Determination of bonding in wood-plastic composites;
Correlation of physical bonding and shear strength in wood plastic interface
Dissertation

For the purpose of obtaining a doctoral degree (Dr. rer. nat.) at the faculty of
Mathematics, informatics and natural sciences
Department of Biology
Institute for Wood Science
Universität Hamburg

Submitted by

Pouria Rezaee Niaraki

Born in Teheran, Iran

Hamburg 2020

1. Examiner: Univ. Prof. Dr. Andreas Krause
Universität Hamburg, Germany

2.Examiner: Univ. Prof. Dr. Holger Militz

Date of Disputation: 01.12.2020

Dedicated to my dear mother,

Mehri Biashad

Acknowledgement

Hereby, I would like to thank my dear Prof. Dr. Andreas Krause. You guided me over the whole period of my PhD in a way wherein I could not only find the true path of doing an academic research study but also discover a new character of me as a person who is ready to devote his entire energy for finding the truth in any aspect of life!

I would sincerely thank Prof. Dr. Holger Militz for accepting the responsibility as the second examiner of my thesis and for the time he spent on the whole process of my doctoral defense.

I appreciate the great support of Dr. Johannes Welling and Prof. Dr. Jörg B. Ressel. May you were not in direct contact of my project but your remarkable roles, as the managing directors of Thünen institute of wood research and department of wood physic at Hamburg university, have always inspired me to work on my thesis with a sense of responsibility.

Special thanks to Sylvia Diestel and Bettina Steffen for doing the statistical analysis of current thesis and answering any questions I had in terms of data analysis.

I would also like to thank Dr. Martin Nopens who helped me not just in terms of my thesis review but also as a nice man that gave me a positive feeling over the whole period of my PhD.

Special thanks to Johannes Beruda. You always helped me in laboratory works and stood by me over the most difficult tasks of my experimental study.

I warmly appreciate Tanja Potsch and Sergej Kashuro who helped me sincerely in terms of anatomic analysis of samples by scanning electron microscopy (SEM) and

electron light microscopy (VHX-6000). I owe you both the best images of my present thesis!

I would like to sincerely thank Prof. Dr. Bodo Saake, Martina Heitmann and Dr. Ralph Lehnen from the chemistry department who have warmly guided me for doing the right procedure of chemical treatment, characterization of wood surfaces by FTIR and exchanging the precious knowledge in terms of polymer science.

Thanks to the unwavering support of Bernd Lütkemeier from the wood biology working group of Prof. Dr. Holger Militz, I could calculate the surface roughness of wood samples by laser-Scanning-Microscope (LSM-Keyence-VK-X100) in the University of Göttingen, Germany.

Thanks to Dr. Henning Storz and Matthias Steffen from Thünen-Institute of Agrartechnologie who did the rheological analysis of used plastics by Rheometer.

I am really thankful of German Academic Exchange Service (DAAD) for affording the research grants of current study.

I would like to also thank my dear friends Dr. Ali Akrami, Katja Butter, Friederike Mennicke and all the colleagues and students of Thünen/UHH -institute of wood research who were kindly helped me through the whole period of my PhD and make me feel as a member of a community that always care about each other.

Finally, I want to thank my family who always support me through the most difficult times of my life. Without your love, Pouria had been lost long time ago!

Zusammenfassung

Holz-Kunststoff-Komposite sind eine neue Generation von Holz-Produkten, die im Vergleich zu Massivholz verschiedene Vorteile bieten. Sie sind kostengünstig, in vielen Varianten verfügbar, dimensionsstabil und wiederverwertbar. Allerdings limitiert die Inkompatibilität der physikalischen und chemischen Eigenschaften von Holz und Kunststoff die Verwendung. Eine Herstellung von Hochfesten Kompositen stellt immer noch eine Herausforderung dar. Insbesondere die Verbindung der Grenzflächen hat einen erheblichen Einfluss auf die Endfestigkeit der Komposite.

Das Phänomen der Adhäsion besteht aus chemischer, physikalischer und mechanischer Verbindung die jeweils einzeln oder zusammen mit der Grenzoberfläche interagieren. Ziel der vorliegenden Arbeit ist die Untersuchung der Grenzoberfläche zwischen Holz und Kunststoff, um herauszufinden welchen Anteil an der Interaktion die chemische Zusammensetzung und die mechanische Verbindung haben. Es soll geklärt werden ob überhaupt eine signifikante Korrelation zwischen der Benetzung und der Scherfestigkeit von Holz-Kunststoff-Kompositen existiert.

Es wurde Fichtefurnier, geschliffen und ungeschliffen, mit „Maleic Anhydride Grafted Polyethylene“ (MAPE) und „Butyric Anhydride“ (BA) behandelt. Die Oberflächenbenetzung der Furniere wurde durch die Messung des Kontaktwinkels und der Oberflächenenergie (Acid-Base-Methode) durchgeführt. Die Resultate zeigen, dass das Schleifen und die MAPE-Behandlung signifikant den Kontaktwinkel erhöhen und die Oberflächenenergie senken. Die mit BA behandelten Proben zeigten keine signifikante Änderung der Oberflächenenergie der Holzoberfläche.

