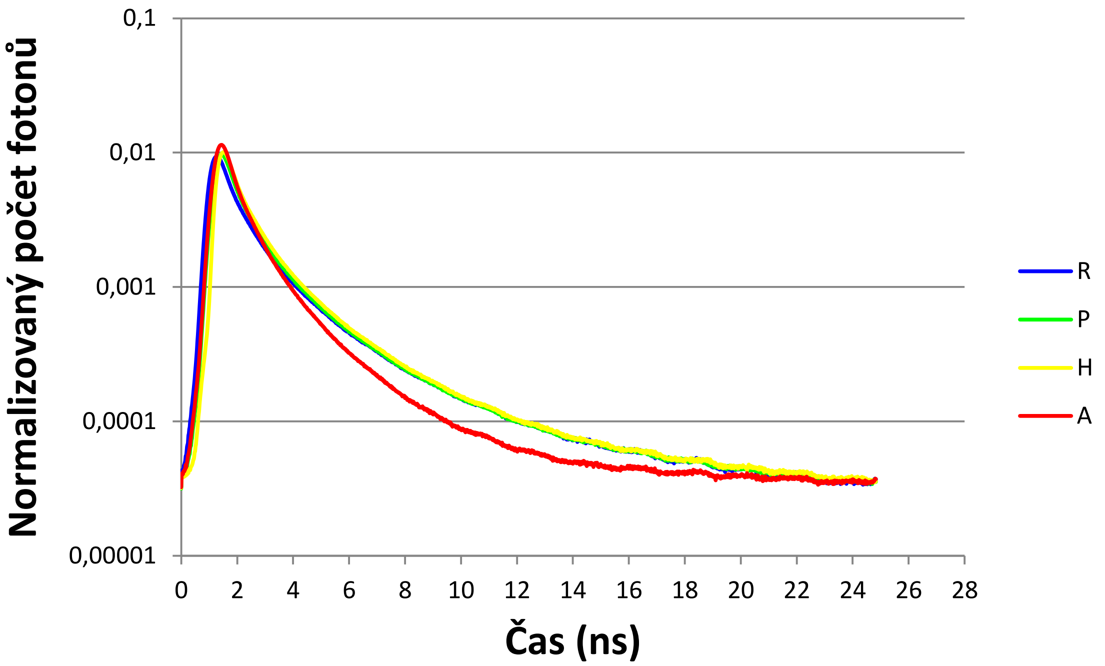
Obrázek 11 Snímky z elektronového mikroskopu povrchu plev (a) neupravené plevy, (b) hydrotermicky upravené plevy, (c) alkalicky upravené plevy a (d) plazmaticky upravené plevy

K pozorování změn v celém objemu modifikovaných plev bylo využito moderní metody v podobě fluorescenční časové zobrazovací mikroskopie (fluorescence lifetime imaging microscopy (FLIM)). Obrázek 12 zachycuje závislost průměrného času trvání fluorescence na typu modifikace. Z grafu je patrný podstatný pokles fluorescence life time u alkalicky modifikovaných plev, který poukazuje na vyšší obsah ligninu.



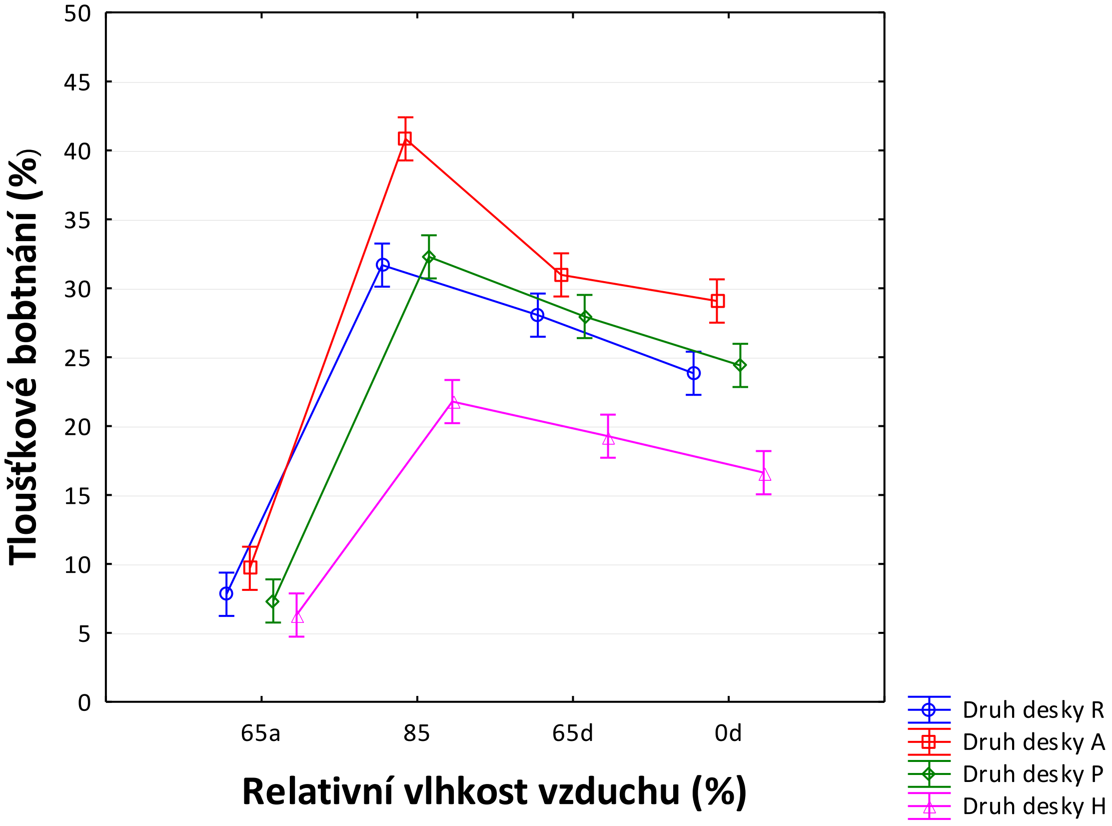
Obrázek 12 Fluorescence lifetime modifikovaných plev, R - neupravené plevy, A - alkalicky upravené plevy, P - plazmaticky upravené plevy, H - hydrotermicky upravené plevy

Pokud zobrazíme normalizovaný počet fotonů zachycených na detektoru jako funkci času (obrázek 13), můžeme opět pozorovat změnu tvaru křivky u alkalicky modifikovaných plev. Histogram normalizovaného počtu fotonů alkalicky upraveného vzorku dosahuje nejvyššího vrcholu a pak prudce klesá. Tento průběh opět odpovídá vyššímu podílu ligninu, nežli u referenčního vzorku. Přestože bylo očekáváno, že množství ligninu po alkalické modifikaci bude nižší (Li a kol. 2007; Tran a kol. 2014), FLIM analýza ukazuje na vyšší obsah ligninu v alkalicky modifikovaných plevách, než v referenčních. Tento pozorovaný výsledek koresponduje i s provedenou FTIR analýzou a lze ho vysvětlit snížením obsahu celulózy a hemicelulóz v důsledku jejich částečného odbourání. Tato reakce nastává, pokud na lignocelulózový materiál působí alkalický roztok a je nazýván peeling reaction (Green a kol. 1977).



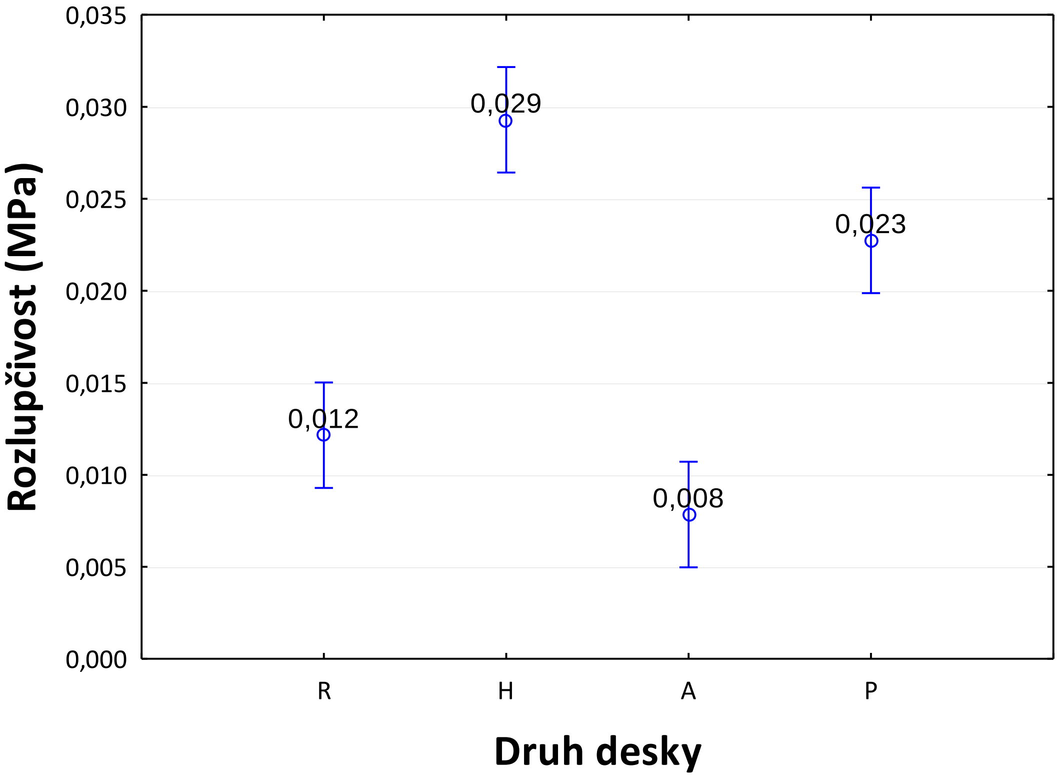
Obrázek 13 Fluorescence decay curves – Histogramy normalizovaného počtu fotonů, R - neupravené plevy, A - alkalicky upravené plevy, P - plazmaticky upravené plevy, H - hydrotermicky upravené plevy

Provedené způsoby modifikace měly vliv i na rovnovážnou vlhkost plev, kdy nejvyšší rovnovážné vlhkosti dosáhly plevy modifikované alkalicky a nejnižší plevy modifikované hydrotermicky. Zvýšení hygroskopicity plev se projevilo i ve zvýšené navlhavosti, nasáklivosti a bobtnání desek z alkalicky upravených plev. Tloušťkové bobtnání desek je uvedeno na obrázku 14 a můžeme pozorovat, že nejnižší tloušťkové bobtnání bylo dosaženo hydrotermicky upravenými deskami. Hydrotermická modifikace snížila obsah karbohydrátů v plevách, zejména xylanů a arabinanů (Carvalho a kol. 2017), což kromě snížení rovnovážné vlhkosti plev vedlo i ke snížení bobtnání vyrobených desek.



Obrázek 14 Tloušťkové bobtnání desek při různých klimatizačních stupních, R - neupravené plevy, A - alkalicky upravené plevy, P - plazmaticky upravené plevy, H - hydrotermicky upravené plevy

Rozlupčivost desek z plev (obrázek 15) dosahovala vesměs velmi malých hodnot, což bylo způsobeno jak vertikálním hustotním profilem, tak nízkou hustotou desek. Jak plazmatická, tak hydrotermická modifikace zvýšily pevnost v tahu kolmo k rovině desky. Zlepšení adheze zapříčinilo působení vyšší teploty, což může být perspektivní způsob modifikace nejen pro úpravu alternativních materiálů, ale i dřeva (Fang a kol. 2017; Tavasolli a kol. 2018). Naproti tomu chemická modifikace snížila pozorovanou mechanickou vlastnost desek. Pravděpodobně se jednalo o příliš agresivní úpravu, která narušila strukturu a zhoršila pevnost plev (pozorováno i pomocí SEM). Snížení rozlupčivosti desek mohl způsobit i zbytkový hydroxid sodný, který nebyl z plev zcela dokonale vymyt. Zatímco močovinoformaldehydová lepidla vytvrzují v kyselém prostředí, hydroxid sodný způsobil alkalické prostředí, což mohlo dále způsobit nedokonalé vytvrzení adhesiva nebo dokonce vytvrzený spoj narušit.



Obrázek 15 Rozlupčivost desek v závislosti na modifikaci, R - neupravené plevy, A - alkalicky upravené plevy, P - plazmaticky upravené plevy, H - hydrotermicky upravené plevy

Kromě výše uvedených způsobů úpravy plev může vést ke zvýšení mechanických vlastností kompozitů na bázi plev i enzymatická modifikace (Mamun and Bledzki 2013). Pro porovnání účinku enzymatické modifikace byly zvoleny třísky ze slámy pšenice ozimé a řepky ozimé. Zvolená enzymy byly: pektináza, xylanáza a směs xylanýzy a pektinázy. Podmínky zpracování třísek jsou uvedeny v tabulce 8. Úprava probíhala za využití přístroje Linitest, s poměrem lázně 1:5.

Tabulka 8 Podmínky enzymatické úpravy

Č. úpravy	Složení lázně	Podmínky	Dokončující operace
1	5% z v.m Texazym BFE 0,5 ml/l Nofome AF	teplota 55°C čas 2 hodiny	Proplach teplá studená voda Volné sušení
2	5% z v.m. Texazym SER 7 conc.	teplota 55°C čas 2 hodiny	Proplach teplá studená voda Volné sušení
3	5% z v.m. Texazym DLG new 0,5 ml/l Nofome AF	teplota 55°C čas 2 hodiny	Proplach teplá studená voda Volné sušení

Legenda: Texazym BFE - hlavní enzymová složka pektináza

Texazym SER 7 conc. - hlavní enzymové složky kombinace xylanázy a pektinázy

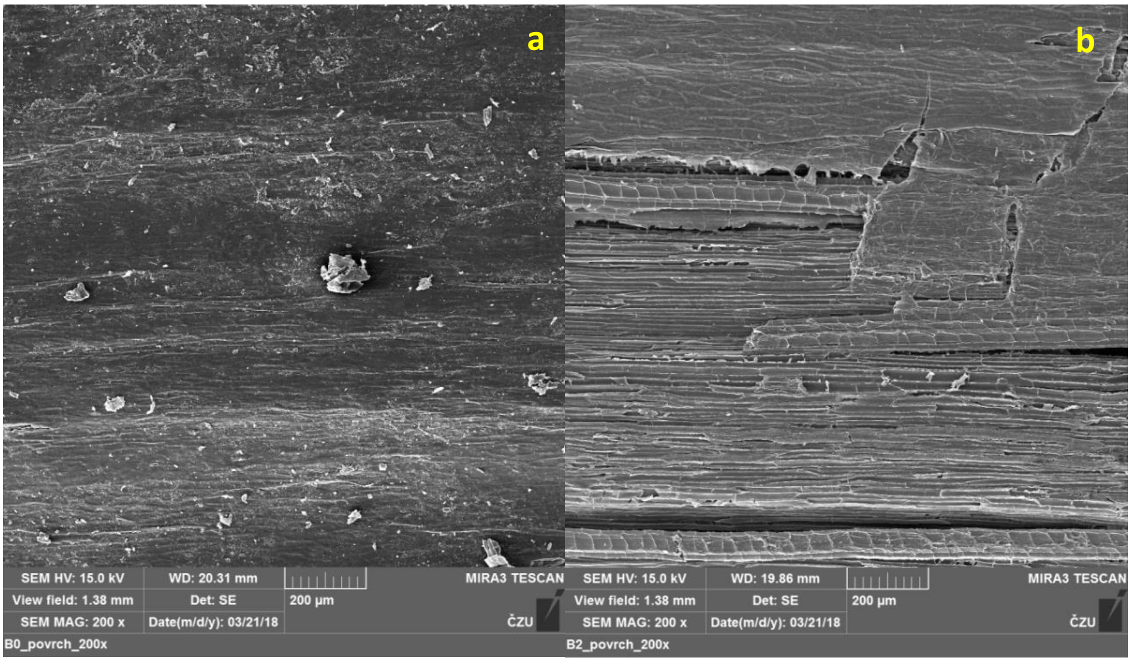
Texazym DLG new - hlavní enzymová složka xylanáza

Nofome AF – odvzdušňovací, odpěňovací, smáčení přípravek

Enzymatická úprava měla vliv na povrchové napětí třísek (tabulka 9), povrchové napětí bylo měřeno pomocí testovacích inkoustů Gamin. Nejvyššího nárůstu bylo dosaženo u řepkových třísek za využití nálevu č. 1, kdy povrchové napětí vzrostlo z 34 mN/m na 42 mN/m. Bylo možné pozorovat i narušení povrchu vlivem působení enzymů. Byl rozrušen povrch jak na vnitřní, tak na vnější straně stonku. Obrázek 16 znázorňuje povrch řepkové třísky před a po úpravě.

Tabulka 9 Povrchové napětí enzymaticky upravených třísek

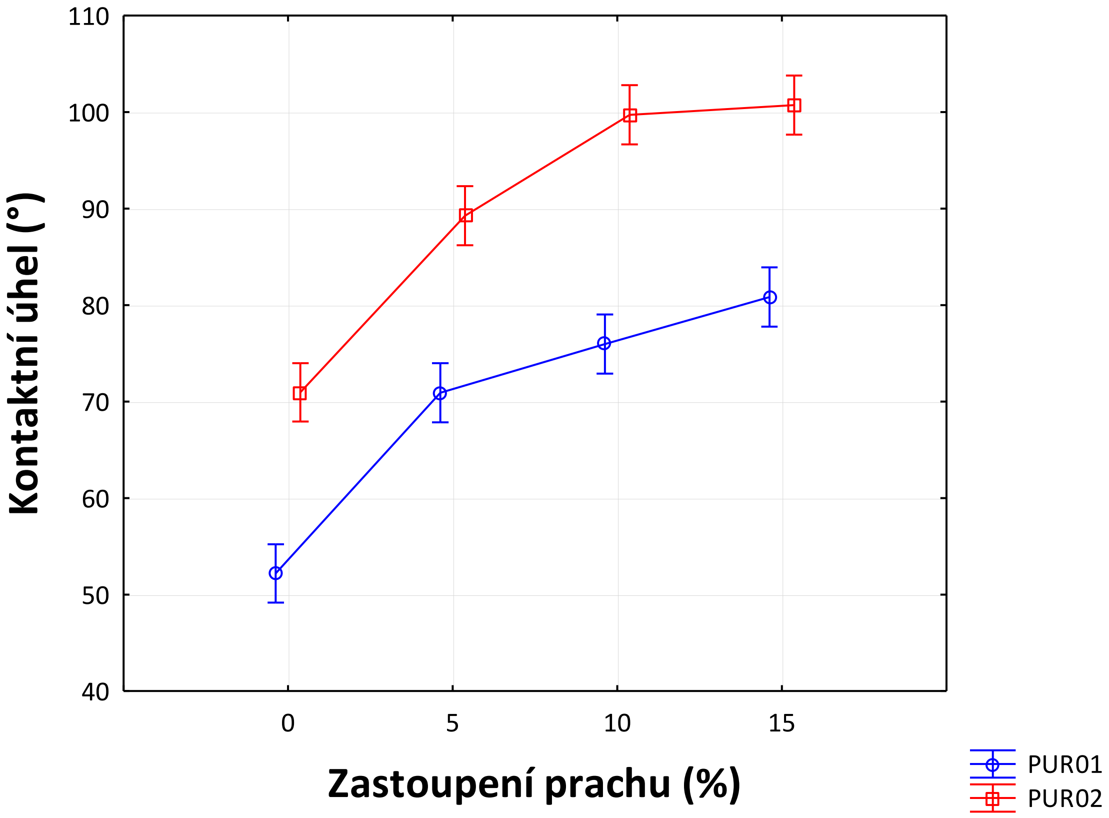
Úprava	**Druh slámy**	**Povrchové napětí (mN/m)**
neupravené	pšenice	26±2
1	pšenice	26±2
2	pšenice	30±2
3	pšenice	26±2
neupravené	řepka	34±2
1	řepka	42±2
2	řepka	38±2
3	řepka	38±2



Obrázek 16 Snímky z elektronového mikroskopu povrchu řepkových třísek (a) neupravený povrch, (b) povrch upravený enzymaticky (č. úpravy 2)

Enzymatická úprava třísek ze slámy pšenice a řepky měla jednoznačný vliv na jejich vlastnosti a na základě předchozích výsledků můžeme konstatovat, že změna těchto vlastností ovlivní i výsledné vlastnosti kompozitního materiálu vyrobeného z takto upravených třísek.

Vlastnosti kompozitního materiálu jsou determinovány vlastnostmi matrice, vyztužovacích prvků a vlastnostmi mezifáze. Během řešení disertační práce proto nebyla věnována pozornost pouze vyztužovacím prvkům v kompozitních materiálech, ale i matrici. Byl zjišťován vliv modifikace polyuretanového adhesiva pomocí drobných prachových částic z recyklované polyuretanové pěny na vlastnosti adhesiva. Experimenty byly prováděny dle metodiky uvedené v publikaci Hýsek a kol. 2018d a výsledky ukázaly, že přídavkem polyuretanového recyklované prášku došlo ke zvýšení pevnosti spojů vařených ve vodě, avšak vzorky ponořené do vody za laboratorních podmínek vykazovaly pokles pevnosti ve smyku s rostoucím obsahem prášku. Kontaktní úhel mezi dřevem a kapkou adhesiva se zvyšoval s rostoucí koncentrací prášku (obrázek 17), avšak nebyl pozorován žádný vliv tohoto kontaktního úhlu na pevnost lepeného spoje.



Obrázek 17 Vliv množství prášku a adhesiva na kontaktní úhel

6 Závěry a přínos

Hlavní přínos této práce spočívá v oblasti před-úpravy vstupních materiálů za účelem kvalitnějšího spojení s adhesivem. Tato otázka je řešena jak z pohledu lignocelulózových částic, tak z pohledu adhesiva. Předkládaný výzkum poskytuje data a informace jak o samotném modifikovaném materiálu, tak o vlastnostech výsledného kompozitu a zkoumá i příčiny, které dané změny vlastností způsobily. V předkládané disertační práci je zhodnocen vliv různých druhů modifikace povrchu lignocelulózových materiálů na vlastnosti kompozitních materiálů vyrobených z takto upraveného materiálu. Konkrétně se jedná o chemickou, termickou, enzymatickou a plazmatickou modifikaci posklizňových zbytků zemědělských plodin, a to plodin, jejichž osevní plochy v České republice a Evropské unii jsou velké a jejichž posklizňové zbytky dostupné ve velkých množstvích (pšenice ozimá, řepka ozimá).

Kromě hlavního přínosu tohoto výzkumu v podobě poznatků týkajících se využití modifikace povrchu vstupní lignocelulózové suroviny pro výrobu kompozitních materiálů a technologie výroby těchto materiálů práce přispívá i k řešení problematiky nedostatku dřevní suroviny pro dřevozpracující průmysl. Práce má tak jednoznačný přínos pro praxi v podobě vývoje technologie výroby kompozitních materiálů z posklizňových zbytků řepky ozimé a pšenice ozimé, přičemž jsou zohledněny jak ekonomické, tak technologické aspekty. Práce však nemá charakter pouze aplikovaného výzkumu, předkládá cenná data i pro výzkum základní, zejména v podobě zachycení vlivu příslušné modifikace na chemické složení modifikovaného materiálu. V neposlední řadě přispívá svými poznatky i do politicko-vědní debaty o využívání obnovitelných zdrojů surovin pro uspokojování potřeb společnosti a o trvale udržitelném rozvoji.

Z disertační práce mohou být vyvozeny následující hlavní závěry:

- Celkové prvkové složení a prvkové složení povrchu zkoumaných posklizňových zbytků bylo nejvýznamněji ovlivněno chemickou modifikací v alkalickém prostředí. Provedené modifikace měly vliv i na makromolekulární složení modifikovaného materiálu, kde alkalická modifikace zapříčinila pokles obsahu celulózy a hemicelulóz.

- Všechny vybrané způsoby modifikace ovlivnily povrchové vlastnosti zkoumaných materiálů. Byly pozorovány morfologické změny v podobě narušení struktury povrchu. Za nejagresivnější způsob modifikace lze z tohoto pohledu opět uvést chemický a enzymatický způsob. Byl zaznamenán vliv modifikace na povrchové napětí posklizňových zbytků. Chemická, hydrotermická, plazmatická i enzymatická modifikace zvýšily povrchové napětí modifikovaných materiálů, čímž byla zlepšena jejich afinita k vodou ředitelným adhesivům.
- Vybrané způsoby modifikace statisticky významně ovlivnily modifikovaný materiál i v celém svém objemu. Zatímco hydrotermická a plazmatická modifikace snížily rovnovážnou vlhkost plev, alkalická ji zvýšila.
- Ukázal se vliv modifikace na termodynamické vlastnosti posklizňových zbytků. Tento vliv lze dokumentovat vlivem modifikace na rozdílné součinitele tepelné vodivosti desek vylisovaných z modifikovaných pšeničných plev a také vlivem plazmatické úpravy třísek z pšeničné slámy na vertikální hustotní profil vylisovaných desek.
- Byl vyvinut lisovací program pro výrobu desek z posklizňových zbytků zemědělských plodin za využití močovinoformaldehydového adhesiva s přesně definovaným průběhem a vstupní vlhkostí třísek s naneseným adhesivem tak, aby při výrobě desek nedocházelo k tvorbě trhlin v deskách. Lisovací program využívaný při výrobě dřevotřískových desek nebylo možné použít z důvodu rozdílných vlastností vstupního materiálu.
- Změny vlastností modifikovaných částic se následně projevily i na vlastnostech vyrobených kompozitních materiálů. Byl pozorován vliv modifikace jak na fyzikální, tak mechanické vlastnosti kompozitního materiálu. Plazmatická úprava zapříčinila statisticky významný nárůst pevnosti v ohybu a rozlupčivosti vyrobených desek a zároveň mírně zvýšila jejich navlhavost. Tloušťkové bobtnání však významně ovlivněno nebylo. Hydrotermická úprava se ukázala jako velmi perspektivní. Ze všech způsobů modifikace zapříčinila nejvyšší nárůst rozlupčivosti desek z plev i řepkové slámy. Zároveň bylo sníženo tloušťkové bobtnání desek z plev. Tloušťkové bobtnání desek z řepkové slámy však narostlo. Zvolená chemická modifikace způsobila nejvyšší afinitu upraveného materiálu k vlhkosti, desky z alkalicky upravených posklizňových

zbytků vykazovaly velkou navlhavost, nasáklivost i tloušťkové bobtnání. Spoj adhesiva a alkalicky modifikované třísky však může být hodnocen jako velmi pevný.

- Výsledky provedené SWOT analýzy ukazují, že posklizňové zbytky řepky ozimé jsou velmi perspektivním materiálem pro výrobu kompozitních materiálů.
- Modifikace jednosložkového vodou vytvrzujícího polyuretanového adhesiva polyuretanovým prachem vedla ke zvýšení pevnosti spojů zatížených působením tepla a vody. Vzorky ponořené ve studené vodě však vykazovaly snížení pevnosti lepeného spoje při nárůstu obsahu polyuretanového prachu.

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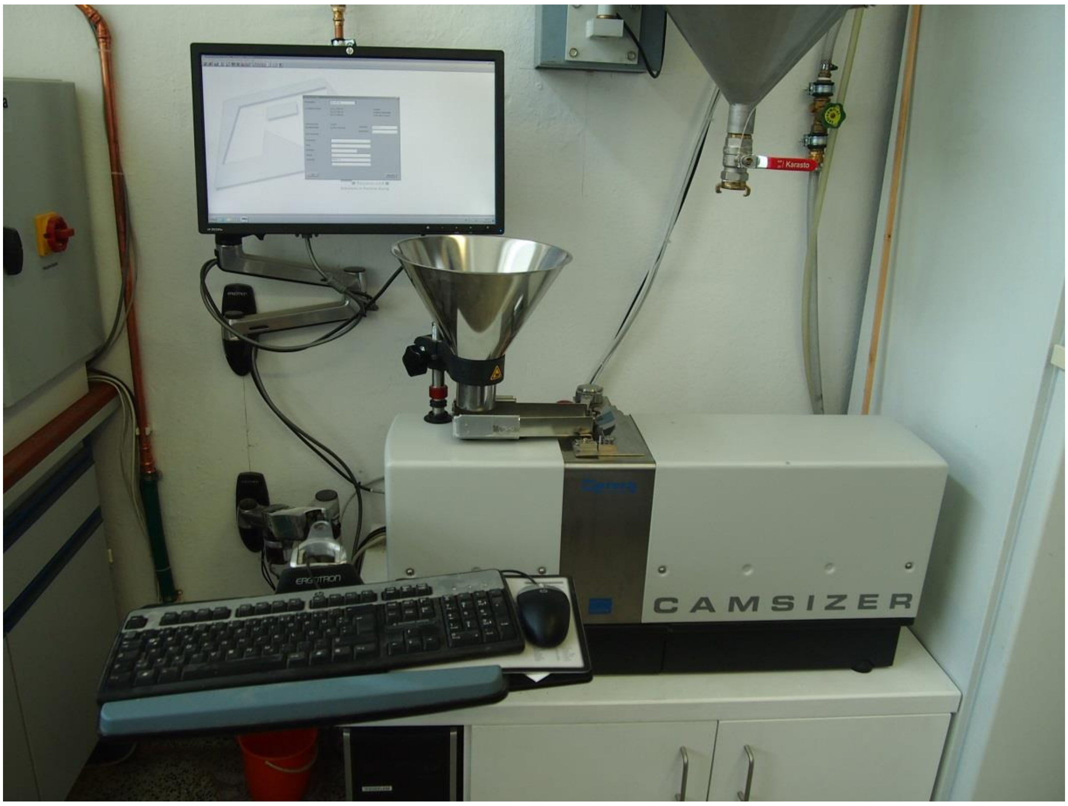
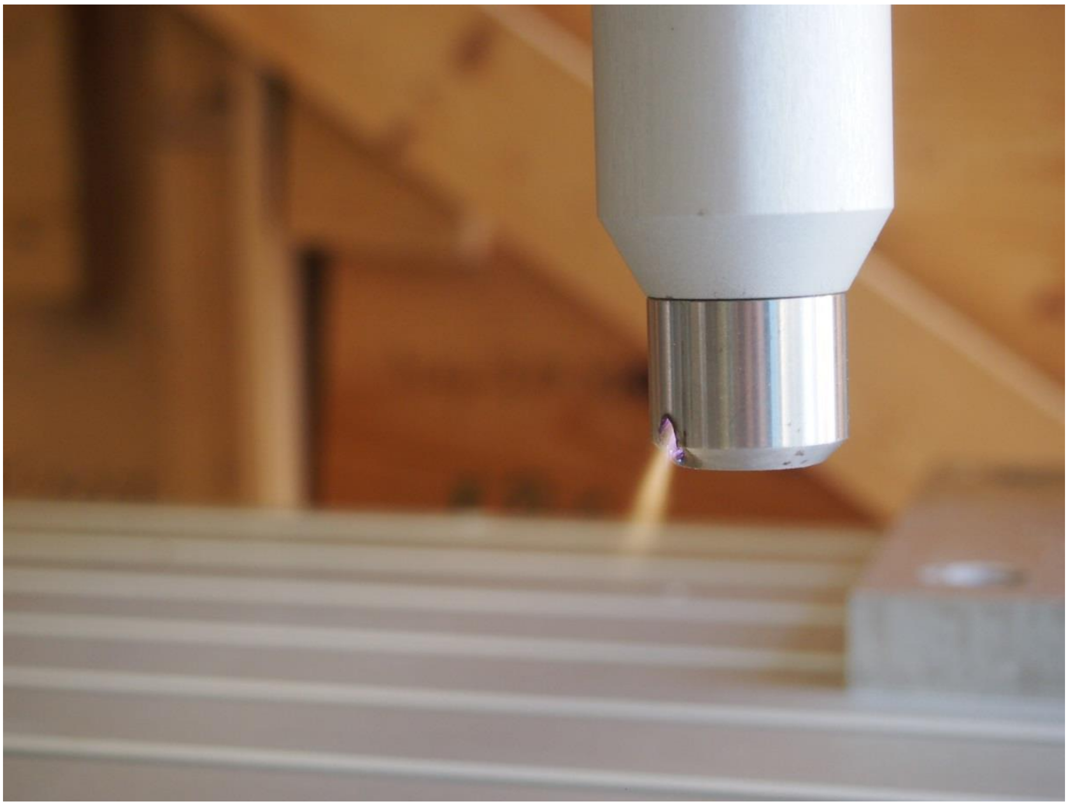
8 Seznam příloh

9 Přílohy



Příloha 1 Camsizer – sestava pro zjišťování frakce třísek

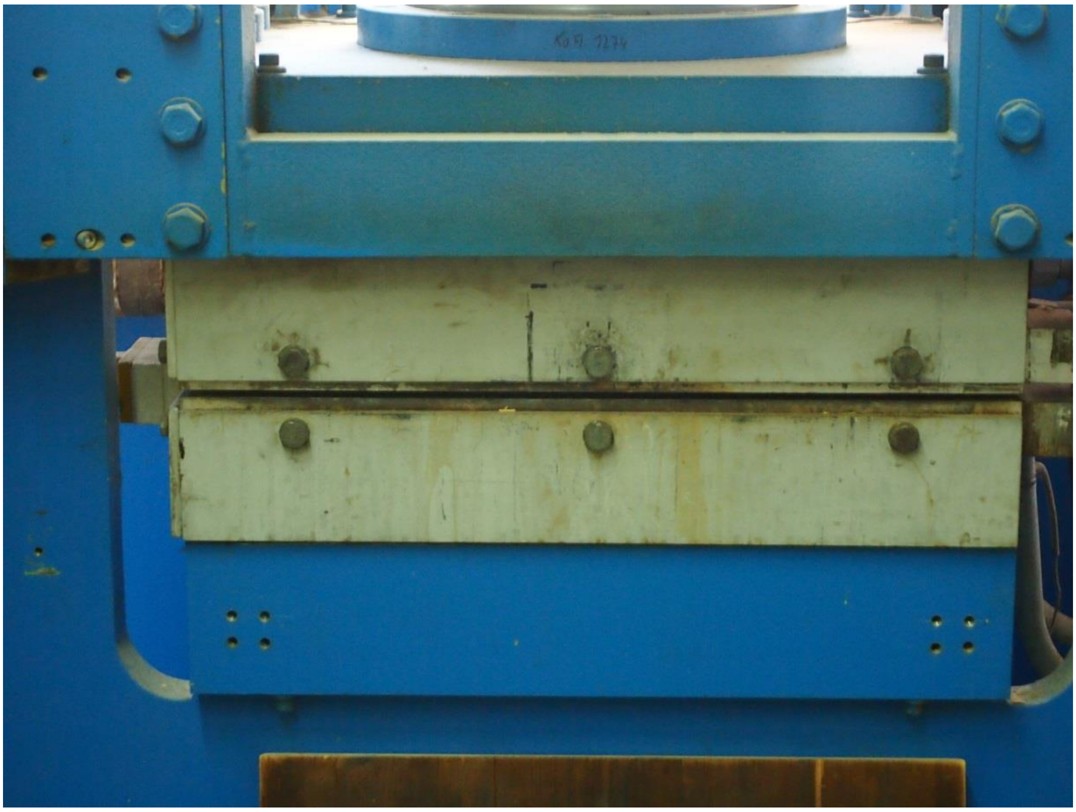


Příloha 2 Tryska pro aplikaci plazmatu

Příloha 3 Přesné zjišťování vlhkosti třísek po aplikaci adhesiva pomocí přístroje Ultra X

Příloha 4 Předlisování třískových desek

Příloha 5 Předlisovaný koberec (třísky ze slámy pšenice ozimé)



Příloha 6 Lisování desek pomocí lisu Höfer

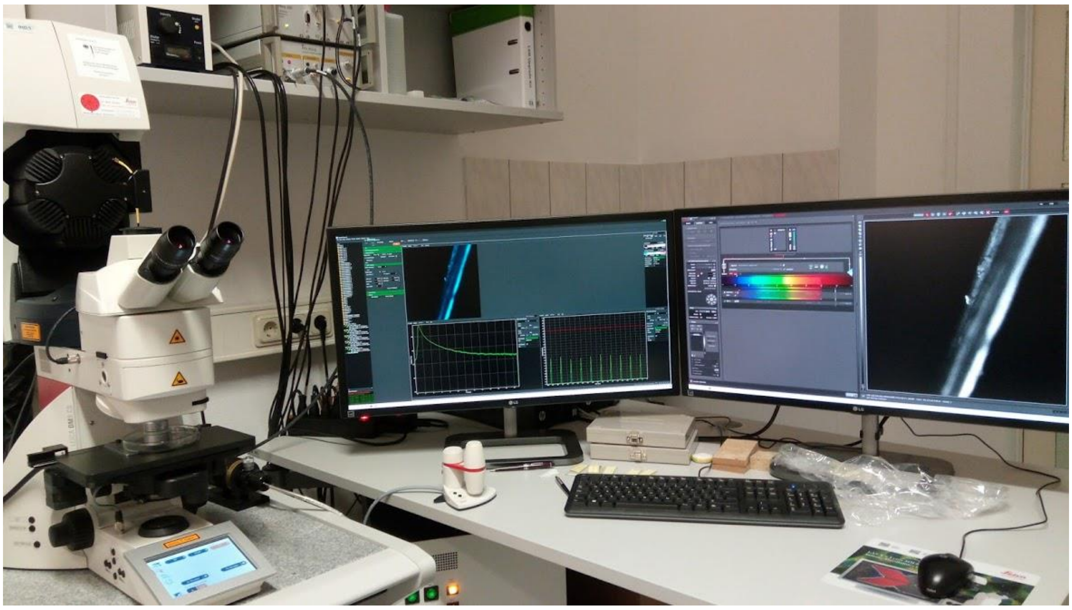
Příloha 7 Vylisovaná deska ze slámy pšenice ozimé

Příloha 8 Přesná kontrola tloušťky desky po vylisování pomocí úchylkoměru (deska z plev pšenice ozimé)

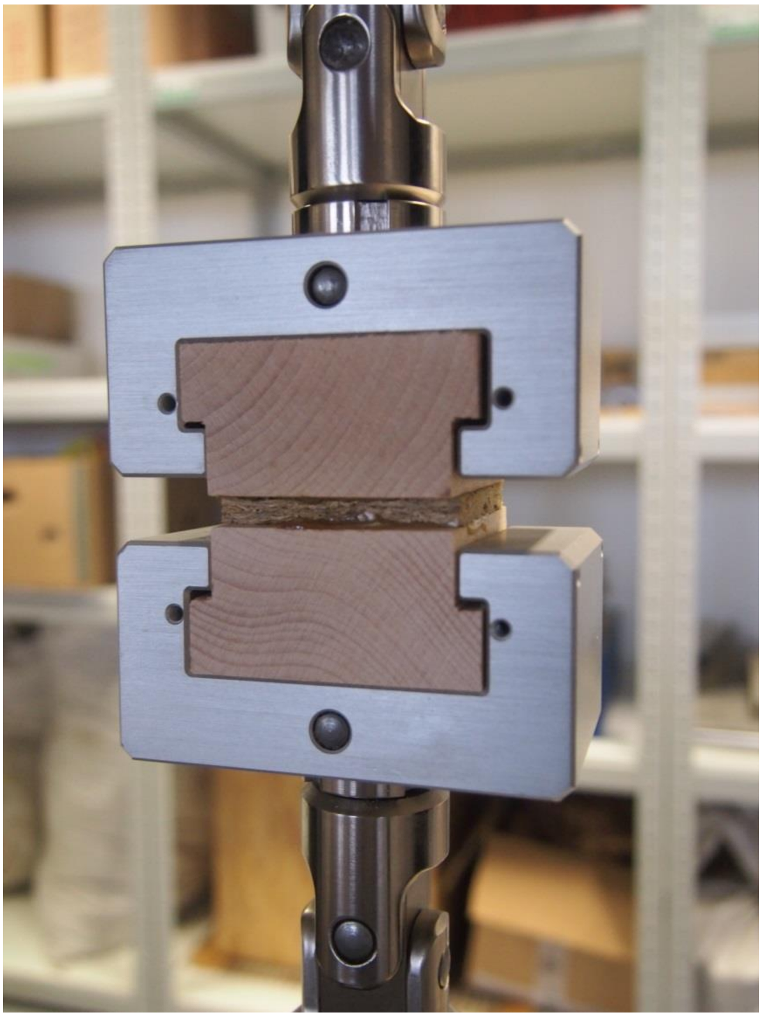
Příloha 9 Pohled na příčný řez desky ze slámy pšenice ozimé – deska s trhlinou

Příloha 10 Pohled na příčný řez desky ze slámy pšenice ozimé – bez vady

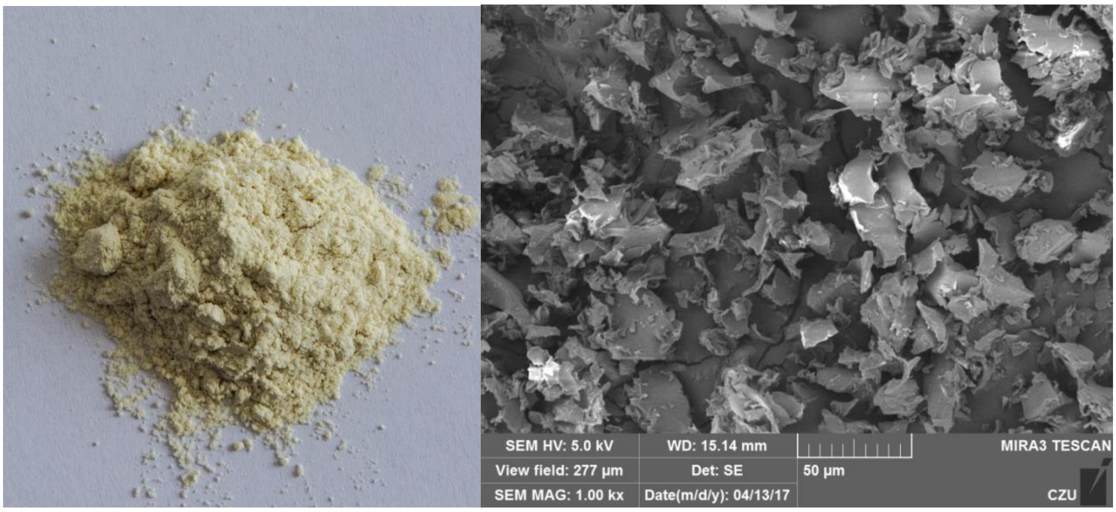
Příloha 11 Desky po zkoušce bobtnání – zleva dřevotřísková deska, deska z řepkových třísek lepená práškovým adhesivem, OSB deska



Příloha 12 Sestava laserového konfokálního mikroskopu pro fluorescenční časovou zobrazovací mikroskopii



Příloha 13 Zkouška rozlupčivosti desek



Příloha 14 PUR recyklovaný prach pro modifikaci adhesiv – vlevo snímek volně nasypaného prachu, vpravo mikroskopický snímek

10 Separáty článků

[1] ČÁSTKOVÁ, T., **HÝSEK, Š.,** SIKORA, A., SCHÖNFELDER, O., a BÖHM, M. 2018, Chemical and physical parameters of different modification of rape straw (Brassica napus L.), *BioResources*, roč. 13, č. 1, s. 104-114.

Chemical and Physical Parameters of Different Modifications of Rape Straw (*Brassica napus* L.)

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Material alternatives to wood, such as rape straw, are needed for the production of composite materials. This study performed an analysis of rape straw as a composite material source for production. There were three types of rape straw particle modification: untreated particles as reference variant, boiling in water, and soaking in sodium hydroxide (NaOH) solution. The pH and calorific value were highest for the variant soaked in NaOH. The total elemental content and the elements on the rape straw surface varied between variants. The modification method chosen influenced the pH, calorific value, elemental composition, and contact angle.

Keywords: Modification of rape straw; Brassica napus; Physical and agrochemical parameters; Scanning electron microscopy

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INTRODUCTION

Recently there has been an effort to develop new composite materials using alternative sources of raw materials. This trend is largely explained by population growth, which contributes directly to a limited supply of natural resources, as well as wood shortage in all wood processing industries (Galor and Weil 2000; Bektas *et al*. 2005; Seintsch 2011; Lauri *et al.* 2012). One alternative source of raw materials is post-harvest rapeseed crop residue (Mohanty *et al*. 2002; Dziurka *et al.* 2015). As a prospective raw material, rapeseed has many advantages, as it is available in large quantities and is not yet used in other products with high added value (Bečka *et al*. 2007; Dukarska *et al*. 2017). However, waxy and siliceous substances are present on the surface of winter rape stems, which prevents the formation of quality adhesion between particle and adhesive (Grigoriou 2000). This is the main disadvantage of particles from annual plants compared to wood particles. The chemical composition differs between internal and external areas of the stem because of cuticles and epicuticular waxes (Wiśniewska *et al.* 2003; Trischler, and Sandberg 2014). The surface has a strong impact on the water contact angle, which deteriorates the wetting of particles by adhesives, since adhesives used in particleboard production are mainly water-based (Wiśniewska *et al.* 2003). Therefore, it is necessary to pre-treat these particles from annual plants before the production of the composite material itself (Mahlberg *et al*. 1999; Cao *et al.* 2017). This modification can be done in various ways (Pelaez-Samaniego *et al*. 2013; Trischler and Sandberg 2014). Boiling in water is regarded favorably as a treatment due to its ease of implementation (Bekhta *et al.* 2013). An alternative is alkaline treatment, which breaks ester linkages between wax and lignocellulose, as well as dissolving wax and lignin (Binod *et al.* 2010; Wan *et al.* 2011). In this study, winter rape chips were modified by applying hydrothermal and chemical (soaking in sodium hydroxide) processes (Xie *et al*. 2010; Bekhta *et al*. 2013). It is assumed that the modification destroys the waxy, siliceous substances on the surface of the chips and consequently improves adhesion in the composite product. This study characterized the physical and chemical properties of raw and modified rapeseed particles to measure the effects of modification on particle properties. This information on the effect of the various particle modifications on particle properties will promote the utilization of this waste material in particleboard production.

EXPERIMENTAL

Materials

Chipped rape straw (*Brassica napus* L.) particles were treated by one of two processes. In the chemical treatment, the particles were soaked in 2% sodium hydroxide solution (NaOH) at 20 °C for 45 min. Alternatively, a hydrothermal treatment was carried out by boiling in water for 45 min. After both modifications, particles were carefully flushed with water and then oven-dried to 6% moisture content. A portion of each sample was dried at 40 °C and milled for determination of the total element content, calorific value, and percentage of volatile solids. Representation of the individual fractions in chopped rape straw is stated in Table 1.

Table 1. Representation of the Individual Fractions in Chopped Rape Straw

Fraction [mm]	0-0.25	0.25-0.5	0.5-0.8	0.8-1.6	1.6-2	2-3.15	3.15-8
Representation [%]	0.3	0.6	5.2	39.9	20.9	23.8	9.3

Methods

The goal of this study was to determine the effects of different particle pre-treatment methods on particle properties. In order to estimate this effect and to determine what happened and changed in the particle after modification, the following characteristics were observed: equilibrium moisture content, pH value, calorific value, total element content, elemental composition of the surface, water contact angle, and microstructure of the particle surface.

Chemical analysis of rape straw

Moisture content was determined by measurement at 105 °C by a ML-50 Moisture Analyzer (A&D Company, Elk Grove Village, IL, USA). The pH was measured in samples mixed with deionized water (1:5 w/v wet basis) using a WTW pH 340 I device (GeoTech, Denver, CO, USA), according to BSI EN 15933 (2012). Total element contents were determined through decomposition in an enclosed microwave, using an Ethos 1 system (MLS GmbH, Leutkirch im Allgäu, Germany). Elemental concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES; Varian VistaPro, Mulgrave, Australia) with axial plasma configuration. The calorific value of the material and the percentage of volatile solids were determined using the Laget MS 10A dry calorimeter (Laget, Staufen im Breisgau, Germany). The sample was burned in a 100% oxygen atmosphere, according to ČSN ISO 1928 (2010).

Scanning electron microscopy (SEM) and elemental analysis

The surface of the rape straw particles was observed with a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector operated at 15 kV acceleration voltage. When rape straw is washed with water, the elements can be changed on the surface, as well as when straw soaked in NaOH. The elemental compositions of the surface were examined by an energy dispersive spectroscopy system (Bruker XFlash X-ray detector, Karlsruhe, Germany, and ESPRIT 2 software).

Contact angle

Contact angle analysis is widely used to determine the wettability of solid materials (Walinder and Ström 2001; Aydin 2004). To determine wetting characteristics of modified particles, the contact angle of the water and particle surface was measured using a DSA 30E goniometer (Krüss GmbH, Hamburg, Germany). Straw particles have both interior and exterior surfaces. However, due to a pith on the interior of the particles, the contact angle of the water droplet could not be measured on the inside, and therefore only the exterior contact angle was measured. Static contact angle was measured for 30 measurements for each straw modification. In order to minimize the influence of variable of straw surface, a new particle was used for each droplet. The volume of distilled each water droplet was 5 µL with the measurement taken 5 s after the application. Contact angle was measured using image analysis software.

Statistical Analysis

All results from the agrochemical analysis represent the mean values of three replicates. Analysis of normality and homogeneity and one-way analysis of variance (ANOVA) were performed with STATISTICA 12 software (StatSoft, Tulsa, OK, USA). ANOVA was based on a 95% confidence level in accordance with Tukey’s range HSD (honest significant difference) test.

RESULTS AND DISCUSSION

In each modification, the pH value of the rape straw was different. The lowest pH value was in the sample modified through maceration in H_2O (6.58), and conversely, the highest pH value was in the sample modified through maceration in NaOH (9.44) (Table 2). This result suggests that the straw was not well washed after soaking in the NaOH solution as there was the highest total content of Na present. Both in this variant and the reference variant, there was a high content of calcium (Ca) on the surface of the straw, which was seen in the elemental analysis (Fig. 2a, c). The equilibrium moisture content was very low in all samples, with no statistically significant difference. The highest moisture content was in the sample modified with H_2O 7.7% (Table 2).

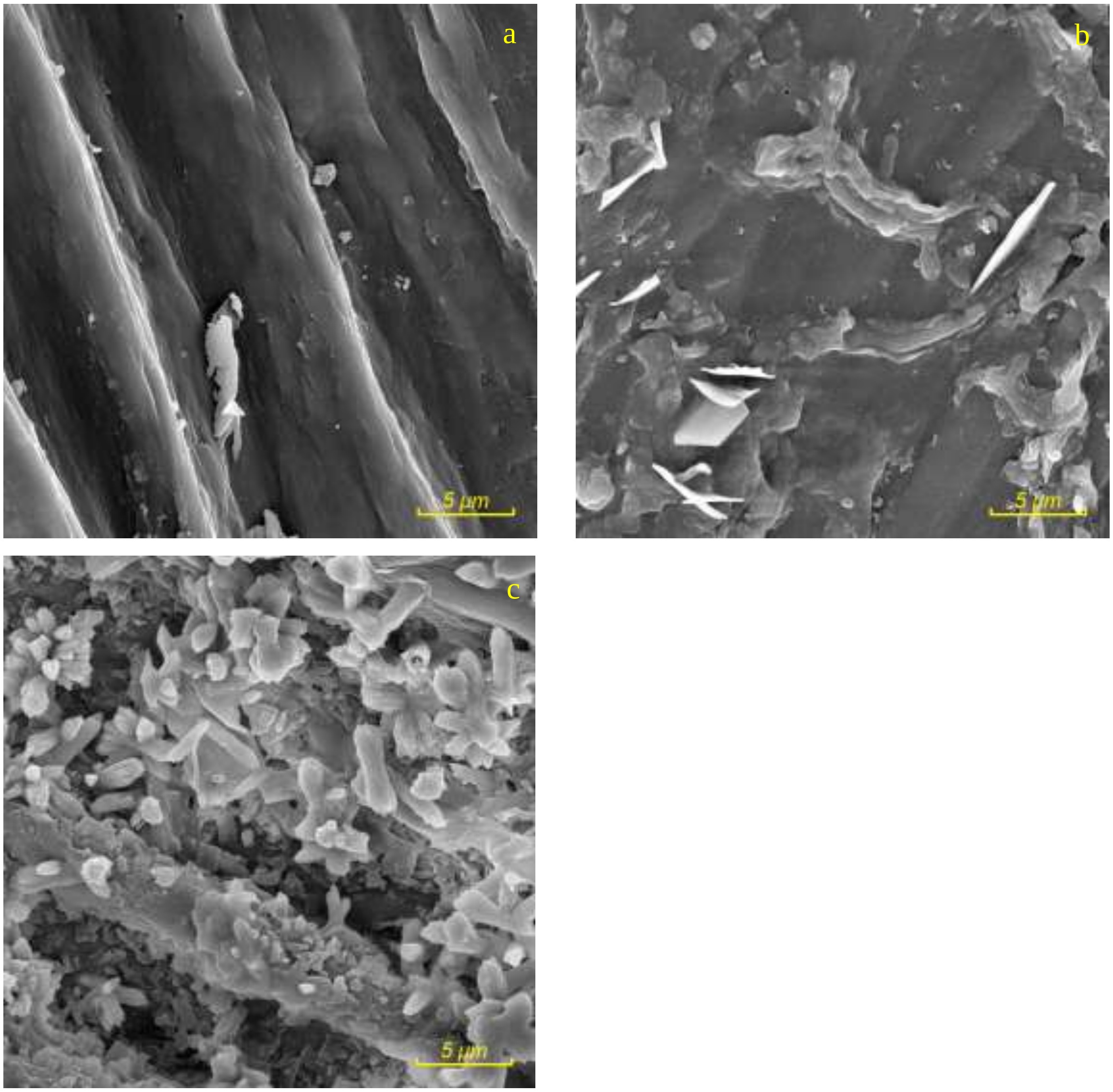

Fig. 1. Electron micrographs of rape straw surfaces (magnification 10000x). (a) Reference variant, (b) variant modified by cooking in H_2O, and (c) variant modified in NaOH solution

Table 2. pH and Moisture Content in Modified Rape Straw

Modification	pH/H_2O	Moisture (%)
Ref.	7.86 ± 0.08 ^{a}	7.6 ± 0.46 ^{a}
H_2O	6.58 ± 0.07 ^{b}	7.7 ± 0.10 ^{a}
NaOH	9.44 ± 0.56 ^{c}	6.9 ± 0.32 ^{a}

Values are the means ± SD (n = 3). Different letters (in superscript) in a column indicate significant differences (Tukey's HSD test, $P < 0.05$).

The percentage of volatile solids present in all modifications was relatively high. The highest value of volatile solids was found in the modification with H_2O (96.97%) (Table 3). It appeared that the H_2O dissolved in the compounds into an improved combustible form. This variant had the highest value of volatile solids, but also the lowest calorific value. In contrast, the variant with NaOH had the highest calorific value of 18.4 MJ.kg^{-1} but the lowest value of volatile solids. The calorific value can be influenced by the content of carbon (C) or sulfur (S) present (Erol *et al*. 2010). As the elemental analysis showed, the highest C content was found in the variant with NaOH (Fig. 2c), explaining the high calorific value of this variant. Total S content was the highest in the reference variant and the lowest in variant with H_2O (Table 4), again explaining its calorific value.

Table 3. Volatile Solids and the Calorific Value of Modified Rape Straw

Modification	**Volatile Solids (%)**	**Calorific Value (MJ.kg^{-1})**
Ref.	95.52	17.9
H_2O	96.97	17.6
NaOH	94.60	18.4

Table 4. Elemental Analysis of Modified Milled Rape Straw

Element / Modification	**Reference**	**H_2O**	**NaOH**
Al (mg/kg)	45.30 ± 4.1 ^{a}	59.73 ± 0.95 ^{b}	61.93 ± 8.95 ^{b}
B (mg/kg)	11.01 ± 0.52 ^{a}	7.85 ± 0.2 ^{b}	7.94 ± 0.9 ^{b}
Ca (mg/kg)	6941.9 ± 99 ^{a}	5858.5 ± 41.6 ^{b}	5705.2 ± 657.7 ^{b}
Cd (mg/kg)	0.08 ± 0.01 ^{a}	0.09 ± 0.01 ^{a}	0.09 ± 0.02 ^{a}
Cr (mg/kg)	0.23 ± 0.0 ^{a}	0.25 ± 0.02 ^{a}	0.25 ± 0.04 ^{a}
Cu (mg/kg)	1.03 ± 0.07 ^{a}	0.82 ± 0.03 ^{b}	0.67 ± 0.07 ^{c}
Fe (mg/kg)	42.67 ± 11.8 ^{a}	46.97 ± 1.39 ^{a}	50.83 ± 8.42 ^{a}
K (mg/kg)	5036,8 ± 198 ^{a}	1026.1 ± 34.5 ^{b}	732.8 ± 88.3 ^{c}
Mg (mg/kg)	998.8 ± 18.38 ^{a}	739.1 ± 11.72 ^{b}	1089.8 ± 107.9 ^{a}
Mn (mg/kg)	8.09 ± 0.3 ^{a}	6.71 ± 0.05 ^{b}	4.80 ± 0.57 ^{c}
Ni (mg/kg)	0.33 ± 0.13 ^{a}	0.10 ± 0.05 ^{b}	0.19 ± 0.1 ^{ab}
P (mg/kg)	248.9 ± 29.72 ^{a}	217.5 ± 9.3 ^{a}	210.3 ± 24.84 ^{a}
S (mg/kg)	1340 ± 45.6 ^{a}	431.5 ± 13 ^{b}	323.4 ± 27 ^{c}
Zn (mg/kg)	1.26 ± 0.08 ^{a}	1.68 ± 0.27 ^{a}	2.50 ± 0.45 ^{b}
Na (mg/kg)	245.5 ± 49.5 ^{a}	663.8 ± 29.1 ^{a}	4187.8 ± 508.5 ^{b}

Values are the means ± SD (n = 3). Different letters (in superscript) in a column indicate significant differences (Tukey's HSD test, $P < 0.05$).

An extensive analysis of element concentrations was performed, including an analysis of the total element content (Table 4) and an analysis of particle surfaces using SEM (Fig. 1a-c; Fig. 2a-c). The total content of arsenic (As) and lead (Pb) were below the detection limit. The total contents of cadmium (Cd), chromium (Cr), and nickel (Ni) were very low and therefore were not statistically different. None of the above elements were found on the surface of the rape straw.

The total contents of copper (Cu), zinc (Zn), manganese (Mn), boron (B), iron (Fe), and aluminum (Al) were low but statistically significant. Specifically, the total content of Mn and Cu was the highest in the reference variant, almost twice as high as in the variant with NaOH (Table 4). Significant differences were not found in the total content of Fe. None of these elements were detectable using SEM (Fig. 2a-c).

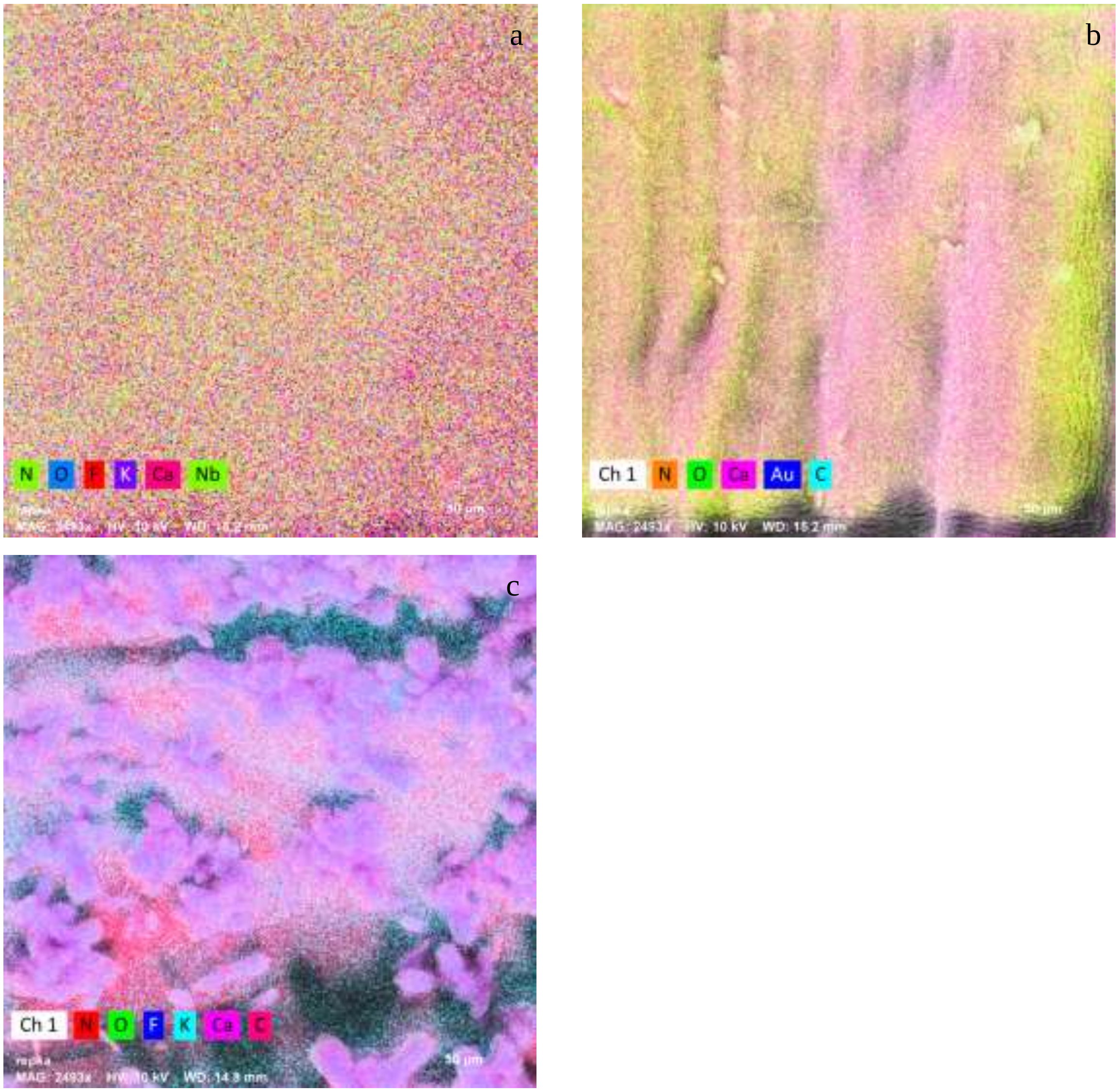

Fig. 2. Elemental content of rape straw surface taken by SEM. (a) Reference variant, (b) variant modified by cooking in H_2O, and (c) variant modified in NaOH solution

The total phosphorus (P) content was over 200 mg/kg in all variants, and no significant differences were found. However, a significant difference was found in the total content of Na. The total content of Na was 17 times higher (4187.8 mg/kg) for the variant with NaOH compared with the reference variant (245.5 mg/kg). As Na was only found on the exterior surface of this variant, it can be assumed that the large amount of Na present was probably caused by poor washing of the NaOH solution.

The total S content of the reference variant was four times higher than in variant with NaOH, which further confirming the calorific value of this variants. Potassium (K) was found only on the surface of the reference variant and the variant with NaOH, as shown in pictures taken by SEM (Fig. 2a-c). In the variant with H_2O, K could have been washed away from the surface. In the variant with NaOH, K could have precipitated on the surface. Total K content was the highest in the reference variant (5037 mg/kg) and was almost 7 times higher in the reference variant than in the variant with NaOH (733 mg/kg).

The lowest magnesium (Mg) content was found in variant with H_2O (739 mg/kg). However, Mg on the surface of the rape straw was found only in the variant with H_2O. The total Ca content corresponds to the content found on the rape straw surface by SEM analysis. The hydroxide precipitated Ca on the surface of the variant with NaOH (Fig. 2c). This Ca deposit created crystals that were observed also by SEM, as can be seen in Fig. 1c. There were no Ca crystals on the surface of reference particles or the particles modified by cooking. Only dust was found on the surface of these particles (Fig. 1a, b). The pith of the rape straw particles was observed also. Figure 3a shows the undisturbed pith of the reference sample. Both hydrothermal and alkaline modification destroyed the pith, which is shown in Fig. 3b and Fig. 3c, respectively.

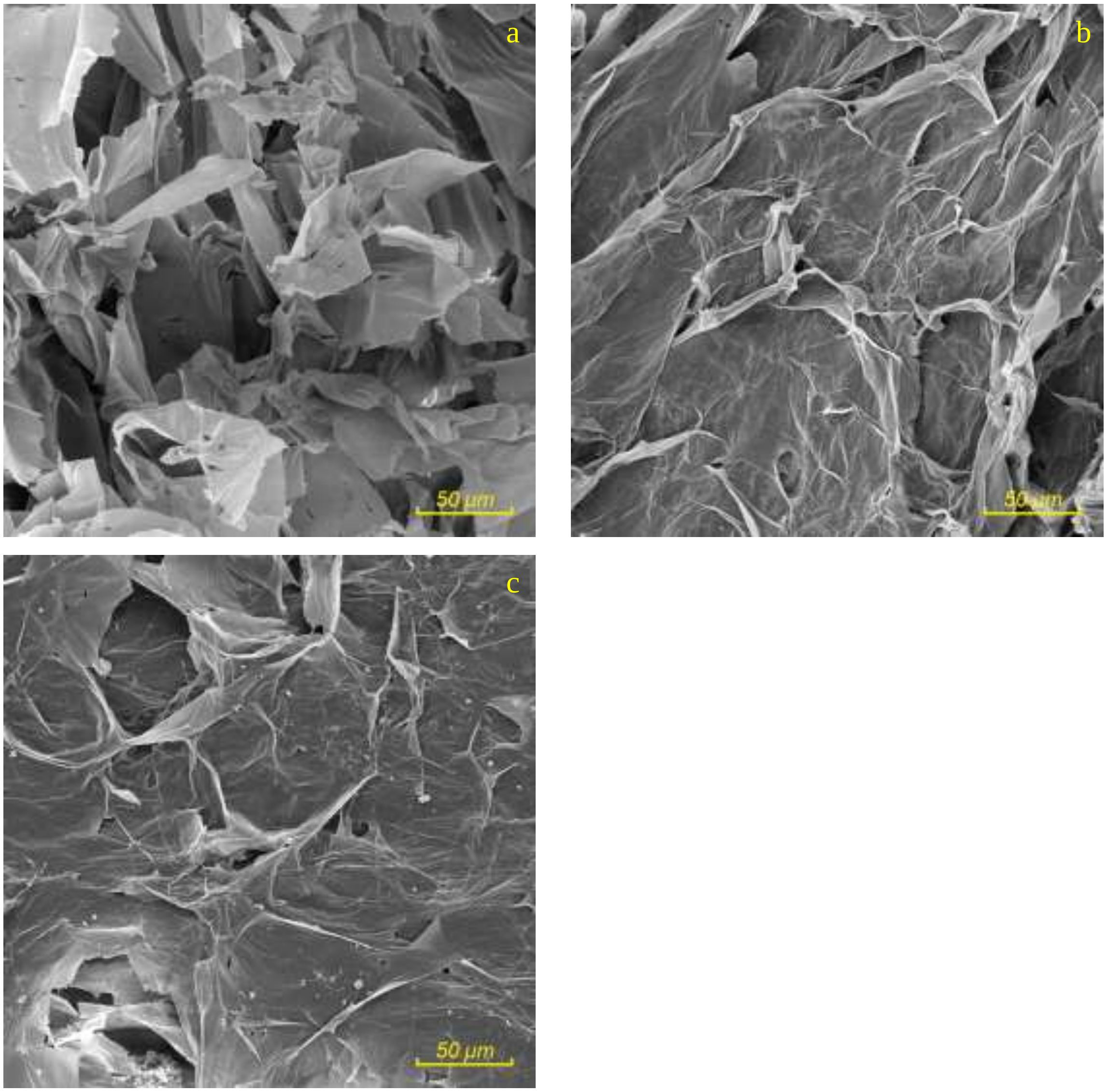

Fig. 3. Electron micrographs of rape straw pith (magnification 1000x). (a) Reference variant, (b) variant modified by cooking in H_2O, and (c) variant modified in NaOH solution

Figure 4 depicts the analysis of contact angle between water droplet and straw particle surface. The vertical columns depict 95% confidence intervals. Both modifications caused the desired decrease in water contact angle, while the contact angle was different for each modification. The largest contact angle was found in the reference variant, with a mean of 94.1° and the lowest mean, 82.7°, was seen in the modification with H_2O. A smaller contact angle is better for the strength of a glued joint (Banea and Silva 2008; Moghadamzadeh *et al*. 2011). The variant with H_2O exhibited a significant difference from the others, but there was no significant difference between the reference and NaOH variants. The alkaline modification resulted in the lowest variability of water contact angle (Fig. 4).

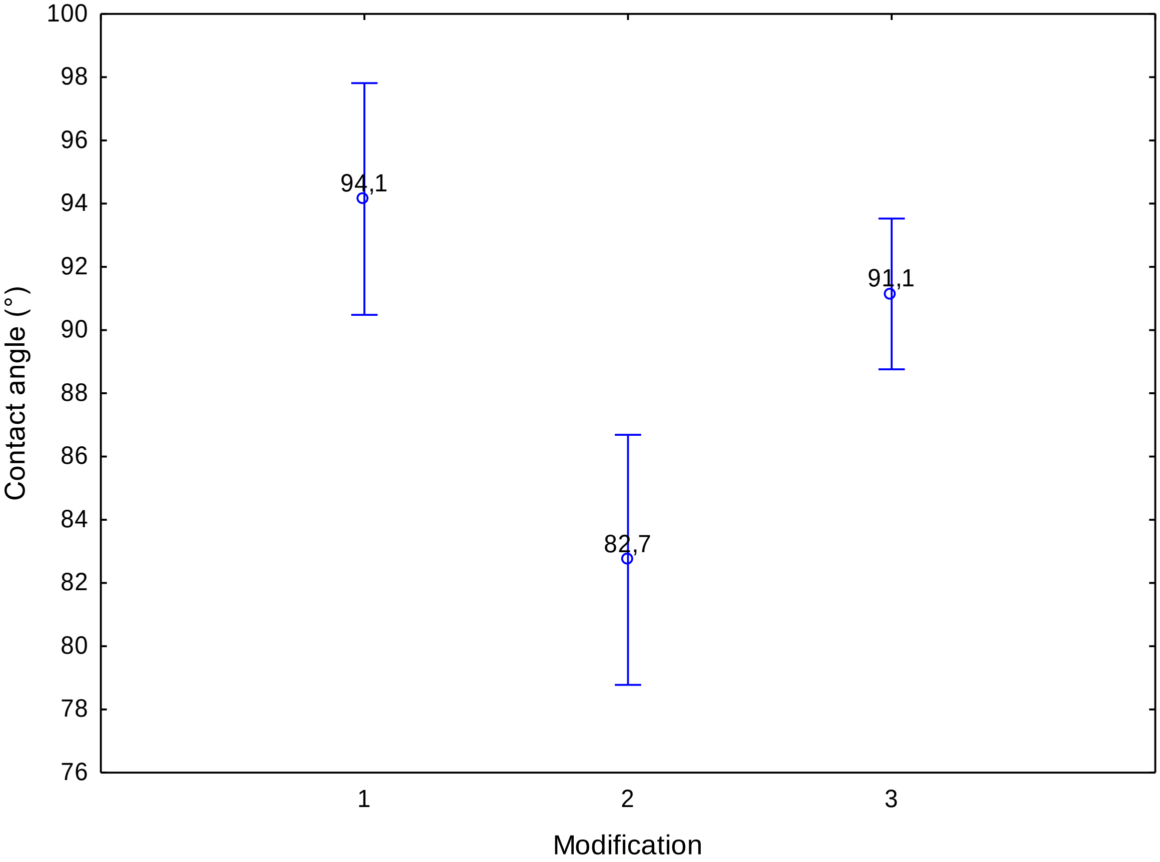

Fig. 4. Influence of modification technique on contact angle: 1-reference variant, 2-variant modified by cooking in H_2O, 3-variant modified in NaOH solution

CONCLUSIONS

1. The elemental composition of surface and the total element content of rape straw are highly influenced by the type of modification.
2. A variant modified with H_2O exhibited the highest value of volatile solids and the

lowest calorific value, but a variant modified with NaOH had the highest calorific value and the lowest value of volatile solids.

3. A disadvantage of soaking rape seed straw particles in NaOH is that it is not possible to rinse out all of the hydroxide. Therefore, the variant modified with NaOH had the highest pH value.
4. Contact angle is also dependent on the type of modification. The variant with the best strength for a glued joint was modified with H_2O.
5. Moisture content is not dependent on the type of modification, as there were no significant differences.

ACKNOWLEDGMENTS

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[2] GAFF, M**., HÝSEK, Š.,** SIKORA, A. a BABIAK, M. 2018, Newly Developed Boards Made from Crushed Rapeseed Stalk and their Bendability Properties, *BioResources*, roč. 13, č. 3, s. 4776-4794.

Newly Developed Boards Made from Crushed Rapeseed Stalk and their Bendability Properties

Milan Gaff, Štepán Hýsek, Adam Sikora,* and Marián Babiak

The bendability of a material can be classified as both a positive and negative characteristic. The classification depends on the intended use of the given material. In the case of materials intended for bending (solid wood), this property is positive; whereas in the case of building materials this property may have a negative effect on the stability and durability of the finished structure. Depending on the use of the material, different characteristics of bendability can be used to describe it. The important characteristics include the force and deflection at the limit of proportionality and at the modulus of rupture. Because the bendability also depends on the material thickness, this characteristic is most often expressed as the ratio of the material thickness to the smallest achievable bent radius. Therefore, an analysis of the minimum curve radius and coefficient of bendability was performed. The bending characteristics were measured for composite materials, which were made of crushed rapeseed stalk and bonded with powder polyester adhesive. The stalks were subjected to different modifications (R, H_2O, and NaOH). The results of this work indicated that rapeseed is a prospective raw material for the production of composite materials with specific properties.

Keywords: Bendability; Modulus of elasticity; Limit of proportionality; Elastic potential; Composite material

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INTRODUCTION

The bendability of a material can be seen as both a positive and negative factor (Požgaj *et al.* 1997; Gaff 2014; Gaff *et al.* 2017b), depending on its specific purpose. While material deflection is undesirable in the construction of conventional furniture, such as table tops and cabinet shelves, it can be desirable in selected applications and certain design elements, and is even indispensable in some cases. The technology for producing bentwood furniture, such as chairs and armchairs, has been used for decades. Larger interior units with spatially wavy and curved elements cause trouble for designers and furniture manufacturers. At present, manufacturers prefer using materials other than lignin- and cellulose-based materials.

Bendable fiberboards made with renewable materials can be found on the market today. Their bendability is achieved by cutting various patterns into the surface or with various sandwich structures, from solid wood and wood particles to polymers (Fathi *et al.* 2013; Gaff *et al.* 2017b). A variety of physical qualities can be used to determine the bendability characteristic, such as the force at the limit of proportionality (F_E), deflection at the limit of proportionality (Y_E), force at the modulus of rupture (F_P), and deflection at the modulus of rupture (Y_P) (Gaff *et al.* 2015; Sikora *et al.* 2017; Svoboda *et al.* 2017).

Unlike the strength, the bendability depends on the thickness of the material. This property is therefore most often expressed as the ratio of the material thickness to the minimum curve radius (*R*min), *i.e.*, the coefficient of bendability (K_{bend}) (Gašparík and Gaff 2015; Gaff *et al.* 2016).

The development of methods, mathematical models, and characteristics used to describe materials is progressing rapidly (Bal 2014). This progress highlights the effort in the development of material engineering to produce materials that meet specific customer requirements, as well as the environmental and economic requirements of production. This development is also associated with the testing of new types of materials that could replace materials that are more expensive and environmentally more valuable, such as wood (Bao *et al.* 2001). There is an increasing need to develop new materials using alternative sources, predominantly lignocellulosic post-harvest residues (Wang and Sun 2002). The main advantages of these raw materials are that they are renewable, recyclable, sustainable, and they can mean a positive difference between the environment of today and that of tomorrow (Guler *et al.* 2006; El-Kassas and Mourad 2013; Marinho *et al.* 2013). The world has a large amount of lignocellulosic residues (approximately 2.4 trillion tons) that is suitable for the production of composite materials and are produced every year after the end of the agricultural season. These residues are either burned or left on the ground, but the fibers of these raw materials have many advantages over some synthetic fibers (Taj *et al.* 2007). These residues include flax, hemp, wheat straw, barley, rapeseed stalks, and more (Bond and Ansell 1998).

Rapeseed (*Brassica napus* L.) is an agricultural crop with a prospective development in the Czech Republic. Although it is not the most widely planted agricultural crop, it is still a relatively important crop for the Czech economy, and the secondary product (stalk) is a suitable material for the production of composite materials. Figure 1 shows the growing tendency for the utilization of sowing areas in hectares for rapeseed in the Czech Republic, according to the Czech Statistical Office. The yield per hectare of rapeseed stalk throughout Europe ranges from 3 tons to 10 tons.

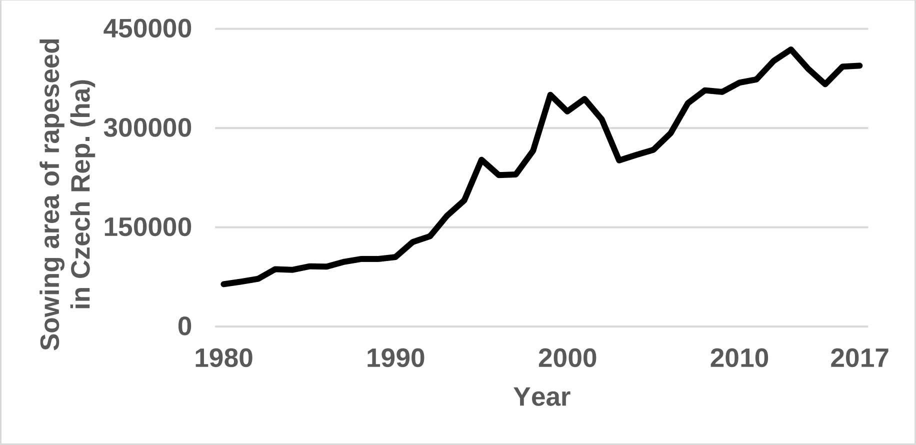

Fig. 1. Increase in the sowing area of rapeseed from 1980 to 2017

The growth of rapeseed, as well as the properties of this material, ranks it among materials with a high potential for use in the manufacture of composite materials (Guntekin *et al.* 2014).

Another equally important factor in the development of the material engineering industry is the correct identification and quantification of material properties (Bal 2014). It has become evident that even today, characteristics that adequately describe important material properties have not been derived and thoroughly examined (Gaff *et al.* 2016, 2017a). A drawback of this industry is that the applied methods are based on approaches introduced in times when the possibilities that modern technology currently offer were non-existent. The implementation of new scientific knowledge (in the form of mathematical models) and the approaches to its identification, on the basis of which important material characteristics can be correctly and quickly identified and quantified, are equally important.

The present study combined the synergistic effect of all of the above-mentioned properties with the implementation of new knowledge in the form of mathematical models in the testing of new materials. New information technology was used to identify important parameters.

EXPERIMENTAL

Materials

Rapeseed chips were used to produce chipboard. The fraction of chips used is shown in Table 1. Two modification methods were chosen, which were hydrothermal modification and modification in an alkaline environment. The hydrothermal modification consisted of boiling the chips in water for 45 min and 100 °C. The boards produced from these chips were marked with H_2O. The modification in an alkaline environment also lasted for 45 min (temperature of solution was 25 °C), and the chips were soaked in a 2% sodium hydroxide solution. The boards produced from these chips were marked with NaOH. To determine the effect of the modifications, boards from raw unmodified rapeseed chips were also produced, and these boards were marked with R. These boards produced by us were 12 mm thick. Two commercial materials were chosen for comparison of the properties of the manufactured boards: a 12-mm thick particle board (PB) (P2 for furniture use) and a 12-mm thick oriented strand board (OSB) (type 3 - load-bearing board for use in humid environments).

Table 1. Representation in the Fractions of the Chopped Rapeseed Straw

Length fraction (mm)	0-0.25	0.25-0.5	0.5-0.8	0.8-1.6	1.6-2	2-3.15	3.15-8
Representation, mass (%)	1.2	2.8	4.8	39.4	20.1	23.1	8.6

DAKOTEX2600, which is a powder glue based on polyester and epoxy resin (Dakota Coatings N. V., Nazareth, Belgium), was used to create the boards. The resination was 10%, and the boards were pressed in a laboratory press (Strozatech, Brno, Czech Republic). The following pressing parameters were chosen: a pressure of 2.3 MPa, press plate temperature of 185 °C, pressing time of 10 min, and press closing speed of 150 s. After 10 min, a temperature of 170 °C was reached in the middle of the boards.

The specimens were conditioned to a standardized equilibrium moisture content under a relative humidity of 65% ± 5% and temperature of 20 °C ± 2 °C in a HCP 108 climate chamber (Memmert, Schwabach, Germany). Thirty samples were used for each set of specimens.

Figure 2 shows the vertical density profiles of the tested materials. While the PB and OSB boards had typical M-shaped vertical density profiles, the boards produced by the authors had opposite density profiles, with the highest density in the middle of the board.

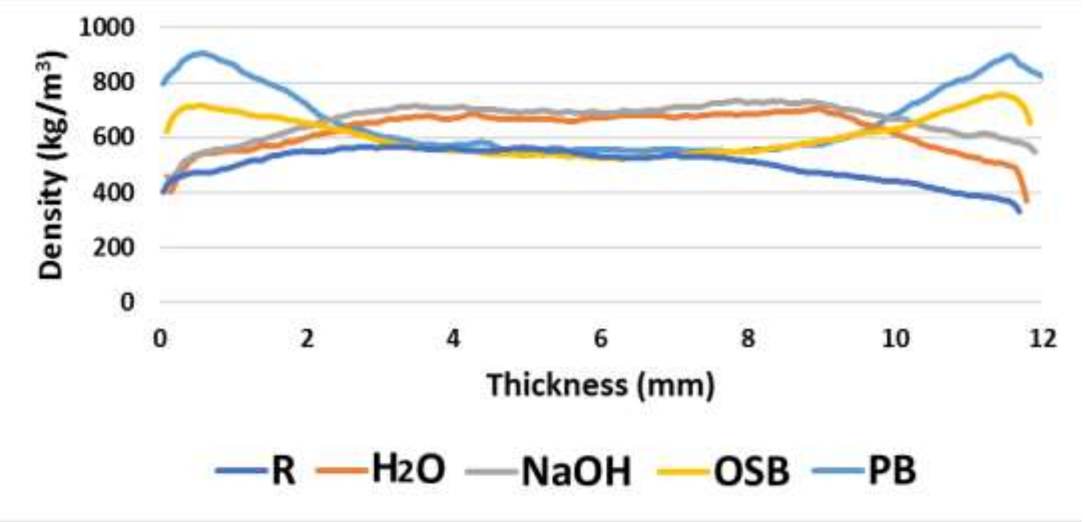

Fig. 2. Density profiles measured for the monitored sets of test samples

Methods

Determination of the characteristics

The bending support span was adjusted to a length of 20 times the thickness. The samples were loaded by three-point bending with a single force in a UTS 50 universal testing machine (TIRA, Schalkau, Germany) according to EN 310 (1993). The loading speed was set to 3 mm/min so that the test duration would not exceed 2 min. The loading forces were measured using the data logger ALMEMO 2690-8 (Ahlborn GmbH, Ilmenau, Germany).

All of the necessary data were obtained from the force-deflection diagrams. To identify the characteristics, a program developed by the authors was used that accurately identified and quantified data that could be obtained from the force-deformation diagram.

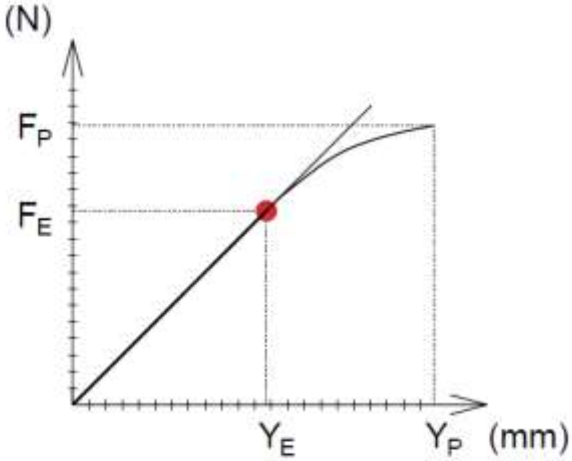

Fig. 3. Force–deflection diagram of bending

Evaluation and calculation

A force-deflection diagram was created using the measured data (Fig. 3), in which a method that the authors developed for accurately identifying boundary points was applied.

Determining the boundary points consisted of determining the exact boundaries between the linear and nonlinear part of the diagram. This is neglected in the standards used today and therefore, subsequent evaluation is quite inaccurate.

In the next part of this study, a bendability evaluation was done using the minimum curve radius and coefficient of bendability. For this analysis, Eqs. 1, 2, 3, and 4 were used, which were deduced by the authors in a previous paper (Gaff *et al.* 2016).

The minimum curve radius (R_{minB}) (Eq. 1) and coefficient of bendability (K_{bendB}) (Eq. 2) were based on the bending geometry, and are as follows:

$$R_{\mathrm{minB}} = \frac{l_0^2}{8\,Y_{\mathrm{max}}} + \frac{Y_{\mathrm{max}}}{2} - \frac{h}{2} \tag{1}$$

$$K_{\mathrm{bendB}} = \frac{h}{R_{\mathrm{minB}}} = \frac{h}{\frac{l_0^2}{8\,Y_{\mathrm{max}}} + \frac{y_{\mathrm{max}}}{2} - \frac{h}{2}} \tag{2}$$

The minimum curve radius (R_{minC}) (Eq. 3) and coefficient of bendability (K_{bendC}) (Eq. 4) are based on the basic bending equations that follow,

$$R_{\mathrm{minC}} = \frac{l_0^2}{12\,Y_{\mathrm{max}}} \tag{3}$$

$$K_{\mathrm{bendC}} = \frac{h}{R_{\mathrm{minC}}} = \frac{h}{\frac{l_0^2}{12\,Y_{\mathrm{max}}}} \tag{4}$$

where R_{minB} is the minimum curve radius based on bending geometry (mm), K_{bendB} is the coefficient of bendability based on bending geometry, R_{minC} is the minimum curve radius based on the basic bending equations (mm), K_{bendC} is the coefficient of bendability based on the basic bending equations, Y_{max} is the maximum deflection (mm), l_0 is the distance between supporting radius (mm), and h is the thickness of the sample (mm).

The wood density was determined before and after testing according to ISO 13061-2 (2014). The moisture content of the samples before and after testing, along with drying to an oven-dry state were performed according to ISO 13061-1 (2014). Drying to an oven-dry state was also performed according to ISO 13061-1 (2014). The bending strength values were converted to those that corresponded to a moisture content of 12%, in accordance with ISO 13061-3 (2014).

The effect of individual factors was evaluated using an analysis of variance (ANOVA), specifically Fisher's F-test, with the STATISTICA 12 software (Statsoft Inc., Tulsa, USA). The results were evaluated using a 95% confidence interval, which represents a significance level of 0.05 ($P < 0.05$). To deepen the acquired knowledge, Duncan's tests were used to compare the tested sets of specimens.

The effect of the density of the tested materials on the monitored characteristics was verified by a correlation analysis, and the degree of dependence between the characteristics was determined based on the coefficient of determination (r^2). To determine the degree of dependence, the interaction between individual monitored characteristics was evaluated, for which a correlation analysis and Spearman's correlation were used.

RESULTS AND DISCUSSION

Table 2 shows the average values of the monitored characteristics, as well as the corresponding coefficient of variation for the evaluated materials. The table also shows the average density values measured over the entire cross section of the boards and the average density of the surface zones (1 mm from the surface) of the material.

Table 2. Mean Values of the Y_E, Y_P, F_P, F_E, R_{minB}, R_{minC}, K_{bendB}, K_{bendC}, and the Coefficient of Variation for the Evaluated Materials

Material	Glue	Y_E (mm)	Y_P (mm)	F_P (N)	F_E (N)	Average Density for Entire Thickness (kg/m^3)	Average Density for a Thickness of 1 mm (kg/m^3)
R	**PSE**	2.9 (17.0)	5.4 (17.4)	108 (18.3)	74 (10.2)	582 (10.4)	456.3 (8.2)
H_2O	**PSE**	3.2 (12.6)	6.6 (16.8)	201 (13.2)	133 (19.4)	621 (5.3)	487.3 (4.5)
NaOH	**PSE**	2.8 (16.0)	6.6 (15.5)	157 (18.5)	93 (10.9)	655 (11.1)	508.7 (6.8)
PB	**UF**	2.0 (16.6)	3.9 (7.8)	238 (9.3)	143 (16.6)	669 (3.0)	862.4 (5.2)
OSB	**MUF**	2.9 (14.3)	5.2 (18.2)	458 (19.6)	309 (15.9)	619 (3.2)	677.9 (6.1)
Material	**Glue**	**R_{minB}**	**R_{minC}**	**K_{bendB}**	**K_{bendC}**	**Average Density for Entire Thickness (kg/m^3)**	**Average Density for a Thickness of 1 mm (kg/m^3)**
R	**PSE**	1282 (21.4)	853 (21.5)	0.009 (17.5)	0.014 (17.5)	582 (10.4)	456.3 (8.2)
H_2O	**PSE**	1063 (22.5)	707 (22.6)	0.011 (16.8)	0.017 (16.8)	621 (5.3)	487.3 (4.5)
NaOH	**PSE**	1093 (15.5)	726 (15.6)	0.011 (15.6)	0.017 (15.7)	655 (11.1)	508.7 (6.8)
PB	**UF**	1897 (7.5)	1263 (7.6)	0.006 (7.7)	0.010 (7.7)	669 (3.0)	862.4 (5.2)
OSB	**MUF**	1487 (29.0)	990 (29.0)	0.009 (28.1)	0.013 (28.2)	619 (3.2)	677.9 (6.1)

Values in parentheses are the coefficients of variation (CV) in %; PSE = hybrid polyester/epoxide adhesive; MUF = melamine-urea-formaldehyde adhesive; UF = urea-formaldehyde adhesive

Based on the level of significance (P), it was apparent that each of the monitored characteristics was significantly affected by the type of material. In all of the monitored cases, the probability that this factor had no effect was 0.00%, which meant that this factor had a statistically significant effect (Tables 3 and 4).

Table 3. Statistical Evaluation of the Factors Influencing the Y_E, Y_P, F_P, and F_E

Y_E (mm)					
Monitored Factor	**Sum of Squares**	**Degree of Freedom**	**Variance**	**Fisher's F - test**	**Significance Level P**
Intercept	1139.804	1	1139.804	4578.769	***
1) Material	22.834	4	5.709	22.932	***
Error	36.095	145	0.249		
The respective model explained roughly 38.7% of the total sum of squares.					
Y_P (mm)					
Monitored Factor	**Sum of Squares**	**Degree of Freedom**	**Variance**	**Fisher's F - test**	**Significance Level P**
Intercept	4623.372	1	4623.372	4255.367	***
1) Material	145.087	4	36.272	33.385	***
Error	157.540	145	1.086		
The respective model explained roughly 47.9% of the total sum of squares.					
F_P (N)					
Monitored Factor	**Sum of Squares**	**Degree of Freedom**	**Variance**	**Fisher's F - test**	**Significance Level P**
Intercept	8088153	1	8088153	1156.170	***
1) Material	2191905	4	547976	78.331	***
Error	1014368	145	6996		
The respective model explained roughly 68.4% of the total sum of squares.					
F_E (N)					
Monitored Factor	**Sum of Squares**	**Degree of Freedom**	**Variance**	**Fisher's F - test**	**Significance Level P**
Intercept	3390107	1	3390107	717.759	***
1) Material	1043529	4	260882	55.234	***
Error	684861	145	4723		
The respective model explained roughly 60.4% of the total sum of squares.					

NS - not significant, *** - significant, where significance was accepted at $P < 0.05$

Figure 4 shows the values of the Y_E and Y_P. It was clear from the values in the graph that the highest Y_E was measured in the material developed with the hydrothermally modified chips (H_2O). In the other cases (R, NaOH, PB, and OSB), the Y_E values were significantly lower. The highest Y_P was measured in the H_2O and NaOH materials, with no statistically significant difference found between the Y_P values of these two materials. The other monitored specimen sets (R, PB, and OSB) had significantly lower values than the modified specimen sets (H_2O and NaOH). The significantly lowest Y_P values were measured with the PB material.

The above results indicated that the materials developed in this work (R, H_2O, and NaOH) had higher bendability values than the commercially available materials (PB and OSB), which was characterized by measured Y_E and Y_P values. Sikora *et al.* (2017) also dealt with the assessment of the bendability based on the values of the Y_E and Y_P. The Y_E values ranged from 1.7 mm to 25.4 mm depending on the material thickness and wood species.

Table 4. Statistical Evaluation of the Factors Influencing the R_{minB}, R_{minC}, K_{bendB}, and K_{bendC}

<table>
<tr><td colspan="6">R_{minB}</td></tr>
<tr><th>Monitored Factor</th><th>Sum of Squares</th><th>Degree of Freedom</th><th>Variance</th><th>Fisher's F - test</th><th>Significance Level P</th></tr>
<tr><td>Intercept</td><td>279314793.519</td><td>1.000</td><td>279314793.519</td><td>3804.955</td><td>***</td></tr>
<tr><td>1) Material</td><td>14099251.711</td><td>4.000</td><td>3524812.928</td><td>48.017</td><td>***</td></tr>
<tr><td>Error</td><td>10644185.168</td><td>145.000</td><td>73408.174</td><td></td><td></td></tr>
<tr><td colspan="6">The respective model explained roughly 100% of the total sum of squares.</td></tr>
<tr><td colspan="6">R_{minC}</td></tr>
<tr><th>Monitored Factor</th><th>Sum of Squares</th><th>Degree of Freedom</th><th>Variance</th><th>Fisher's F - test</th><th>Significance Level P</th></tr>
<tr><td>Intercept</td><td>123635360.870</td><td>1.000</td><td>123635360.870</td><td>3775.832</td><td>***</td></tr>
<tr><td>1) Material</td><td>6286086.973</td><td>4.000</td><td>1571521.743</td><td>47.994</td><td>***</td></tr>
<tr><td>Error</td><td>4747861.022</td><td>145.000</td><td>32743.869</td><td></td><td></td></tr>
<tr><td colspan="6">The respective model explained roughly 100 % of the total sum of squares.</td></tr>
<tr><td colspan="6">K_{bendB}</td></tr>
<tr><th>Monitored Factor</th><th>Sum of Squares</th><th>Degree of Freedom</th><th>Variance</th><th>Fisher's F - test</th><th>Significance Level P</th></tr>
<tr><td>Intercept</td><td>0.013</td><td>1.000</td><td>0.013</td><td>4259.588</td><td>***</td></tr>
<tr><td>1) Material</td><td>0.000</td><td>4.000</td><td>0.000</td><td>37.744</td><td>***</td></tr>
<tr><td>Error</td><td>0.000</td><td>145.000</td><td>0.000</td><td></td><td></td></tr>
<tr><td colspan="6">The respective model explained roughly 100% of the total sum of squares.</td></tr>
<tr><td colspan="6">K_{bendC}</td></tr>
<tr><th>Monitored Factor</th><th>Sum of Squares</th><th>Degree of Freedom</th><th>Variance</th><th>Fisher's F - test</th><th>Significance Level P</th></tr>
<tr><td>Intercept</td><td>0.030</td><td>1.000</td><td>0.030</td><td>4218.593</td><td>***</td></tr>
<tr><td>1) Material</td><td>0.001</td><td>4.000</td><td>0.000</td><td>37.675</td><td>***</td></tr>
<tr><td>Error</td><td>0.001</td><td>145.000</td><td>0.000</td><td></td><td></td></tr>
<tr><td colspan="6">The respective model explained roughly 100% of the total sum of squares.</td></tr>
</table>

NS - not significant, *** - significant, where significance was accepted at $P < 0.05$

Figure 5 shows the F_E and F_P measured for the monitored sets of test specimens. It was clear from the values in the graph that the highest values of the F_E and F_P were measured in the OSB materials. In contrast, the significantly lowest values were measured in the R material developed in this work.

The results also showed that the H_2O material can withstand the same stress as the PB material at the modulus of rupture, as well as the limit of proportionality, which was considered a positive property of this material. The results of Svoboda *et al.* (2017) showed that for aspen wood a force of 600 N is needed to achieve deflection at the limit of proportionality, and a 1100-N force is needed to achieve deflection at the modulus of rupture.

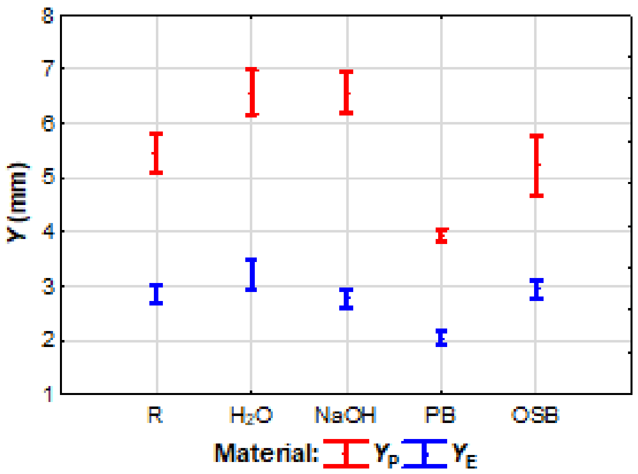

Fig. 4. Effect of the material on the Y_E and Y_P

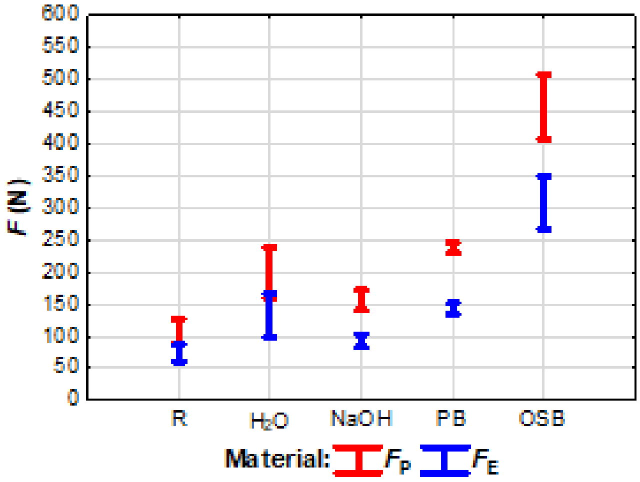

Fig. 5. Effect of the material on the F_E and F_P

Figure 6 shows the values of the minimum curve radius evaluated according to the methodology of Gaff *et al.* (2016). The difference between the R_{minB} and R_{minC} values was approximately 51%, which was consistent with the data reported by Gaff *et al.* (2016). The highest minimum curve radius values were measured in the PB. The lowest minimum curve radius was measured in the H_2O and NaOH samples. The difference between these sets of specimens was statistically insignificant.

The highest K_{bend} was measured in the H_2O and NaOH sets of specimens, and the lowest values were measured in the PB set of test specimens (Fig. 7). The results showed that the materials developed in this work (R, H_2O, and NaOH) had significantly higher bendability values than the commercially available materials (PB and OSB).

In the study (Gaff *et al.* 2016), the K_{bendB} and K_{bendC} of beech and aspen wood were analyzed, and the results of the work showed that there was a 51% difference in the measured values, which coincides with the data measured in this study.

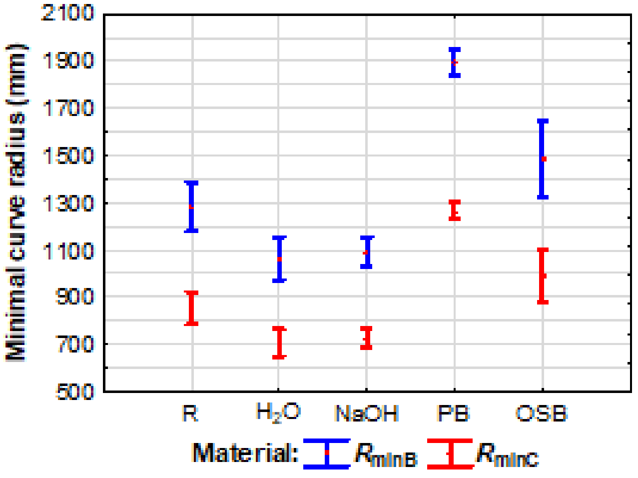

Fig. 6. Effect of the material on the minimum curve radius

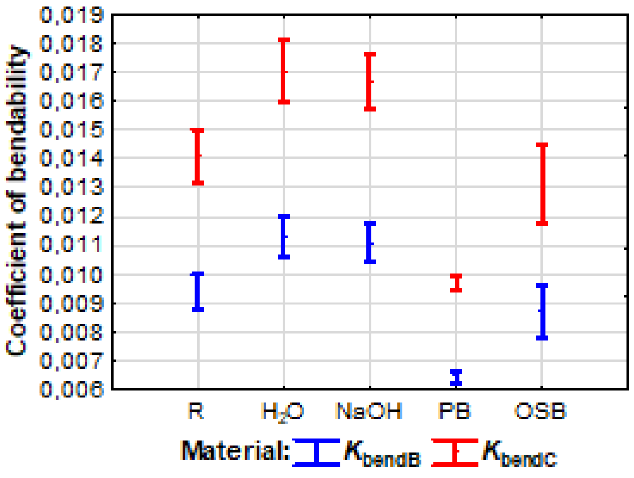

Fig. 7. Effect of the material on the coefficients of bendability

The Duncan's test results show differences between the monitored characteristics of the compared sets of specimens, and are shown in Tables 5 and 6. The data in Table 5 indicated the following findings:

- In the case of the Y_E, there was no statistically significant difference between the R and NaOH specimens (P = 0.467), OSB and NaOH specimens (P = 0.222), and R and OSB specimens (P = 0.566). In the other monitored cases, statistically significant differences in the measured values with a significance level of 0.000 were found.
- In the case of the Y_P, a statistically insignificant difference was confirmed between the H_2O and NaOH specimens (P = 0.990), and R and OSB specimens (P = 0.427). In the other monitored cases, statistically significant differences in the measured values with a significance level of 0.000 were found.
- In the case of the F_P, a statistically insignificant difference was found between the H_2O and PB specimens (P = 0.0083). Between the other sets of test specimens, the difference was statistically very significant with a significance level of 0.000.
- The last monitored characteristic in Table 5 was the F_E. Based on the significance level, it was concluded that there was no significant difference between the values measured for the R and NaOH specimens (P = 0.271), and H_2O and PB specimens (P = 0.589). In the other monitored cases, the differences in the measured values were statistically very significant with a significance level of 0.000.

Table 5. Comparison of the Effect of the Material on the Y_E, Y_P, F_P, and F_E using Duncan's Test

Y_E (mm)						
Material		**(1) 2.8527**	**(2) 3.2083**	**(3) 2.7590**	**(4) 2.0362**	**(5) 2.9266**
1	**R**		0.008	0.467	0.000	0.566
2	**H_2O**	0.008		0.001	0.000	0.029
3	**NaOH**	0.467	0.001		0.000	0.222
4	**PB**	0.000	0.000	0.000		0.000
5	**OSB**	0.566	0.029	0.222	0.000	
Y_P (mm)						
Material		**(1) 5.4463**	**(2) 6.5733**	**(3) 6.5765**	**(4) 3.9303**	**(5) 5.2323**
1	**R**		0.000	0.000	0.000	0.427
2	**H_2O**	0.000		0.990	0.000	0.000
3	**NaOH**	0.000	0.990		0.000	0.000
4	**PB**	0.000	0.000	0.000		0.000
5	**OSB**	0.427	0.000	0.000	0.000	
F_P (N)						
Material		**(1) 107.80**	**(2) 200.67**	**(3) 156.70**	**(4) 238.15**	**(5) 457.72**
1	**R**		0.000	0.024	0.000	0.000
2	**H_2O**	0.000		0.042	0.083	0.000
3	**NaOH**	0.024	0.042		0.000	0.000
4	**PB**	0.000	0.083	0.000		0.000
5	**OSB**	0.000	0.000	0.000	0.000	
F_E (N)						
Material		**(1) 73.540**	**(2) 133.10**	**(3) 93.085**	**(4) 142.70**	**(5) 309.25**
1	**R**		0.001	0.271	0.000	0.000
2	**H_2O**	0.001		0.024	0.589	0.000
3	**NaOH**	0.271	0.024		0.007	0.000
4	**PB**	0.000	0.589	0.007		0.000
5	**OSB**	0.000	0.000	0.000	0.000	

The data in Table 6 indicated the following findings:

- The R_{minB} was significantly affected by the material with a significance level of 0.000. The effect of the material was not confirmed between the H_2O and NaOH materials, which had a significance level of 0.671.
- In the case of the R_{minC}, the same conclusions as for the R_{minB} were reached.
- Very significant differences between the K_{bendB} and K_{bendC} were confirmed by Duncan's test, which indicated a very significant difference between the values measured in the individual materials, with a significance level of 0.000. An insignificant difference was measured between the R and OSB sets of specimens (P = 0.148), and H_2O and NaOH specimens (P = 0.632).

Table 6. Comparison of the Effect of the Material on the R_{minB}, R_{minC}, K_{bendB}, and K_{bendC} using Duncan's Test

R_{minB}						
Material		**(1) 1282.5**	**(2) 1063.1**	**(3) 1092.9**	**(4) 1897.0**	**(5) 1487.4**
1	**R**		0.002	0.007	0.000	0.003
2	**H_2O**	0.002		0.671	0.000	0.000
3	**NaOH**	0.007	0.671		0.000	0.000
4	**PB**	0.000	0.000	0.000		0.000
5	**OSB**	0.003	0.000	0.000	0.000	
R_{minC}						
Material		**(1) 852.18**	**(2) 706.56**	**(3) 726.40**	**(4) 1263.3**	**(5) 989.88**
1	**R**		0.002	0.007	0.000	0.003
2	**H_2O**	0.002		0.671	0.000	0.000
3	**NaOH**	0.007	0.671		0.000	0.000
4	**PB**	0.000	0.000	0.000		0.000
5	**OSB**	0.003	0.000	0.000	0.000	
K_{bendB}						
Material		**(1) .00937**	**(2) .01130**	**(3) .01108**	**(4) .00645**	**(5) .00872**
1	**R**		0.000	0.000	0.000	0.148
2	**H_2O**	0.000		0.632	0.000	0.000
3	**NaOH**	0.000	0.632		0.000	0.000
4	**PB**	0.000	0.000	0.000		0.000
5	**OSB**	0.148	0.000	0.000	0.000	
K_{bendC}						
Material		**(1) .01409**	**(2) .01701**	**(3) .01668**	**(4) .00969**	**(5) .01310**
1	**R**		0.000	0.000	0.000	0.150
2	**H_2O**	0.000		0.631	0.000	0.000
3	**NaOH**	0.000	0.631		0.000	0.000
4	**PB**	0.000	0.000	0.000		0.000
5	**OSB**	0.150	0.000	0.000	0.000	

Correlation Dependence of the Monitored Characteristics and Density

The statistical significance of the monitored factors is shown in Table 7.

Table 7. Analysis of the Dependence of the Individual Factors on the Material Density using Correlation Analyses and Coefficient of Determination of the Y_E, Y_P, F_P, and F_E

Average Density for Entire Thickness					
Material	**Glue**	**r^2 for Y_E (mm)**	**r^2 for Y_P (mm)**	**r^2 for F_P (N)**	**r^2 for F_E (N)**
R	**PSE**	***	***	****	**
H_2O	**PSE**	*	*	***	*
NaOH	**PSE**	**	**	**	**
PB	**UF**	*	*	***	****
OSB	**MUF**	*	*	**	**

Average Density for a Thickness of 1 mm					
Material	**Glue**	**r^2 for Y_E (mm)**	**r^2 for Y_P (mm)**	**r^2 for F_P (N)**	**r^2 for F_E (N)**
R	**PSE**	*	*	*	*
H_2O	**PSE**	*	*	*	*
NaOH	**PSE**	**	**	**	**
PB	**UF**	*	**	**	*
OSB	**MUF**	*	*	*	*

*r^2 < 10% - low tightness; **10% ≤ r^2 < 25% - slight tightness; ***25% ≤ r^2 < 50% - significant tightness; ****50% ≤ r^2 < 80% - high tightness; *****80% ≤ r^2 - very high tightness

Table 8. Analysis of the Dependence of the Individual Factors on the Material Density using Correlation Analyses and Coefficient of Determination of the R_{minB}, R_{minC}, K_{bendB}, and K_{bendC}

Average Density for Entire Thickness					
Material	**Glue**	**r^2 for R_{minB} (mm)**	**r^2 for R_{minC} (mm)**	**r^2 for K_{bendB}**	**r^2 for K_{bendC}**
R	**PSE**	*	***	***	***
H_2O	**PSE**	*	*	*	*
NaOH	**PSE**	*	**	**	**
PB	**UF**	*	*	*	*
OSB	**MUF**	*	*	*	*

Average Density for a Thickness of 1 mm					
Material	**Glue**	**r^2 for R_{minB} (mm)**	**r^2 for R_{minC} (mm)**	**r^2 for K_{bendB}**	**r^2 for K_{bendC}**
R	**PSE**	*	*	*	*
H_2O	**PSE**	*	*	*	*
NaOH	**PSE**	*	**	**	**
PB	**UF**	*	**	**	**
OSB	**MUF**	*	*	*	*

*r^2 < 10% - low tightness; **10% ≤ r^2 < 25% - slight tightness; ***25% ≤ r^2 < 50% - significant tightness; ****50% ≤ r^2 < 80% - high tightness; *****80% ≤ r^2 - very high tightness

The statistical significances of the correlation coefficients among the factors are shown in Table 8.

Correlation Analysis of the Dependence Between the Monitored Characteristics in the Monitored Materials

The results of the correlation analysis showed that there was a high degree of dependence between all of the monitored characteristics in the case of the R material.

The degree of dependence between the monitored characteristics in the H_2O, NaOH, PB, and OSB materials was not as clear as in the case of the R material. There were relationships between characteristics with degrees of dependence where the significance level was less than 50%.

A graphical representation of the correlation dependencies found in individual materials is shown in Figs. 8 to 12. The results presented in Table 9 and Figs. 8 to 12 showed a clear relationship between the increase in the values of one of the monitored characteristics, which affected the increase or decrease in other monitored characteristics.

Table 9. Spearman's Correlation for Each Evaluated Material

R								
Variable	**Y_E (mm)**	**Y_P (mm)**	**F_E (N)**	**F_P (N)**	**R_{minB}**	**R_{minC}**	**K_{bendB}**	**K_{bendC}**
Y_E (mm)	1.000	0.428	0.721	0.614	-0.443	-0.443	0.420	0.420
Y_P (mm)	0.428	1.000	0.616	0.685	-0.990	-0.990	0.994	0.994
F_E (N)	0.721	0.616	1.000	0.962	-0.660	-0.660	0.633	0.633
F_P (N)	0.614	0.685	0.962	1.000	-0.728	-0.728	0.705	0.705
R_{minB}	-0.443	-0.990	-0.660	-0.728	1.000	1.000	-0.997	-0.997
R_{minC}	-0.443	-0.990	-0.660	-0.728	1.000	1.000	-0.997	-0.997
K_{bendB}	0.420	0.994	0.633	0.705	-0.997	-0.997	1.000	1.000
K_{bendC}	0.420	0.994	0.633	0.705	-0.997	-0.997	1.000	1.000
H_2O								
Variables	**Y_E (mm)**	**Y_P (mm)**	**F_E (N)**	**F_P (N)**	**R_{minB}**	**R_{minC}**	**K_{bendB}**	**K_{bendC}**
Y_E (mm)	1.000	0.654	0.430	0.028	-0.606	-0.606	0.636	0.636
Y_P (mm)	0.654	1.000	0.191	0.214	-0.983	-0.983	0.991	0.991
F_E (N)	0.430	0.191	1.000	0.783	-0.202	-0.202	0.203	0.203
F_P (N)	0.028	0.214	0.783	1.000	-0.271	-0.271	0.240	0.240
R_{minB}	-0.606	-0.983	-0.202	-0.271	1.000	1.000	-0.996	-0.996
R_{minC}	-0.606	-0.983	-0.202	-0.271	1.000	1.000	-0.996	-0.996
K_{bendB}	0.636	0.991	0.203	0.240	-0.996	-0.996	1.000	1.000
K_{bendC}	0.636	0.991	0.203	0.240	-0.996	-0.996	1.000	1.000

NaOH								
Variable	**Y_E (mm)**	**Y_P (mm)**	**F_E (N)**	**F_P (N)**	**R_{minB}**	**R_{minC}**	**K_{bendB}**	**K_{bendC}**
Y_E (mm)	1.000	0.073	0.484	0.242	-0.065	-0.065	0.052	0.052
Y_P (mm)	0.073	1.000	0.166	0.423	-0.962	-0.962	0.980	0.980
F_E (N)	0.484	0.166	1.000	0.905	-0.307	-0.307	0.254	0.254
F_P (N)	0.242	0.423	0.905	1.000	-0.566	-0.566	0.519	0.519
R_{minB}	-0.065	-0.962	-0.307	-0.566	1.000	1.000	-0.994	-0.994
R_{minC}	-0.065	-0.962	-0.307	-0.566	1.000	1.000	-0.994	-0.994
K_{bendB}	0.052	0.980	0.254	0.519	-0.994	-0.994	1.000	1.000
K_{bendC}	0.052	0.980	0.254	0.519	-0.994	-0.994	1.000	1.000
PB								
Variable	**Y_E (mm)**	**Y_P (mm)**	**F_E (N)**	**F_P (N)**	**R_{minB}**	**R_{minC}**	**K_{bendB}**	**K_{bendC}**
Y_E (mm)	1.000	0.172	0.751	0.233	-0.254	-0.254	0.208	0.208
Y_P (mm)	0.172	1.000	0.138	0.486	-0.979	-0.979	0.995	0.995
F_E (N)	0.751	0.138	1.000	0.635	-0.242	-0.242	0.188	0.188
F_P (N)	0.233	0.486	0.635	1.000	-0.549	-0.549	0.518	0.518
R_{minB}	-0.254	-0.979	-0.242	-0.549	1.000	1.000	-0.990	-0.990
R_{minC}	-0.254	-0.979	-0.242	-0.549	1.000	1.000	-0.990	-0.990
K_{bendB}	0.208	0.995	0.188	0.518	-0.990	-0.990	1.000	1.000
K_{bendC}	0.208	0.995	0.188	0.518	-0.990	-0.990	1.000	1.000
OSB								
Variable	**Y_E (mm)**	**Y_P (mm)**	**F_E (N)**	**F_P (N)**	**R_{minB}**	**R_{minC}**	**K_{bendB}**	**K_{bendC}**
Y_E (mm)	1.000	0.317	0.332	0.268	-0.355	-0.355	0.340	0.340
Y_P (mm)	0.317	1.000	-0.299	-0.051	-0.992	-0.992	0.996	0.996
F_E (N)	0.332	-0.299	1.000	0.884	0.258	0.258	-0.273	-0.273
F_P (N)	0.268	-0.051	0.884	1.000	0.008	0.008	-0.022	-0.022
R_{minB}	-0.355	-0.992	0.258	0.008	1.000	1.000	-0.997	-0.997
R_{minC}	-0.355	-0.992	0.258	0.008	1.000	1.000	-0.997	-0.997
K_{bendB}	0.340	0.996	-0.273	-0.022	-0.997	-0.997	1.000	1.000
K_{bendC}	0.340	0.996	-0.273	-0.022	-0.997	-0.997	1.000	1.000

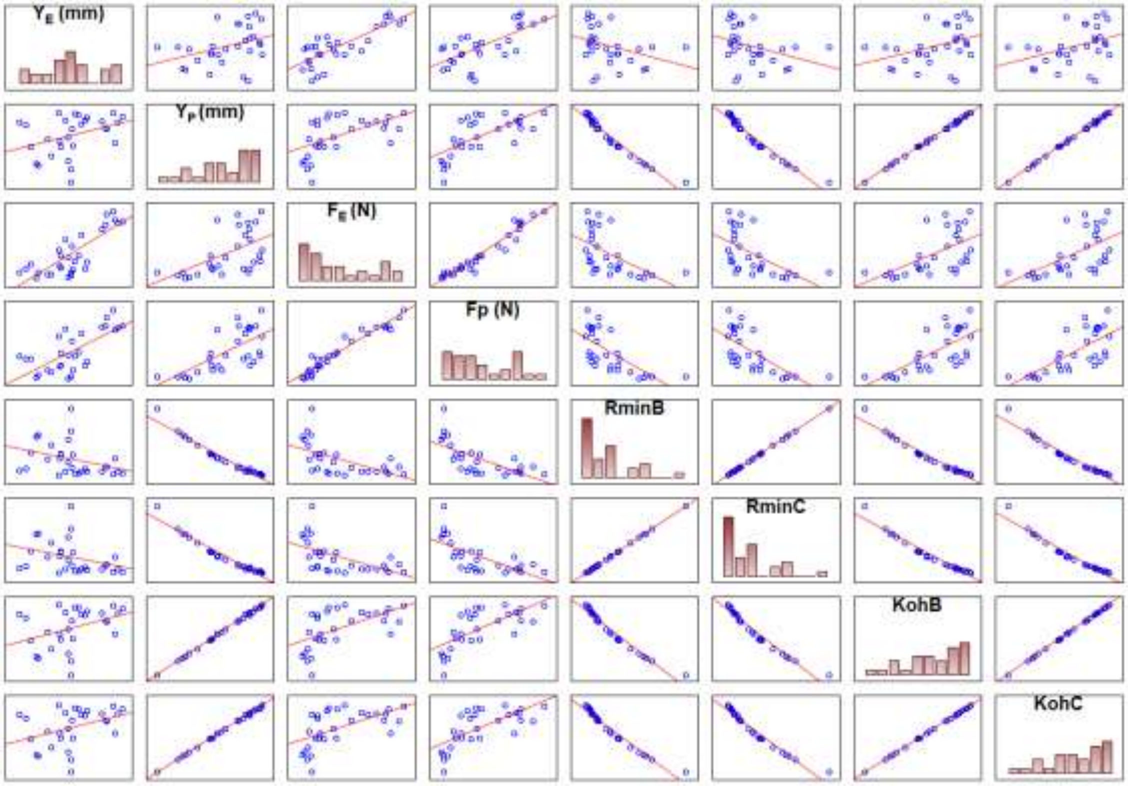

Fig. 8. Correlation matrix of the evaluated characteristics for the R material

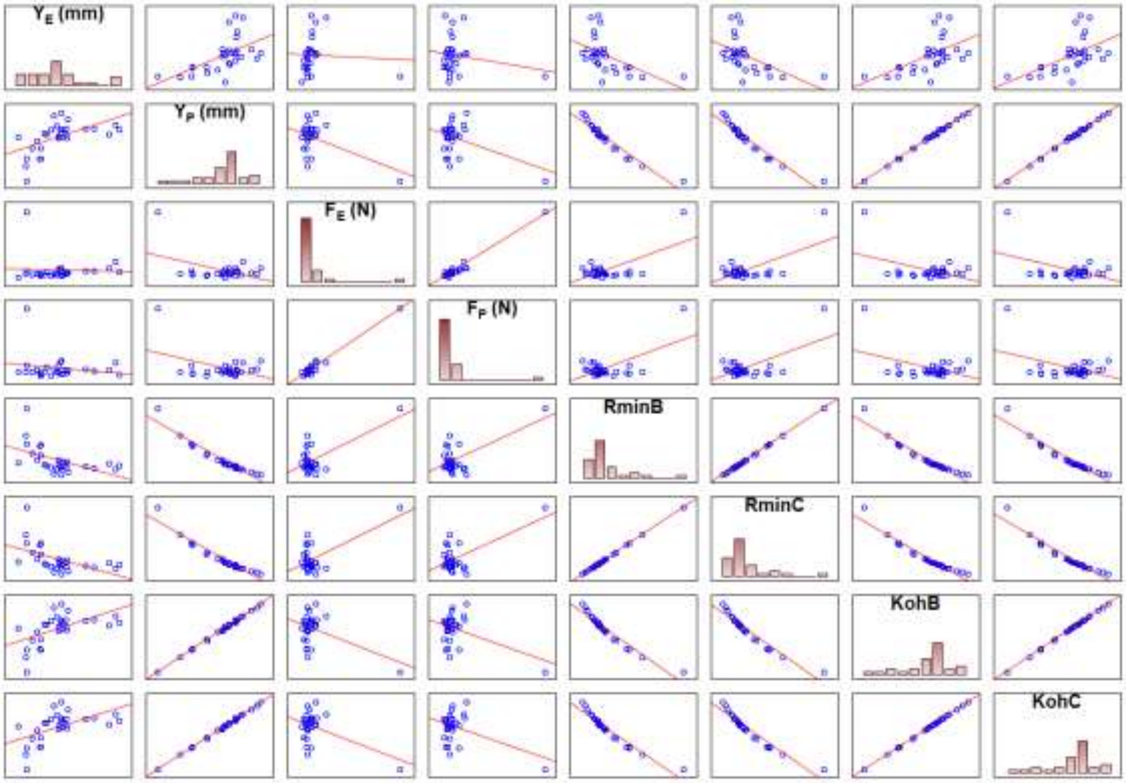

Fig. 9. Correlation matrix of the evaluated characteristics for the H_2O material

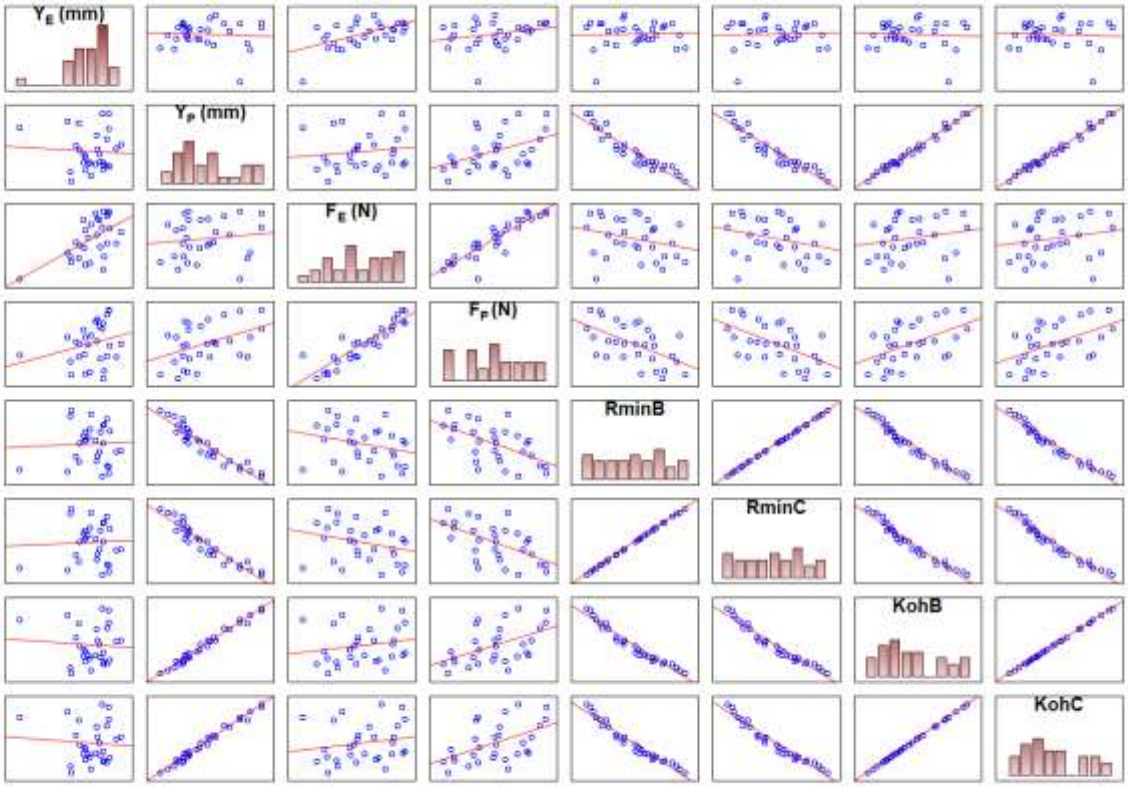

Fig. 10. Correlation matrix of the evaluated characteristics for the NaOH material

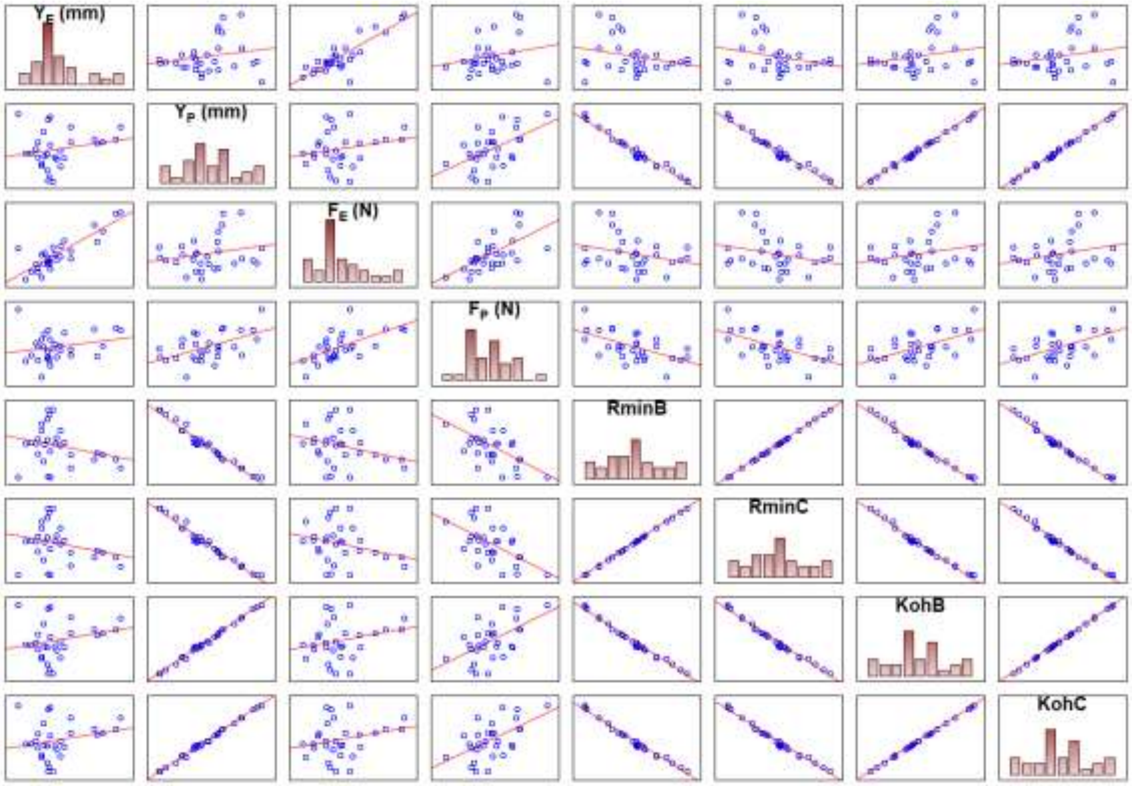

Fig. 11. Correlation matrix of the evaluated characteristics for the PB material

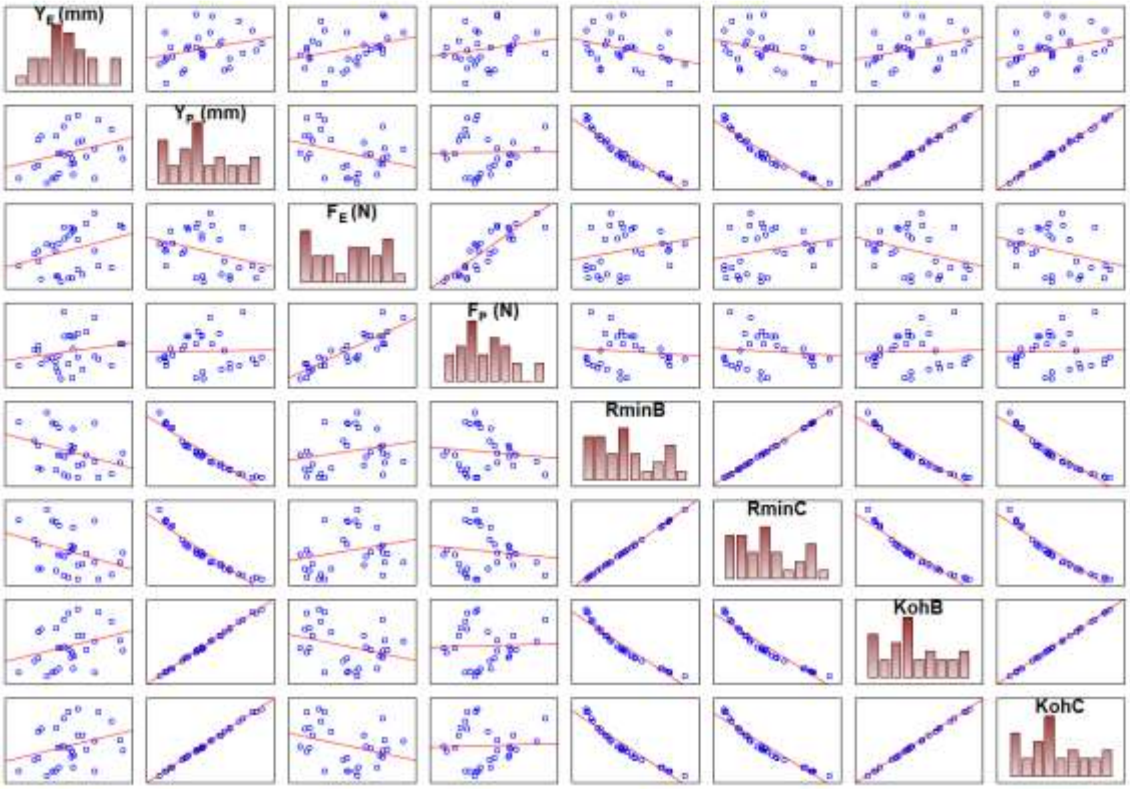

Fig. 12. Correlation matrix of the evaluated characteristics for the OSB material

CONCLUSIONS

1. This article described the bendability of composite materials using completely new software and mathematical models.
2. The results provided comprehensive information about the properties of new composite materials produced from rapeseed residues, as well as commercially available materials with properties that have been unknown until now (PB and OSB).
3. The results indicated that rapeseed can fully replace precious raw materials (wood), and thus increase the protection of the natural environment and ensure the better utilization of waste, which undoubtedly has an impact on the economic indicators of society.
4. The results showed that the materials developed by the authors had significantly higher bendability values (H_2O and NaOH) than the commercially produced materials (PB and OSB). These materials can replace commercially produced materials, which are used for the production of bent furniture components. The properties of the rapeseed boards can be technologically modified.
5. The research showed that biocomposites produced with renewable and available raw materials have excellent bending characteristics, and it is possible to use these materials for special applications.

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Utilisation of Winter Rapeseed in Wood-based Materials as a Solution of Wood Shortage and Forest Protection

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Due to various factors, there is evidence that there will be a future lack of wood materials in the woodworking and energy sectors, as well as other sectors. This has been confirmed definitively through the most recent developments. Possible solutions include the partial replacement of wood in composite materials by post-harvest remnants of agricultural crops. Unlike wood matter, however, these stems need surface pre-treatment before they can be used to produce composite materials. In this study the effects were compared for two pre-treatments of stems (alkaline and hydrothermal) of rapeseed (*Brassica napus* L.), maize (*Zea mays* L.), and wheat (*Triticum aestivum* L.). The effects were compared using the contact angle between water and the surfaces of the stems. Hydrothermal modification yielded a statistically significant reduction in the contact angle between water and the stem surfaces of winter rapeseed and maize; likewise, alkaline modification yielded a statistically significant reduction in the contact angle between water and the stem surface of maize. The possibility of using winter rape to produce composite materials was further evaluated and comprehensively assessed using SWOT analysis.

Keywords: Rapeseed; Wheat; Maize; Straw; Wood; Forest; Surface modification

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INTRODUCTION

Forests are a source not only of goods but also of ecological services and socio-cultural benefits (Stenger *et al*. 2009; Šišák *et al.* 2016). The increased demand for wood, however, can pose a threat to the performance of these non-production functions of forests (Balest *et al. In Press*). Locally and globally, the demand for wood material is increasing, with the greatest needs for its supply, in terms of volume, coming from not only various wood and energy sectors but also from the paper, chemical, and other sectors of national economies (Seintsch 2011; Lauri *et al*. 2012). For example in the Czech Republic, where the production potential of forests is well known (Pulkrab *at al.* 2015), wood-processing companies are facing a shortage of logs even now, with their economic performance declining (Sujová *et al*. 2017). Unfortunately, the growth figures for wood matter are not large enough to meet the ever-increasing demand for its supply (Bostedt e*t al*. 2016). It is estimated that by 2030 there will be an increase of 73% in the demand for wood (compared with 2010), with a shortfall of 316 million m^3 (Mantau *et al*. 2010). To avert the threat of a shortage of wood for industrial use, other actions need to be implemented in cooperation with silvicultural actions, strategies, and measures (Mburu *et al*. 2007; Ye *et al*. 2007; Dieter and Seintsch 2012; Temperli 2017). Legal regulation for the protection of forests appears to be an evident and necessary instrument for coordinating the expected situation.

Comprehensive legislation does not exist within the European Union, even though forest cover accounts for 38% of the surface area of the region. The main reasons for this are the distinct types of geoclimatic diversity and the circumstance that only six member states occupy some two thirds of the total area. This would make any compact European legislation quite extensive or even confusing and, in most member states, impossible to apply in practice. Therefore, member states stipulate the conditions for the protection of forests at the national legislative level (European Parliament 2017). In the Czech Republic, Czech Parliament Act No. 289/1995 (1995) is the main piece of legislation and is further supplemented, in particular, by decrees issued by the Ministry of Agriculture. The main task of the Forest Act is, according to the provisions of its Section 1, to specify the prerequisites for the preservation, management, and regeneration of forests as a national resource while still allowing permanent economic activities in the area; such activities are possible in forests, whether national or private, but compliance with all the conditions for the sustainable development of forests is required.

In the future, demand for wood will continue to increase because of the need to reduce CO_2 emissions and, in particular, to replace energy-consuming materials such as concrete and steel. Another driver of demand will be the goal to eliminate fossil raw materials in both the energy and processing industries, motivated not only by the need to reduce CO_2 emissions but also because deposits of fossil raw materials will gradually become exhausted in the long term (Lauri *et al*. 2012; Temperli *et al*. 2017). This implies that, in addition to forestry and legal measures, which alone cannot fully protect the performance of the non-production functions of forests in the long term, it will be necessary to look for other natural sources of cellulose and lignin. This involves annual and biennial plants because their stems, which also consist of cellulose and lignin, can be utilised for the manufacture of materials (Halvarsson *et al*. 2010; Marinho *et al*. 2013; Hýsek *et al*. 2016) as well as for energy purposes (Haq *et al*. 2016; Taha *et al*. 2016). Post-harvest remnants of agricultural crops appear to be promising materials (Guler *et al*. 2006; Belini *et al*. 2012; El-Kassas and Mourad 2013; Částková *et al*. 2018). Unlike with wood matter. However, the production of composite materials from the stems of agricultural crops typically requires that the surfaces of these stems be pre-treated, in order to disrupt the waxy layer that inhibits high-quality bonding between the particle and the adhesive (Bekhta *et al.* 2013; Částková *et al*. 2018).

Pre-treatment of rapeseed particles by both boiling in water or soaking in NaOH solution led to morphological changes of the particle surface and statistical significant decrease of some elements (Ca, K, Mg, and S) in the particle mass (Částková *et al.* 2018). Bekhta *et al.* 2013 reported that soaking in acetic anhydride solution, as well as boiling in soapy solution or in water enhanced the adhesion between wheat straw particle and urea formaldehyde adhesive, which consequently led to increase of mechanical properties.

This aim of this report is to determine the effects of different types of stem pre-treatment on the surface properties of the stems of rape, maize, and wheat modified in this way. Furthermore, the report seeks to evaluate more comprehensively the possibility of using stems of winter rapeseed for the production of composite materials.

EXPERIMENTAL

Materials

In order to compare the effect of modification on contact angle between stalk surface and water, three kinds of stalks were used: rapeseed (*Brassica napus* L.), maize (*Zea mays* L.), and wheat (*Triticum aestivum* L.). All plants were grown in the Czech Republic in the Central Bohemian Region.

Methods

Two kinds of surface pre-treatment (modification) were tested: hydrothermal modification and alkaline modification. A third group was left untreated as a control. The hydrothermal treatment was carried out by boiling in water for 45 min. In the chemical treatment, the particles were soaked in 2% sodium hydroxide (NaOH) solution at 20 °C for 45 min. After both modifications, particles were carefully flushed with water and then oven dried to 6% moisture content (Částková *et al*. 2018).

To determine the wettability of treated and untreated surface of stalks, the contact angle of the water and stalk surface was measured using a DSA 30E goniometer (Krüss GmbH, Hamburg, Germany). The contact angle was measured only on the exterior surface of stalks. Thirty (30) measurements of static contact angle were made for each straw modification. The volume of each distilled water droplet was 5 µL, with the measurement taken 5 s after the application. Contact angle was measured using image analysis software (Částková *et al*. 2018).

The morphological changes of surface of stalks were observed with a MIRA 3 scanning electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector operated at 15 kV acceleration voltage.

To evaluate measured data, descriptive statistics (arithmetic mean, minimum, maximum, standard deviation, and coefficient of variation) were calculated. A two-way analysis of variance was used to determine whether any of the pairwise differences among the various arithmetic means were significant. The Tukey post hoc test was employed to determine the significant differences between group means. Computations were carried out using Statistica 12 software (StatSoft, Tulsa, OK, USA). A significance level of $\alpha = 0.05$ was selected.

An analysis of strengths, weaknesses, opportunities, and threats (SWOT analysis) was made for boards based on oilseed rape stems in order to evaluate the possibilities of using winter oilseed rape for the production of composite materials; it is presented in the Results and Discussion section.

RESULTS AND DISCUSSION

Surface Modification

Table 1 lists the arithmetical averages, minimum and maximum figures, standard deviations, and coefficients of variation for the data sets of measured contact angles between water and the surfaces of three types of plant stems for three surface treatment variants. In accordance with theoretical assumptions, the greatest contact angles between water and the straw surfaces were achieved in untreated stems in all three species of plants. The highest figures were reached for maize; however, the differences between plants were not statistically significant. Both types of modification caused the desired effect, a reduced contact angle between water and the surfaces of the stems. The lowest figures were recorded for maize stems modified in an alkaline environment.

Table 1. Descriptive Statistics of Measured Contact Angle Values

Straw	Modification	Mean (°)	Minimum (°)	Maximum (°)	Standard Deviation (°)	Coefficient of Variation (%)
Rapeseed	Hydrothermal	82.7	68.85	112.70	10.4	12.6
	Alkaline	91.1	79.01	100.90	6.3	6.9
	Untreated	94.1	70.70	109.90	9.6	10.2
Maize	Hydrothermal	83.9	71.59	98.15	6.9	8.2
	Alkaline	76.8	53.39	97.09	8.6	11.2
	Untreated	94.8	79.13	104.82	5.6	5.9
Wheat	Hydrothermal	89.6	70.73	108.50	11.4	12.8
	Alkaline	85.0	69.42	98.41	7.7	9.1
	Untreated	91.3	62.40	107.05	10.8	11.8

The two-factor analysis of variance shown in Fig. 1 depicts the relationship between the contact angle and the type of stem or surface treatment; Table 2 shows the statistical significance for pairwise differences. The results show that the hydrothermal modification significantly reduced the contact angle between the water and the surfaces of the maize and rape stems. Alkaline modification, in contrast, yielded a statistically significant reduction in contact angle in maize stems only. Using a 0.05 level of significance, alkaline modification of wheat stems did not have a statistically significant effect on the contact angle. Modification by sodium hydroxide solution did reduce the contact angle between water and rape stems, but this difference was not statistically significant either. For rape straw, hydrothermal modification seems to be a suitable type of surface treatment, based on these results. For maize stems, alkaline modification can be used in addition to the hydrothermal variant; however, if a cheaper variant is preferred, hydrothermal modification would be sufficient. From the results obtained, the selected types of modification seem to be inappropriate for modification of the surface of wheat straw.

The contact angle generally presents a high variability among plant materials (Oberhofnerová and Pánek 2016), and increased variability is also evident from the results obtained in this work. The considerable variability of the measured data, unfortunately, caused some of the rather large differences to be statistically insignificant. For example, no statistically significant difference between hydrothermal and alkaline modifications was demonstrated for maize stems, and no influence of modification at all was demonstrated for the contact angle of wheat straw.

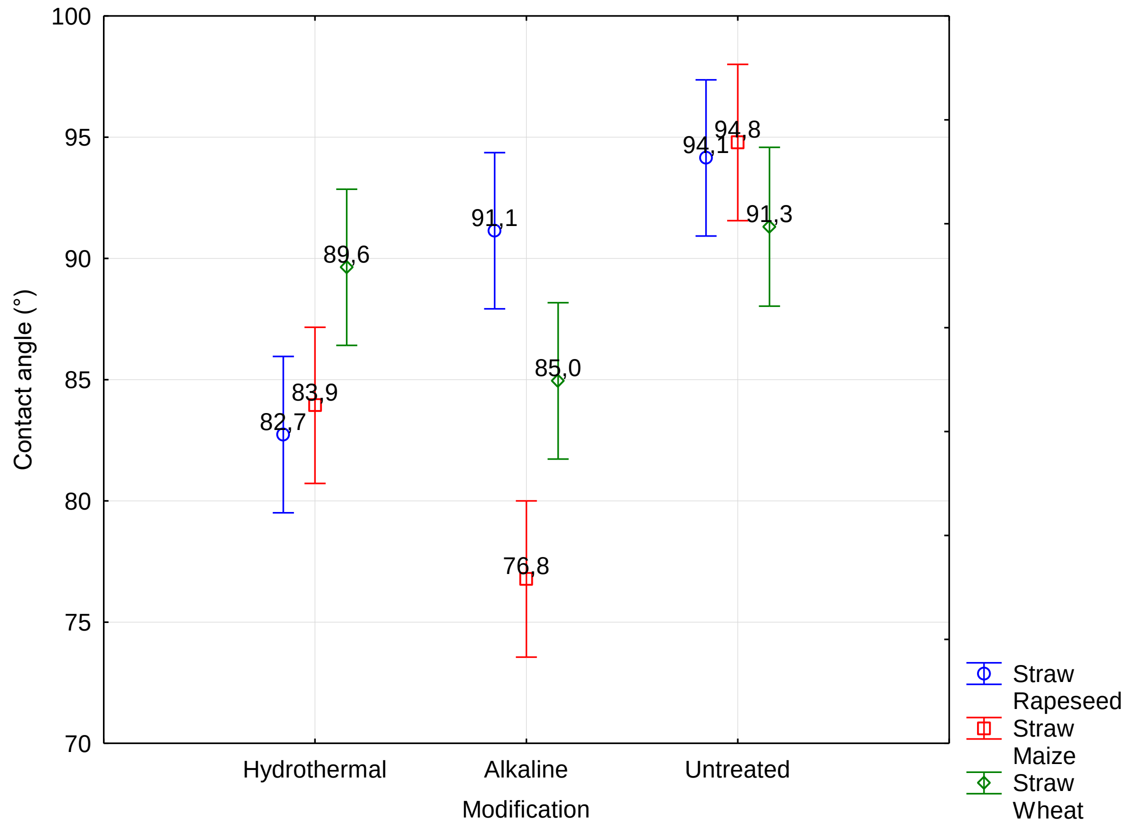


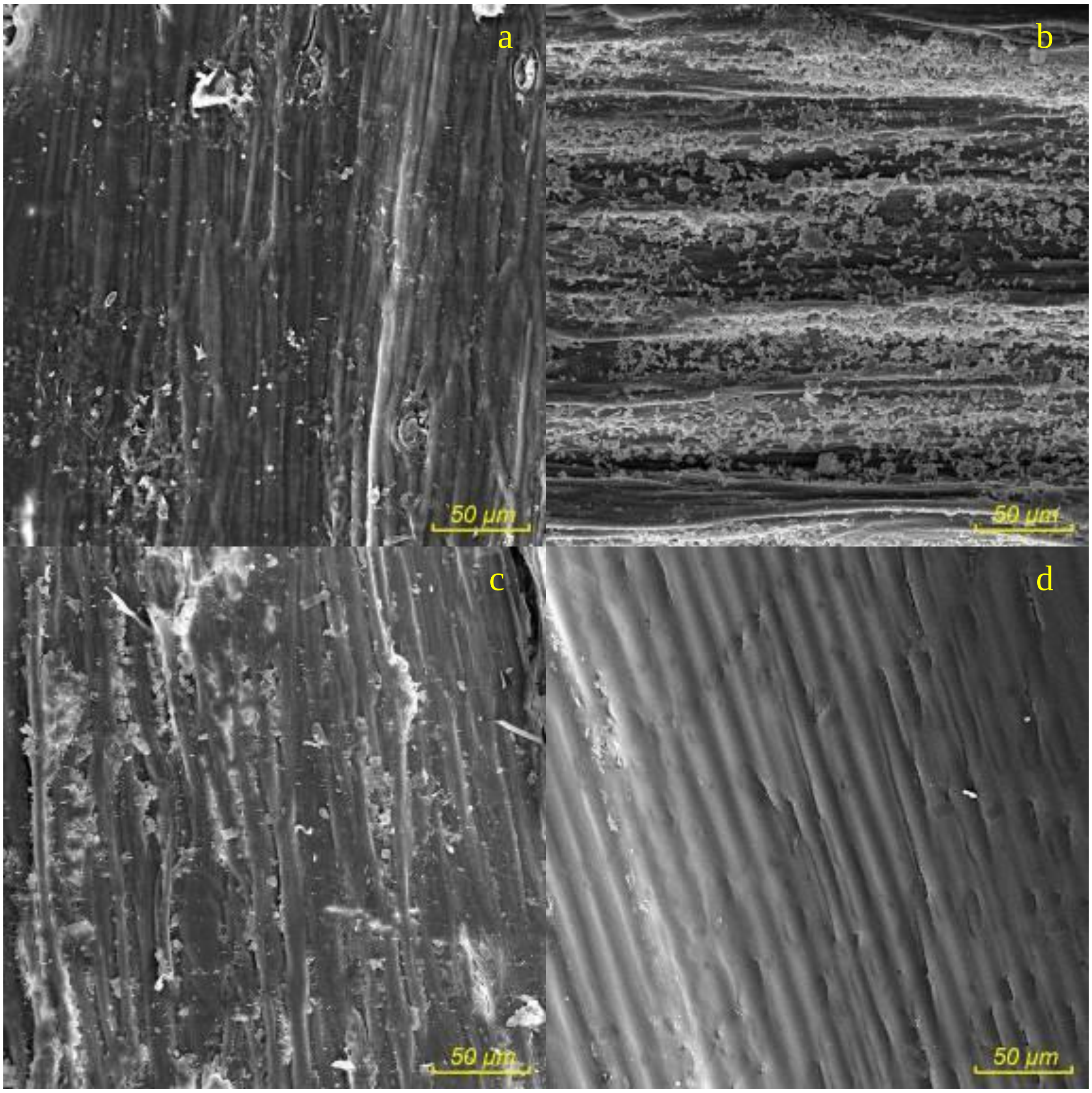
Fig. 1. ANOVA – effect of straw and modification on contact angle (Note: vertical bars depict 95% confidence intervals)

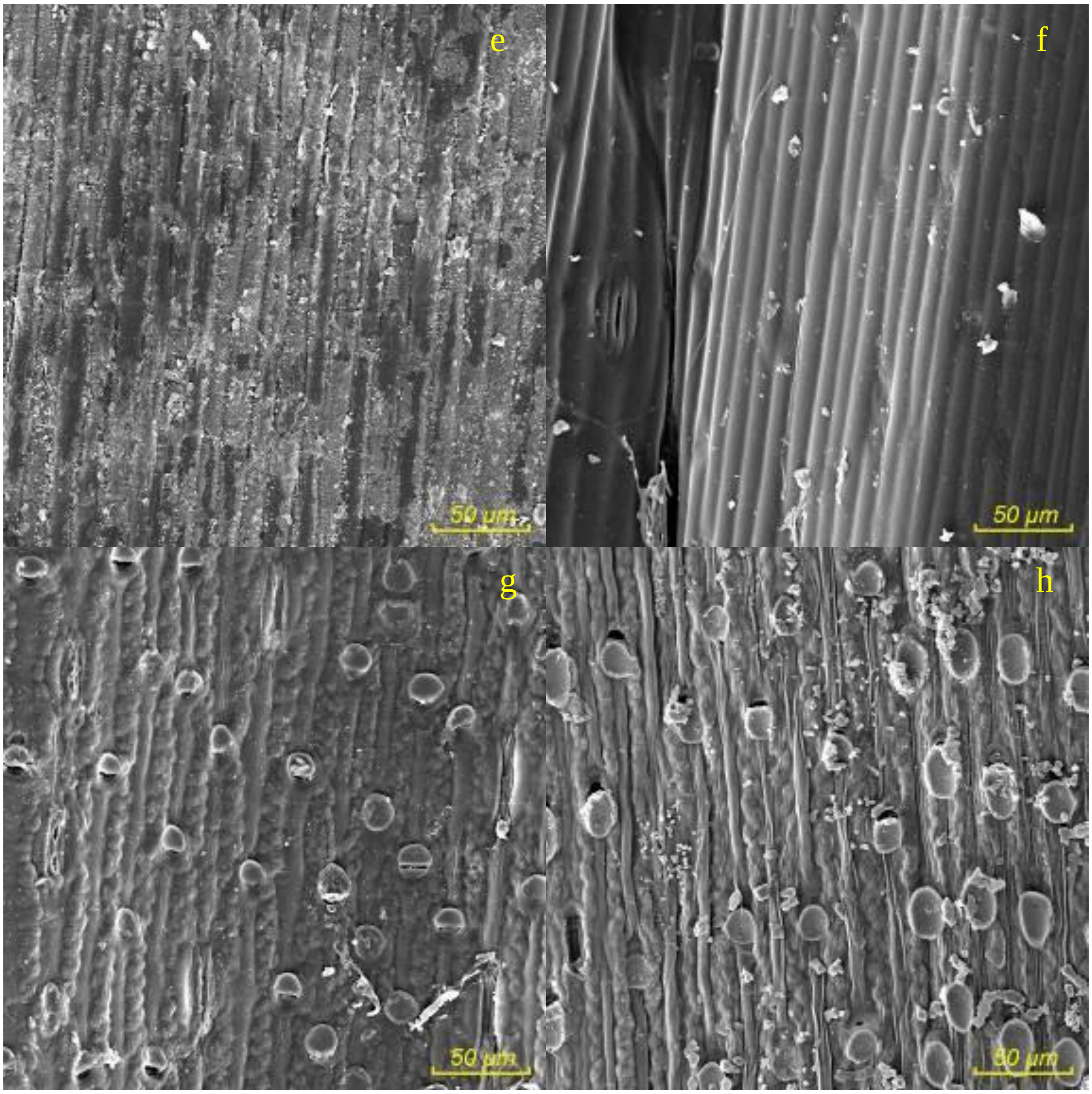
Table 2. Appropriate Statistical Significances of Differences in Fig. 1

	Straw	R	R	R	M	M	M	W	W	W
Straw	Modification	H	A	U	H	A	U	H	A	U
R	H		s.	s.	n.s.	n.s.	s.	n.s.	n.s.	s.
R	A	s.		n.s.	s.	s.	n.s.	n.s.	n.s.	n.s.
R	U	s.	n.s.		s.	s.	n.s.	n.s.	s.	n.s.
M	H	n.s.	s.	s.		n.s.	s.	n.s.	n.s.	s.
M	A	n.s.	s.	s.	n.s.		s.	s.	s.	s.
M	U	s.	n.s.	n.s.	s.	s.		n.s.	s.	n.s.
W	H	n.s.	n.s.	n.s.	n.s.	s.	n.s.		n.s.	n.s.
W	A	n.s.	n.s.	s.	n.s.	s.	s.	n.s.		n.s.
W	U	s.	n.s.	n.s.	s.	s.	n.s.	n.s.	n.s.	

Note: R = Rapeseed, M = Maize, W = Wheat; H = Hydrothermal, A = Alkaline, U = Untreated; s. = significant, n.s. = not significant

In Fig. 2a-i are depicted morphological changes of rapeseed, maize and wheat stalks after different modifications. It can be seen that both hydrothermal and alkaline modification caused visible changes in the surface structure of stems. In Figs. 2g-h one can observe loss of the top layer (epidermis) of the wheat stem surface. Pores of untreated stems are sunk in the top layer, whereas pores of modified stems are protruding, because the top layer is missing. Maize stalks exhibited visual changes of stem surface only after alkaline treatment. The damage of maize stem surface by hydrothermal treatment was not visible, despite the fact that the decrease of water contact angle was significant. It can be assumed that boiling water did not cause any morphological changes of the maize surface, but only washed the stems and thus the water contact angle was lower. Also any damage of rapeseed stem surface was caused by hydrothermal treatment. Rapeseed stems evidenced changes of surface only after alkaline modification. On the rapeseed, maize and wheat stems were deposited crystals of Ca after alkaline treatment. These crystals were precipitated by sodium hydroxide (Částková *et al*. 2018).

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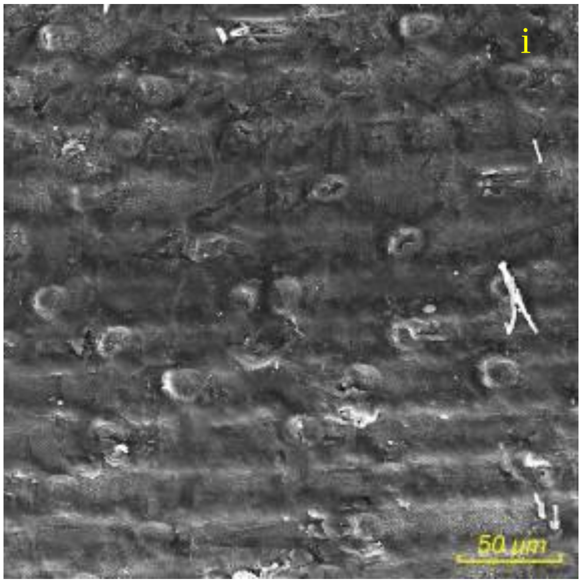

Fig. 2. Electron micrographs of rape, maize and wheat straw surfaces (magnification 1000x). (a) Hydrothermal modified rape stalk, (b) alkaline modified rape stalk, (c) untreated rape stalk, (d) hydrothermal modified maize stalk, (e) alkaline modified maize stalk, (f) untreated maize stalk, (g) hydrothermal modified wheat stalk, (h) alkaline modified wheat stalk, and (i) untreated wheat stalk

Scientific reports that evaluate the possibility of using post-harvest remnants of crops have focused mainly on the characteristics of the material produced. If, however, the present results are to be commercialised, then the issue of producing composite materials from these crops needs a more comprehensive assessment. Therefore, the strengths, weaknesses, opportunities, and threats of the production of particle board from rape stems were analysed. Stems of winter rapeseed were selected as a promising material, with their production amounting to about 42 million tonnes per annum in the European Union (Eurostat 2016); unlike stems of wheat and maize, however, they have not yet found any considerable application. In the European Union, 29.1 million m^3 of particle board was produced in 2015 (EPF 2017). Therefore, the current rape stem production already has the potential to replace almost two times the wood used in particle boards in the EU (ca. 0.75 tonnes of raw materials are required to produce 1 m^3 of particleboards). The possibility of successful replacement of wood in wood-based materials by rapeseed stems has already been demonstrated (Dziurka *et al.* 2015; Dukarska *et al.* 2017), and the effect of rapeseed particle pre-treatment by hydrothermal and alkaline treatment on the disrupting of the surface layer has also already been estimated and reported (Částková *et al.* 2018).

SWOT Analysis of Making Particle Board from Rape

Strengths

- **Low purchasing costs (waste not used):** Rape stems are currently not used; they are turned to chips during harvest and left on the field or used for energy purposes at the most (Karaosmanoğlu *et al*. 1999; Zabaniotou *et al*. 2008; Díaz *et al*. 2009). As this involves unused harvest remnants, low purchasing costs can be assumed.
- **Widespread availability:** In 2017, there was in The Czech Republic a total of 407 thousand hectares of land sowed with rape, which represents 16.5% of the total

sowing area of this country (CSO 2017). For stems, yield per hectare in Europe is 3 to 10 t/ha, meaning that in 2014 the European Union produced around 42 million tonnes of stems (Eurostat 2016). Widespread availability and huge produced amounts of rape stems are reported from all over the word, as from China (Huang *et al.* 2016), Poland (Dukarska *et al.* 2017), Iran (Yousefi 2009), Canada and United States (Oh and Jamaludin 2015).

- **Renewable resource:** It is a renewable resource that can be harvested annually to source lignin and cellulose (Karaosmanoğlu 1999).
- **Policies of the EU and the Czech Republic:** European Union policy supports sowing large areas of winter oilseed rape, meaning that the crop is highly financially advantageous for farmers. The European Union has set itself an objective (European Parliament (EP) Directive 2009/28/EC 2009) to reduce greenhouse gas emissions by 20% compared with the values in 1990. In addition, a directive was adopted (European Parliament (EP) Directive 98/70/EC 1998) concerning fuel quality that tasks fuel suppliers to reduce, by 2020, the intensity of greenhouse gas emissions in fuel mixtures by 6% in comparison with 2010; this provides an incentive for more extensive use of low-carbon fuels in transportation. Because most of this 6% consists largely of rape, there is an assumption of high consumption of rape (European Commission (EC) Report COM(2017) 284 2017). This issue is also elaborated at the national level; the mandatory content of mineral oil is governed by Czech Parliament Act No. 353/2003 (2003), where it is established that a mixture of medium oils and heavy gas oils shall contain at least 30% methyl ester of rapeseed oil (§ 45(2)(c)). Despite the fact that in the European Union 2nd generation biofuels are regarded as having better prospects, in the Czech Republic biofuels 1st generation from rapeseed are highly supported, the financial concession can be found in the excise taxes (Act No. 353/2003 (2003).
- **Good mechanical and physical properties:** The chemical composition of stems and the dimensions of rape fibres are similar to those of the wood of broad-leaf trees (Adapa *et al*. 2009; Tofanica *et al.* 2011). The characteristics of composite materials made of this raw material are comparable with commercially available products based on wood (Huang *et al*. 2016; Nikvash *et al*. 2012; Dziurka *et al*. 2015; Dukarska *et al*. 2017).
- **The existing technology of particle and fibre boards can be leveraged:** Given the similarities in the composition of rape fibres and particles and those of wood, existing board production technology could presumably be utilised after modifications.
- **Stems can be compressed for storage:** Stems of annual and biennial plants contain pulp, allowing compression of the straw into bales for transportation, handling, and storage.
- **Annual cycle of rape cultivation:** The annual cycle of the cultivation of winter oilseed rape (Su *et al*. 2014), and the consequent production of straw, is an important benefit permitting rapid response to changes in the market.
- **Low energy intensity of production:** The bulk density of rape straw is around 270 kg/m^3 for 10% moisture content; the particle density is 1,550 kg/m^3 (Adapa *et al.* 2009). Compared with wood, which has a significantly higher density, the stems are easier and require less energy to disintegrate (Zhu and Pan 2010).

- **CO_2 emissions reduction:** Unlike burning stems in solid form or using them for biofuel production, making boards binds CO_2 in the product for several decades (Schlamadinger and Marland 1996).

Weaknesses

- **Variability of the properties:** The properties of natural materials exhibit higher variability compared with artificial materials (Anandjiwala and Blouw 2007; Das *et al*. 2012; Hýsek *et al*. 2016).
- **Soaking and moistening capacity:** With free hydroxyl groups contained in the cellulose fibres, rape fibres can absorb molecules of water from both the air and liquid water (Hofstetter *et al*. 2006), which in turn influences the properties of soaking and moistening of materials produced from these fibres. In composite materials, however, soaking and moistening capacity can be substantially reduced by appropriate adhesives and additives (Dukarska *et al*. 2017).
- **The technology of collecting straw from fields is not fully developed:** Currently, winter oilseed rape stems are being turned into chips when harvested and left lying in the fields. For collecting stems, it would be appropriate to use collecting and packaging units that are already being used for collecting post-harvest remnants of other crops (Carvalho *et al*. 2017; Tang *et al*. 2017).
- **Production technology is not fully developed:** Boards made of rape particles are not yet commercially produced, though research is currently underway, with objectives including the development of board production technology. In the case of water-assisted particle pre-treatment, waste water management could raise costs of this production.
- **Demand for environmentally friendly products still low:** Demand for environmentally friendly products is rising, yet only a quarter (26%) of the EU population “often buy environmentally-friendly products” (Flash Eurobarometer 2013).
- **Drawing nutrients from the soil:** Compared with ploughing stems into the soil, nutrients are removed from the soil, with the subsequent need for fertilising using inorganic fertilisers (Su *et al*. 2014). However, the straw still needs to be ploughed into the soil for the nutrients to be absorbed. Through the widely used practice of shallow ploughing, instead of deep ploughing, the quantity of nutrients absorbed is significantly reduced (Su *et al*. 2015; Zhu *et al*. 2016).
- **Bulkiness of the raw material:** Pulp represents a substantial portion of the stem. Due to the pulp, the density of the stems is 270 kg/m^3 for approximately 10% humidity, and bulkiness is greater in comparison with wood (Adapa *et al*. 2009).
- **Degradation by biotic factors:** Stems of rape can degrade through the action of biotic factors when stored improperly, as can any other natural lignin-cellulose material (Anandjiwala and Blouw 2007; Das *et al*. 2012).
- **Seasonal nature of the harvest:** Given the seasonality of the harvest (Tofanica *et al*. 2011), it is necessary to put the material into storage in large quantities, with an associated cost.

Opportunities

- **An extensive market of large-area composite materials for construction and furniture-making applications:** In the European Union, 53.8 million m^3 of wood-based, large-area composite materials were produced in 2015 (EPF 2017).
- **Improved economic situation of farmers:** Using straw as a by-product from the production of winter rape provides a significant monetary income to farmers.
- **Addressing the situation of the wood raw materials shortage:** The partial replacement of wood in lignin- and cellulose-based composite materials by winter rape can significantly contribute to addressing the lack of wood in various wood-processing and energy sectors (Ye *et al*. 2007; Dziurka *et al*. 2015). This contributes to protecting the equally important non-production functions of forests as a very important positive externality.
- **Legislative support for environmentally-friendly products:** Support from national governments for environmentally-friendly solutions is assumed in the future and can enhance their propagation in relation to products from non-renewable resources.
- **Low energy consumption in production:** Energy demands for the production of final products made of wood-based composites is significantly lower than for products made from concrete, steel, or glass. It is assumed that the production of boards from rape will use even less energy than production from wood.
- **Expansion into sectors other than just the furniture-making and construction industries:** While the furniture-making and construction sectors are assumed to be the major industries in which products made of rape stems could find applications (in the form of large-area materials), composite materials made of rape stems, such as composites from fibres and shaped moulded pieces, could find applications in automotive, shipbuilding, and other industries.
- **Utilising the stems of plants other than rape:** There could be more than just winter oilseed rape fibres or particles present in the composite materials produced; they could be combined with other natural fibres or particles according to the purpose (Nikvash *et al*. 2012; Oh and Jamaludin 2015).

Threats

- **Competition from composite materials made of other renewable raw materials:** Research is underway, focusing on the use of other renewable raw materials. Possible examples for potential use include bamboo (Marinho *et al*. 2013), sugar cane (Belini *et al*. 2012), reeds (Han *et al*. 2001), flax, hemp, and kenaf (Aisyah *et al*. 2013; Papadopoulou *et al*. 2014).
- **Concrete lobby:** The lobbying activities of conventional construction companies could significantly hamper the propagation of materials based on wood and other natural resources; this currently involves legislative disadvantages and the limits applied to wood structures.
- **Low consumer awareness:** In general, any further growth in production using renewable raw materials in Europe might be prevented through low consumer awareness. In Eastern European countries especially, consumers still prevail who prefer cheaper variants using non-renewable resources to those involving renewable resources.
- **Pests:** As with any other monoculture, fields of rape are at risk of being damaged by pests. As the area of monoculture grows, this threat is increasing, making it necessary

to take agronomic measures. In the case of winter oilseed rape, this involves selective breeding, proper agronomic practices, treatment of crops against pests, and other measures (Zegada-Lizarazu and Monti 2010).

- **Competition from biofuel production:** Producing biofuels provides an alternative to using post-harvest remnants of agricultural crops to produce composite materials; this primarily involves bioethanol production. Raw materials for producing biofuels are also not subject to quality requirements of such a high level as are materials intended for the production of composite materials (Haq *et al*. 2016; Taha *et al*. 2016).
- **Reduced rape production volume:** Any reduced production of winter rape, whether from a change in the policy that currently results in a higher volume of rape production compared with other raw materials or from other factors such as decreased demand for rapeseed oil, poses a significant threat. According to Directive 98/70/EC (1998) on the quality of fuels, the European Commission does not propose extending the reduction of emissions of greenhouse gases through fuels after 2020 (European Commission (EC) Report COM(2017) 284 2017).

CONCLUSIONS

1. Hydrothermal and alkaline modification of the surface of plant stems has an effect on the contact angle between the stem surface and water.
2. Specifically, hydrothermal modification yielded a statistically significant reduction in the contact angle between water and the stem surfaces of winter oilseed rape and maize; likewise, alkaline modification yielded a reduction in the contact angle between water and the stem surface of maize.
3. SWOT analysis suggests that winter rape stems are a very promising material for the production of composites.
4. Partial replacement of wood in wood-based composites with winter rape stems brings positive externalities, one of the most important being a contribution to the protection of the non-production functions of forests.

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Effect of Cold Plasma Surface Pre-treatment of Wheat Straw Particles on Straw Board Properties

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Effects of the plasma treatment were evaluated for particles from winter wheat stalks relative to the properties of particleboards manufactured from such treated particles. Using urea-formaldehyde adhesive, boards with a nominal density of 540 kg/m^3 and a thickness of 6 mm were manufactured. Two degrees of plasma treatment were selected: cold plasma applied at atmospheric pressure by jet system, with a generator output voltage of 26.9 V and a current of 6.9 A; and in the second treatment, a maximum voltage of 28.6 V was used with a current of 8.7 A. The physical properties (equilibrium moisture content and thickness swelling depending on relative humidity) and mechanical properties (bending strength and tensile strength perpendicular to the plane of the board) were determined. The results showed that the plasma pre-treatment of particles had a statistically significant effect on the resulting composite properties. The mechanical properties of the boards increased with both plasma treatments, but the physical properties changed negatively. Boards manufactured from particles treated with a higher degree of plasma treatment resulted in significantly higher equilibrium moisture contents and thickness swelling than the reference boards.

Keywords: Cold plasma; Wheat straw; Particleboard; Surface modification; Water uptake

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INTRODUCTION

Cellulose and lignin-based plant materials are often used in composite materials, where they can act as fillers and reinforcing materials. It is always important to ensure the thorough bonding of the plant particle and the polymer. It has been proposed that a basic prerequisite for solid particle-polymer bonding is the presence of reactive groups on the interface of both materials to provide high surface energy (Mwaikambo and Ansell 2002; Bekhta *et al.* 2013). In composites hardened by plant materials, the opposite phenomenon is usually encountered, in which the solid bond between polar cellulose and nonpolar polymer is not easily formed. The wettability of a natural fibre or a particle by polymer is further worsened by the waxy substances that natural fibres often contain. In addition, the presence of water and free hydroxyl groups, in particular in amorphous portions, reduce the possibility of creating a strong bond between plant materials and most adhesives. Furthermore, a high water and moisture uptake causes dimensional changes in plant fibres, implying a reduction in the mechanical and physical properties of the composite material (Mwaikambo and Ansell 2002; Xie *et al.* 2010; Gajdačová *et al.* 2018).

Chemical modification of the fibre not only can improve the adhesion between the surface of the fibre and the polymer, but the specific fibre strength can increase, the water absorption by the composite can be decreased, and the mechanical properties of the entire composite material can also be improved (Li *et al.* 2007). However, the disadvantage of traditional methods of chemical surface modification is the production of hazardous substances that may endanger the environment and human health. From this perspective, surface treatment using plasma is a more benign method toward the environment.

Plasma is an ionized gas containing ions, electrons, neutral and excited molecules, and photons (Baltazar-y-Jimenez *et al.* 2008). Two methods of surface treatment using plasma can be distinguished at low pressure and at atmospheric pressure. Plasma surface treatment at atmospheric pressure is less demanding for instrumentation and has been a progressive method in recent years (Cheng *et al.* 2010). The interaction of plasma with a solid surface results in varying changes in surface properties depending on the type of gas used. Surface energy may be increased or decreased, cross-linking of cellulose in the surface layer may occur, or the forming of free reactive groups may take place (Podgorski *et al.* 2000; Baltazar-y-Jimenez *et al.* 2008).

Cold plasma does not cause any changes deeper in the material, but rather only affects the surface layers (Mahlberg *et al.* 1999). The most important parameters when treating a surface with plasma are the plasma surface contact time, the distance between nozzle and surface, and the size of the current (Baltazar-y-Jimenez *et al.* 2008). Primarily the following gases are used to modify the surface of lignocellulosic materials to better bond with the polymer: oxygen (Mahlberg *et al.* 1999), air (Baltazar-y-Jimenez *et al.* 2008), and argon (Zanini *et al.* 2005).

The aim of this research was to clarify the effect of a cold plasma surface treatment of crushed winter wheat stalk particles, prior to board manufacturing, on the physical and mechanical properties of thereof produced particleboards. Specifically, this is a determination of the impact of plasma treatment on the bending strength, tensile strength perpendicular to the plane of the board (internal bonding), vertical density profile, water uptake, and thickness swelling of boards manufactured from plasma-treated wheat straw bonded with urea-formaldehyde adhesive.

EXPERIMENTAL

Materials

Straw particles

Commercially-sold chopped wheat straw particles were used to manufacture the boards (Mikó Stroh, Borota, Hungary). Using digital image analysis, the proportion of individual fractions was defined per 100 g of material sample using a particle analyzer CAMSIZER (Retsch Technology GmbH, Haan, Germany). The sample was poured into the feed chute, allowing the material to enter the measurement field through the feed guide, which prevented unwanted turbulence of the particles and gave the particles the correct orientation. The maximum range was set to 50 mm. The shortest (width) and the longest particle distance (length), measured by the Feret diameter during the projection, was assessed.

Methods

Plasma application method

The wheat straw surface was modified by atmospheric cold plasma in a mixing agent designed to treat particles and other loose materials (Fig. 1). The base consisted of an iron vessel (outer diameter of 415 mm) attached to a rotating platform. At the top, the container was covered with transparent polycarbonate (PC) to close the plasma application environment and to enable visualization of the course of the modification. Inside the container was an eccentrically-positioned cylinder (outer diameter of 110 mm) that was attached to a fixed arm that held it in a stable position relative to the bowl.

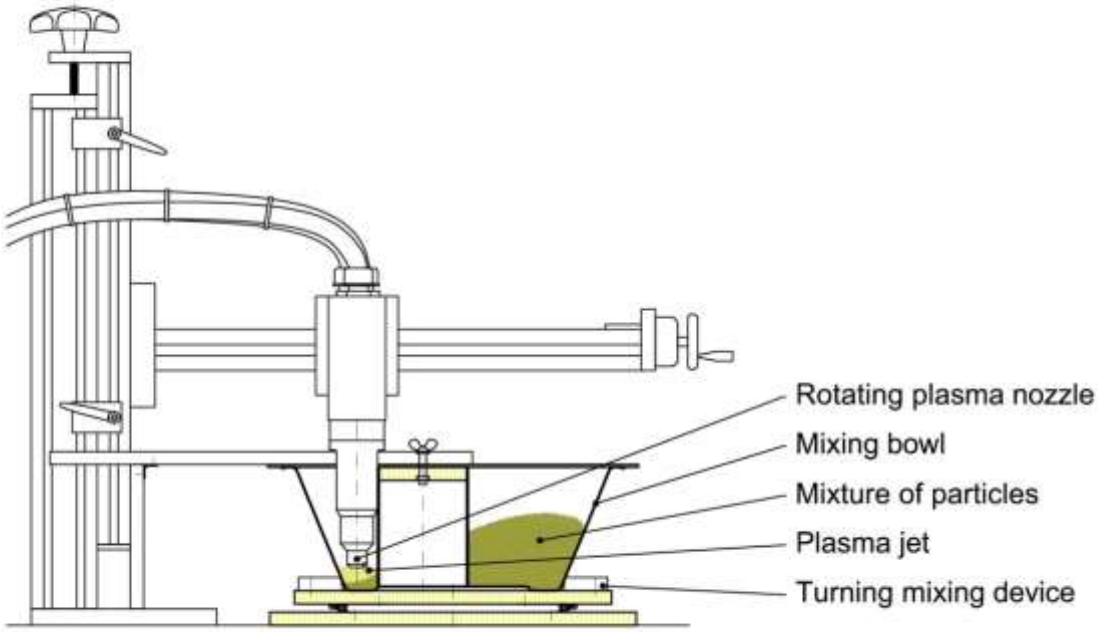

Fig. 1. Side view of the set-up of the stationary plasma aggregate with designed mixing agent

The plasma beam was generated by a high-voltage discharge from the FG 1001 generator (PlasmaTreat GmbH, Steinhagen, Germany) with a maximum output of 1000 VA, and it was distributed to the surface of the particles using compressed air (2 bar). Cold air plasma generated at atmospheric pressure was used. The rotary system of the nozzle of plasma aggregate RD1004 (PlasmaTreat GmbH, Steinhagen, Germany) with the standard AGR 131A (25°) nozzle produced a conical beam shape. To compare the effect of the treatment on wheat-straw using plasma, two variants of surface treatment and one reference variant without treatment (R) were proposed. The variants of plasma application are shown in Table 1.

Table 1. Variants of Plasma Modifications

	Voltage (Generator Set Up)	Current (Generator Set Up)
Modification A	26.9 V	6.9 A
Modification B	28.6 V	8.7 A

The plasma was applied to 100 g of wheat straw for 4 min, and during the treatment, the Alther 2590 digital thermometer (Ahlborn Mess- und Regelungstechnik GmbH, Holzkirchen, Germany) recorded the maximum temperature inside the particle blend.

The degree of plasma surface activation of particles was evaluated with the use of Arcotest (Arcotest GmbH, Moensheim, Germany) test inks designed to measure surface tension. The ink value was identified 2 s after it was applied to the surface, and then an image was recorded using the DTX 90 digital microscope (Levenhuk, Tampa, USA). Testing was conducted until the ink started to coalesce into drops. When it coalesced, a lower-value ink was used, and the boundary between the two inks was sought out.

Adhesive mixture application

After activation of the surface, the particles were resinated with a preformed urea-formaldehyde (UF), hardener (ratio solids hardener / dry adhesive was 10%), and paraffin emulsion mixture (ratio solids hydr. agent / dry particles was 1%). The solid content was 50%. A resin dosage of 10% solids on wood dry mass was applied in a planetary mixer M 301 (Bonnet, Mitry-Mory, France). The mixture was subsequently placed in a drying chamber EHR-K 15/40/20 II (Helios Ventilatoren GmbH, Villingen-Schwenningen, Germany), where it was dried at 30 °C to a moisture content of 8%. The ISI10 scale (Sartorius AG, Göttingne, Germany) was used to continuously monitor water loss, and the final moisture was determined on a moisture tester Ultra X 3011 instrument (A&P instruments, Detmold, Germany). *Via* gradual pouring, the prepared mixture (175 g) was manually layered into a mold with internal dimensions of 128 mm × 355 mm. The layer was spread evenly along the horizontal guiding lines on the inside of the mold.

Pre-pressing and hot-pressing

The mold was then closed and a cold pre-press was performed on the HLP350 hydraulic press (Höfer Presstechnik GmbH, Taiskirchen, Austria). The pressing conditions were set manually by means of the controller to an initial pressure of 4 bars for 1 min. The pre-pressed board was then removed from the mold and continued to be pressed by two heated plates set to 165 °C. The pressing plates were always separated on both sides using waxed paper to avoid adhesion of the boards to the press plate. The pressing was performed according to the pre-set program on the resulting board thickness of 6 mm. The press cycle is shown in Table 2. The total number of six boards for each variant was manufactured. The boards were then allowed to cool down and, further on, they were conditioned at 20 °C and a relative humidity (RH) of 65% for 14 days.

Table 2. Pressing Cycle

Phase No.	Thickness at the End (mm)	Moving Time (s)	Remaining Time (s)
1	40	0.1	0
2	9	4	0
3	5.9	4	6
4	6	5	5
5	6.3	3	0
6	6	3	50
7	6.5	25	0
8	500	0.1	0

Physical and mechanical properties estimation

Test samples were made from the manufactured boards with a rectangular shape for four-point bending, internal bonding, vertical density profile measurement, and samples for water uptake with thickness swelling. Before the mechanical properties measurement, the test specimens were air-conditioned at 65% RH and a temperature of 20 °C.

Strength tests (Fig. 2) were performed on a TIRA test 2850 (TIRA GmbH, Schalkau, Germany) universal testing machine. The maximum force, F_{max}, was always recorded with 1% accuracy. The maximum load was always achieved within 60 s ± 30 s. Before loading, the test specimens were placed in an air-conditioned chamber at 65% RH and a temperature of 20 °C.

The basis of the bending test was to place the test specimen (50 mm × 300 mm) flat on two parallel cylindrical supports (d = 30 mm). Another two supports (d = 30 mm) had a constant loading force, F, cantered above the axis of the board and the maximum force, F_{max}, derived by the machine was measured. The total bending strength was calculated as the arithmetic mean of the values of the following equation for each group of specimens,

$$\mathrm{f_m}\ (\mathrm{N} * \mathrm{mm}^{-2}) = \frac{3 * \mathrm{F_{max}} * \mathrm{l_m}}{2 * \mathrm{b_m} * \mathrm{t_m^2}}, \qquad (1)$$

where l_{m} is the length (mm), b_{m} is the width (mm), and t_{m} is the thickness (mm) of the test specimen for four-point bending. Tests were not performed according to EN 798 (2004) because no characteristic values of board properties were determined. Using this measuring method, it is possible to compare measured strength values with previously obtained data from the authors' research.

The internal bonding of boards was estimated according to EN 319 (1993) on samples with dimensions of 50 mm × 50 mm.

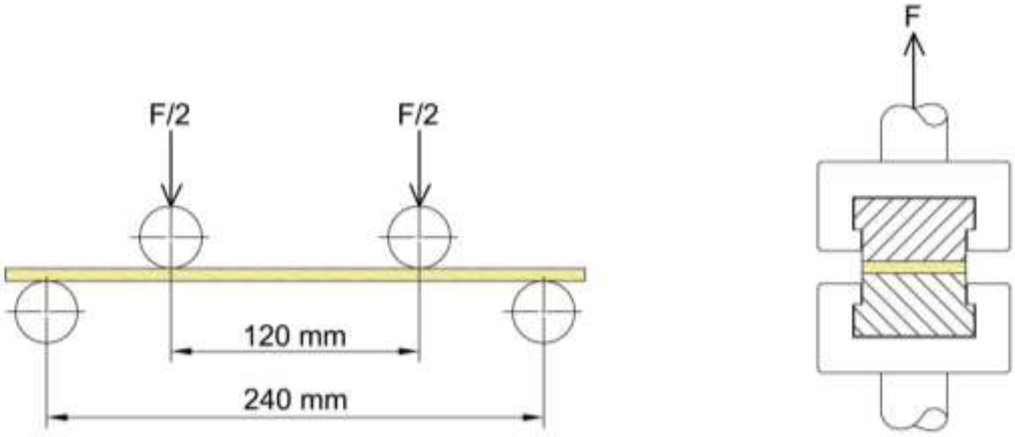

Fig. 2. Diagram of mechanical properties testing

According to Eq. 2, dimensional changes at different air-conditioning stages were determined for water uptake and thickness swelling. The test specimens were first dried to 0% board moisture at 103 °C (air-conditioning stage 0). The samples were then air-conditioned at 20 °C and 65% RH (air-conditioning stage 1) and then at 85% RH (air-conditioning stage 2).

This was reverted to desorption at 65% RH (air-conditioning stage 3), and the last phase was the reverse drying of the samples back to 0% moisture at 103 °C (air-conditioning stage 4). Weight with dimensions of test specimens at marked points was determined at each stage.

$$\beta_x(\%) = \frac{l_x - l_0}{l_0} \text{ x } 100 \tag{2}$$

Measuring points were indicated to ensure repeatability by measuring (mm) in the same position for all air-conditioning stages (x = 0 to 4). Furthermore, the moisture content of samples w_x (%) according to Eq. 3 was determined, where m_0 is the dry sample weight (g) and mass m_x is the weight of the samples at air-conditioning levels (g). The density of the samples ρ_x (kg/m^3) was again calculated from the mass m_x and the sample volume V_x according to Eq. 4:

$$w_x\ (\%) = \frac{m_x - m_0}{m_0} \text{ x } 100 \tag{3}$$

$$\rho_x\ (\text{kg} * \text{m}^{-3}) = \frac{m_x}{V_x} \tag{4}$$

The vertical density profile of boards was measured on a Compact X-ray density profile Analyser DPX300-LTE (Imal, Modena, Italy). The test samples had dimensions of 50 mm × 50 mm and were air-conditioned at 20 °C and 65% RH.

Scanning electron microscopy (SEM) of ruptured samples, after internal bonding tests were performed using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector, operated at 15 kV acceleration voltage.

Statistical methods

Besides descriptive statistics, an analysis of variance was used to determine whether any of the pairwise differences from the number of means were significant. The Tukey *post hoc* test was employed to determine the significant differences between group means. A significance level of $\alpha = 0.05$ was selected and all computations were performed using Statistica12 software (StatSoft CR s.r.o., Prague, Czech Republic).

RESULTS AND DISCUSSION

Particle size analysis

A digital imaging analysis revealed a heterogeneous proportion of the used wheat straw particles from which the boards were made. As shown in Fig. 3, there are also a number of dust particles in addition to the wheat straw stalks. Nevertheless, it was found that from 100 g of the sample, 30.9% of the particle was from 1.657 mm to 2.696 mm wide. In terms of length (Feret diameter), 29.1% of particle sizes ranged from 8.393 mm to 13.656 mm.

The projection of some deformed particles may result in inaccuracies in measurements, which may be due to the processing of, for example, broad and thin or narrow and long stalks. To avoid distortion of the results, a sufficiently large set of 100 g was chosen to cover these inaccuracies.

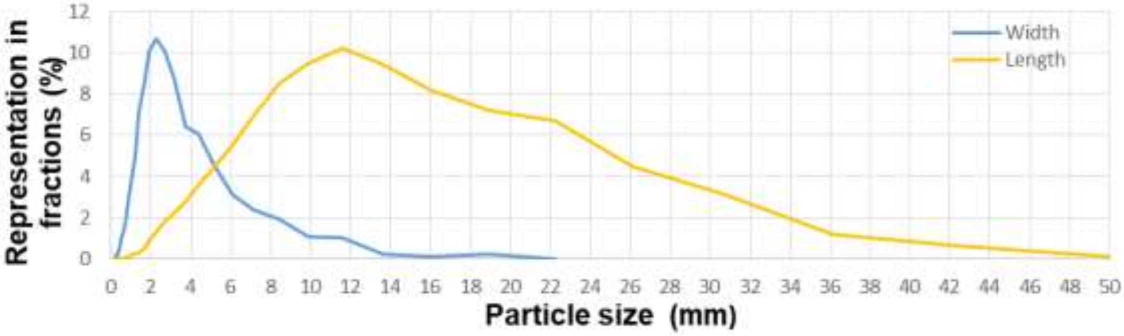

Fig. 3. Results of the particle size analysis

Plasma application and surface tension changes

Due to the designed enclosed mixer, it was possible to modify the particle mixture homogeneously using plasma. Two modification degrees of lower (26.9 V/6.9 A) and maximum power (28.6 V/8.7 A) were used to treat the straw. Despite the fact that cold plasma was used, the maximum average vessel temperature reached 81 °C at lower power, while at maximum power it increased up to 86 °C. As a result, most likely a small effect of thermal treatment has to be taken in consideration in addition to the plasma treatment of the wheat straw. This effect led to a pre-drying of the particles.

After plasma treatment, test inks on the outer sides of the straw determined a change in the surface energy of the modified particles, which were compared with the reference particles without modification. The surface tension on the outside of the reference straw covered range values from 24 mN/m to 28 mN/m. Wheat straw with a lower degree of plasma treatment (A) ranged from 28 mN/m to 30 mN/m, and at a higher degree of modification (B), the surface tension was from 30 mN/m to 32 mN/m. The variability of the unmodified particles was thus higher than that of the plasma-treated particles. Therefore, the testing inks confirmed that both degrees of cold plasma treatment increased the surface wettability and changed the surface energy. However, these results could be affected by the different moisture of particles. Plasma-treated particles in the missing agent were partly dried and then immediately examined by test inks. The treated particles were not conditioned because the effect of cold air plasma on the physical properties of modified material decreases with time after the plasma application (Klímek *et al.* 2016).

Density and vertical density profile

The average density of the reference boards was 540.0 kg/m^3. Boards with a lower degree of modification reached 524.9 kg/m^3 and boards with a higher degree of modification had an average density of 545.7 kg/m^3. Due to manual layering, the density also exhibited considerable variability (Table 3). Further, it was noticed that the boards manufactured from the reference particles had the steepest density profile (Fig. 4a). The different average density, the variability of the density, and the shape of the density profile have to be taken into consideration while interpreting the physical and mechanical properties measured. Figure 4b shows a cross-sectional cut of the board showing individual particles of winter wheat stalk.

Table 3. Density of Straw Board at 25 °C and 65% Relative Humidity

Density	Ref.	Modification	
		A	B
Mean (kg/m^3)	540.0	524.9	545.7
Median (kg/m^3)	540.5	528.8	553.4
Standard deviation (kg/m^3)	27.9	31.5	31.0
Minimum (kg/m^3)	486.2	473.8	491.8
Maximum (kg/m^3)	613.2	586.4	607.1

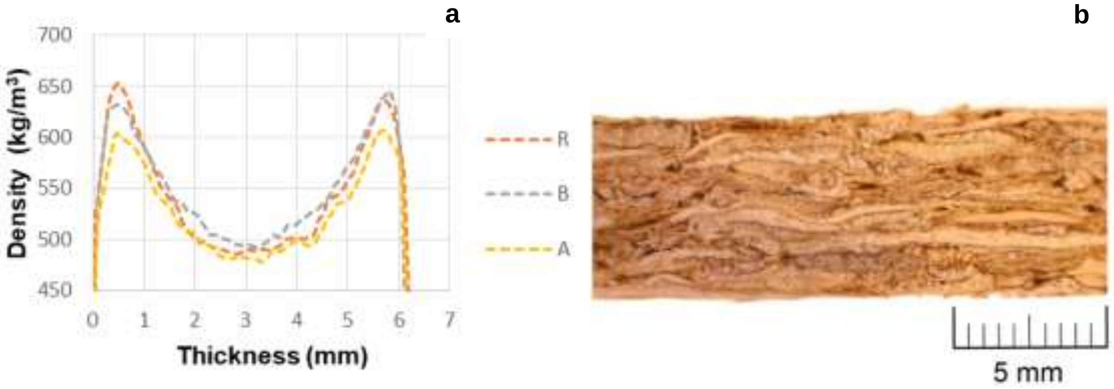

Fig. 4. (a) Vertical density profile of straw boards at 25 °C and 65% relative humidity; (b) side view of pressed board with nominal thickness of 6 mm

Equilibrium moisture content and thickness swelling

Figure 5 shows a graph of the dependency of equilibrium moisture content of the boards on relative humidity, and Fig. 6 shows a graph of the dependency of thickness swelling on relative humidity, and these average values are subsequently specified numerically in Table 4. The highest values of equilibrium moisture and thickness swelling were obtained from boards manufactured from particles modified by a higher degree of plasma treatment (type B), and all of the differences in the given moisture level were statistically significant (Table 5). Adversely, the lowest values of equilibrium moisture were obtained from the boards manufactured from unmodified particles. In terms of the equilibrium moisture of boards manufactured from particles treated with a lower degree of plasma treatment and untreated particles, a statistically significant difference only appeared in the first air-conditioning stage (20 °C/RH 65%, absorption cycle).

Type B boards once again exhibited the highest thickness swelling. As expected, the lowest values of thickness swelling were not reached by boards from the reference particles (Fig. 6). Except for in the first air-conditioning stage (this difference was not statistically significant (Table 6)), a higher thickness swelling in the reference boards was ascertained than in the boards manufactured from modified particles with a lower degree of plasma treatment. This was explained by a variation in the average density of boards, where the average density of the reference boards was 540.0 kg/m^3 and boards with a lower degree of modification reached 524.9 kg/m^3.

Table 4. Average Values of Thickness Swelling and Equilibrium Moisture of Boards on the Given Level

Board Type	Relative Humidity (%)	Thickness Swelling (%)	Moisture (%)
R	0a	0.0	0.0
R	65a	8.3 (0.7)	8.8 (0.4)
R	85	45.9 (5.7)	19.3 (0.6)
R	65d	37.9 (5.5)	11.0 (0.6)
R	0d	30.7 (4.8)	0.0
A	0a	0.0	0.0
A	65a	9.4 (1.6)	9.8 (0.8)
A	85	39.9 (4.5)	19.7 (0.7)
A	65d	33.8 (4.2)	11.4 (0.8)
A	0d	27.9 (2.6)	0.0
B	0a	0.0	0.0
B	65a	10.1 (1.3)	10.8 (0.3)
B	85	53.1 (4.2)	23.0 (0.4)
B	65d	45.3 (3.9)	13.1 (0.3)
B	0d	36.6 (3.3)	0.0

Note: a = absorption, d = desorption, values in parentheses are standard deviations

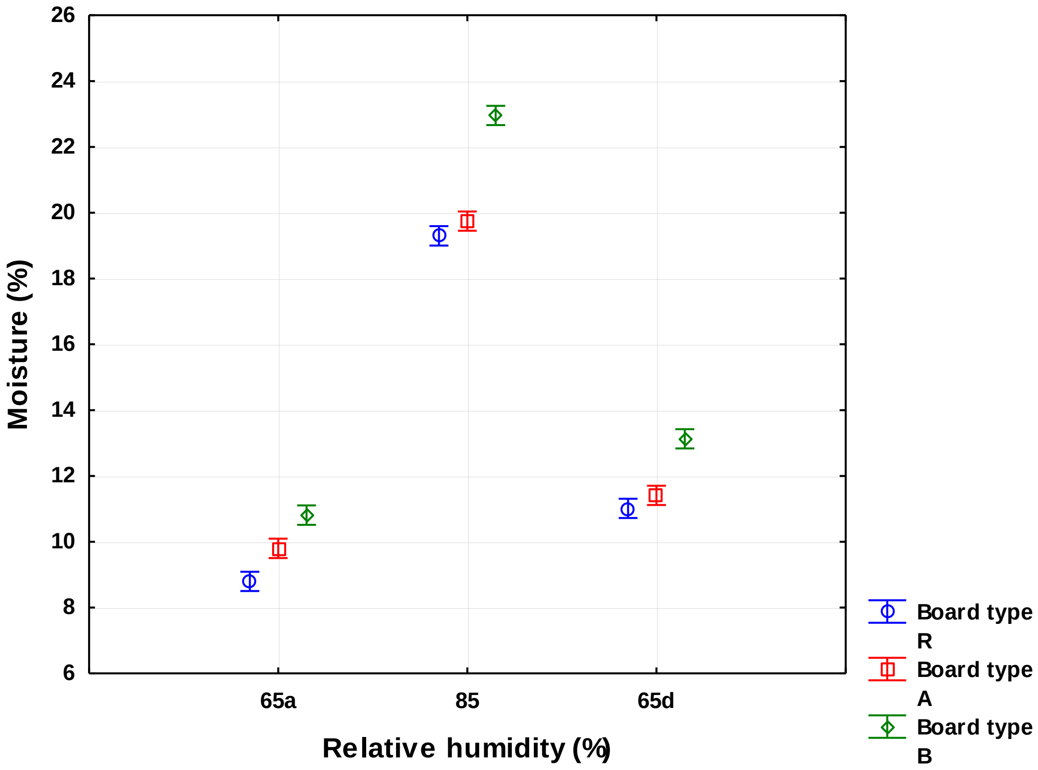

Fig. 5. Graph of the dependency of equilibrium moisture of the boards on relative humidity, a = absorption, d = desorption

Table 5. Appropriate Statistical Significances of Differences in Fig. 5

T = 20°C, RH = 65%, Absorption			
	R	A	B
R		s.	s.
A	s.		s.
B	s.	s.	

T = 20°C, RH = 85%			
	R	A	B
R		n.s.	s.
A	n.s.		s.
B	s.	s.	

T = 20°C, RH = 65%, Desorption			
	R	A	B
R		n.s.	s.
A	n.s.		s.
B	s.	s.	

Note: s. = statistically significant, n.s. = not significant, and α = 0.05

In comparison with commercially produced particleboards, non-recoverable thickness changes of produced boards reached relatively high values. This was explained by the material used. From the authors' previous study it is already known that boards produced from after harvest remains reached non-recoverable thickness changes higher than 30% (Hýsek *et al.* 2018). It was concluded that the plasma treatment of the particles had a statistically significant effect on the equilibrium moisture content of the boards and their thickness swelling; however, the thickness swelling values were negatively affected by the different average densities of the boards. In contrast, when non-recoverable changes were compared with the bending strength results, it can be assumed that modification A was the better level of plasma pre-treatment for the purpose of this study. These boards reached lower non-recoverable thickness changes as well as higher bending strength. Therefore, it was assumed that the lower level of plasma modification caused better adhesion, in comparison to the more aggressive modification B.

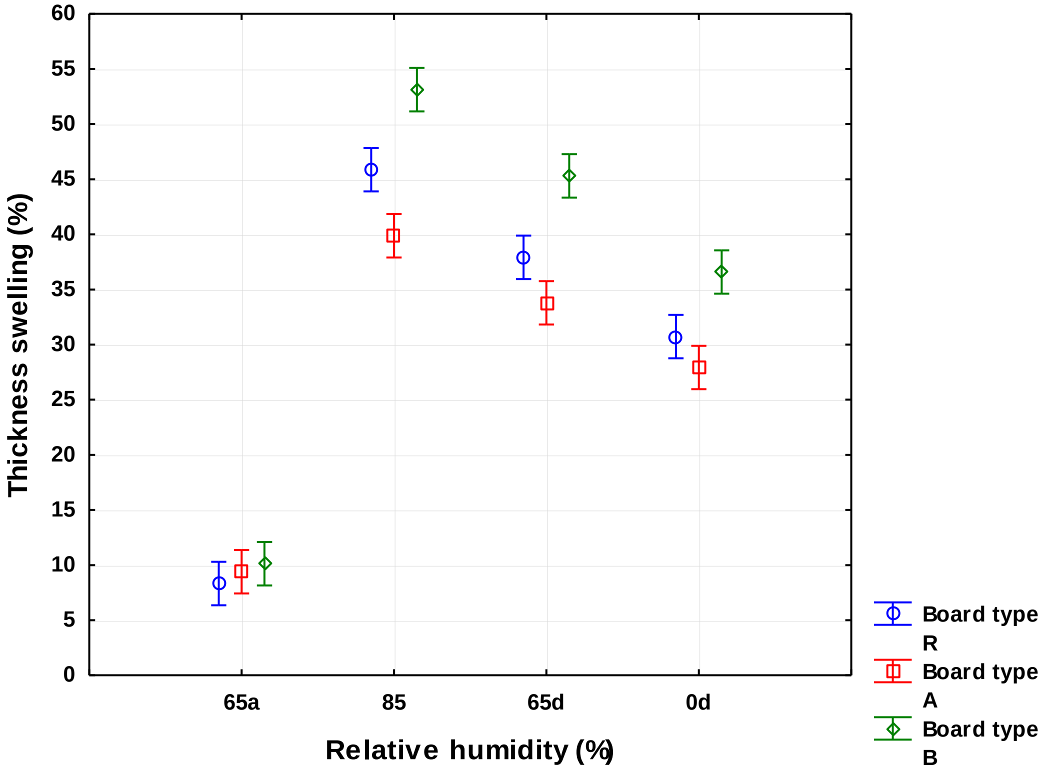

Fig. 6. Graph of the dependency of thickness swelling on relative humidity, a = absorption, d = desorption

Table 6. Appropriate Statistical Significances of Differences in Fig. 6

T = 20°C, RH = 65%, Absorption			
	R	A	B
R		n.s.	s.
A	n.s.		n.s.
B	s.	n.s.	

T = 20°C, RH = 85%			
	R	A	B
R		s.	s.
A	s.		s.
B	s.	s.	

T = 20°C, RH = 65%, Desorption			
	R	A	B
R		s.	s.
A	s.		s.
B	s.	s.	

T = 103°C, Desorption			
	R	A	B
R		n.s.	s.
A	n.s.		s.
B	s.	s.	

Note: s. = statistically significant, n.s. = not significant, and α = 0.05

Bending strength and internal bonding

Table 7 shows the average values with basic descriptive statistics for the bending strength of boards. Figure 7 shows the bending strength variation analysis and Table 8 shows data on the statistical significance of the differences. The results show that in both cases of plasma treatment of the particles there was an increase in flexural strength compared to the reference material, but the increase was only statistically significant for modification A. There was also no statistically significant difference in the flexural strength between the two different plasma treatments.

Table 7. Average Values with Basic Bending Strength Descriptive Statistics

Bending Strength	Ref.	Modification	
		A	B
Mean (MPa)	4.9	5.5	5.1
Median (MPa)	4.8	5.5	5.4
Standard Deviation (MPa)	0.5	0.3	0.7
Minimum (MPa)	4.2	5.0	3.9
Maximum (MPa)	5.6	6.0	5.9

Table 8. Appropriate Statistical Significances of Differences in Fig. 7

	R	A	B
R		s.	n.s.
A	s.		n.s.
B	n.s.	n.s.	

Note: s. = statistically significant, n.s. = not significant, and α = 0.05

Table 9 shows the average values with the basic descriptive statistics for the internal bonding of the boards. Figure 8 shows the internal bonding variation analysis and Table 10 shows data on the statistical significance of the differences. The results showed that in both cases of plasma treatment there was a statistically significant increase in internal bonding. There was no statistically significant difference between the different plasma treatments. Both observed mechanical properties reached lower values than the boards made form rapeseed stalk particles, where internal bonding was 0.34 MPa to 0.50 MPa and the bending strength was 5 MPa to 10 MPa (Hýsek *et al.* 2018). However, in previous research, boards with an average density of 600 kg/m^3 and with an inverse vertical density profile (maximal density in the middle of the board) were produced.

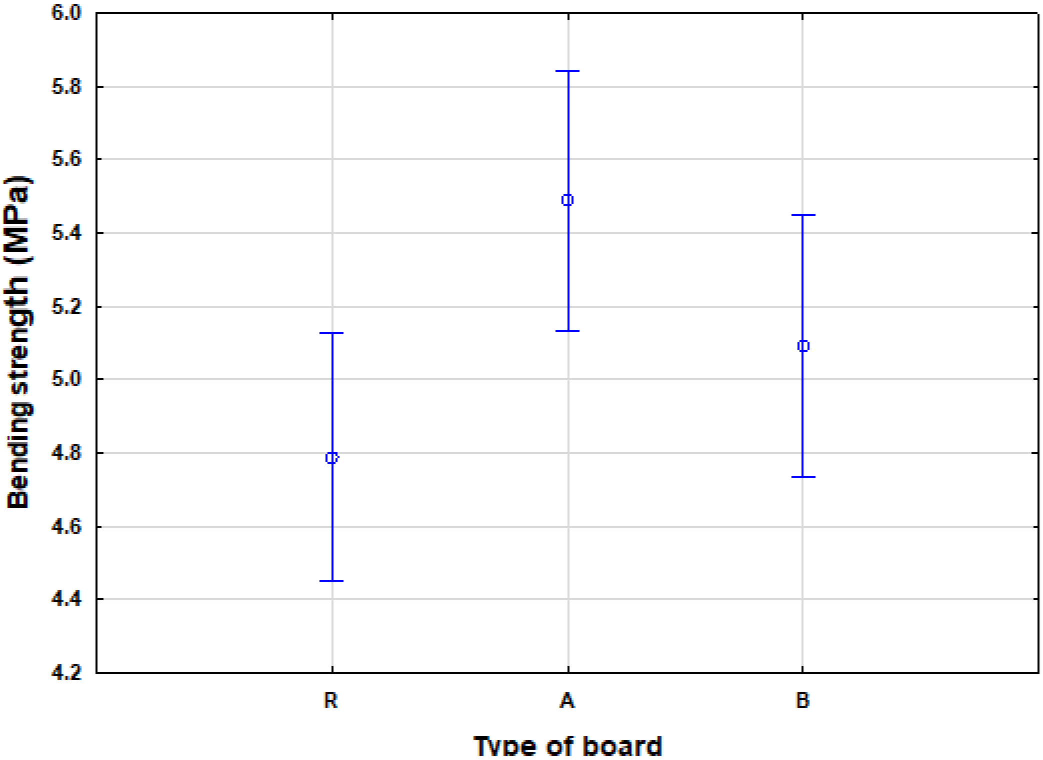

Fig. 7. Analysis of variance - dependence of flexural strength on modification of particles

Table 8. Appropriate Statistical Significances of Differences in Fig. 7

	R	A	B
R		s.	n.s.
A	s.		n.s.
B	n.s.	n.s.	

Note: s. = statistically significant, n.s. = not significant, and α = 0.05

Table 9. Average Values with Basic Internal Bonding Descriptive Statistics

Transverse Tensile Strength	Ref.	Modification	
		A	B
Mean (MPa)	0.037	0.058	0.061
Median (MPa)	0.036	0.054	0.063
Standard deviation (MPa)	0.006	0.019	0.017
Minimum (MPa)	0.028	0.033	0.039
Maximum (MPa)	0.050	0.092	0.098

Table 10. Appropriate Statistical Significances of Differences in Fig. 8

	R	A	B
R		s.	s.
A	s.		n.s.
B	s.	n.s.	

Note: s. = statistically significant, n.s. = not significant, and α = 0.05

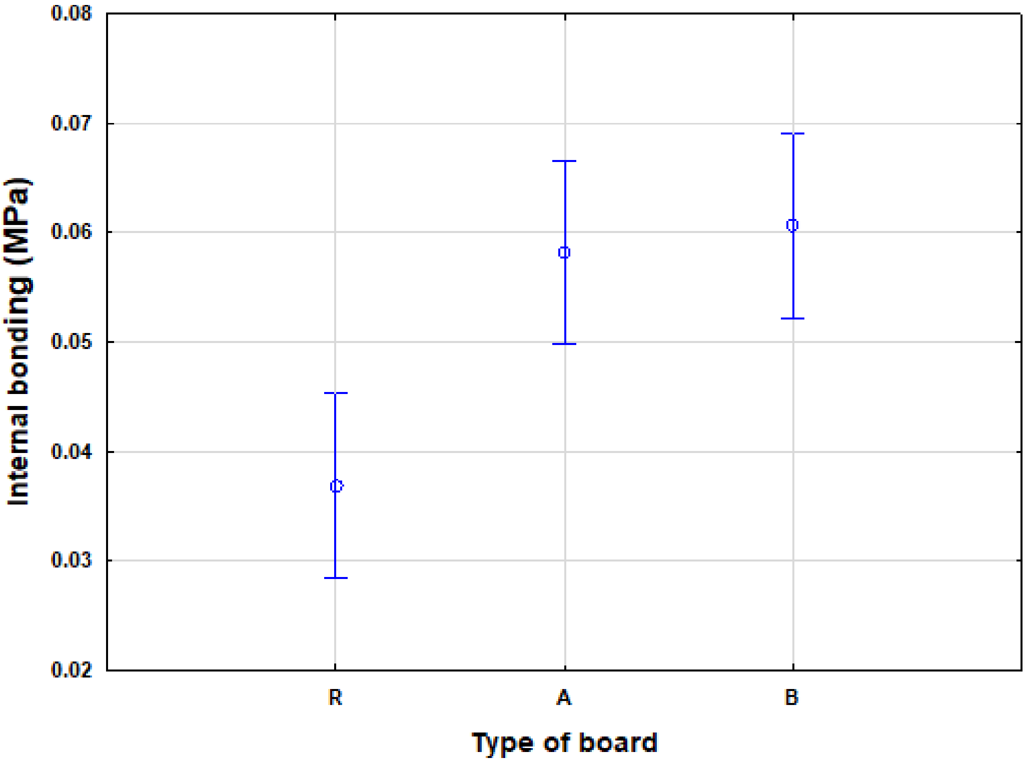

Fig. 8. Analysis of variance – dependence of internal bonding on modification of particles

Figure 9 shows a SEM microscopic image of the damaged joint from the tensile test perpendicular to the plane of the boards. The image shows the noticeable impact of the modification on the nature of the damage. In terms of boards manufactured from the reference unmodified particles (Fig. 9a), there was only adhesion damage between the adhesive and the particle surface. In terms of boards made from plasma-modified particles (Figs. 9b, 9c), cohesive breakage in the particle material was also observed, which indicated a better joint of the modified particle-adhesive.

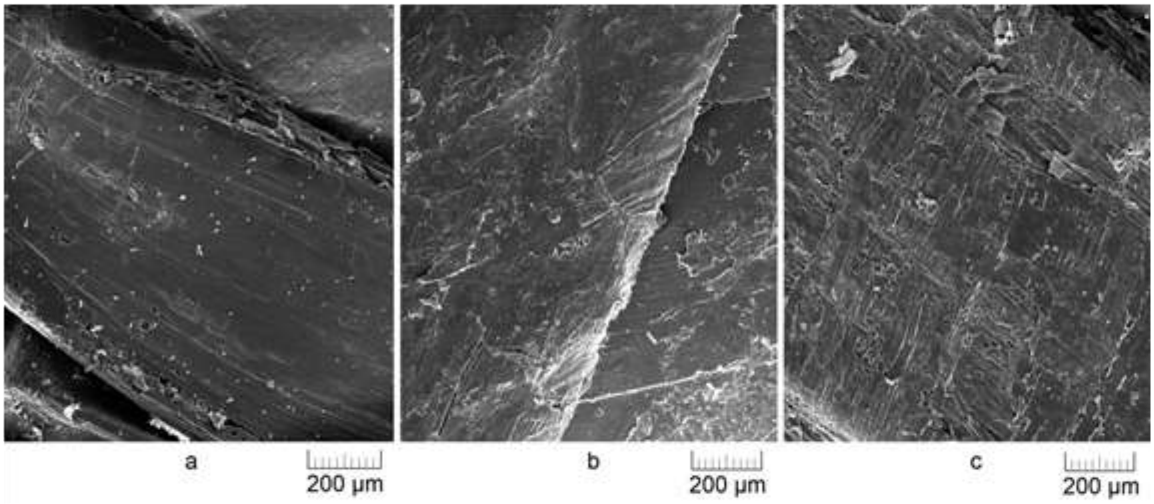

Fig. 9. SEM analysis of particle of boards after strength testing: (a) reference, (b) modification A, and (c) modification B

CONCLUSIONS

1. The effect of plasma treatment on the properties of composite material made from winter wheat stalk particles was investigated. Test inks showed an increase in surface energy and confirmed that plasma treatment influences surface properties of the particles.
2. The plasma treatment of the particles had a statistically significant effect on the equilibrium moisture content of the boards and on their thickness swelling, with increased degrees of plasma treatment the equilibrium moisture content also increased.
3. Opposite of the physical properties, the positive effect of plasma pre-treatment of the particles was observed in the mechanical properties. Both the flexural strength and internal bonding of the boards were increased. The highest increase in flexural strength was achieved by the type A plasma treatment, whereas a difference between the individual types of plasma treatment was not observed in the internal bonding.
4. A better joint of the modified particle-adhesive was reached by the plasma treatment. A noticeable impact of the modification on the nature of the damage in produced composite materials was observed through SEM analysis.

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[5] **HÝSEK, Š.,** ŠEDIVKA, P., BÖHM, M., SCHÖNFELDER, O. a BERAN, R. 2018, Influence of using recycled polyurethane particles as a filler on properties of polyurethane adhesives for gluing of wood, *BioResources*, roč. 13, č. 2, s. 2592-2601.

Influence of Using Recycled Polyurethane Particles as a Filler on Properties of Polyurethane Adhesives for Gluing of Wood

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Fillers can greatly affect the properties of adhesives, and this research aimed at enhancing the performance of adhesives by using different concentrations of fillers. This paper describes the influence of using recycled polyurethane particles (powder of particle size from 10 µm to 50 µm) as a filler on some properties of polyurethane adhesives for the gluing of wood. Two kinds of one-component, moisture-curing polyurethane adhesives were used. The observed properties were the contact angle between the wood and adhesive droplet, and the strength of bonded joints (shear strength). From the results, it was concluded that the contact angle increased with an increase in filler (in the entire observed range from 0% to 15% filler). The content of filler also affected the strength of bonded joints and their thermal stability. The strength of bonded joints decreased with an increase in filler content when samples were conditioned in cold water. However, the strength of bonded joints increased with an increase in filler content when samples were boiled in water.

Keywords: Adhesive; Polyurethane; Recycled foam; Wood; Contact angle; Strength of joints

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INTRODUCTION

The use of polyurethane adhesives in many industrial fields is becoming increasingly common. Their range of application includes not only the construction, automotive, and wood processing industries, but also the manufacturing of wind turbines and aircrafts (Desai *et al.* 2003b; Patel *et al.* 2009; Clerc *et al.* 2017; Najib *et al.* 2017). Because polyurethane adhesives cure without the need to add a curing agent, they are characterised by an easier reticulation method than epoxy adhesives, leading to reduced production costs. Another advantage of polyurethane adhesives is the high flexibility of the bond, which contributes to resistance to dynamic strain and good shock-absorbing properties (Clauß *et al.* 2011; Najib *et al.* 2017).

For many years, research has endeavoured to develop properties of polyurethane adhesives for various application areas by combining different modifications (Deka and Karak 2009; Patel *et al.* 2009). The physical and chemical properties of adhesives can be adjusted by changing the components comprising the adhesive mixture, which are added during prepolymer synthesis (Desai *et al.* 2003a; Deka and Karak 2009; Volkova *et al.* 2013). Besides plasticisers, organic solvents, wetting agents, rheological agents, and catalysers, fillers are commonly used as well. Fillers are used for various purposes, and the replacement of a more expensive polymer is but one of the many reasons (Sedliačik *et al.* 2006; Šmidriaková and Kollár 2010). In addition, fillers can improve the mechanical properties, workability, thermal and dimensional stability, and flame retardation of polymers (Li *et al.* 2008; Clauß *et al*. 2012). Various types of filler materials are used for improvement of the aforesaid properties in adhesives.

Inorganic filler materials include silicon, calcium, kaolin, chalk, *etc.* These materials have been studied in combination with various types of adhesives, such as phenol-formaldehyde, urea-formaldehyde, and epoxy adhesives (Clauß *et al.* 2011, 2012). Modification of polyurethane adhesives using organic fillers can be achieved by adding plant- or animal-based polymers to factory-made adhesive mixtures (Šmidriaková and Kollár 2010). Another solution is the addition of polyurethane (PUR) powder and polyurethane dispersion (Clauß *et al*. 2012). Mansouri and Pizzi (2007) studied the addition of particles of a PUR fraction to urea-formaldehyde and phenol-formaldehyde adhesives. Their research indicates that addition of polyurethane particles to the adhesive mixture significantly improves the physical properties of the adhesive and its water resistance. Another possible type of modification used currently is the modification of adhesive polymers using nanotechnologies (Dodiuk *et al.* 2006; Deka and Karak 2009).

The goal of this research project was to modify a polyurethane adhesive for the gluing of wood using a powder made of recycled polyurethane foam. The use of the powder as a filler in a polyurethane adhesive can considerably modify the base polyurethane. Therefore, this approach may provide unique combinations of properties, and reduce the costs of input materials in polyurethane manufacturing through utilization of waste.

EXPERIMENTAL

Materials

Two kinds of one-component (1C), moisture-curing, polyurethane adhesives were formulated: PUR01, which was made of polyether polyol with an initial molar mass of 2000 g/mol to 3000 g/mol (405 g) + catalyst (0.8 g) + polyisocyanate based on 4,4,-diphenylmethan-diisocyanate (620 g) + UV-stabilizers (10.3 g), and PUR02, which was made of polyether polyol with an initial molar mass of 1000 g/mol to 2000 g/mol (405 g) + catalyst (0.5 g) + polyisocyanate based on 4,4,-difenylmethandiisocyanate (540 g). The recycled polyurethane foam was used as a filler to modify the polyurethane adhesives. The recycled foam was powder from PUR/PIR (combination of polyurethane and polyisocyanurate) foam and contained particles of dimensions from lower than 50 µm (see Fig. 2). Micro-milling of foam on a two-cylinder grinder was used to produce the powder from rigid PUR/PIR foam (utilized as heat insulation in civil engineering) with a closed cell structure. The initial molar mass of PUR/PIR foam was 500 g/mol to 1000 g/mol. The powder was mixed with the adhesives using weight powder ratios of 5%, 10%, and 15%, with 0% as a reference. All of the chemicals were supplied by STACHEMA CZ s.r.o. (Kolín, Czech Republic). Beech wood (*Fagus sylvatica*) obtained from the Central Bohemian Region, Czech Republic, was used to produce samples for the determination of strength of bonded joints. Beech wood with straight graining and a nominal density (700 kg/m^3 ± 50 kg/m^3) was selected. The angle between the tree rings and the bonded surface was between 30° and 90°.

Methods

The structure of the raw and modified adhesives was characterized using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic), with a secondary electron detector operated at 15 kV acceleration voltage.

Contact angle analysis is widely used to characterize the interaction between liquid and solid materials (Walinder and Ström 2001; Aydin 2004). To determine the wetting properties of the modified adhesives, the contact angle of the adhesives and a wood surface (planned radial beech wood) was measured using a Krüss DSA 30E goniometer (Krüss GmbH, Hamburg, Germany). The static contact angle was measured and 30 measurements were taken for each adhesive modification type. To minimize the influence of variation in the wood surface, five wood samples for each adhesive modification type were used, and on each sample, six droplets were deposited. The volume of the resin droplet was 10 µL and a measurement was made 5 s after the deposition.

Preparation of test specimens, measurements of the strength of bonded joints, and an evaluation of the results were conducted in accordance with the standards EN 204 (2001) and EN 205 (2003). Test specimens were manufactured according to Fig. 1 from beech wood, which was air-conditioned at 20 °C with a relative humidity (RH) of 65%. The adhesive weight was 160 g/m^2 to 180 g/m^2. Then, 60 test specimens (2 types of adhesives × 4 degrees of powder content × 10 test samples) were produced with test procedure number 1, 60 test specimens were produced with test procedure number 2, and 60 test specimens were produced with test procedure number 3.

The first test was conducted 7 days after bonding (test sequence number 1, further marked as a1), and the specimens were air-conditioned at 20 °C with a relative humidity (RH) of 65%.

After 7 days in standard conditions, specimens from the second test group were immersed for 4 days in water at 20 °C ± 5 °C, and then immediately tested (test sequence number 2, further marked as a2).

The third test was conducted in such a way that after 7 days the samples were immersed for 6 h in boiling water and then placed in water at 20 °C ± 5 °C for 2 h, and then immediately tested (test sequence number 3, further marked as a3). These three tests were performed for each adhesive combination.

The shear test was performed using a TIRAtest 285 E222 universal testing machine (TIRA GmbH, Schalkau, Germany). The specimen was strained with a tensile force until breach, and the greatest exerted force, F_{max}, was recorded. The speed of the loading was constant at 6 m/min as required by EN 205 (2003).

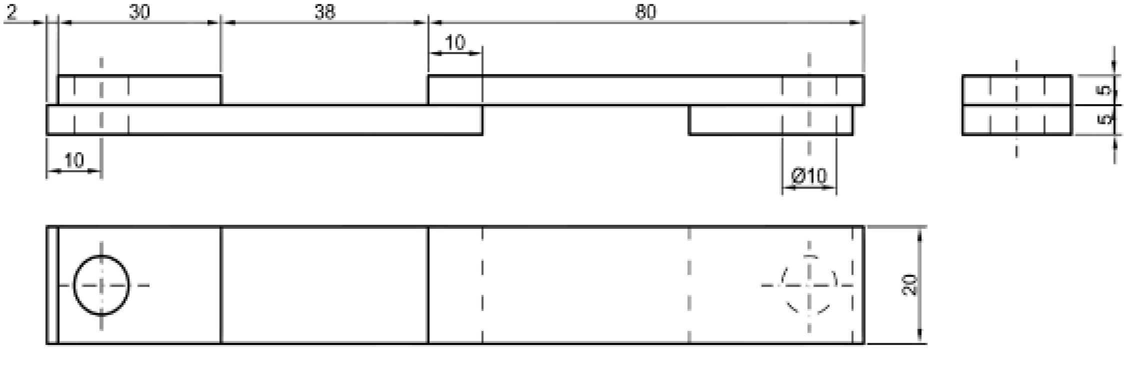

Fig. 1. Diagram of the lapped test sample

Expression of results

The strength of the bonded joint (τ; N/mm^2) was calculated using the following formula,

$$\tau = \frac{F_{max}}{l_2 \times b} \tag{1}$$

where F_{max} is the greatest exerted force (N), l_2 is the length of the bonded test surface (mm), and b is the width of the bonded test surface (mm).

A one-way analysis of variance (ANOVA) was used for statistical data evaluation. The post-hoc Tukey (HSD) test was employed to determine the significant differences between group means. Computations were conducted using Statistica12 software (StatSoft CR s.r.o., Prague, Czech Republic). A significance level of $\alpha = 0.05$ was selected.

RESULTS AND DISCUSSION

Figure 2 depicts a scanning electron microscope (SEM) picture of a PUR/PIR powder, and Fig. 3 depicts the surfaces of hardened PUR02 and the surface of hardened PUR02 modified by the PUR/PIR powder. In Fig. 2, one can see that particle dimensions of used filler were higher, than in previous studies (Dodiuk *et al.* 2006; Clauß *et al.* 2012). Therefore it was expected that used powder would behave as inert filler. Figure 3 shows typical changes in structure of modified adhesives (Clauß *et al.* 2012); these changes are visible not only on the cross section, but also on the surface. It can be seen that there was a difference between the reference adhesive and modified adhesive. The adhesives modified with powder had a rougher surface that was caused by the powder particles.

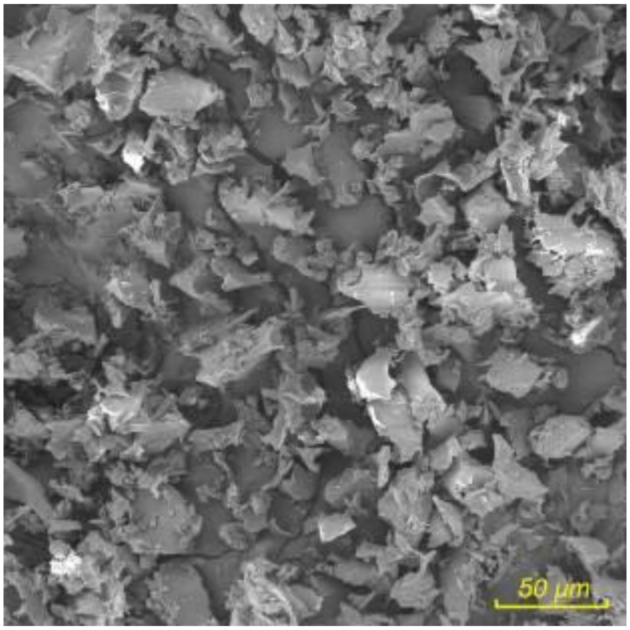

Fig. 2. SEM image of polyurethane powder

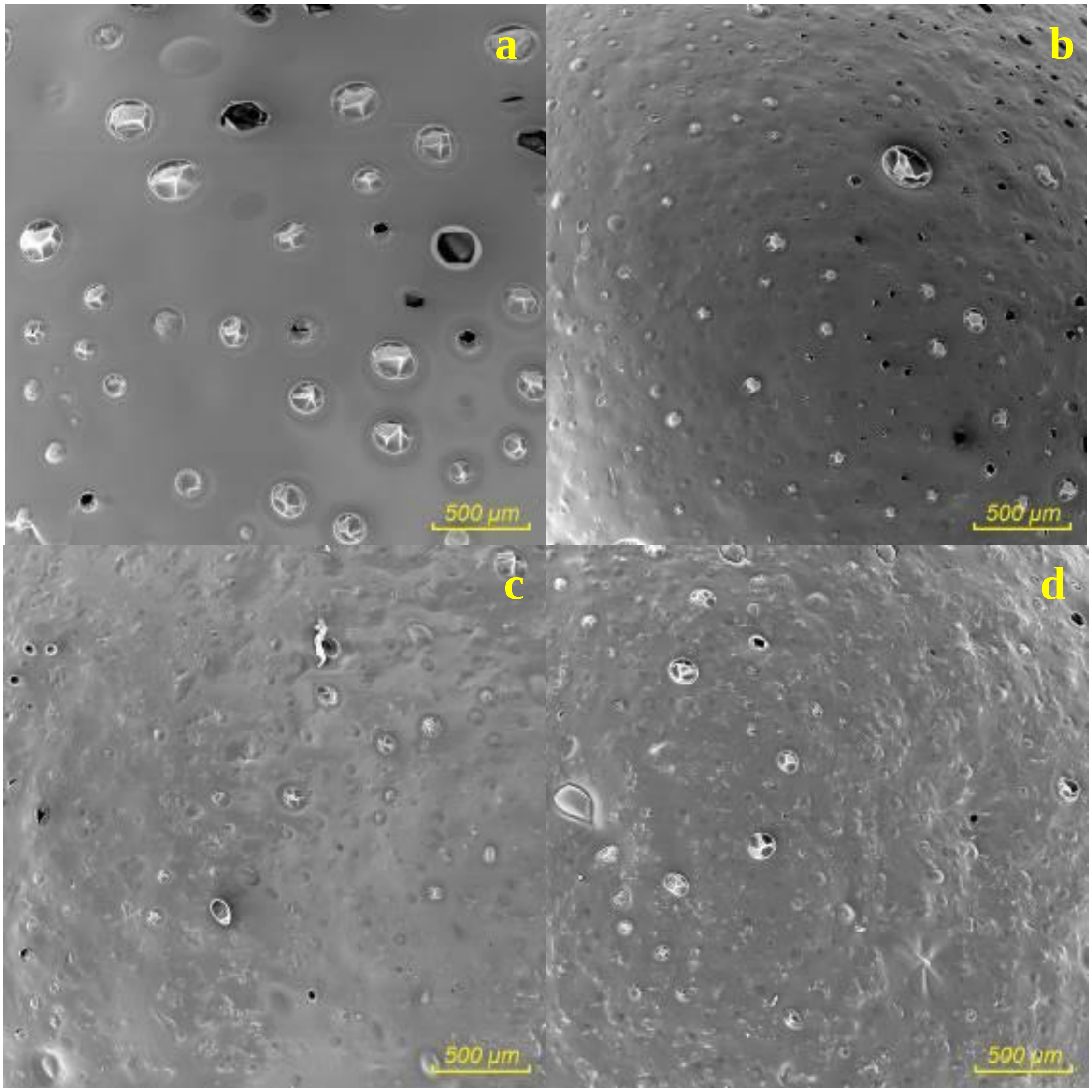

Fig. 3. Surface of hardened PUR02 without powder (a), hardened PUR02 with 5% powder (b), hardened PUR02 with 10% powder (c), and hardened PUR02 with 15% powder (d)

Figure 4 shows the results from an analysis of variance of the measured contact angles. The appropriate statistical significances of the differences are stated in Table 1. As shown, for both kinds of polyurethane adhesives the contact angle increased with an increase in powder content, within the entire interval of powder content of 0% to 15%. However, the particular increments of the contact angle decreased with an increase in powder content. Fillers have a significant effect on viscosity of modified adhesives (Benhadjala *et al.* 2015; Ruanpan and Manuspiya 2018), which affect contact angle as well. Since the increasing viscosity and adhesive contact angle is an undesirable effect, further decreasing of filler's particle dimensions could lead to modified adhesive with lower contact angle between wood and adhesive (Benhadjala *et al.* 2015).

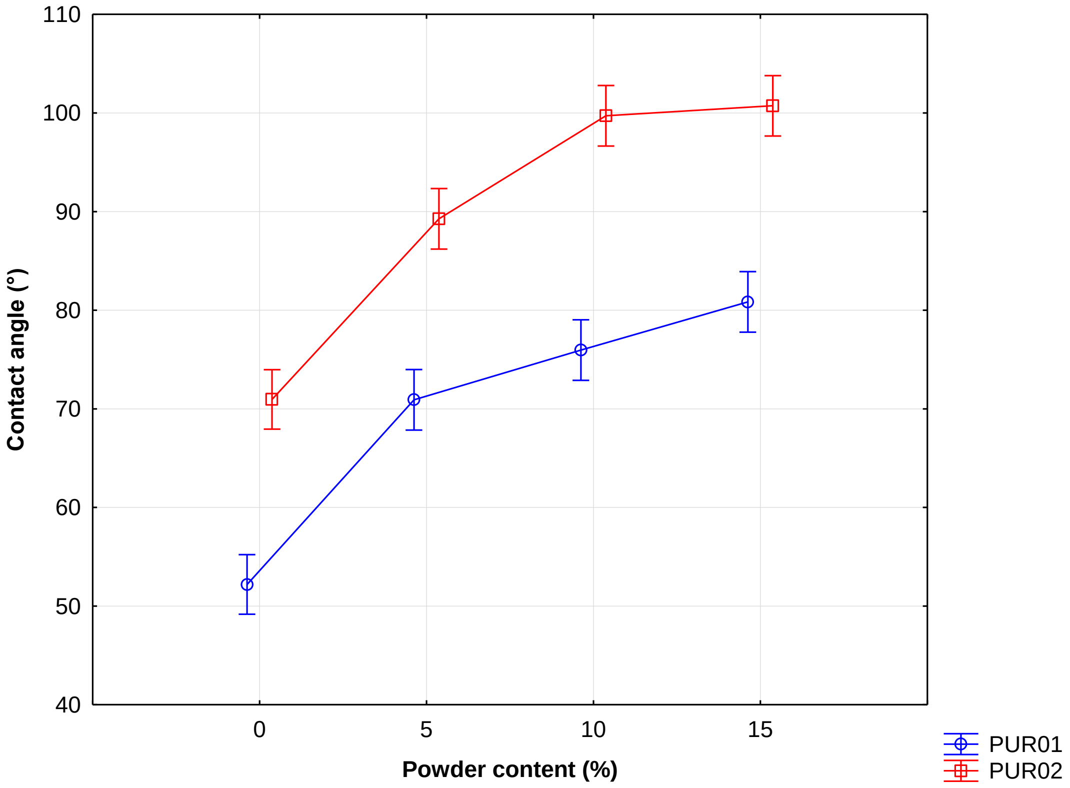

Fig. 4. Effect of powder content and adhesive type on contact angle

Table 1. Statistical Significance of Differences in Fig. 2 (According to Tukey Test)

Powder Content (%)		0	0	5	5	10	10	15	15
Powder Content	Adhesive Type	PUR01	PUR02	PUR01	PUR02	PUR01	PUR02	PUR01	PUR02
0	PUR01		s.	s.	s.	s.	s.	s.	s.
0	PUR02	s.		n.s.	s.	n.s.	s.	s.	s.
5	PUR01	s.	n.s.		s.	n.s.	s.	s.	s.
5	PUR02	s.	s.	s.		s.	s.	s.	s.
10	PUR01	s.	n.s.	n.s.	s.		s.	n.s.	s.
10	PUR02	s.	s.	s.	s.	s.		s.	n.s.
15	PUR01	s.	s.	s.	s.	n.s.	s.		s.
15	PUR02	s.	s.	s.	s.	s.	n.s.	s.	

s.- significant; n.s.- not significant

Figure 5, where a three-factor analysis of variance is depicted, shows the influence of the strength of joints (shear strength) on powder content, adhesive type, and conditions. As shown, the powder content affected the strength of joints. By conditioning under laboratory conditions (a1), the greatest shear strength was shown by the glue joints with 10% powder, and the effect of powder content on the strength of joints was unclear. By conditioning in water (a2), the strength of joints decreased with an increase in powder content. Finally, by conditioning in boiling water (a3), the addition of PUR/PIR powder increased the average values of the strength of joints, and it seemed that the optimum level was a 5% powder content. By hot water conditioning (a3) the addition of powder (5% ratio) increased the shear strength from 0.7 MPa to 1.7 MPa for PUR01, resp. from 0.7 MPa to 2.4 MPa for PUR02. The increase of thermal stability of 1C PUR adhesives was also reached by addition of chalk as filler (Clauß *et al*. 2011); however in this study higher shear strength of bonded joints was reached.

From these results, it can be concluded that boiling water rapidly decreased the strength of bonded joints; however, the modification of PUR adhesives with PUR/PIR powder increased the thermal stability of bonded joints. In contrast, the resistance to cold water decreased with increase of powder content (Fig. 4). Due to the effect of higher temperature, which caused better crosslinking of reactive groups, the adhesive was hardened more (Clauβ et al. 2011). Recycled foam has a high specific surface area of particles, and due to physical depolymerisation is the particle surface polar and contains functional groups (hydroxy- and amino-). The higher temperature caused degradation of steric barriers and thus additional reactions of functional groups with isocyanate groups of adhesive. This effect indicated that the PUR/PIR powder performed partly as an inert filler and partly as a catalyst. In general, the strength of joints was low; the level of 10 MPa (performance requirement for one component polyurethane for load-bearing timber structures according EN 15425 (2017) for conditioning a1) was reached in only two cases – PUR02 via conditioning type a1 and with powder content 0% and 10%. The performance requirement for conditioning a2 and a3, which is according EN 15425 (2017) 6 MPa, was not reached by any variant. When the results from the contact angle analysis were compared with the results of shear strength, the contact angle between the adhesive and wood surface for all levels of powder content was higher for PUR02. However, the shear strength of bonded joints with PUR02 was higher in all cases except one. The adhesive with lower wetting of the wood surface reached higher values of shear strength in these experiments; however, the wetting ability of an adhesive is not the only adhesive characteristic that affects the strength of bonded joints (Okkonen and River 1988; Banea and Silva 2009; Custódio *et al.* 2009; Moghadamzadeh *et al.* 2011; Budhe *et al.* 2015). In this case, a different adhesive formulation probably affected the results (Banea and Silva 2009; da Silva *et al.* 2009). Moreover, there was a big difference between the adhesives in conditioning type a1, the differences decreased when the bonds were soaked in water and boiling water.

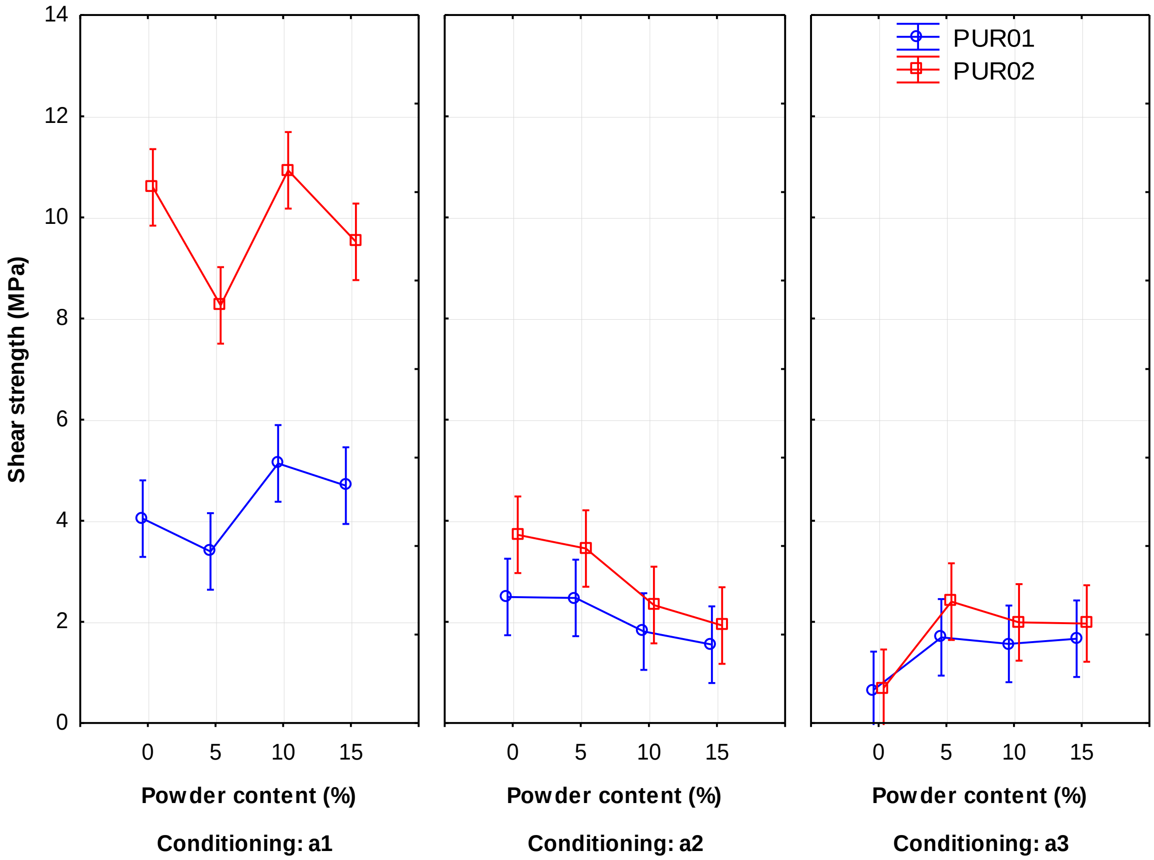

Fig. 5. Effect of powder content, adhesive type, and conditioning on the strength of bonded joints

CONCLUSIONS

1. The addition of polyurethane powder as a filler to 1C moisture-curing polyurethane adhesives increased the strength of bonded joints boiled in water; however, samples immersed in cold water showed a decrease in the strength of bonded joints.
2. The contact angle between the wood and adhesive droplet increased with an increase in polyurethane powder content. However, the contact angle was not observed to have any influence on the strength of bonded joints.
3. The addition of polyurethane powder as a filler to 1C moisture-curing polyurethane adhesives affected the structure of hardened adhesives, which was observed by SEM on the surface of the hardened adhesive.

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Effect of Wheat Husk Surface Pre-Treatment on the Properties of Husk-Based Composite Materials

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Abstract

The effect of different types of winter wheat husks treatments (alkaline, hydrothermal and plasma treatment) on the properties of the particle material, as well as on composite materials made from such pre-treated husks, was studied. After pre-treatment, the surface energy, equilibrium moisture content, surface morphology using SEM, elemental content on the surface and the fluorescence life time (FLIM) of husks were estimated, as well as the IR spectra (FTIR) of pre-treated husks. Boards with target density of 450 kg/m^3 were produced using urea-formaldehyde resin (resination 9%) and the equilibrium moisture content, thickness swelling, vertical density profile, internal bonding and insulation properties of boards were examined. Modification in 2% sodium hydroxide solution caused noticeable erosion of husks resulting in higher lignin content, higher equilibrium moisture of husks and consequently higher thickness swelling of boards made from pre-treated husks and lower internal bonding of those boards. Both hydrothermal (boiling in water) and plasma treatment (air plasma at atmospheric pressure, jet system of application) resulted in the desired effect in terms of an increase in the surface energy of husks, decrease of husk equilibrium moisture content and increase of internal bonding of boards. All of the manufactured boards exhibited good thermal conductivity that ranged from 0.0714 W/(mK) to 0.0783 W/(mK).

Keywords

Wheat husk, renewable resources, composite material, particleboard, pre-treatment

1. Introduction

At present, the main raw material for particle board production is low quality wood, and its share in the production of particle board is about 70%. Nevertheless, thanks to improved woodworking technologies, this wood is increasingly being used in the production of glued laminated timber or cross-laminated timber, where its value increases (Klímek and Wimmer 2017). However, the lack of lower quality logs is not only caused by the above-mentioned competition, as the potential mass for the production of chips is also used by the paper, energy and chemical industries. The requirements for the supply of this wood material are increasing and have already resulted in its shortage, which is reflected, for example, by a reduction in the profits of woodworking enterprises (Seintsch 2011, Lauri et al., 2012, Sujová et al., 2017), and the increased demand for this raw material necessarily increases wood prices. This increase in the price of the main input raw material can cause supply outages or reduce the competitiveness of the particle board, and growth of wood in Europe do not cover this growing demand (Bostedt et al., 2016). A possible solution may be partial replacement of wood by post-harvest crop residues in the production of composite materials, and this solution seems appropriate both economically and politically (Klímek and Wimmer 2017). The question of the use of alternative raw materials for the production of composite materials must be dealt with in terms of production technology. It is well known from an extensive amount of research that wax and siliceous substances occur on their surfaces in the stems of annual plants, which cause difficulties when they are glued (Bekhta et al., 2004; Částková et al., 2018), and we also observed this phenomenon when gluing wheat husks. The husks are a by-product in the production of grain and constitute an available source of cellulose and lignin in large quantities. Wheat husks contain 36% cellulose, 18% hemicellulose, 16% lignin, 9% starch, 6% protein and 5% fat (Bledzki et al. 2010). Due to their high cellulose content and fibrous structure, the husks have the potential to be used in cellulose-based composites. Based on the weight ratio between wheat and husk production of about 5:1 (McCartney et al. 2006; Bledzki et al 2010, Djorđević and Antov 2016), we are able to estimate that approximately 30 x 10^6 tonnes of wheat husk (Eurostat 2017) are produced annually in the European Union, which, in terms of weight, represents 1.5 times the amount of wood needed for particle board production in the European Union (Klímek and Wimmer 2017). The husks are currently used for feeding livestock or biofuel production (Bledzki et al 2010). Research activities are also evident in the area of bio-composites (Mavani et al. 2006; Sobhy and Tammam 2010; Mamum and Bledzki 2013) or heavy metals absorption materials (Sud et al., 2008).

This paper describes the effect of different types of winter wheat husks surface pre-treatments on the properties of the iparticle material, as well as on composite materials made from such pre-treated raw materials. Specifically, this concerns the chemical, hydrothermal and plasma pre-treatment of winter wheat husks, namely crops with large sowing areas in the Czech Republic and the European Union, and whose post-harvest residues are available in large quantities.

2. Materials and Methods

2.1. Wheat husks

Wheat husks (Fig. 1) were supplied by a local supplier from the Central Bohemia Region in the Czech Republic. Digital image analysis was used in order to characterize distribution of particle dimensions. The proportion of individual fractions was defined per 100 g of material sample using a CAMSIZER analyser (Retsch Technology GmbH, Haan, Germany).

Figure 1 Wheat husks

2.2.Wheat husk pre-treatment

Three types of wheat husk pre-treatments were selected; hydrothermal pre-treatment (marking H), alkaline pre-treatment (marking A) and plasma pre-treatment (marking P). Untreated husks were also used as a reference (marking R). The hydrothermal pre-treatment was carried out by boiling in water for 45 min and the chemical pre-treatment was executed by soaking the husks in 2% sodium hydroxide solution (NaOH) at 25 °C for 45 min. After both treatments, the husks were flushed with water and then oven-dried to 6% moisture content. Plasma pre-treatment was carried out using jet plasma generator. Cold air plasma was used. The parameters of plasma jet of voltage 26.9 V and current 6.9 A were set. The application of plasma on the husks was performed using circulation of 80 g husks in an application bowl for 3 min. The principle of the application is shown in Figure 2 and this method is further described in Hýsek et al. 2018.

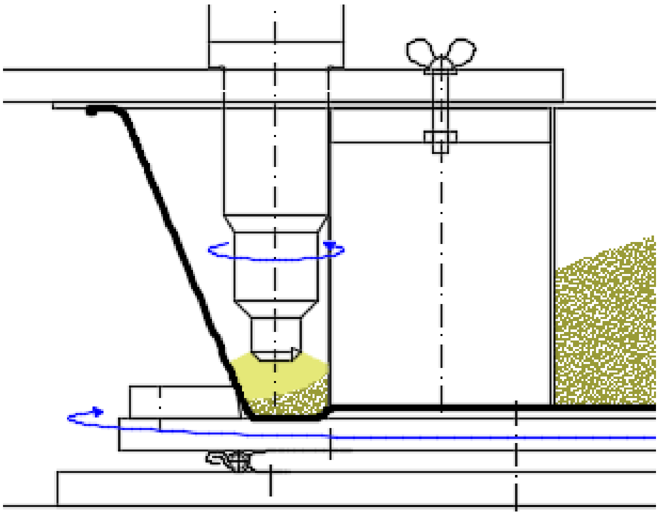

Figure 2 Principle of plasma treatment

2.3.Characterization of modified material

After the wheat husk pre-treatment, several analyses were used in order to characterize the modified particle material. Scanning electron microscopy (SEM) and elemental analysis of wheat husks were performed using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector operated at 15 kV acceleration voltage. The elemental compositions of the husk surface were examined by an energy dispersive spectroscopy system (Bruker XFlash X-ray detector, Karlsruhe, Germany, and ESPRIT 2 software). The surface tension of pre-treated husks was estimated using the test ink method; non-toxic test inks Arcotest (Arcotest GmbH, Moensheim, Germany) were used. The equilibrium moisture content of the modified husks was estimated using moisture analyser Ultra X 3011 (A&P instruments, Detmold, Germany) after conditioning of husks in an environment of 65% relative humidity and 20 °C. In order to characterize chemical changes in the mass, samples for FLIM (Fluorescence-lifetime imaging microscopy) and FTIR (Fourier transform infrared spectroscopy) analyses were disintegrated and homogenized using laboratory ball mill cooled with liquid nitrogen. In order to perform FTIR, powder from husks was placed directly on the ATR (attenuated total reflection) crystal and pressed with reproducible pressure. IR spectroscopy was performed using a Paragon 1000 FTIR spectrometer (PerkinElmer, Waltham, Massachusetts, USA). The spectral range was recorded from 3800 cm^{-1} to 500 cm^{-1} with a count of 10 scans each. For the FLIM analysis, the Leica SP8 module with TCSPC (Time-Correlated Single Photon Counting) capability was employed. A pulsing laser at 405 nm with pulsing frequency of 40 MHz was used for specimen excitation. The expose period was 1.5 ns and the signal was taken from square of 581 x 581 µm in dimension. A five-component multi-exponential decay model was fitted to the fluorescence decay data, which was found to provide the optimum fit measured by minimising the χ^2 value.

2.4.Particleboard manufacturing

Urea-formaldehyde resin K350S was used as an adhesive to produce boards made from the wheat husks. The composition of the adhesive mixture is specified in Table 1.

Table 1 Adhesive mixture composition

Component	Representation
Hydrophobic agent	Paraffin emulsion
Ratio solids hydr. agent / dry husk	1%
Adhesive	K350S
Ratio solids adhesive / dry husk	9%
Hardener	Ammonium nitrate
Ratio solids hardener / dry adhesive	10%
Ratio solid content of adhesive mixture / adhesive mixture	42.7%

Adhesive mixture was applied on husks using a laboratory blender, and after adhesive mixture application, the husks were dried to 7% moisture content. Boards of a target thickness of 6 mm and target density of 450 kg/m^3 were manufactured using a laboratory press; the husk fleece was first pre-pressed at a pressure of 14 bar for 60 s. The pressing cycle lasted 105 s and the pressing temperature was 170 °C. The pressing diagram is shown in Fig. 3.

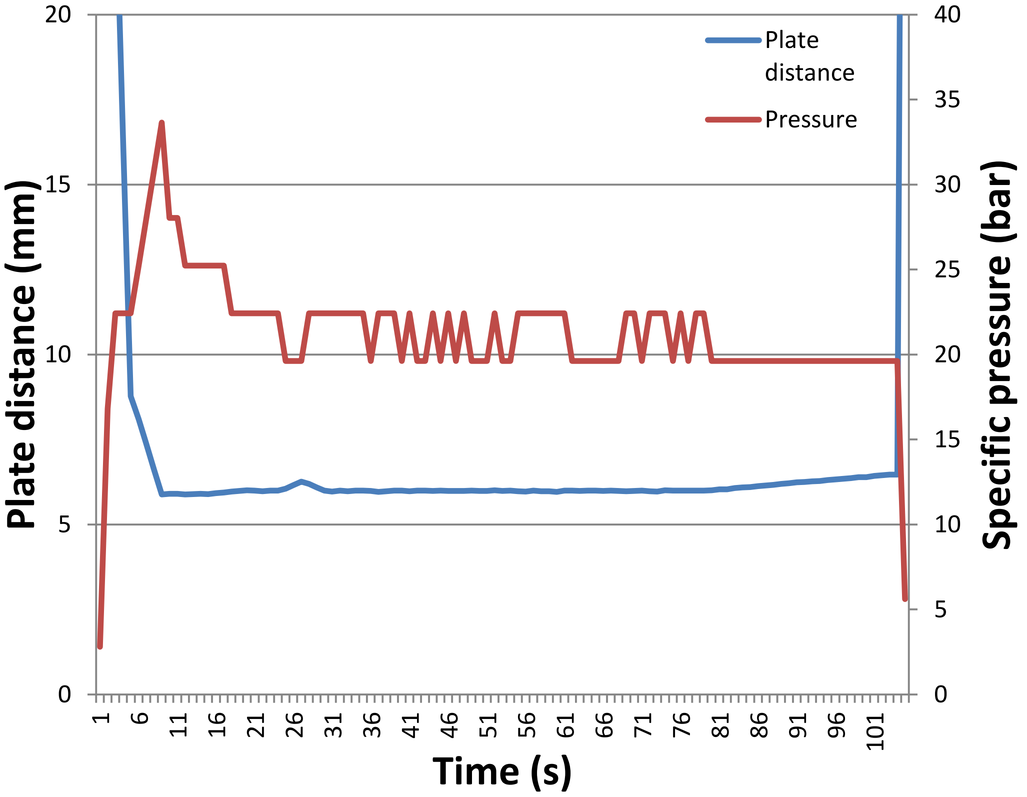

Figure 3 Press scheme

2.5.Determination of physical and mechanical board properties

The swelling behaviour and moisture content were determined by measuring the dimensions and weight during absorption and desorption cycles under the following conditions. Absorption: 103 °C/relative humidity (RH) 0%; 20 °C/RH 65%; 20 °C/RH 85%. Desorption: 20 °C/RH 85%; 20 °C/RH 65%; 103 °C/RH 0%. The cycles started at 103 °C/RH 0% because of the possibility of non-recoverable thickness changes estimation. The vertical density profile of the board was measured using compact X-ray density profile analyser DPX300-LTE (Imal, Modena, Italy). The measurements of internal bonding, characterized as the tensile strength of the composite material perpendicular to the board's plane, were carried out according to EN 319. The tensile tests were performed using a universal testing machine TIRA test 2850 (TIRA GmbH, Schalkau, Germany). Thermal conductivity of boards was estimated using guarded hot plate apparatus λ-Meter EP500e (Lambda-Messtechnik GmbH, Dresden, Germany) according EN 12664.

2.6.Statistical analysis

A statistical analysis was carried out using Statistica12 software (Stat Soft, Dell Inc.). Data was described by descriptive statistics and an analysis of variance was used to determine whether any of the pairwise differences were significant. The Tukey HSD test was employed in order to determine the significant differences between group means. A significance level of α = 0.05 was selected.

3. Results and Discussion

3.1.Particle material characterization

The results from the digital image analysis are shown in Table 2. The most numerous length class is 8.136 – 9.739 mm and the most numerous width class is 2.765 – 3.310 mm.

Table 2 Representation of the individual fractions of wheat husks

Length class (mm)	**Representation (%)**	**Width class (mm)**	**Representation (%)**
< 2.765	0.3	< 1.125	0.9
2.765 - 3.310	0.3	1.125 - 1.346	1.1
3.310 - 3.962	0.8	1.346 - 1.612	2
3.962 - 4.743	2	1.612 - 1.929	3.7
4.743 - 5.678	3.2	1.929 - 2.310	7.1
5.678 - 6.797	6.4	2.310 - 2.765	13.8
6.797 - 8.136	13.9	2.765 - 3.310	22.5
8.136 - 9.739	29.2	3.310 - 3.962	23
9.739 - 11.659	23.8	3.962 - 4.743	12.6
11.659 - 13.957	11.2	4.743 - 5.678	6.6
13.957 - 16.707	4.7	5.678 - 6.797	4.3
16.707 - 20.000	2.4	6.797 - 8.136	1.5
> 20.000	1.8	> 8.136	0.9

3.2.Morphological changes in husks

In Fig. 4a-d are depicted morphological changes in the wheat husk surface after different pre-treatments. The surface of untreated husk can be seen in Fig. 4a, where the knots (trichome remnants) on the husks are sunk into the top layer (epidermis). In Fig. 4b (hydrothermal treatment), the knots are protruding because the top layer is missing. The alkaline pre-treatment (Fig. 4c) even destroyed the knots, and holes in the husk surface can therefore be seen. Such a disruption of einkorn wheat husks was not observed by Tran et al. (2014) until husks were treated in 5% solution of sodium hydroxide for 24 hours. This may be explained by the harder and more resistant husks of einkorn wheat compared to winter wheat. The plasma pre-treatment (Fig. 4d) did not cause any visible morphological changes on the husk surface.

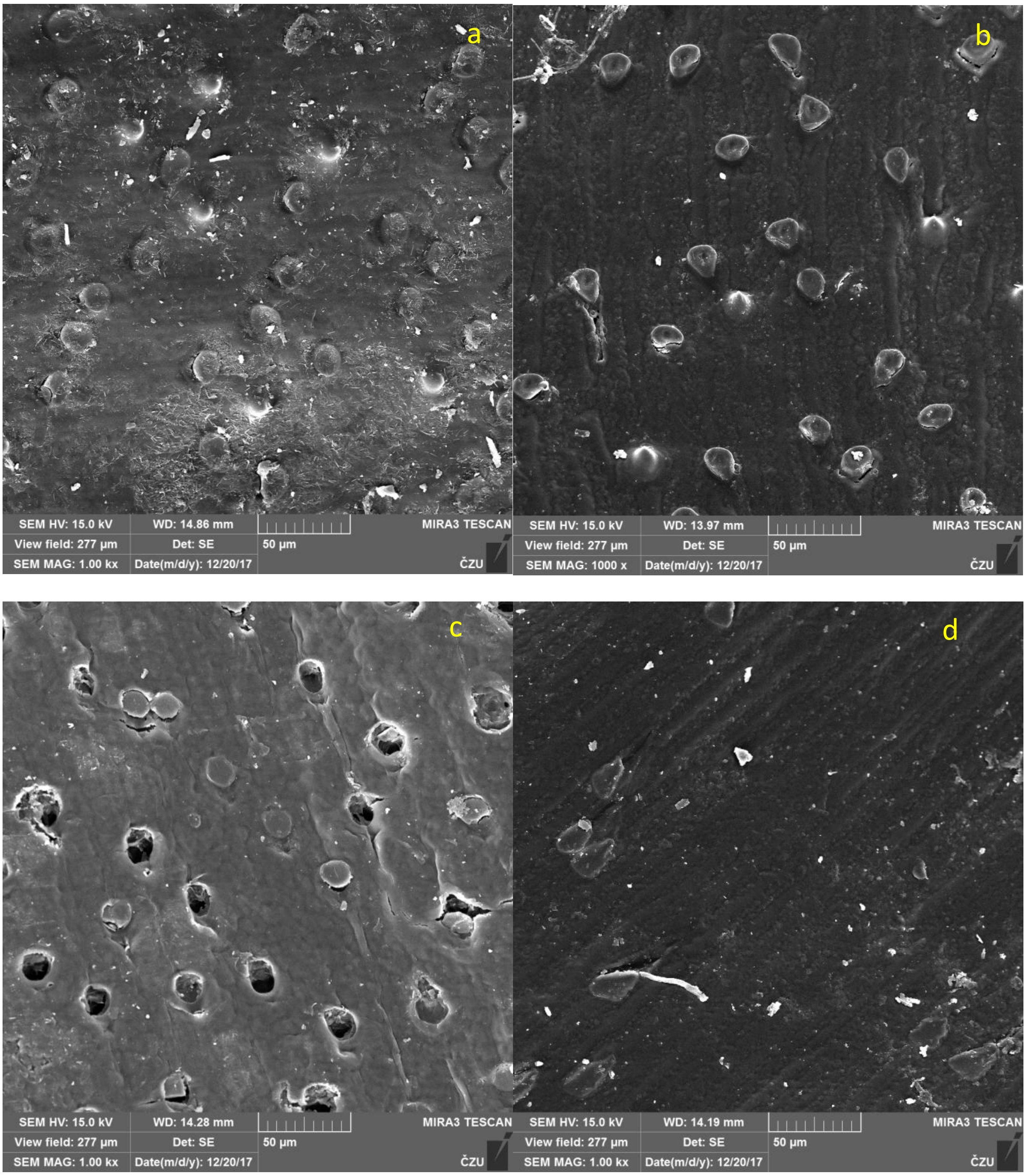

Figure 4 Electron micrographs of wheat husk surfaces (magnification 1000x). (a) Untreated husk, (b) hydrothermal treated husk, (c) alkaline treated husk and (d) plasma treated husk

3.3.Elemental content on the surface

The elemental compositions of the husk surface taken by an energy dispersive spectroscopy system (EDS) are depicted in Fig. 5. As the primary components of natural materials, oxygen and carbon have the greatest representation (as well as hydrogen, but this element is not detectable by the method used). It can be seen that silicon is present mainly on the trichome remnants of wheat husks; it was removed using alkaline treatment, as was also revealed by Tran et al. (2014). They further hypothesized that wheat husks have a very thin film of lignin covering the surface, and this film can be dissolved easily using sodium hydroxide at low concentrations (Tran et al. 2014). The alkaline treatment caused higher concentration of sodium on the husk surface, which was caused by imperfect washing of the treated husks.

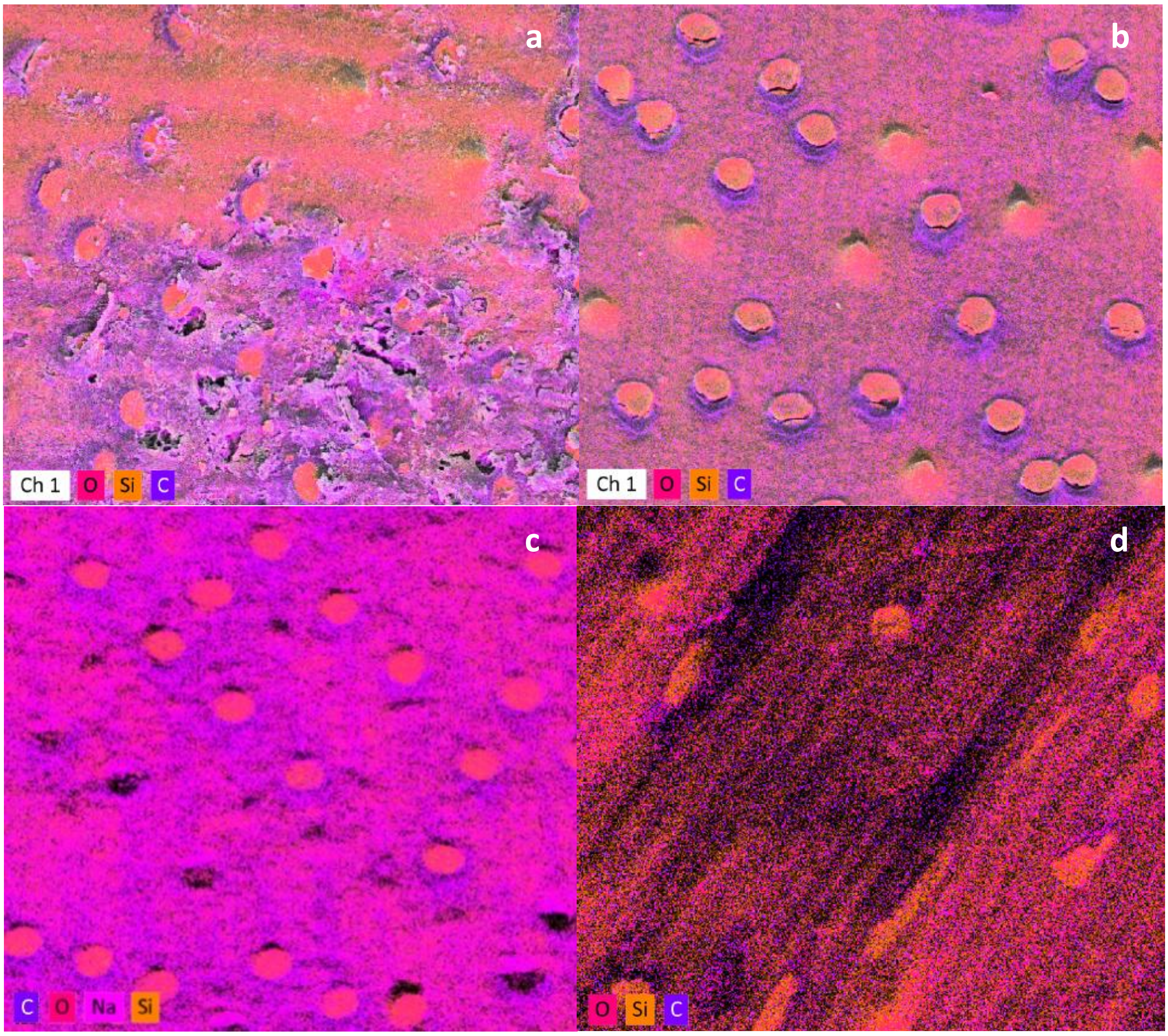

Fig 5 Elemental content of wheat husk surface taken by EDS (magnification 2000x). (a) Untreated husk, (b) hydrothermal treated husk, (c) alkaline treated husk and (d) plasma treated husk

3.4.FLIM analysis

The graph in Figure 6 depicts the influence of the mean fluorescence lifetime on chosen husk pre-treatment. Untreated husks exhibited the highest fluorescence lifetime, whereas alkaline pre-treated husks had the lowest fluorescence lifetime. Both hydrothermal and plasma pre-treatment did not cause statistical significant differences in fluorescence life time in comparison to the reference. The decrease of fluorescence lifetime caused by alkaline pre-treatment can be explained by the higher lignin content.

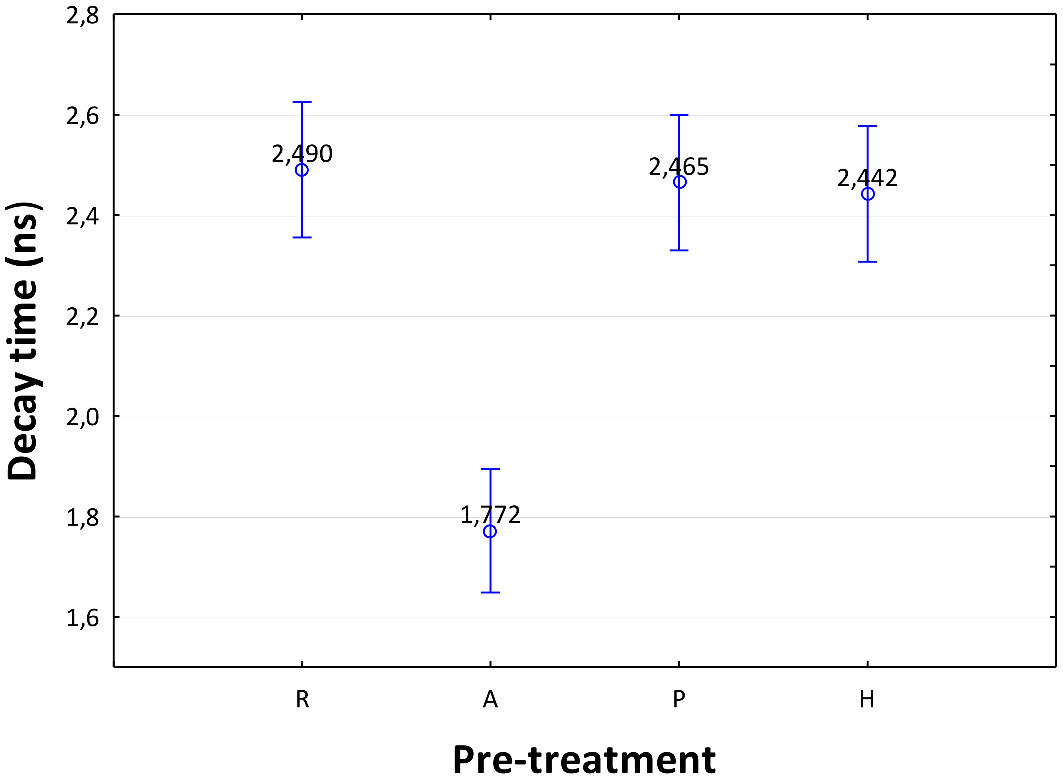

Figure 6 Fluorescence lifetime of modified husks

When the normalized photon count as a function of time is displayed (Figure 7), it can be seen that the alkaline pre-treatment differs most in the shape of the fluorescence decay curve, which corresponds to the shorter lifetime in Figure 6. The histogram for normalized photon count from an alkaline treated specimen achieved the highest peak and then the count decreased rapidly. As both cellulose and lignin have the characteristic shape of a fluorescence decay curve, the ratio between lignin, cellulose and hemicelluloses could be estimated from the shape of the decay curve before and after modification. Lignin is characterized by a shorter fluorescence lifetime; the peak of its decay curve is closer to the zero point and is followed by a steep decrease in the photon count (Donaldson and Radotic 2013; Coletta et al. 2013), whereas decrease in the photon count emitted from cellulose and hemicelluloses is slower. Despite the fact that lignin was supposed to be reduced by the alkaline treatment (Li et al. 2007; Tran et al. 2014), the FLIM analysis indicates a higher lignin content in chemical treated husks than in untreated husks. This result corresponds to the results from FTIR analysis, where a higher ratio of lignin in chemical treated husks was also observed. The reduction of cellulose and hemicelluloses content can be explained by a peeling reaction, which occurs when the ligno-cellulose material is immersed in an alkaline solution (Green et al. 1977).

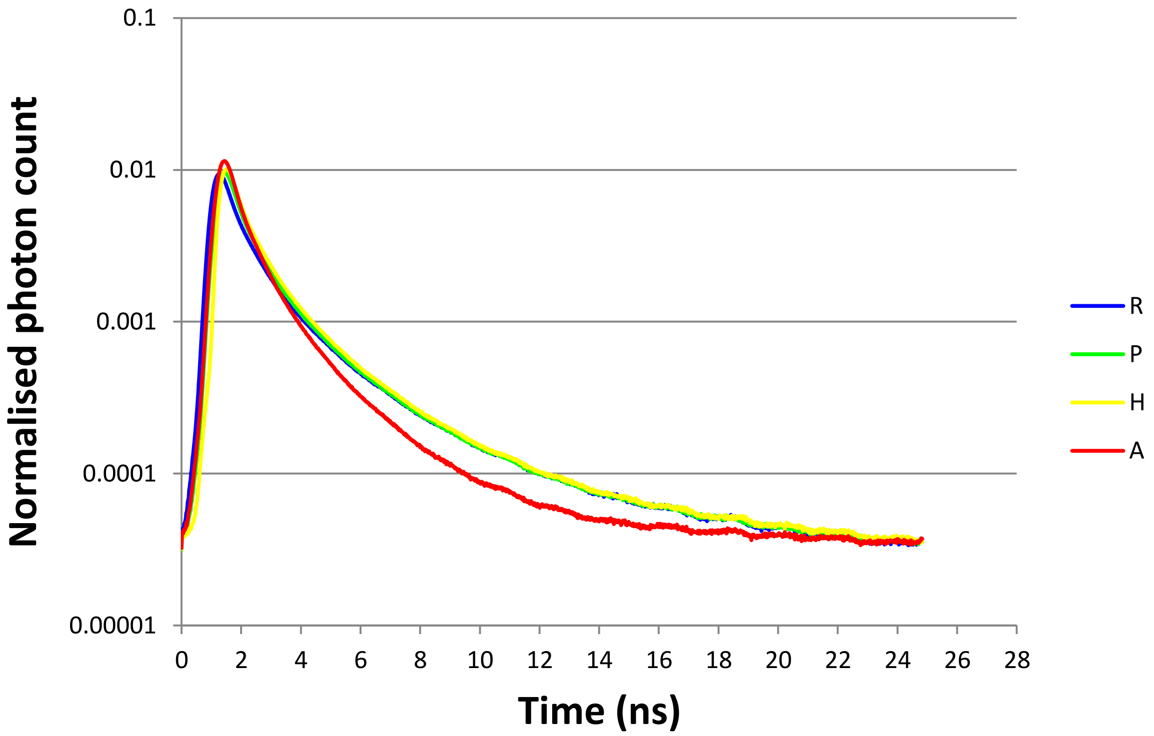

Figure 7 Fluorescence decay curves – Histograms of normalised photon counts

3.5.FTIR analysis

The various chemical constituents present in untreated and pre-treated husk were analysed by FTIR (Fig. 8). Slight variations in the FTIR spectra of different treated husks can be seen. The broad absorption band around the peak of 3336 cm^{-1}, which is ascribed to the hydrogen-bonded O-H stretching present in aliphatic or aromatic alcohols (Tran et al. 2014), has the same intensity and shape for all of the tested materials. The signal from alkaline treated husks has higher absorbance than from untreated, plasma and hydrothermally treated husks, up to the wavenumber of 1800 cm^{-1}. At the two peaks around 2922 cm^{-1}, which correspond to the C-H stretching from aliphatic saturated compounds, the highest absorbance was achieved by alkaline, followed by hydrothermally treated husks. This indicates a higher content of aliphatic compounds in cellulose and hemicelluloses. A steep double peak detected at 2360 cm^{-1} corresponds to CO_2. The peak at 1738 cm^{-1} is reflective of the C=O function of the acetyl and ester group of hemicelluloses or waxes and natural fatty components (Seki 2009; Tran et al. 2014) and reflects the presence of hydrophobic compounds. The highest absorbance of this band was achieved by hydrothermal and plasma treated husks, whereas reference and alkaline treated husks achieved lower absorbance. This absorption band was completely removed by alkaline treatment (siloxane treatment) of jute fibres (Seki 2009) and also reduced by sodium hydroxide treatment of wheat and rice husks (Tran et al. 2014) or wheat straw (Yang et al. 2016). The band around 1650 cm^{-1} is ascribed to the H-O-H bend of bonded water in crystalline cellulose, and highest absorbance on this peak was achieved by untreated and alkaline treated husks. The C=C aromatic skeletal vibrations at about 1510 cm^{-1} represent lignin, and it can be seen that alkaline treated husks achieved the highest absorbance there. This could be caused by a reduction in cellulose and hemicelluloses with sodium hydroxide solution (Green et al. 1977). The lignin units are also slightly prominent for hydrothermally treated husks, as hemicelluloses were partially removed by boiling in water (Carvalho et al. 2018; Gallina et al. 2018). Wavelengths of 1430-1460 cm^{-1} correspond to C-H deformation (asymmetric) and aromatic skeletal vibration and the wavelengths around the peak of 1366 cm^{-1} are assigned to the symmetric and asymmetric C-H deformations in methyl and phenolic alcohol or C-H rocking in alkanes (Tran et al. 2014); whereas in the first band, higher absorbance is achieved by alkaline treated material, while hydrothermally treated husks have higher absorbance in the second bands. The intense peak at 1034 cm^{-1} is attributed to asymmetric and symmetric Si-O-C and Si-O-Si stretching bonds corresponding to silica present in wheat husks (Tran et al. 2014). In the poplar wood, Gierlinger et al. (2008) also reported at 1033 cm^{-1} aromatic C-H in-plane deformation assigned to lignin overlays with the C-O stretching band of cellulose at 1035 cm^{-1}.

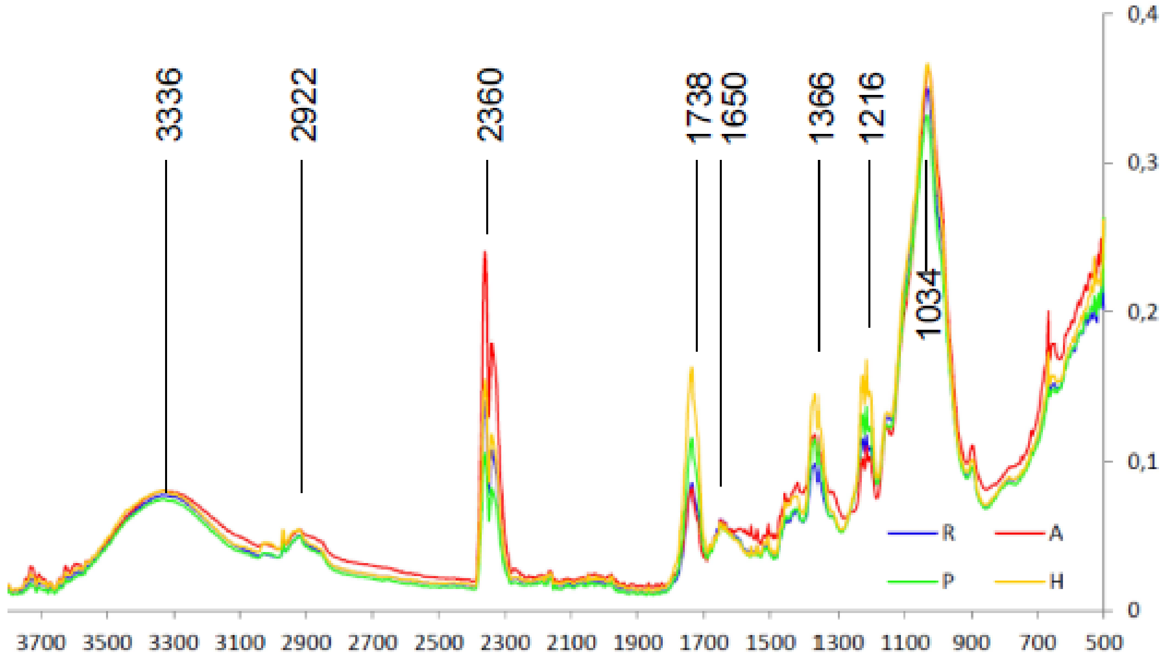

Figure 8 FTIR Spectrum of husks

3.6.Equilibrium moisture content and surface tension of husks

Figure 9 shows the equilibrium moisture content of wheat husks. Each of the variants differ statistically significant (p=0.05) to the others. While the mean moisture of untreated husks was 12.7%, the alkaline pre-treatment shifted this value up to 13.7%. The sodium hydroxide solution broke ester linkages between wax and lignocellulose and dissolved wax and lignin, and the cellulose was thus more accessible for water (Wan et al. 2011). Tran et al. (2014) also revealed that alkaline treatment using a sodium hydroxide solution dissolved a fraction of waxes, lignin and hemicellulose so that the polarity of their surface was increased and the alkaline treated husks were therefore more sensitive to moisture. The hydrothermal and plasma pre-treatment had the opposite effect - the equilibrium moisture content decreased. It seems that these two types of modifications did not dissolve compounds and that the thermal treatment caused a decrease in husk hygroscopicity in the same way it did for wood (Nakano and Miyazaki 2003; Esteves et al. 2007). Using hydrothermal treatment, the content of carbohydrate in the particles, especially mannan, xylan and arabinans, was decreased (Carvalho et al. 2018), which resulted in lower equilibrium moisture content and subsequently lower thickness swelling of the manufactured boards. Despite the fact that the effect of cold air plasma on the physical properties of the modified material decreases over time after plasma application (Klímek et al. 2016), we still observed statistical significant changes in the treated husks after 14 days in an air-conditioned chamber. These changes were likely also caused by the high temperature in plasma mixing device during plasma treatment. The internal temperature rose during plasma application up to 70 °C. In addition to the mentioned modifications, enzymatic modification was reported as a method for reducing the equilibrium moisture content of wheat husks. Using amylase–xylanase, laccase, pectinase and protease enzymes, the equilibrium moisture content of wheat husks was reduced by 35% (Mamun and Bledzki 2013).

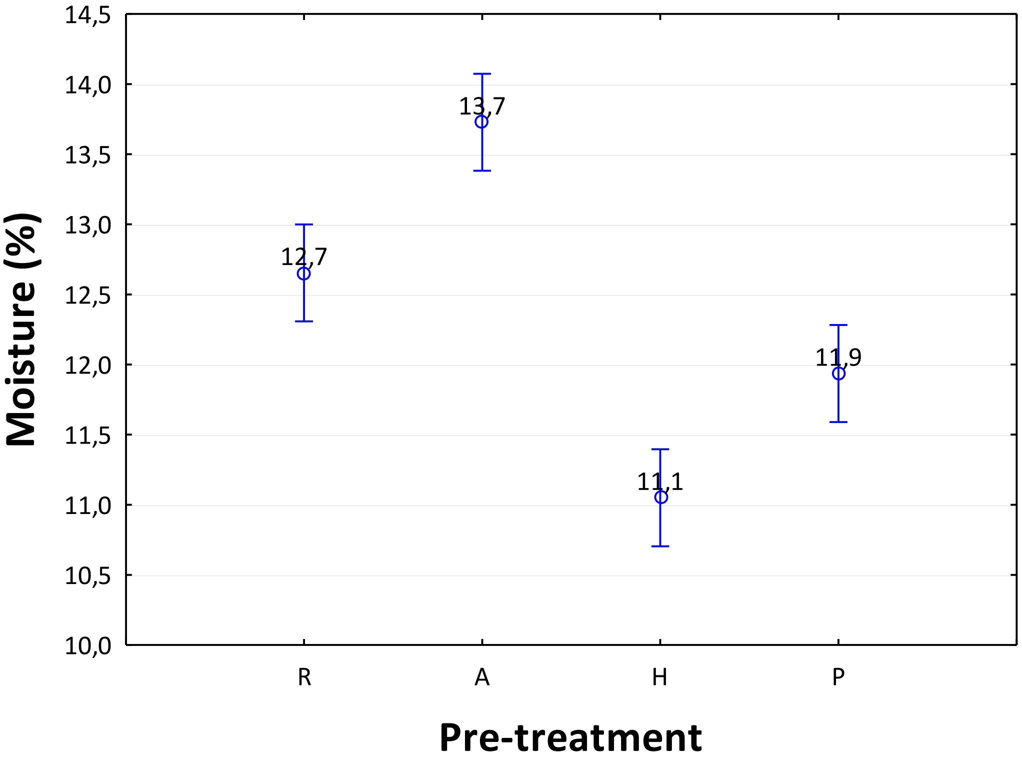

Figure 9 Equilibrium moisture content of wheat husks

The values of surface tension of husks are specified in Table 3. It can be seen that all of the modifications caused the desired effect in terms of an increase in the surface tension. The highest increase was caused by alkaline pre-treatment, whereas hydrothermal pre-treatment had the lowest effect.

Table 3 Surface tension of husks

Pre-treatment	Surface tension (mN/m)
untreated	34±2
hydrothermal treated	40±2
alkaline treated	54±2
plasma treated	44±2

3.7.Physical properties of boards

Boards made from all four types of materials were produced using the same production method, and in particular the moisture of husks and the pressing programme were the same for all of the alternatives. Therefore, differences in board densities and vertical density profiles can be considered as a function of husk pre-treatment. Certain variability (Table 4) was caused due to manual layering or due to the presence of small amount of wheat grains, as a natural part of husks, which could be spread unevenly. However, coefficients of variation are lower compared to other research where boards were produced manually from alternative materials (Nguyen et al. 2017). The lowest average density was achieved by boards made from alkaline treated husks due to higher thickness. The higher thickness (it can be seen on the vertical density profile in Fig. 10) was caused by higher thickness swelling over a longer period of storage (3 days) since directly after hot-pressing no spring back was observed. Compared to boards made from pre-treated particles, the boards manufactured from the reference particles had the steepest density profile. It had already been observed in a previous study that particle pre-treatment slightly affects the vertical density profile due to changes in plasticization behaviour of the particles (Hýsek et al. 2018).

Table 4 Average densities of boards measured after conditioning at 20 °C and RH 65%

Board type	Density* [kg/m^3]	Standard deviation	Coeff. of variation (%)
R	466,5	26,2	5,6
P	483,9	26,6	5,5
H	481,8	22,0	4,6
A	458,6	18,2	4,0

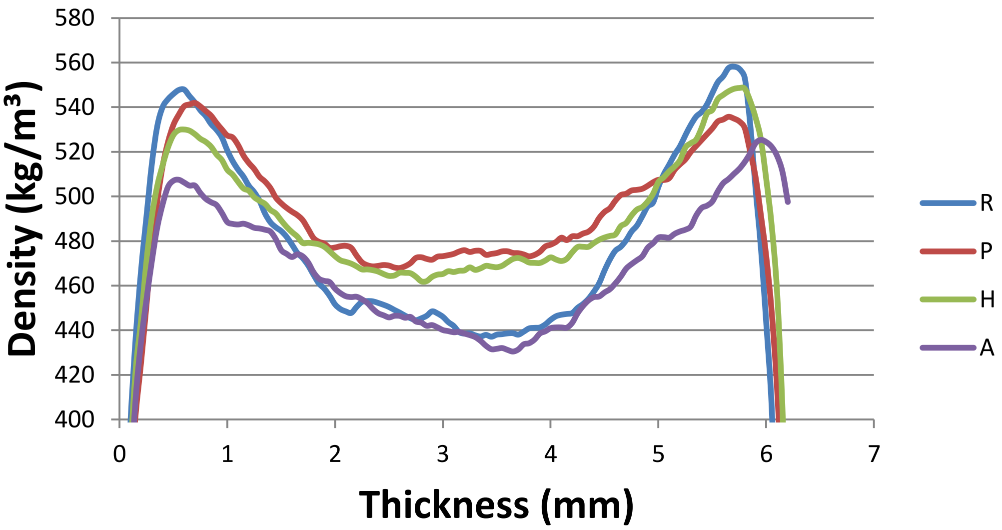

Figure 10 Vertical density profiles of boards measured after conditioning at 20 °C and RH 65%

The thermal conductivity of the manufactured boards (Table 5) was in the range from 0.0714 W/(mK) to 0.0783 W/(mK), where boards made from plasma treated husks achieved the lowest value. When we compare the achieved values with other natural thermal-insulation materials composed of renewable resources, it can be stated that the achieved thermal conductivity of husk boards is quite low. Thermal insulation of binderless cotton stalk fibreboard with density of 450 kg/m³ was reported as 0.0815 W/(mK) (Zhou et al. 2010), insulation fibreboards made from bamboo fibres and bone glue with density of 382 kg/m³ achieved thermal conductivity of 0.082 W/(mK) and fibreboards made from bamboo fibres and bone glue modified with sodium lignosulfonate with density of 442 kg/m³ achieved a value of 0.081 W/(mK) (Nguyen et al. 2017).

Table 5 Thermal conductivity of boards made from wheat husks

Pre-treatment	**Density* [kg/m³]**	**$\lambda_{10}^{23/50}$ [W/(mK)]**
untreated	466	0.0728
hydrothermal treated	483	0.0783
alkaline treated	461	0.0765
plasma treated	487	0.0714

*Density was measured after conditioning at 20 °C and RH 65%

Thickness swelling caused by conditioning of specimens in different relative humidity is shown in Fig. 11. It can be seen that at all conditioning stages, the boards produced from alkaline treated husks achieved the biggest thickness swelling, which was caused by elimination of hydrophobic substances from husks. The lowest thickness swelling was achieved at all stages by boards made from hydrothermally treated husks. With the exception of the first stage, all of the differences in the other materials are statistical significant. The thickness swelling of type H boards was the lowest, despite the fact that their average density was higher than those made from alkaline treated and untreated husks. Relatively high non-recoverable thickness changes were observed after the samples were dried in an oven. However, high non-recoverable thickness changes had already been observed on boards made from pre-treated after harvest remains (Hýsek et al. 2018).

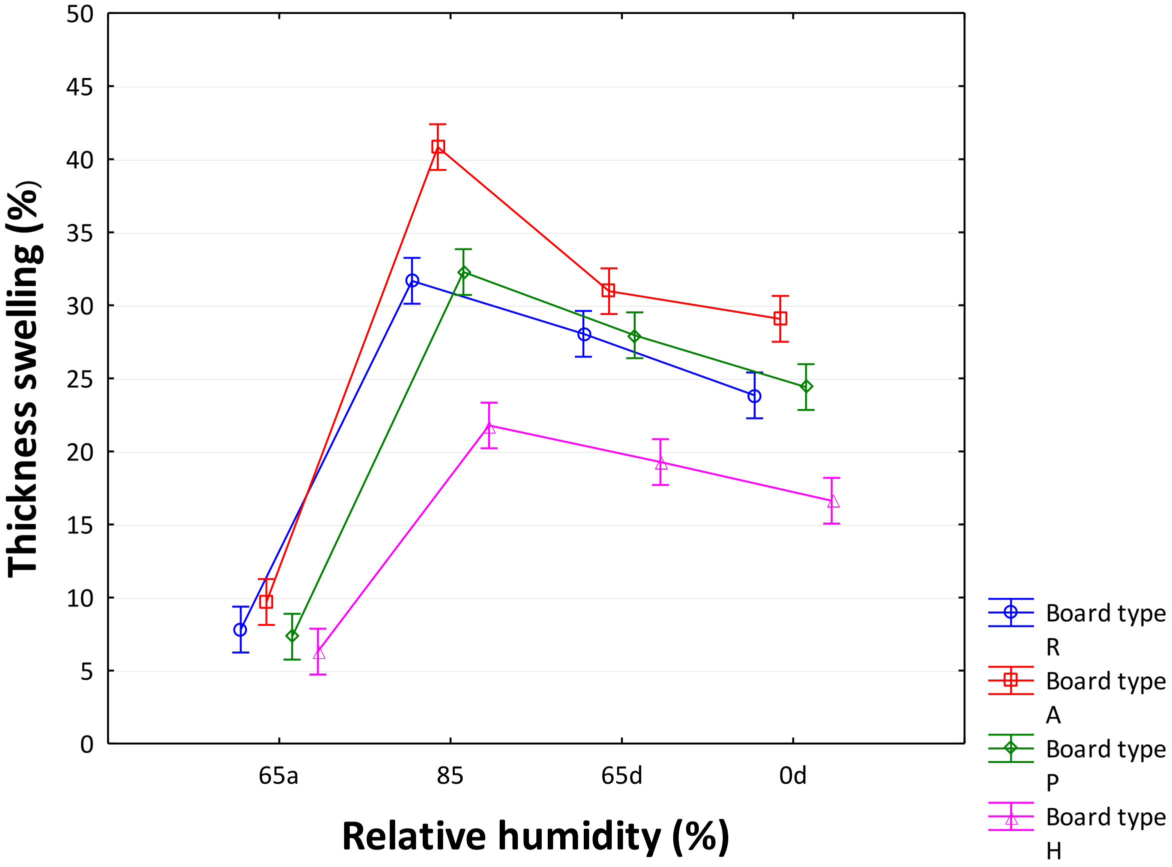

Figure 11 Thickness swelling of boards at different conditioning stages

The influence of wheat husk pre-treatment on the equilibrium moisture content of boards is shown in Fig. 12. Similarly to thickness swelling, the highest moisture was achieved by boards made from chemically treated husks. However, the increase in moisture uptake in the climate of 85% RH was noticeably higher for these boards than at other conditioning stages. High moisture uptake of alkaline treated husks and boards from those husks could by also partly caused by residual sodium hydroxide presented on those husks, which has great hygroscopic properties. Boards made from untreated husks achieved the lowest equilibrium moisture content in all climates, and both hydrothermal and plasma treatment caused same moisture uptake of boards. This does not correspond to moisture uptake of treated husks, where the lowest moisture was achieved by hydrothermally treated husks, and the difference between plasma and hydrothermal treatment was statistically significant. This can be explained by the average density of boards, which was lower for boards made from untreated husks. In addition, boards made from hydrothermally treated wood strands exhibit both lower thickness swelling and equilibrium moisture content, which could be caused by a reduction in carbohydrates (Carvalho et al. 2018). The overall high level of moisture may also be caused by the presence of grains in boards, due to starch, which, as a natural compound, is able to absorb a great amount of moisture (Mamun and Bledzki 2013). It can be expected that the effect of plasma treatment on thickness swelling could occur for resin content lower than 9%. Thickness swelling and water uptake of boards made from wood particle treated with direct dielectric plasma discharge at atmospheric pressure were only improved when compared to the respective control samples at an adhesive content of 3% and not at 5% and 8% (Altgen et al. 2015). It can also be hypothesized that the plasma application method could affect the treatment effect on husks properties. When particles were plasma treated in previous research, surface discharge plasma was used for the application, and particles have greater contact with ionised gas during this application (Altgen et al. 2015; Klímek et al. 2016). However, a jet system for plasma application was used in our study and an application apparatus was developed for this purpose.

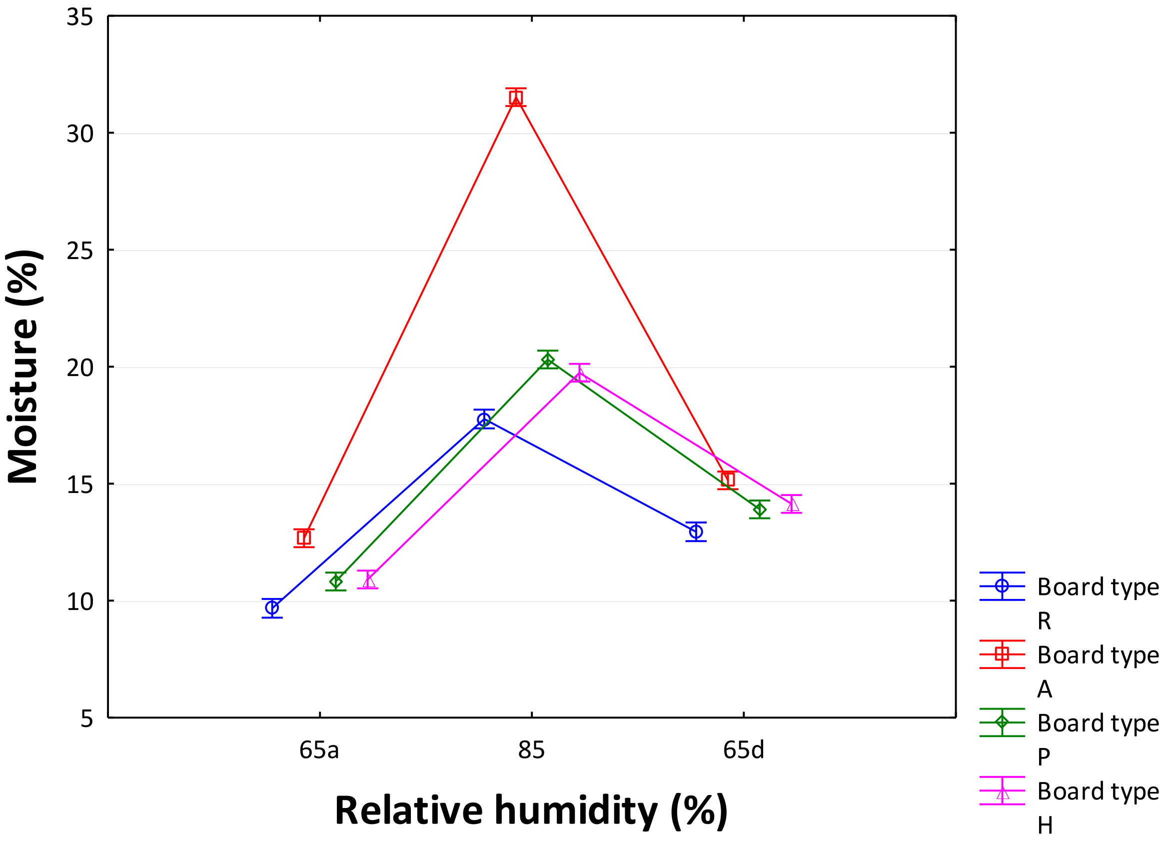

Figure 12 Equilibrium moisture content of boards at different conditioning stages

3.8.Internal bonding

Internal bonding was characterized to display the effect of husk pre-treatment on the mechanical properties of boards made of those husk particles (Fig. 13). Both plasma and hydrothermal pre-treatment caused the desired effect in terms strength increase. The greatest enhancement in husk-adhesive adhesion was caused by the high temperature, which can be seen as promising in terms of better adhesion not only for pre-treatment of alternative materials, but also for pre-treatment of wood (Fang et al. 2017; Tavasolli et al. 2018). The chemical treatment, however, caused a decrease in internal bonding. This treatment was most likely too aggressive for treatment of wheat husks and its material was destroyed (observed by SEM). Nevertheless, a lower-percentage solution of sodium hydroxide could have an opposite effect. Yao et al. (2015) and Orue et al. (2016) had already observed enhancement of mechanical properties of composites after alkaline pre-treatment of raw material. In the research specified above, the concentration of the used sodium hydroxide solution was higher than 2% and the treatment time longer that 45 minutes; however, the treated materials were obviously more resistant. However, effect of 10% solution of sodium hydroxide on the mechanical properties of composites from treated rice husks was also unclear (Huner 2017). In the other study, einkorn wheat husks were immersed in sodium hydroxide solutions at 2%, 5% and 10% for 24 h at room temperature, and the mechanical properties of composites from treated husks increased. However, the husks were only used as a filler in reinforced poly(lactic acid) composites, where the husk weight content was only 20% compared to our composites where husk weight content was 91% (Tran et al. 2014). It can be therefore assumed that the residual sodium hydroxide in imperfectly washed husks caused a poor adhesion of adhesive, because used urea-formaldehyde resin is an acid-hardening adhesive and sodium hydroxide caused an alkaline environment. The interaction between adhesive and residual sodium hydroxide could also cause higher thickness swelling of boards (Fig. 10 and 11). Altgen et al. (2015) reported an increase in internal bonding of boards after wood particle treatment with direct dielectric plasma discharge at atmospheric pressure. The increase was by approximately 0.1 MPa compared to the respective controls for all adhesive ratios (3%, 5% and 8%). However, the modulus of rupture, modulus of elasticity and water related properties were only improved at the lowest adhesive content. It is therefore concluded that the discharge plasma treatment can improve the bonding quality and water related properties of wood based particleboards particularly at low adhesive contents (Altgen et al. 2015). Apart from reported modifications, using enzymatic modification can also lead to an increase in the mechanical properties of the husk based composites (Mamun and Bledzki 2013).

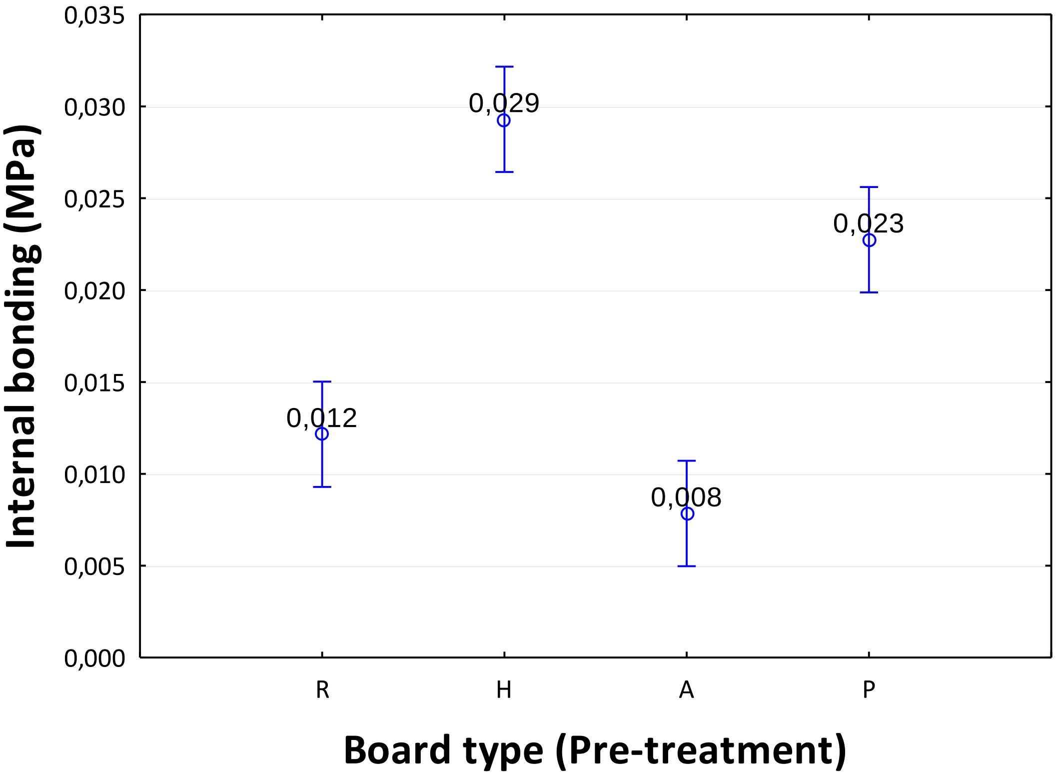

Figure 13 Tensile strength perpendicular to the plane of the board

4. Conclusions

Hydrothermal, plasma and alkaline treated and untreated wheat husks were used for board production. Treatment in 2% sodium hydroxide solution increased the surface energy of husks and reduced waxes and natural fatty components; however, the husk structure was eroded and thus the internal bonding of the boards decreased. Promising results were achieved using hydrothermal treatment - boards made from such treated husks achieved the highest internal bonding and significantly lower thickness swelling caused by moisture uptake. Compared to the reference samples, of all of the selected pre-treatments, plasma treatment caused the lowest changes in material characteristics.

5. Acknowledgement

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[7] **HÝSEK, Š.,** SIKORA, A., SCHÖNFELDER, O. a BÖHM, M. 2018, Physical and Mechanical Properties of Boards Made from Modified Rapeseed Straw Particles, *BioResources*, roč. 13, č. 3, s. 6396-6408.

Physical and Mechanical Properties of Boards Made from Modified Rapeseed Straw Particles

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Composites made from annual plants, such as winter rapeseed, can be used as an alternative to wood-based composites because of their ecological character, low price, as well as physical and mechanical properties. The goal of this study was to prepare such boards and evaluate their properties. Unmodified material and chemically and hydrothermally modified rapeseed particles glued by powder polyester glue were used. The characteristics measured were the internal bonding, swelling and moisture uptake over time, and surface soundness. The results showed that modification of the raw material influenced the properties of the resulting composites. The highest swelling values were exhibited by the boards with particles that were alkaline-modified. Boards made from hydrothermally modified particles achieved the highest strengths compared with the commercially produced boards. The alkaline modification of the particles resulted in a stronger adhesive bond between the particle and adhesive. During the internal bonding test, the boards made from the alkaline-modified particles exhibited cohesive failures in the particles. Therefore, the modification of the particles increased the mechanical properties of the boards, but the physical properties deteriorated.

Keywords: Rapeseed; Particleboard; Internal bonding; Surface soundness; Non-recoverable thickness changes; Thickness swelling

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INTRODUCTION

Raw wood is the main component used in the production of composite materials. With increasing demands in the woodworking industry, the importance of alternative sources for the production of wood-based materials is increasing and becoming more topical (Dziurka *et al.* 2015). Various materials based on cellulose and lignin are currently used for the production of agglomerated materials (Ye *et al.* 2007). Agricultural products that are used to produce composite materials include rice stalk, coconut fiber (de Melo *et al.* 2010; Zhang and Hu 2014), corn stalk (Akinyemi *et al.* 2016), jute (Goswami *et al.* 2008), bagasse (Silva *et al.* 2016), bamboo (Widyorini *et al.* 2016), wheat straw (Zhang *et al.* 2011), and rapeseed (Dziurka *et al.* 2005). This study primarily focused on the production of composite materials made from rapeseed. Using post-harvest rapeseed residues, which have not yet been industrially used as the main component in composite materials, has the potential to contribute to solving the shortage of wood in the woodworking industry in the European Union.

The yield per hectare of rapeseed stalk is 3 t to 10 t, which means there is a production of 42 million t of post-harvest rapeseed residue in the European Union (Eurostat 2015). The chemical composition of rapeseed stalk is slightly different from that of wood. Rapeseed particles contain less cellulose and lignin, and more hemicellulose and extractive substances. The cellulose contained in stalks positively affects the resulting mechanical and physical properties of composite boards (Dziurka and Mirski 2013; Dukarska *et al.* 2017). There are different requirements for the mechanical and physical properties of composite materials, depending on their use. The change in the shape of a material caused by moisture is one of the most discussed physical properties. The effects of moisture have a major impact on the resulting properties and use of a composite material (Halligan 1970).

These effects mostly manifest themselves as a reduction in the strength of the boards, their durability, and changes in their shape (Gaff 2014). Dimensional changes can be prevented by the type of adhesive used, which can also affect the resulting usability of a material in the furniture and construction industries (Mirski *et al.* 2012; Gaff and Gašparík 2013). In terms of practical utilization, the internal bonding and surface soundness of materials are tested.

The objectives of this study were to evaluate selected mechanical and physical properties of composite materials made from rapeseed particles and to assess the effects of surface modification on these properties. The monitored mechanical properties were surface soundness and internal bonding. Because it is believed that the modification of particles disrupts the waxy and siliceous substances on the particle surface, the swelling and moisture of the boards over time were also observed. The resulting properties were compared with the properties of oriented strand board (OSB) and particleboard.

EXPERIMENTAL

Materials

Test specimens based on rapeseed stalk particles were used in this research. For the particle characteristics, a screen analysis was performed; the percentages of individual fractions are shown in Table 1. DAKOTEX2600 (Dakota Coatings N.V., Nazareth, Belgium), a powder adhesive made of polyester and epoxy resin, was used for board production. Table 2 lists the markings of the manufactured and commercial boards that were further used in the study.

Table 1. Representation of the Fractions in the Chopped Rapeseed Stalk

Fraction (mm)	0 - 0.25	0.25 - 0.5	0.5 - 0.8	0.8 - 1.6	1.6 - 2	2 - 3.15	3.15 - 8
Frequency (%)	1.2	2.8	4.8	39.4	20.1	23.1	8.6

Table 2. Marking of the Manufactured Boards and Commercial Boards

Mark	Type of Board
1	Board made from unmodified rapeseed particles
2	Board made from hydrothermally modified rapeseed particles
3	Board made from rapeseed particles modified in an alkaline environment
4	Particleboard
5	OSB

Methods

Boards made from raw and modified rapeseed particles were compared with commercially available wood-based materials, namely OSB (load-bearing board for use in humid conditions with thickness of 12 mm and density of 620 kg/m^3) and particleboard (panel for interior use in dry conditions with thickness of 12 mm and density of 670 kg/m^3). In order to disrupt the waxy layer on the surface of stems that could inhibit high-quality bonding between the particle and the adhesive, the particles were pre-treated (Částková *et al*. 2018). To achieve a better particle-adhesive bond, the rapeseed particles were hydrothermally (submerged in boiling water for 45 min) and chemically (soaked in a 2% NaOH solution at a water temperature of 25 °C) modified. To remove residual substances from the NaOH solution, the modified particles were thoroughly rinsed and dried.

Boards with a thickness of 12 mm and nominal density of 620 kg/m^3 were made. The adhesive was applied to the particles using a laboratory adhesive applicator (Imal, Modena, Italy). A resin dosage of 10% on straw dry mass was applied. After the adhesive was applied, a uniform particle sheet with the uniform area density was created on steel panels. This particle sheet was placed in a laboratory press (Strozatech, Brno, Czech Republic). The pressing was performed at a pressure of 2.3 MPa and board temperature of 185 °C for 10 min. At the end of the press cycle, a temperature of 170 °C was reached in the center of the boards. The closing speed of the press was 150 s. After the press was opened, the boards were removed and allowed to cool slowly.

The thickness of the boards was levelled to 12 mm, and then 50-mm × 50-mm × 12-mm test specimens were randomly cut from the boards. The vertical density profile of the boards was determined for these specimens. A Compact X-ray density profile Analyser DPX300-LTE (Imal, Modena, Italy) was employed.

Specimens with the dimensions 50 mm × 50 mm × 12 mm intended for the internal bonding and surface soundness testing were conditioned to an equilibrium moisture content in a climatic chamber at a relative humidity of 65% and temperature of 20 °C for 14 d. The specimens for monitoring the swelling over time were dried in an oven at 103 °C down to 0% moisture content. A total of 15 pieces of each type of board were made to monitor the swelling, 15 pieces were made for the internal bonding testing, and 15 pieces were made for the surface soundness testing.

The first monitored property was the swelling of a specimen over time. Rapeseed, OSB, and particleboard test specimens were dried to a 0% moisture content, and their dimensions and weight were measured in their oven-dry state. The monitored characteristics were the dimensions increase over time in all board directions and the moisture increase. The swelling and absorption were determined by measuring the dimensions and weight; the time intervals between measurements were 10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 6 h, 12 h, 1 d, 2 d, and 3 d. The change in the dimensions was determined according to Eq. 1,

$$\beta_t = \frac{\beta_{wt} - \beta_o}{\beta_o} \cdot 100 \ [\%] \tag{1}$$

where β_t is the increase in individual directions depending on the monitored time (%), β_o is the dimensions (mm) of the specimen in the oven dry state, and β_{wt} is the dimensions (mm) of the specimen in individual directions after each interval.

After testing of the swelling, the test specimens were oven-dried again and the non-recoverable thickness changes in the test specimens were determined according to Eq. 2,

$$NRC = \frac{t_2 - t_1}{t_1} . 100\ [\%] \qquad (2)$$

where NRC is the non-recoverable thickness change (%), t_2 is the thickness of the specimen after the second drying (mm), and t_1 is the thickness of the specimen after the first drying (mm).

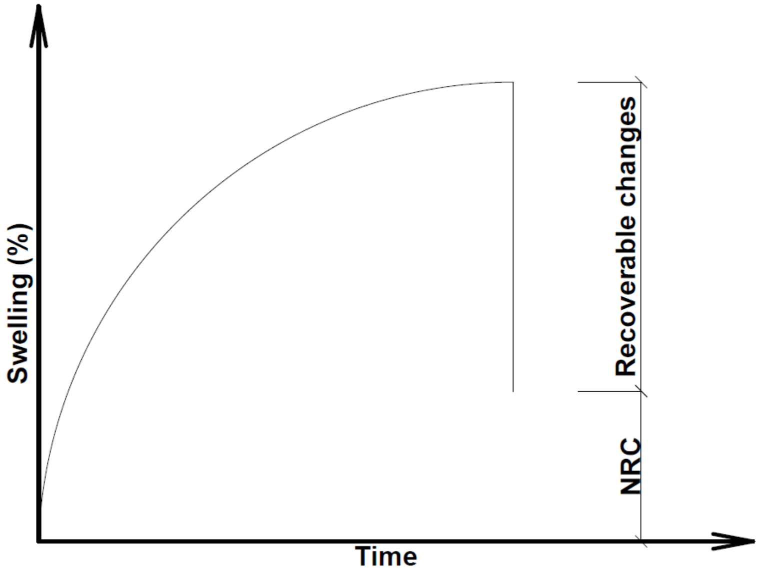

Fig. 1. Graphical representation of the calculation of the *NRC* according to Eq. 2

Internal bonding is the tensile strength of a composite material perpendicular to the plane of a board, where the board breaks down its center in the applied adhesive or material that forms the composite. The internal bonding was determined by following the standard EN 311 (2002). The test blocks to which the test specimens were glued were made of hard T-shaped ash wood, where the base of the block was identical to the dimensions of the test specimen (50 mm × 50 mm) and the dimensions of the top of the block were the same as those of the jaws of the universal testing machine (TIRA test 2850, TIRA GmbH, Schalkau, Germany). Epoxy glue was applied to the surface of a test specimen, which was glued to the wooden blocks and weighed down. After the glue hardened, the test specimens were returned to the climatic room to achieve an equilibrium moisture content. The tensile strength perpendicular to the plane of a board was determined according to Eq. 3,

$$\sigma = \frac{F_{max}}{a \cdot b} [MPa] \qquad (3)$$

where $F_{\max}$ is the maximum tensile force applied to the specimen at the moment of failure (N), and a and b are the dimensions of the test specimen (mm).

Surface soundness is another examined mechanical property. Surface soundness is the tensile strength when the surface layer is torn from the surface of a wood-based board. It is determined by measuring the force required to tear a steel rivet from a test specimen (EN 319 1993). The surface soundness test was performed according to the relevant standard EN 319 (1993). The test was performed on test specimens with the dimensions

(100 × 100) mm, and these specimens were randomly selected from the board. Test pads were glued to the test specimens with the required dimensions using epoxy adhesive. The prepared test specimens were then climatized in a climatic chamber at 65% relative humidity and 20 °C. The climatized specimens were then used to test the surface soundness with a Comtest adhesion tester (Coming Plus a.s., Prague, Czech Republic), and each specimen was tested in at least 12 places.

Scanning electron microscopy (SEM) of the broken bonds after tensile testing perpendicular to the plane of the boards were performed using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic) with a secondary electron detector, operated at 15 kV acceleration voltage.

An analysis of variance (ANOVA) (Fisher's F–test) and Tukey’s honest significant difference (HSD) test were used to evaluate the statistical significance of the individual factors (type of boards). A level of significance (α) of 0.05 was used for all of the statistical analyses. The statistical analyses were performed using STATISTICA 12 software (StatSoft CR s.r.o., Prague, Czech Republic).

RESULTS AND DISCUSSION

Figure 2 shows the course of water absorption by the specimens immersed in water. As was expected, the amount of water absorbed rapidly increased after immersion (Huner 2015). It is clear from the graph that the moisture increase was the steepest up to approximately 1000 min, then from 1000 min to 3000 min the moisture was almost constant, and afterwards the absorption slightly increased. Similar results were reported by Cruz *et al.* (2011). This trend did not apply to the specimens made from OSB; these specimens exhibited a continuous increase in the moisture over the measured time. The highest moisture values were achieved in the rapeseed boards made from the hydrothermally modified particles. In contrast, the lowest moisture values were achieved with the specimens made from the particleboard. Although all of the differences in the moisture content of the boards after the experiment were statistically significant, the effect of particle modification on the water absorption over time was not as great as the effect on the swelling of the boards, which is shown in Fig. 3.

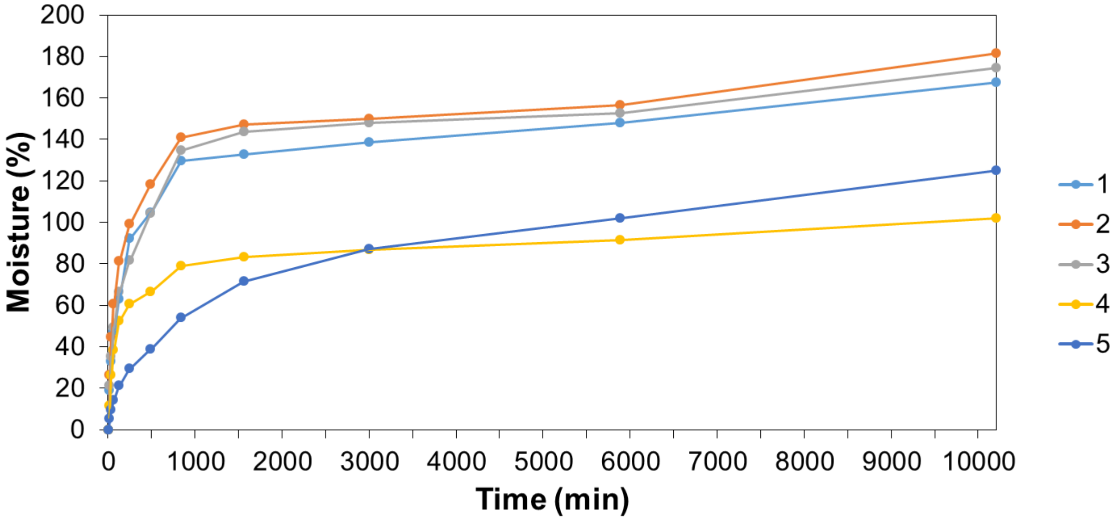

Fig. 2. Water absorption of the specimens immersed in water

Based on these results, it was concluded that boards made from rapeseed particles with the use of powder polyester adhesive can be used only for interior use, and a negative effect of particle modification on water absorption was found. The higher moisture values in the rapeseed-based particleboards were because of the absence of paraffin and other hydrophobic additives in the adhesive mixture. The figure also showed a clear effect from the particle modification on the higher resulting moisture content of the boards; the disruption of surface layer of particles led to higher water uptake (Hýsek *et al.* 2018). The differences between the moisture content of the boards at the end of the experiment were statistically significant ($p < 0.01$). A higher water absorption for hydrothermally modified materials was also reported by Huner (2015).

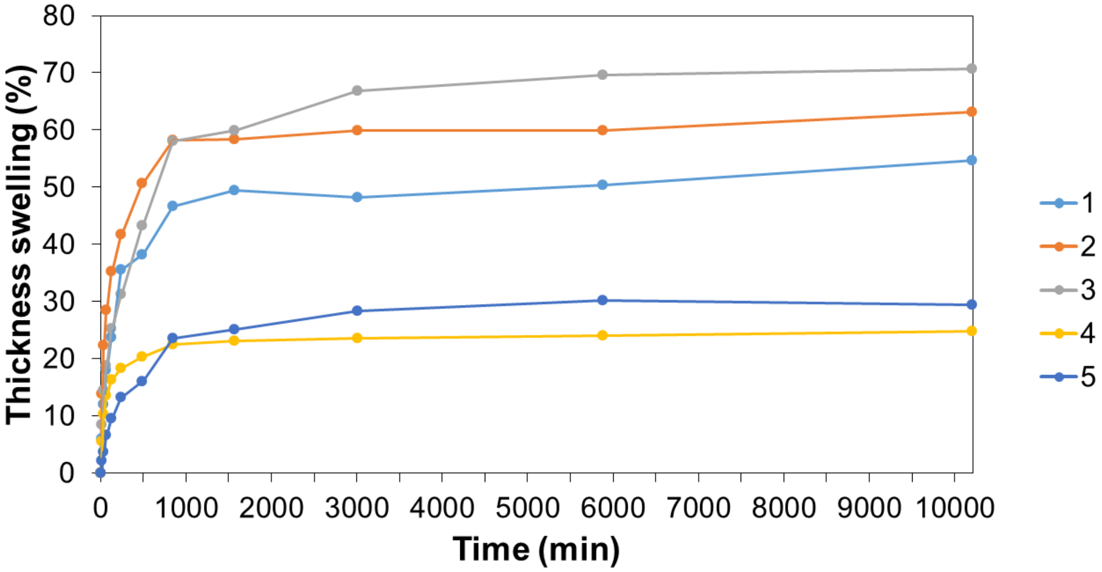

Fig. 3. Thickness swelling of the test specimens over time

Figure 3 shows the thickness swelling of the test specimens over time. The thickness swelling was increased steadily to 1000 min, as was the case with the moisture absorption over time. After this time, the thickness swelling was almost constant. The highest thickness swelling values were achieved by the test specimens made from the chemically modified particles, and the lowest swelling values were achieved by the specimens made from the particleboard, as was the case when the moisture content was monitored. The highest swelling values were achieved by the boards made with rapeseed particles. Both the hydrothermal and alkaline modifications increased the thickness swelling of the boards. Although these modifications caused a higher strength particle-adhesive bond, removing the waxy and siliceous substances from the particle surface resulted in greater particle swelling. The effect of the hydrothermal and alkaline modifications on removing waxy substances from particle surfaces was reported on in a previous study (Gajdačová *et al.* 2018). Furthermore, the alkaline modification caused a more heterogenic surface on the modified particles, which ensured better adhesive-particle bonding (Mohanty *et al.* 2000; Kim *et al.* 2006). Despite the better adhesion, removing hydrophobic substances caused a high thickness swelling. In contrast to this research, where the thickness swelling of the boards made from rapeseed particles achieved a swelling of 45% to 65% after 24 h, Dukarska *et al.* (2017) reported that the thickness swelling of rapeseed boards after 24 h increased by only 14% when a mixture of MDI (4.4′-

methylenediphenyl Isocyanate) and PF (phenol–formaldehyde) adhesive was used. The same values for rapeseed board swelling achieved by Dziurka and Mirski (2013) and Dukarska *et al.* (2017) were also achieved by Dziurka and Mirski (2013), but with the use of pMDI adhesive. Mirski *et al.* (2012) used OSB to achieve a thickness swelling of 8.9% after 24 h.

The figure also shows a clear effect of the particle modification on the resulting thickness swelling of the boards. The differences between the moisture content of the boards at the end of the experiment were statistically significant ($p < 0.01$).

Table 3 depicts the *NRC* and the thickness swelling of the boards. Boards made from the alkaline-modified particles had the highest thickness swelling values (70.7%), while the boards made from the hydrothermally modified particles achieved the highest *NRC* (37.8%). The OSB specimens exhibited the highest variability in the measured data.

Table 3. Thickness Swelling and *NRC* of the Boards

Type of Board	Thickness Swelling (%)	*NRC* (%)
Reference	54.7 (7.7)	30.5 (8.9)
Hydrothermal Treatment	63.1 (7.1)	37.8 (12.2)
Alkaline Treatment	70.7 (9.8)	29.8 (8.7)
Particleboard	24.8 (4.0)	8.6 (9.3)
OSB	29.4 (15.0)	12.1 (16.5)

Values in parentheses are the coefficients of variation in %

Figure 4 shows the volumetric swelling of the test specimens. The volumetric swelling pattern was identical to that of the thickness swelling (see Fig. 3). The differences between the achieved volumetric swellings of the boards at the end of the experiment were also statistically significant ($p < 0.01$).

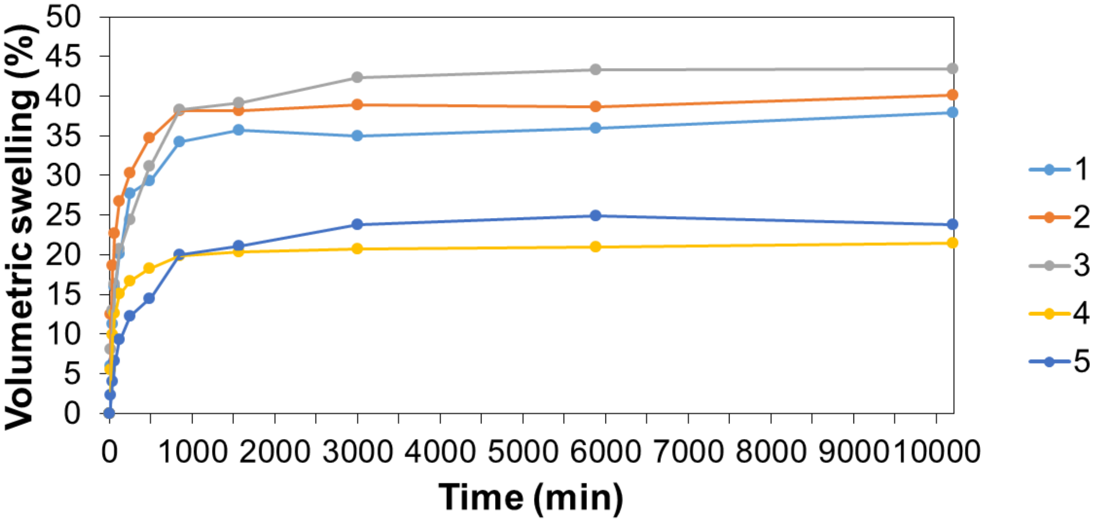

Fig. 4. Volumetric swelling of the test specimens

Figure 5 shows that the highest internal bonding (0.505 MPa) was achieved with hydrothermally modified rapeseed board specimens (bars show 95% confidence intervals). Similar results were obtained by Dukarska *et al.* (2017), who examined the internal bonding of rapeseed particleboards using a mixture of MDI and PF adhesive, with a result of 0.48 MPa. Similar values were obtained by Dziurka *et al.* (2005), who used a UF adhesive constituting 14% of the total particle volume and reported a resulting strength of 0.51 MPa. In contrast, the highest strength values were achieved by Dziurka and Mirski (2013), who reported internal bonding values of 0.82 MPa with the use of a pMDI adhesive.

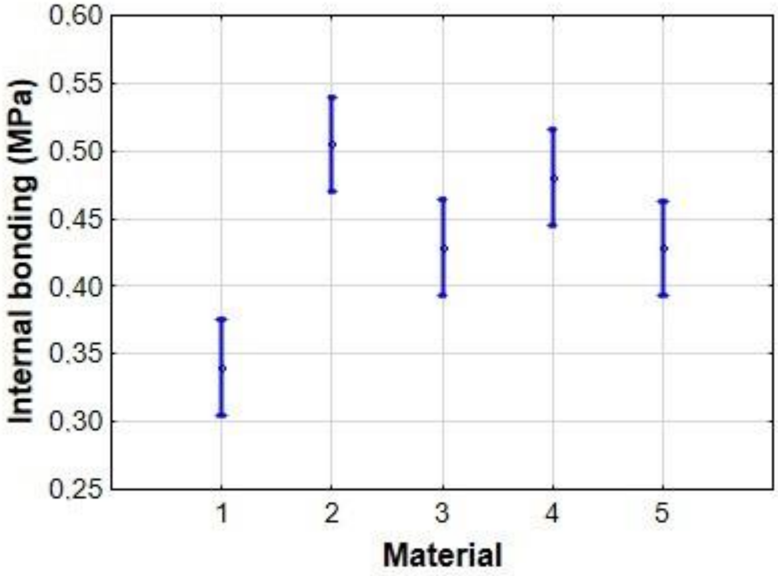

Fig. 5. Internal bonding of the boards

The results in this study indicated that the modification of the rapeseed particles improved the internal bonding of the boards in comparison with the reference set of rapeseed specimens, which achieved the lowest internal bonding values (0.340 MPa). By comparing the internal bonding results of the commercially produced OSB specimens with the results obtained by Mirski *et al.* (2012), lower internal bonding values were found in our study. The high internal bonding values may have been caused by the unusual vertical density profile of the boards made from rapeseed stalks. Because of the long press closing time, the highest density of the produced boards was reached in the middle of the vertical profile. An evaluation of the statistical significance of the differences in the tensile strength perpendicular to the plane of a board, corresponding with Fig. 5, is shown in Table 4.

Table 4. Statistical Significance of the Internal Bonding Differences

Type of Board	1	2	3	4	5
1	-	s.	s.	s.	s.
2	s.	-	s.	n.s.	s.
3	s.	s.	-	s.	n.s.
4	s.	n.s.	s.	-	n.s.
5	s.	s.	n.s.	n.s.	-

Statistical significance done according to Tukey's HSD test; s.- statistically significant; n.s. – no significant difference

Figure 6 shows a graphical representation of the results of the surface soundness tests (vertical columns represents 95% confidence intervals). The surface soundness test was not performed on the OSB specimens because this characteristic is not usually controlled in OSB. It is clear from Fig. 6 that the best results were achieved with material 4, which was a commercially available particleboard (0.325 MPa), and the worst results were achieved with material 3, *i.e.* a reference board developed by the authors without any modifications (0.119 MPa). When the modified particles were used in the materials developed by the authors, there was a trend of improvement in the tested properties with respect to the reference board; the properties of the water-modified boards (Material 2) improved by 16.7%, and the properties of the alkaline-modified boards (Material 1) improved by 33.5%. Although higher values were achieved by modifying the raw materials, the boards developed by the authors were still far behind the particleboards in terms of their values. In the article by Shalbafan *et al.* (2016), which also dealt with the surface soundness of particleboards, it was demonstrated that the results of this test were significantly affected by the board density. Shalbafan *et al.* (2016) tested boards with an approximate density of 600 kg/m^3, and in the case of the current study the density of the particleboards with a 1-mm thickness was approximately 862 kg/m^3. This density was significantly greater than the density of the boards developed in this study at a corresponding thickness (450 kg/m^3 to 500 kg/m^3), which explained the reason for the large difference in the surface soundness.

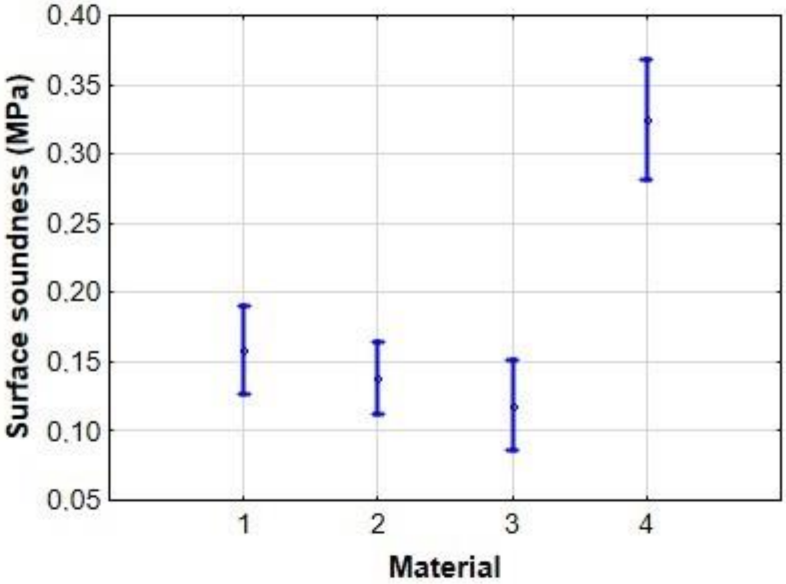

Fig. 6. Surface soundness of the boards

A statistical analysis according to Tukey's HSD test was also performed. The result of this analysis, which is shown in Table 5, was that no significant difference was observed between the developed boards (*i.e.* 1, 2, and 3). A significant difference was observed between all of the developed boards and particleboards.

Figure 7 shows SEM microscopic images of the broken bonds after tensile testing perpendicular to the plane of the boards. The effect of the modification on the nature of the failure was clear from the images. In the case of the boards made from untreated particles (Fig. 7b), there was only a failure between the adhesive and surface of the particle. In the case of the boards made from the alkaline-modified particles (Fig. 7a), a cohesive failure of the particle material was observed, which indicated that the modified particle-adhesive bond was stronger.

Table 5. Statistical Significance of the Surface Soundness Differences

Type of Board	1	2	3	4
1	-	n.s.	n.s.	s.
2	n.s.	-	n.s.	s.
3	n.s.	n.s.	-	s.
4	s.	s.	s.	-

Statistical significance determined according to Tukey's HSD test

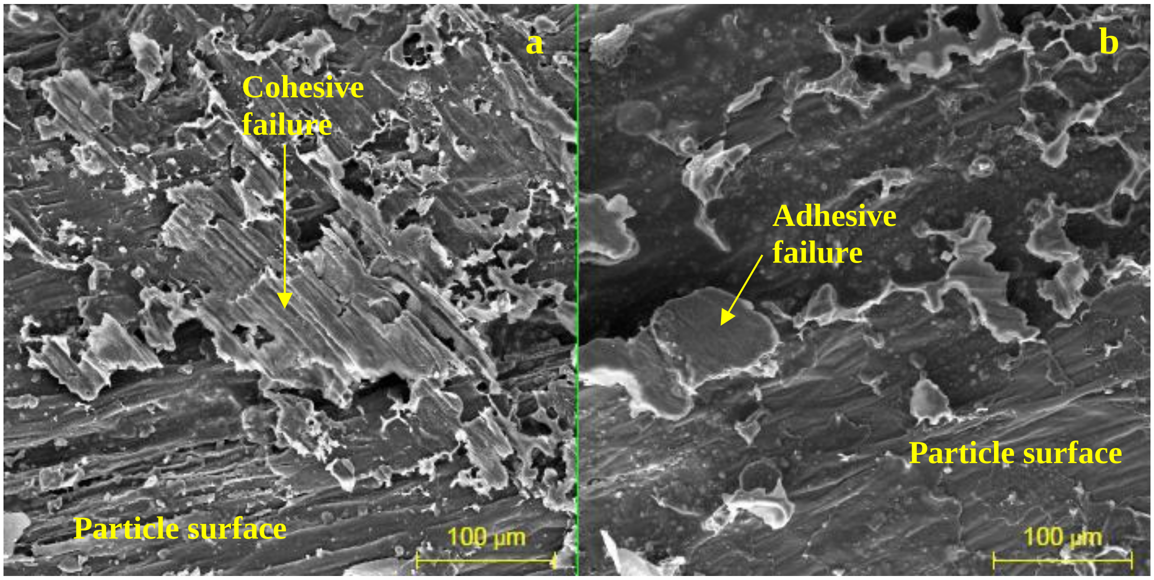

Fig. 7. SEM pictures of the ruptured internal bonding samples: particles treated in NaOH – cohesive failure in the particle (a), and untreated particles – adhesive failure (b)

CONCLUSIONS

1. The results indicated that the modification of the rapeseed particles had a statistically significant effect on the moisture absorption, thickness, and volumetric swelling. The highest swelling values were exhibited by boards with alkaline-modified particles. Conversely, the lowest swelling values were achieved by the boards with unmodified particles.
2. An effect from the modification of the rapeseed particles on the internal bonding was shown to occur. Boards made from the hydrothermally modified particles achieved the highest strength values compared with the commercially produced boards.
3. Compared with the particleboard, the surface soundness was not as high, but the highest mean internal bonding value was achieved with the boards containing unmodified rapeseed particles.

4. The alkaline modification of the particles resulted in a stronger adhesive bond between the particles and adhesive. During an internal bonding test, boards made from these particles exhibited cohesive failures in the particles. Therefore, the modification of the particles increased the mechanical properties of the boards, but the physical properties deteriorated.
5. Modification of rapeseed particles before particleboard production could improve some properties of the boards. However further research needs to be carried out in order to eliminate negative effects of modification that were observed in this study.

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The plasticity of composite material based on winter rapeseed as a function of selected factors

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ABSTRACT

The development of new composite materials using alternative sources of raw materials is of great importance nowadays due to the lack of raw wood material and the economic development of the market. The main objective of this article is to determine selected mechanical properties of new composite materials based on cellulose and lignin. We focused on the mechanical properties measured in the plastic range during the bending of composite materials. We monitored the effect of factors such as the method of modification (raw, boiled in water and soaked in a lye bath), and the effect of the adhesive used to bind components (polyester powder and urea formaldehyde). The monitored characteristics were the bending strength **"MOR"**, plastic potential **"Pp"** and the moduli of plasticity $\mathbf{CH_M}$, $\mathbf{E_E}$, $\mathbf{E_{MV}}$ and $\mathbf{E_P}$. The results constitute an important basis that is inevitably necessary in the production of new types of materials with specific properties for their intended use. The output of this article forms a part of a project whose goal is to create a mathematical model that will enable us to anticipate changes in the monitored characteristics, with regard to the required modifications.

1. Introduction

Composite materials can generally be defined as a combination of two or more materials that differ in size or composition on a macroscale. The components in them retain their identity, although they appear to be in synergy (synergistic effect). Each component can be physically identified, and there is a boundary between it and other components [1]. In the wood industry, composite materials predominantly contain either wood elements or wood fibers. A natural or synthetic adhesive is used to bond these elements [2].

Today, there is an effort to develop new composite materials using alternative sources. The main reason for this trend is population growth, which is closely linked to a scarcity of natural resources [3]. Agricultural waste is an excellent alternative material to replace wood components in composite materials, because it is inexpensive, easy to process and there is a lot of it [4,5]. Natural fibers have many remarkable advantages over synthetic fibers. Today, we are familiar with different kinds of natural fibers [6]: flax, hemp, jute straw, wood, rice bran, wheat, barley, oats, rye, sugar cane, grass, reed, kenaf, ramie, coconut fiber, water hyacinth, silk paper, banana fiber, pineapple fiber, papyrus, and rapeseed have been examined for utilization in composite materials [7]. Rapeseed (*Brassica napus L.*) currently has a strong position in both Czech and European agriculture as a result of its extensive use, with markedly increasing non-food utilization. Rapeseed is primarily used to produce fat. From the global production (about 50 million tons) of seeds, about 19 million tons of fat is extracted, of which 13–14 million tons of oil goes to the food industry. Therefore, the remaining 5–6 million tons are primarily used for biofuels. This non-food utilization of rapeseed is almost exclusively tied to EU27 [8].

In terms of applicability, composite materials have to achieve certain mechanical properties. Flexural characteristics in the plastic range are an important mechanical property. Loading composite materials by bending is a very topical issue. In terms of the use of composite materials in the exterior and interior, these bending characteristics are very important. These characteristics include bending strength, plastic potential and modulus of plasticity. Most research deals with the elastic range of the diagram up to the limit of proportionality, while only a small amount of research deals with deformations in the plastic range, from the limit of proportionality to the yield point where plastic deformation occurs. The existence of plasticity moduli is nothing new. In literature, these moduli can be found under different names [9]. Plasticity moduli can be defined as the relationship between the stress and strain at a certain point of the curve between the limit of proportionality and the bending strength [10]. It is clear from much research that the mechanical properties of composite materials are generally significantly affected by the type of adhesive and its modification [11].

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The mechanical properties of composite materials in terms of the adhesive used are largely influenced by the chemical composition of the adhesive, in interaction with the chemical components of the components used in the composite materials [12].

The aim of this study was to determine the effect of rapeseed modification in interaction with the use of urea formaldehyde and polyester adhesive on the bending characteristics of composite material in the plastic range, and to subsequently compare these characteristics with those of standard composite materials. Standard composite materials such as chipboard and OSB boards were selected to compare the monitored characteristics. In addition, the plastic properties of both commercially produced materials (PB, OSB) and newly developed materials have not yet been investigated.

2. Experimental

2.1. Materials

The main component of the test specimens used in the research were chips from rapeseed stalk (*Brassica napus L.*). A network analysis was used to determine the percentage of individual chip fractions, as shown in Table 1.

The monitored bending characteristics (Fig. 1) were compared using boards produced with different chip modifications. The reference values were found in boards produced from raw chips without further modification (this type of chip was labeled R). The bending characteristics were further observed in boards with hydrothermally modified chips; this modification was performed by boiling the chips in water for 45 min at approx. 100 °C (this type of modified chips were labeled H_2O), and chips modified by soaking in a chemical solution, which was performed by soaking them for 45 min in a 2% NaOH solution under laboratory conditions (this type of modified chips were labeled NaOH).

The abovementioned modifications were used to improve the adhesion of the glue to the chip. After the modification, the chips were thoroughly rinsed with water and dried.

For mixing adhesive DAKOTEX2600, which is a powder glue based on polyester and epoxy resin (Dakota Coatings N. V., Belgium) with our modified particles we used a laboratory adhesive applicator (Imal, Modena, Italy). After that we layered these mix into molds to form a chip sheet. These prepared molds were placed in a laboratory press (Strozatech, Brno, Czech Republic) and pressed at a pressure of 2.3 MPa. Temperature of a pressing plate was 185 °C for 10 min. After 10 min, a temperature of 170 °C was reached in the middle of the boards. The closing speed of the press was 150 s. This procedure is shown in Fig. 2.

All the obtained results were compared with commonly sold material. For comparison, we chose a 14 mm thick three-layer P2 particleboard (PB) and a 14 mm thick type 3 oriented strand board (OSB).

The specimens were conditioned to a standardized equilibrium moisture content (EMC) under conditions of $\phi = 65 \pm 1\%$ and $t = 20 \pm 1$ °C, in climate chamber HCP 108 (Memmert, Germany). 30 samples were used for each set of specimens.

The density profile was also measured for all the tested materials; these density profiles are shown in Fig. 3. The figure shows that the highest density values in PB and OSB boards were measured in the surface layers. However, in the case of the boards pressed by us (H_2O, NaOH and R), there was an opposite trend, i.e. a higher density was measured in the middle layers than in the surface layers.

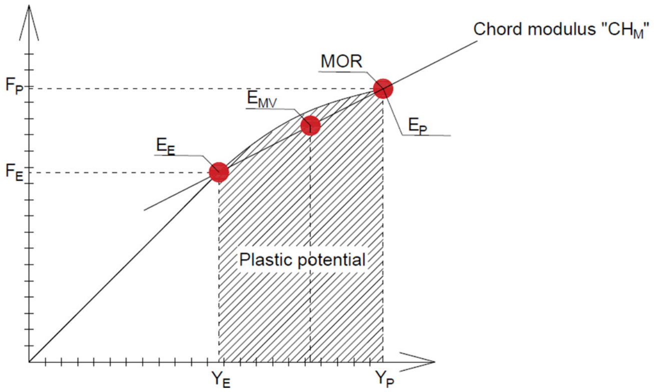

Fig. 1. The monitored bending characteristics in plastic area of force deformation diagram.

3. Methods

3.1. Determination of the monitored characteristics

The support span was adjusted to $L_1 = 20 \times h$ (support span was changed in relation to thickness of specimens). The samples were loaded by three-point bending with single force in a universal testing machine UTS 50 (TIRA, Germany) according to EN 310 [13]. The loading speed was set to 3 mm/min so that the test duration would not exceed 2 min. Loading forces were measured using datalogger ALMEMO 2690-8 (Ahlborn GmbH, Germany).

All the necessary data were obtained from the measured force-deformation diagrams. To identify the characteristics, a program developed by us with the task of accurately identifying and quantifying data that can be obtained from the force-deformation diagram was used.

3.2. Evaluation and calculation

1. The bending strength (MOR) was calculated in accordance with ISO 13061-3 [14] and Eq. (1),

$$MOR_w = \frac{3F_{\max} l_0}{2bh^2} \tag{1}$$

where MOR_W is the modulus of rupture of wood (MPa), Fmax is the maximum (breaking) force (N), l_0 is the distance between the centers of the supports (mm), b is the width of the specimen (mm), and h is the thickness of the specimen (mm). The bending strength values were converted to a moisture content of 12% in accordance with ISO 13061-3 [14].

2. The plastic potential was calculated based on Eqs. (2) and (3) published in the article [9]:

$$\overline{A} = \frac{a}{3}\cdot[Y_P^3 - Y_E^3] + \frac{b}{2}\cdot[Y_P^2 - Y_E^2] + c\cdot[Y_p - Y_E] \tag{2}$$

By dividing Eq. (6) by the volume of the specimen within the stressed area, the calculation of the potential in the viscoplastic range can be obtained according Eq. (7):

$$P_P = \overline{A}/(b\cdot h_0\cdot l) \tag{3}$$

where Pp is the plastic potential (MPa), A is the work of deformation in the viscoplastic range (mJ), b is the width of the specimen (mm), h is

Table 1
Representation in individual fractions of chopped rape straw.

Fraction (mm)	0–0.25	0.25–0.5	0.5–0.8	0.8–1.6	1.6–2	2–3.15	3.15–8
Representation (%)	1.2	2.8	4.8	39.4	20.1	23.1	8.6

Fig. 2. The production of our developed materials: a) mixing adhesive wit modified particles, b) layering particles, c) pressing in laboratory press.

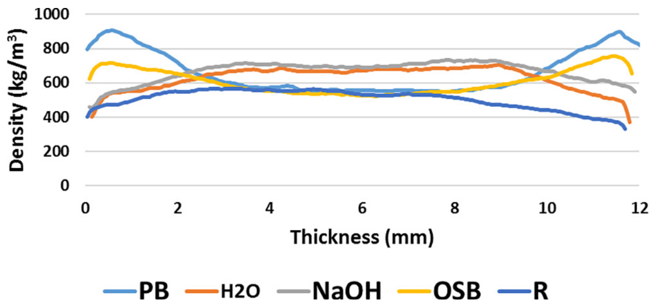

Fig. 3. The density profile measured in monitored sets of test samples.

the thickness of the specimen (mm) and l0 is the support span (mm). It is necessary to emphasize the fact that integrating the given equation neglects elastic deformation over time, which occurs in the limit range above the force at the limit of proportionality "F_E". Y_P is the deflection at the modulus of rapture (mm), Y_E is the deflection at the limit of proportionality (mm).

The tangent modulus is defined as the first derivative of the stress – strain or force-displacement diagram. For the calculation, we used derivations (4–8) published in the article [15]:

3. Tangent modulus at the Limit of proportionality "E_E"

$$E_E = \frac{F_E}{Y_E}\cdot\frac{l_0^3}{48\cdot I} \tag{4}$$

4. Tangent modulus at the middle value of plasticity "E_{MV}"

$$E_{MV} = \frac{F_E}{Y_{MV}}\cdot\frac{l_0^3}{48\cdot I} \tag{5}$$

5. Tangent modulus at the modulus of rapture "E_P"

$$E_P = \frac{F_P}{Y_P}\cdot\frac{l_0^3}{48\cdot I} \tag{6}$$

where I is the moment of inertia:

$$I = \frac{b\cdot h^3}{12} \tag{7}$$

6. The chord modulus of three-point bending was calculated using the following Eq. (5):

$$CH_M = \frac{F_P - F_E}{Y_P - Y_E}\cdot\frac{l_0^3}{4\cdot b\cdot h^3} \tag{8}$$

where F_P is the force at the elastic limit (N), F_E is the force at the proportionality limit (N), Y_P is the deflection at the elastic limit (mm), and Y_E is the proportionality limit (mm).

If the above-mentioned condition is not strictly fulfilled, it can be a source of substantial errors.

The middle value of the tangent modulus is the value for $Y_{MV} = (Y_E + Y_P)/2)$.

3.3. Statistical analysis

For the evaluation of the results, a four-factor variance analysis as to the effect of individual factors on the characteristics was used. Based on the P-level value, it was determined whether a given evaluated factor affected the values of the coefficient of bendability. Diagrams were constructed for the 95% confidence interval, and the results were verified with Duncan's tests.

Fig. 1 shows that the distribution of the density in the cross section varies in the evaluated materials. A significant difference can be primarily seen in the surface layers down to a thickness of 2 mm, and also in the middle layer. The properties of the surface layers may have an effect on the monitored characteristics, as these layers are under the greatest stress during loading.

For this reason, we decided to apply a correlation analysis to the evaluation of the relationship between the monitored characteristics MOR, PP, $_{CH}M$, $_EE$, $_EMV$ and $_EP$, and the average density measured in the entire cross section, as well as the average density measured in the surface layer (1 mm from the surface) of the observed materials (R, H_2O, NaOH, PB and OSB).

4. Results and discussion

4.1. Modulus of rapture "MOR"

The average MOR values measured in the monitored materials are shown in Table 2. The average density of individual materials measured over the entire thickness and the average density measured in the surface layer at 1 mm from the surface are also listed in the table. The coefficient of variation is also listed for all the characteristics.

Based on the level of significance "P" given in Table 3, we can say that the type of evaluated material is a factor that statistically very significantly affects the MOR values.

It is evident from the data in Fig. 2 that the highest statistically significant MOR values were measured in OSB materials. The difference

Table 2
Mean values of MOR for the individual sets of test specimens and the coefficient of variation for evaluated materials.

Material	Glue	MOR (MPa)	Average density in entire thickness (kg/m^3)	Average density at a thickness of 1 mm (kg/m^3)	N
R	PE	5 (14.1)	582 (10.4)	456.3 (8.2)	30
H_2O	PE	10 (18.9)	621 (5.3)	487.3 (4.5)	30
NaOH	PE	8 (16.7)	655 (11.1)	508.7 (6.8)	30
PB	UF	10 (11.6)	669 (3.0)	862.4 (5.2)	30
OSB	MUF	21 (17.6)	619 (3.2)	677.9 (6.1)	30

Values in parentheses are coefficients of variation (CV) in%, PSE = hybrid polyester/epoxide adhesive, MUF = melamine-urea-formaldehyde adhesive.

Table 3
Statistical evaluation of the factors affecting the MOR values.

Bending strength "MOR"					
Monitored factor	Sum of squares	Degree of freedom	Variance	Fisher's F – Test	Significance level P
Intercept	17857.603	1.000	17857.603	1091.153	***
1) Material	4207.762	4.000	1051.941	64.277	***
Error	2373.042	145.000	16.366		
The respective model explains roughly 63.9% of the total sum of squares.					

NS – not significant, *** – significant, Significance was accepted at $P < 0.05$.

between H_2O and PB materials was not confirmed, where we measured 52.3% lower values than in OSB materials.

The lowest MOR values were measured in R materials.

Standard EN 312 [16] defines a bending strength requirement of 11 MPa for P2 boards with a thickness of 6–13 mm, which must be met by the 5th percentile of the set of samples. Rapeseed-based boards do not meet this standard requirement, but neither do PB boards. While rapeseed boards have an opposite density profile – with the highest density in the middle – and the bending strength can be further improved by optimizing the density profile, this is not true for commercially produced PB, whose density profile is already optimized in an M shape, with the highest density in the surface layers of the board. If we compare the measured values with results obtained in other studies concerning composite materials based on rapeseed, we will find that the composite materials studied in this article achieve a lower bending strength [17,18]. However, this can be explained by the opposite density profile as well as the adhesive used. In our research, we used a non-formaldehyde hybrid powder adhesive, whose strength characteristics are not very good, but it is more environmentally friendly and is not harmful to health. If we compare the results of our boards with other lignin and cellulose-based composites such as bamboo [19], we find that bamboo composites have better bending properties. However, this can be explained by the use of different types of materials and different production technologies.

Table 4 shows the results of Duncan's test, which confirm the results from Fig. 4. There was no statistically significant difference between PB and H_2O materials in the measured values ($P = 0.738$). There was a statistically significant difference in MOR values measured in the other monitored materials, with a significance level of $P = 0.000$.

4.2. Plastic potential "Pp"

Table 5 shows the average P_P values, the average density values of individual materials measured over the entire thickness, and the average density values measured in the surface layer at a thickness of 1 mm from the surface of the board on the monitored materials. The coefficient of variation is also listed for all the characteristics.

Based on the results of a one-factor analysis of variance evaluating the effect of the material on P_P values (Table 6), we can state that the

Table 4
Comparison of the effect of the type of material on MOR values using Duncan's test.

Bending strength "MOR"						
	Material	(1) 5.4493	(2) 10.024	(3) 7.8106	(4) 10.373	(5) 20.898
1	R		0.000	0.024	0.000	0.000
2	H_2O	0.000		0.034	0.738	0.000
3	NaOH	0.024	0.034		0.019	0.000
4	PB	0.000	0.738	0.019		0.000
5	OSB	0.000	0.000	0.000	0.000	

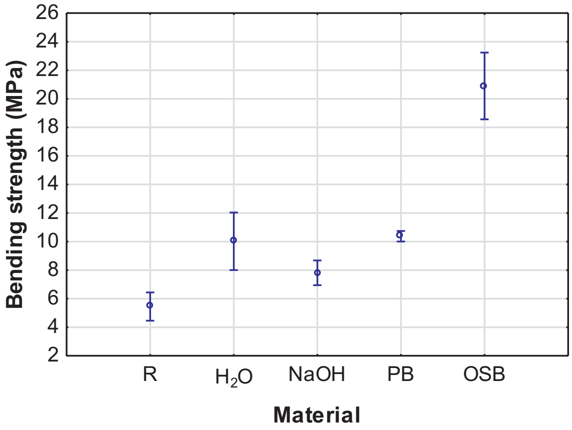

Fig. 4. The effect of the type of material on the MOR.

Table 5
Mean values of Pp for the individual sets of test specimens and the coefficient of variation for evaluated materials.

Material	Glue	Pp (MPa)	Average density in entire thickness (kg/m^3)	Average density at a thickness of 1 mm (kg/m^3)	N
R	PE	1,6 (12.1)	582 (10.4)	456.3 (8.2)	30
H_2O	PE	3,2 (14.1)	621 (5.3)	487.3 (4.5)	30
NaOH	PE	2,9 (12.8)	655 (11.1)	508.7 (6.8)	30
PB	UF	2,0 (12.5)	669 (3.0)	862.4 (5.2)	30
OSB	MUF	5,1 (18.1)	619 (3.2)	677.9 (6.1)	30

Values in parentheses are coefficients of variation (CV) in %, PSE = hybrid polyester/epoxide adhesive, MUF = melamine-urea-formaldehyde adhesive.

Table 6
Statistical evaluation of the factors affecting the values of Pp.

Plastic potential "Pp"					
Monitored factor	Sum of squares	Degree of freedom	Variance	Fisher's F – Test	Significance level P
Intercept	1308.648	1.000	1308.648	404.023	***
1) Material	216.620	4.000	54.155	16.719	***
Error	469.661	145.000	3.239		
The respective model explains roughly 31.6% of the total sum of squares.					

NS – not significant, *** – significant, Significance was accepted at $P < 0.05$.

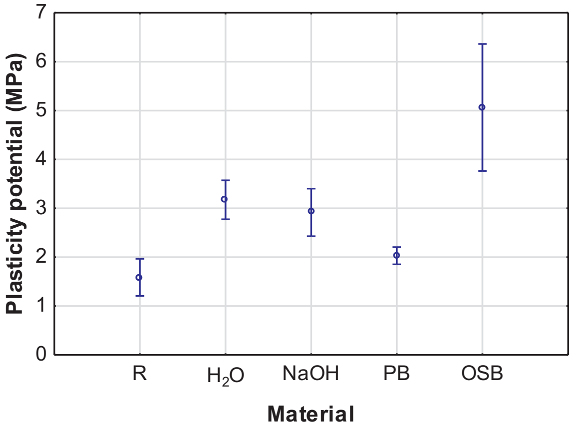

Fig. 5. The effect of the material on the tangent modulus.

Table 7

Comparison of the effects of the material on the P_P values using Duncan's test.

Plastic potential "Pp"						
Material		(1) 1.5874	(2) 3.1737	(3) 2.9152	(4) 2.0291	(5) 5.0630
1	R		0.001	0.006	0.342	0.000
2	H_2O	0.001		0.578	0.019	0.000
3	NaOH	0.006	0.578		0.057	0.000
4	PB	0.342	0.019	0.057		0.000
5	OSB	0.000	0.000	0.000	0.000	

material is a factor that has a statistically significant effect on the values of the monitored characteristic.

It is evident from Fig. 5 that the highest plastic potential values were measured in OSB materials. From the materials developed within our project, H_2O and NaOH materials have the highest plastic potential values. The overall lowest P_P values were measured in R materials, the values of which are significantly different from those measured in PB material. Comparing our plastic potential results with those published in the article [9], in which they also dealt with the plastic potential of wooden lamellas, we found that our tested materials reached much higher values than the beech and ash lamellas mentioned in this article.

The results of Duncan's test (Table 7) indicate a statistically insignificant difference between R and PB (P = 0.342), as well as between H_2O and NaOH (P = 0.578), and NaOH and R (P = 0.057), which is in accordance with the results shown in Fig. 4.

4.3. Chord modulus "CH_M" and tangent moduli in different points: "E_E", "E_{MV}" and "E_P"

Table 8 shows the average values of the monitored characteristics as well as the corresponding coefficient of variation for evaluated materials.

Table 9 shows the results of the one-factor analysis of variance evaluating the effect of the material on the monitored plasticity characteristics CH_M, E_E, E_{MV} and E_P. Based on the level of significance "P", it is obvious that each of the monitored characteristics is statistically very significantly affected by the type of material.

It is evident from the results shown in Fig. 6 that the lowest tangent modulus values were measured at the modulus of rapture "E_P", and the highest values were measured at the limit of proportionality "E_E". There was no statistically significant difference between the chord modulus "CH_M" and tangent modulus at the middle value of plasticity "E_{MV}".

The values of the monitored characteristics (R, H_2O a NaOH) in all the materials developed by us, CH_M, E_E, E_{MV} and $E_{P,}$ were statistically significantly lower than the values measured in commercially available PB and OSB materials. It is evident that their ability to withstand mechanical stress within the plastic section is significantly lower.

Table 8

Mean values of CH_M, E_E, E_{MV}, E_P and individual sets of test specimens, and the coefficient of variation for evaluated materials.

Material	Glue	CH_M (MPa)	E_E (MPa)	E_{MV} (MPa)	E_P (MPa)	Density (kg/ m^3)	N
R	PE	512 (13.1)	743 (19.7)	505 (14.9)	267 (19.1)	582 (10.4)	30
H_2O	PE	911 (19.9)	1334 (19.5)	920 (18.2)	506 (12.9)	621 (5.3)	30
NaOH	PE	673 (17.7)	1071 (14.9)	671 (17.9)	272 (18.9)	655 (11.1)	30
PB	UF	2026 (10.6)	2435 (9.2)	2081 (10.4)	1727 (14.3)	669 (3.0)	30
OSB	MUF	2961 (16.6)	3558 (12.0)	2950 (14.7)	2462 (10.4)	619 (3.2)	30

Values in parentheses are coefficients of variation (CV) in %, PSE = hybrid polyester/epoxide adhesive, MUF = melamine-urea-formaldehyde adhesive

Table 9

Statistical evaluation of the factors affecting the values of CH_M, E_E, E_{MV} and $E_{P.}$

Chord Modulus "CH_M"

Monitored factor	Sum of squares	Degree of freedom	Variance	Fisher's F – Test	Significance level P
Intercept	297948383	1	297948383	743.736	***
1) Material	128190403	4	32047601	79.997	***
Error	58088512	145	400610		

The respective model explains roughly 68.8% of the total sum of squares.

Tangent modulus at the limit of proportionality „E_E"

Monitored factor	**Sum of squares**	**Degree of freedom**	**Variance**	**Fisher's F – Test**	**Significance level P**
Intercept	494144628	1	494144628	933.667	***
1) Material	154002170	4	38500542	72.745	***
Error	76741437	145	529251		

The respective model explains roughly 66.7% of the total sum of squares.

Tangent modulus at the middle value of plasticity "E_{MV}"

Monitored factor	**Sum of squares**	**Degree of freedom**	**Variance**	**Fisher's F – Test**	**Significance level P**
Intercept	298047502	1	298047502	831.470	***
1) Material	125665059	4	31416265	87.643	***
Error	51976499	145	358459		

The respective model explains roughly 70.7% of the total sum of squares.

Tangent modulus at the modulus of rapture "E_P"

Monitored factor	**Sum of squares**	**Degree of freedom**	**Variance**	**Fisher's F – Test**	**Significance level P**
Intercept	158567506	1	158567506	420.947	***
1) Material	111312270	4	27828067	73.875	***
Error	54620331	145	376692		

The respective model explains roughly 67. 1% of the total sum of squares.

NS – not significant, *** – significant, Significance was accepted at $P < 0.05$.

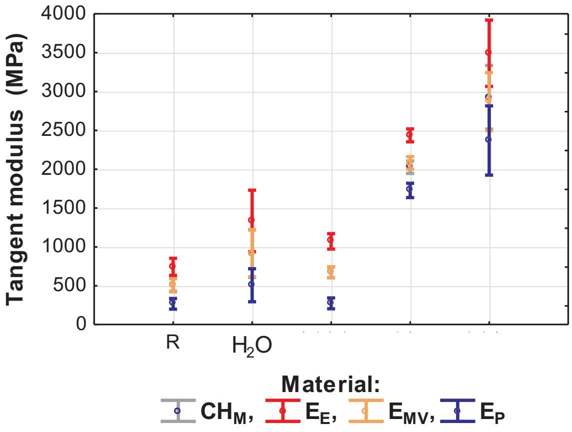

Fig. 6. The effect of the material on the chord modulus and tangent moduli in different point.

Duncan's tests listed in Table 10 show the differences in the monitored characteristics measured in individual materials in detail (CH_M, E_E, E_{MV} and E_P).

The results indicate that differences between chord modulus values "CH_M" were statistically insignificant between R and NaOH materials (P = 0.323), and R and H_2O materials (P = 0.146).

In the case of the tangent modulus at the limit of proportionality

Table 10

Comparison of the effect of the material on **CH_M, E_E, E_{MV}** and **E_P** values using Duncan's test.

Chord Modulus “CH_M”

	Material	(1) 511.82	(2) 910.89	(3) 673.37	(4) 2025.7	(5) 2925.1
1	R		0.020	0.323	0.000	0.000
2	H_2O	0.020		0.146	0.000	0.000
3	NaOH	0.323	0.146		0.000	0.000
4	PB	0.000	0.000	0.000		0.000
5	OSB	0.000	0.000	0.000	0.000	

Tangent modulus at the limit of proportionality “E_E”

	Material	**(1)** **752.60**	**(2)** **1334.3**	**(3)** **1070.7**	**(4)** **2435.0**	**(5)** **3492.5**
1	R		0.002	0.081	0.000	0.000
2	H_2O	0.002		0.161	0.000	0.000
3	NaOH	0.081	0.161		0.000	0.000
4	PB	0.000	0.000	0.000		0.000
5	OSB	0.000	0.000	0.000	0.000	

Tangent modulus at the middle value of plasticity “E_{MV}”

	Material	**(1)** **504.70**	**(2)** **920.05**	**(3)** **671.50**	**(4)** **2081.2**	**(5)** **2870.6**
1	R		0.010	0.281	0.000	0.000
2	H_2O	0.010		0.108	0.000	0.000
3	NaOH	0.281	0.108		0.000	0.000
4	PB	0.000	0.000	0.000		0.000
5	OSB	0.000	0.000	0.000	0.000	

Tangent modulus at the modulus of rapture “E_P”

	Material	**(1)** **266.79**	**(2)** **505.82**	**(3)** **272.25**	**(4)** **1726.7**	**(5)** **2369.2**
1	R		0.156	0.973	0.000	0.000
2	H_2O	0.156		0.141	0.000	0.000
3	NaOH	0.973	0.141		0.000	0.000
4	PB	0.000	0.000	0.000		0.000
5	OSB	0.000	0.000	0.000	0.000	

“E_E”, there was also a confirmed statistically insignificant difference between R and NaOH materials ($P = 0.081$), and R and H_2O materials ($P = 0.161$).

Similar statistically insignificant differences were also found in the tangent modulus at the middle value of plasticity “E_{MV}” between R and NaOH materials ($P = 0.281$), and R and H_2O materials ($P = 0.108$).

In comparison with other characteristics, the tangent modulus at the modulus of rupture “E_P” is characterized by other dependencies. There was no significant difference between R and H_2O materials ($P = 0.156$), R and NaOH materials ($P = 0.973$), or H_2O and NaOH materials ($P = 0.141$).

In the other monitored cases, the differences were statistically very significant with a significance level of $P = 0.000$.

Fig. 7 shows the average values of the monitored characteristics (E_E, E_{MV} and E_P) measured in individual sets of test specimens. It is clear from the data in the graph that the plastic properties of the materials decrease linearly on the interval of values from the limit of proportionality to the ultimate strength. It is also evident that OSB, followed by PB, is most resistant to stress in the plastic range of the stress-strain diagram during bending. The materials developed by us, NaOH, H_2O and R, are the least resistant.

4.4. Correlation dependence of the monitored characteristics and material density

Table 11 shows the results of dependence of the total average density and average density at 1 mm thickness of material on the individual observed characteristics of the all compared materials. In the case of R and H_2O materials, there is a significant difference between these dependencies. NaOH and OSB materials exhibit essentially the same dependence in both cases. PB material exhibits a similar dependence of the difference as the materials R and H_2O only a minor. In general, it has been shown that the average density at 1 mm of material thickness does not affect the characteristics observed to such an extent as the total average density.

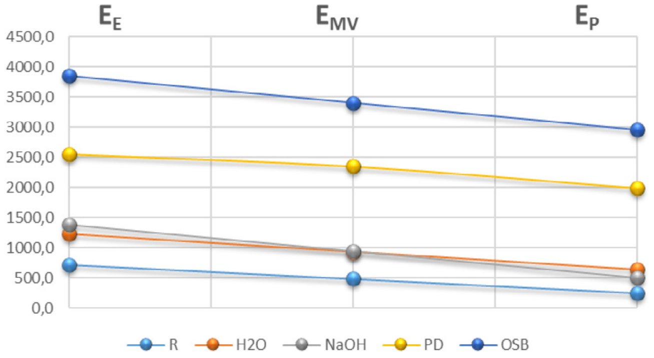

Fig. 7. The tangent modulus of each material.

Table 11

Dependence of the individual factors on the material density using correlation analyses and Coefficient of determination r^2.

Average density in entire thickness

Material	Glue	r^2 for MOR (MPa)	r^2 for P_P (MPa)	r^2 for CH_M (MPa)	r^2 for E_E (MPa)	r^2 for E_{MV} (MPa)	r^2 for E_P (MPa)
R	PSE	*****	****	****	****	****	***
H_2O	PSE	*	*	****	****	****	***
NaOH	PSE	**	**	**	**	**	**
PB	UF	***	*	**	***	***	**
OSB	MUF	**	*	*	*	*	*

Average density at a thickness of 1 mm

Material	**Glue**	**r^2 for MOR (MPa)**	**r^2 for P_P (MPa)**	**r^2 for CH_M (MPa)**	**r^2 for E_E (MPa)**	**r^2 for E_{MV} (MPa)**	**r^2 for E_P (MPa)**
R	PSE	*	*	*	**	**	*
H_2O	PSE	*	*	*	*	*	*
NaOH	PSE	**	**	**	**	**	**
PB	UF	*	*	*	*	*	*
OSB	MUF	*	*	*	*	*	*

PSE = hybrid polyester/epoxide adhesive, MUF = melamine-urea–formaldehyde adhesive.

* $r^2 < 10\%$ – Low tightness.

** $10\% \le r^2 < 25\%$ – Slight tightness.

*** $25\% \le r^2 < 50\%$ – Significant tightness.

**** $50\% \le r^2 < 80\%$ – High tightness.

***** $80\% \le r^2 <$ – Very high tightness.

4.5. Correlation analysis

The results of the correlation between individual characteristics in all the monitored materials are shown in Table 12 and Figs. 8–12. A high degree of dependence between the individual characteristics in all the monitored materials is already clear from the significance level data (70%–100%). There are obvious differences in the degree of dependence caused by the type of material.

It is evident from Figs. 8–12 that the degree of dependence causes an increase in characteristics in most cases, but there are also interactions that cause a decrease in another characteristic when one of the

Table 12

Spearman's correlation for each monitored material.

R

Variables	MOR (MPa)	P_P (MPa)	CH_M (MPa)	E_E (MPa)	E_{MV} (MPa)	E_P (MPa)
MOR (MPa)	1.000	0.911	0.939	0.958	0.941	0.754
P_P (MPa)	0.911	1.000	0.813	0.898	0.830	0.583
CH_M (MPa)	0.939	0.813	1.000	0.941	0.977	0.879
E_E (MPa)	0.958	0.898	0.941	1.000	0.961	0.756
E_{MV} (MPa)	0.941	0.830	0.977	0.961	1.000	0.876
E_P (MPa)	0.754	0.583	0.879	0.756	0.876	1.000

H_2O

Variables	**MOR (MPa)**	**P_P (MPa)**	**CH_M (MPa)**	**E_E (MPa)**	**E_{MV} (MPa)**	**E_P (MPa)**
MOR (MPa)	1.000	0.761	0.596	0.643	0.610	0.479
P_P (MPa)	0.761	1.000	0.310	0.466	0.317	0.010
CH_M (MPa)	0.596	0.310	1.000	0.955	0.994	0.832
E_E (MPa)	0.643	0.466	0.955	1.000	0.952	0.691
E_{MV} (MPa)	0.610	0.317	0.994	0.952	1.000	0.846
E_P (MPa)	0.479	0.010	0.832	0.691	0.846	1.000

NaOH

Variables	**MOR (MPa)**	**P_P (MPa)**	**CH_M (MPa)**	**E_E (MPa)**	**E_{MV} (MPa)**	**E_P (MPa)**
MOR (MPa)	1.000	0.809	0.832	0.931	0.834	0.370
P_P (MPa)	0.809	1.000	0.467	0.726	0.460	−0.135
CH_M (MPa)	0.832	0.467	1.000	0.889	0.999	0.723
E_E (MPa)	0.931	0.726	0.889	1.000	0.884	0.380
E_{MV} (MPa)	0.834	0.460	0.999	0.884	1.000	0.732
E_P (MPa)	0.370	−0.135	0.723	0.380	0.732	1.000

PB

Variables	**MOR (MPa)**	**P_P (MPa)**	**CH_M (MPa)**	**E_E (MPa)**	**E_{MV} (MPa)**	**E_P (MPa)**
MOR (MPa)	1.000	0.480	0.342	0.498	0.481	0.378
P_P (MPa)	0.480	1.000	−0.090	0.328	0.054	−0.210
CH_M (MPa)	0.342	−0.090	1.000	0.818	0.929	0.947
E_E (MPa)	0.498	0.328	0.818	1.000	0.897	0.758
E_{MV} (MPa)	0.481	0.054	0.929	0.897	1.000	0.949
E_P (MPa)	0.378	−0.210	0.947	0.758	0.949	1.000

OSB

Variables	**MOR (MPa)**	**P_P (MPa)**	**CH_M (MPa)**	**E_E (MPa)**	**E_{MV} (MPa)**	**E_P (MPa)**
MOR (MPa)	1.000	0.316	0.509	0.798	0.465	0.272
P_P (MPa)	0.316	1.000	−0.405	−0.018	−0.307	−0.592
CH_M (MPa)	0.509	−0.405	1.000	0.858	0.897	0.935
E_E (MPa)	0.798	−0.018	0.858	1.000	0.789	0.675
E_{MV} (MPa)	0.465	−0.307	0.897	0.789	1.000	0.866
E_P (MPa)	0.272	−0.592	0.935	0.675	0.866	1.000

characteristics increases.

5. Conclusions

1. The article highlights the plastic properties of material based on rapeseed residues, while using innovative knowledge to identify material characteristics with the application of new mathematical models.
2. We have found that in terms of the quality of these materials, it is important to ensure the proper density profile of the boards during their production. This has a positive effect on all the monitored mechanical characteristics. The degree of dependence between the monitored characteristics can be increased to more than 60% with a suitably adjusted density profile. It is clear that after these technological processes have been resolved, rapeseed can fully replace wood in the production of composite materials.
3. This article described the entire plastic course of the force-deformation diagram. The chord modulus, tangent modulus at the limit of proportionality, tangent modulus at the middle value of plasticity, and tangent modulus at the middle value of plasticity were used for this description. The results were compared with these characteristics measured in wood. However, research on biocomposites has not yet been conducted in this area, and further research of the plastic range of biocomposites is therefore desirable.
4. The plastic range of the force-deformation diagram of biocomposites is an important area of material engineering that has yet to be examined. The results of these analyses will be of importance in nonstandard applications of these materials. This study partially illustrated the behavior of composite material based on a renewable source in the plastic range of the force-deformation diagram, and thanks to these results we can partially predict the behavior of these materials under stress.

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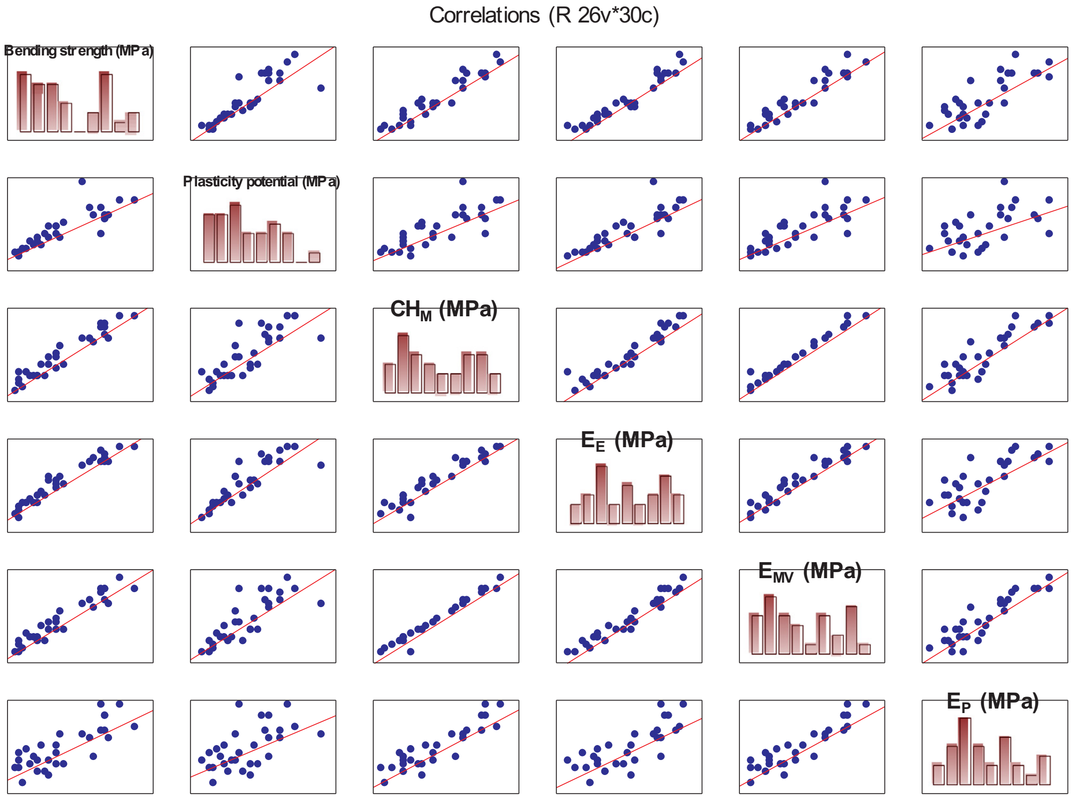

Fig. 8. Correlation matrix of plasticity characteristics of R material.

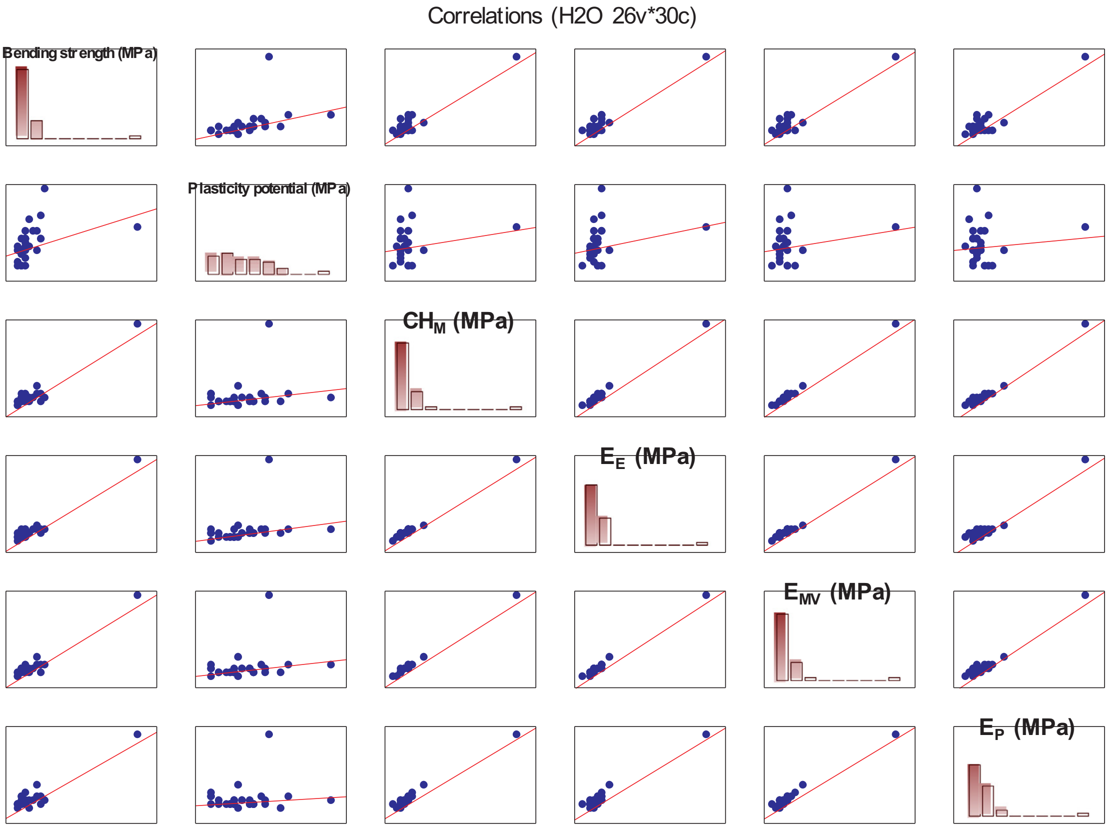

Fig. 9. Correlation matrix of plasticity characteristics of H_2O material.

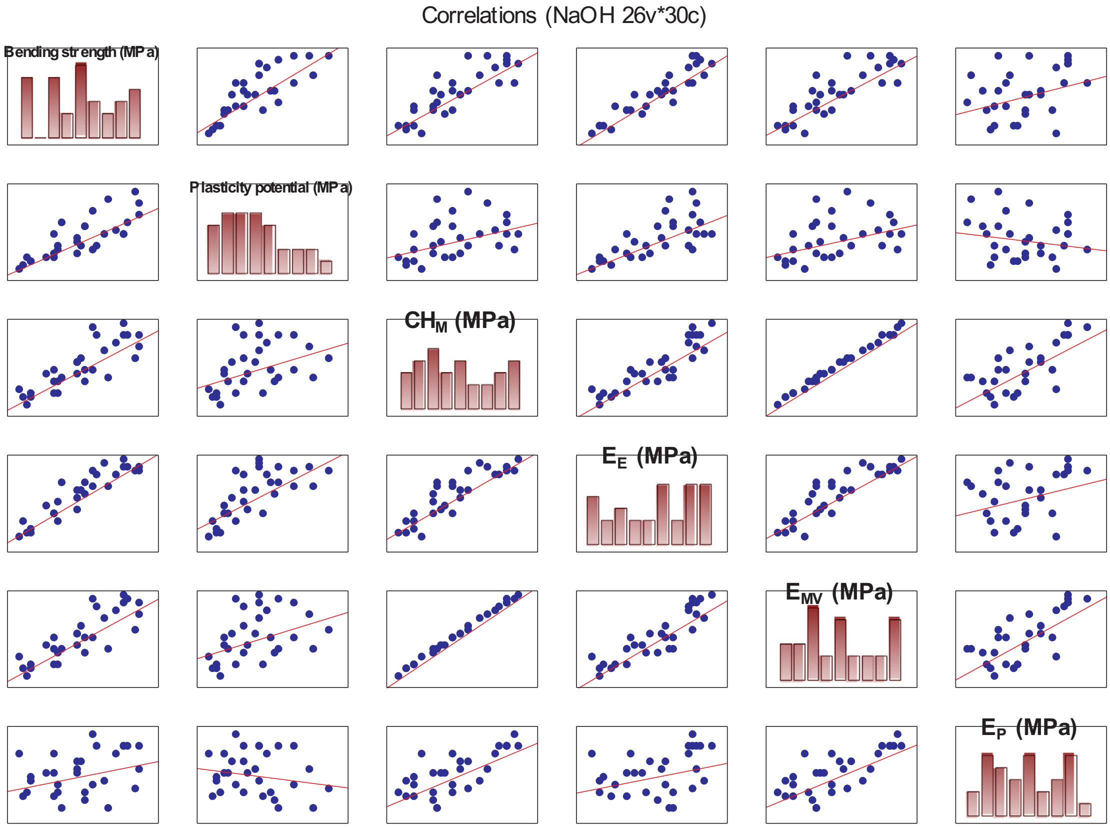

Fig. 10. Correlation matrix of plasticity characteristics of NaOH material.

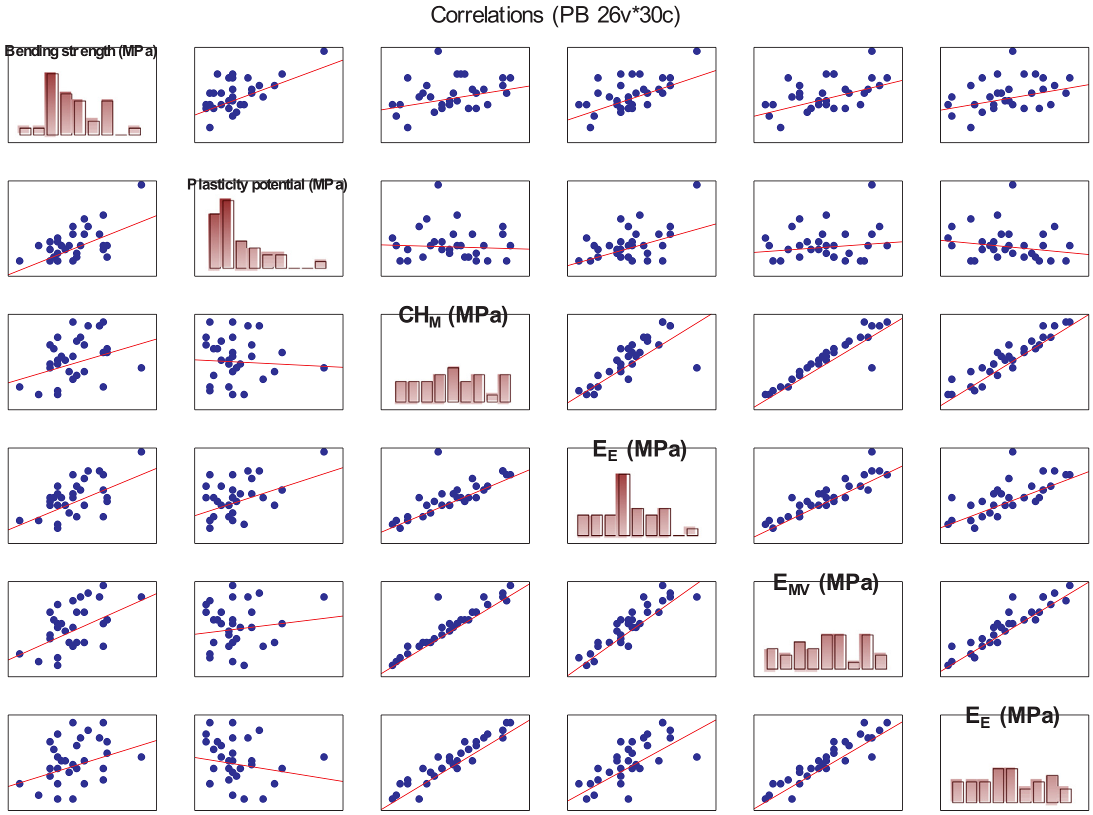

Fig. 11. Correlation matrix of plasticity characteristics of PB material.

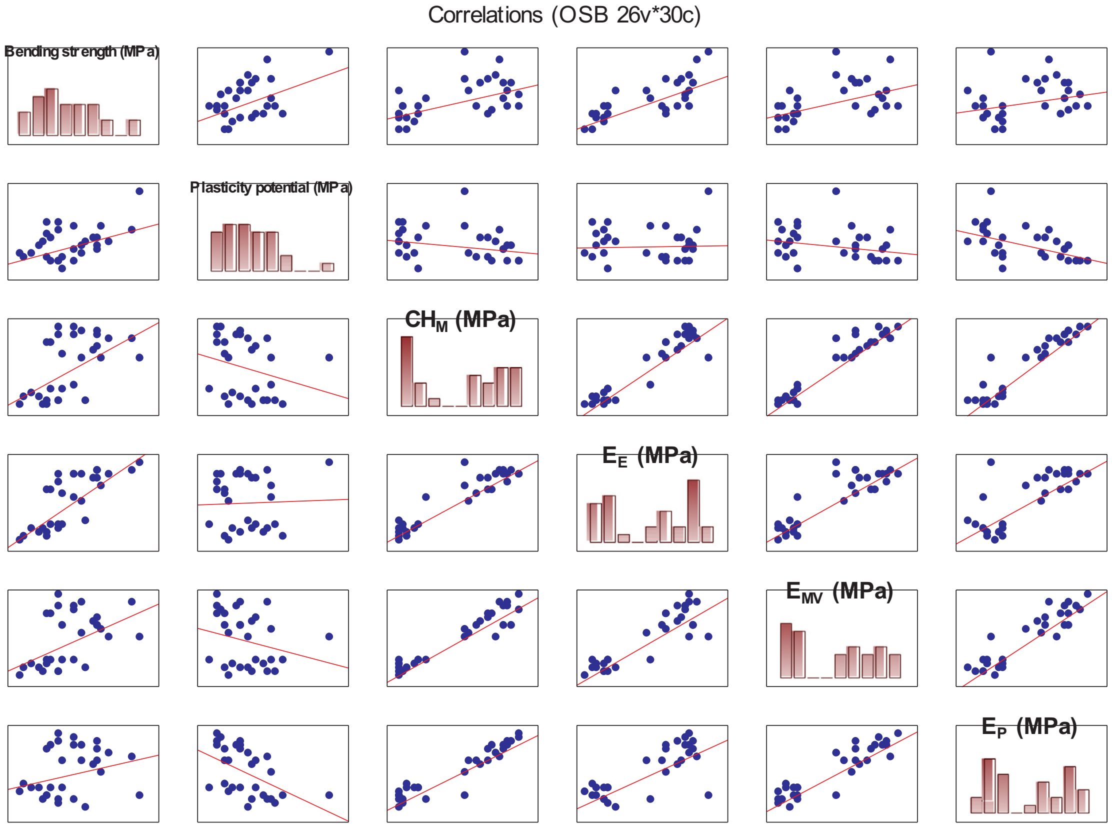

Fig. 12. Correlation matrix of plasticity characteristics of OSB material.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compstruct.2018.04.019.

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