Um die Benetzbarkeit zwischen Holz und Kunststoff bei hohen Temperaturen zu untersuchen wurden drei verschiedene Polymere: high density of Polyethylene (HDPE), eine Mischung aus 3% MAPE mit HDPE (MHDPE) und „Poly Lactic Acid“ (PLA), geschmolzen und als Tropfen auf die Furnieroberfläche aufgebracht. Die Untersuchungen zeigen, dass MAPE die Benetzbarkeit von Holz verbessert, da die HDPE Tropfen einen niedrigeren Kontaktwinkel im Vergleich zu den anderen Polymeren

aufweisen. Die Oberflächenbehandlung durch Schleifen hat ebenfalls den Kontaktwinkel aller Polymere verringert (in der Reihenfolge PLA, MDHDPE und HDPE). Die Grenzflächenscherfestigkeit zwischen Holz und Kunststoff wurde mit einem „Automated Bonding Evaluation System“ (ABES) untersucht. Hier zeigten die ungeschliffenen und geschliffenen PLA-Proben mit 7.14 N/mm2 und 8.19 N/mm2 die höchsten Werte. Die Vorbehandlung durch Schleifen hat die Klebeverbindung durch die mechanische Verzahnung zwischen Holz und Kunststoffoberfläche signifikant verbessert.

Aus den Untersuchungen kann geschlossen werden, dass die MAPE-Behandlung und das Schleifen der Proben die Oberflächenenergie reduziert und zu einer Steigerung der Grenzflächenscherfestigkeit zwischen Holz und Kunststoff führt. Außerdem zeigen die Untersuchungen in dieser Arbeit, dass insbesondere bei höheren Temperaturen die Benetzbarkeit mehr von den Rheologischen Eigenschaften des Kunststoffs abhängt und die Oberflächenenergie eine untergeordnete Rolle bei der Bindung in Holz-Kunststoff-Kompositen darstellt.

Abstract

Wood plastic composites are known as a new generation of wood-based products, that in comparison to using solid wood alone, have many remarkable advantages. These include a low cost, easy accessibility of the raw materials (wood dust and recyclable polymers) and high dimensional stability, owing to their low moisture permeability. However, due to the inherent incompatibility between the physio-chemical properties of wood and plastics, making a high strength composite had always been considered a major challenge. It has been already confirmed that interfacial bonding at the interface will significantly influence the final strength of the composite. In fact, the adhesion phenomenon is the sum of three mechanisms, known as chemical, physical and mechanical bonding, each acting alone or along with others at the interface region.

This thesis aims to investigate the interaction of chemical composition and mechanical interlocking on the interfacial bonding at the wood – polymer interface simultaneously, and to find out whether there is any significant correlation between the wetting property and shear strength of a wood plastic composite. To this end, spruce veneers were divided into two groups of sanded and un-sanded; each groups treated with either maleic anhydride, grafted with polyethylene (MAPE) or butyric anhydride (BA). Surface wetting of all veneers was first characterised by measuring the contact angle (CA) and application of the Acid-Base method in order to calculate the surface free energy (SFE). The result showed that both sanding and MAPE treatments significantly increased the CA and decreased the SFE subsequently. However, treated samples with Butyric anhydride showed no meaningful changes in the SFE of wood surfaces. To simulate surface wetting between wood and plastic interface at high temperature, three sorts of plastics (high density of polyethylene (HDPE), mixture of 3% MAPE with HDPE (coded as MHDPE) and Poly lactic acid (PLA)) were additionally melted and applied to the wood surfaces. Based on this experiment, MAPE treatment was shown to have improved wetting properties of the wood-polymer interface once again, as the CA of the HDPE droplet was significantly lowered on veneers treated with this chemical. Sanding moderately lowered the contact angle of all plastic types on the surface in PLA, MHDPE

and HDPE respectively. This may imply the positive effect this treatment has on interfacial bonding when the chemical components of wood and plastic are close to each other. Finally, the interfacial shear strength (ISS) between wood and plastic was measured by automated bonding evaluation system (ABES), once at a constant temperature (200°C) and once at a constant viscosity (732 Pa) for all applied plastics. The results showed a slight improvement when the samples were tested at a constant temperature using PE adhesives, however this difference was not significantly evaluated for other plastics. PLA showed the highest values of ISS for both un-sanded and sanded veneers (7.14 N/mm^2; 8.19 N/mm^2). Sanding significantly contributed to the glue bonding by creating a fresh surface and forming a mechanical interlocking between the wood and polymer interphases. Overall, it was concluded that MAPE treatment and/or sanding resulted in a lower SFE and may thereby gave rise to a higher ISS being obtained at the wood polymer interface. However, the outcomes of this study support the theory that, at higher temperatures, wetting is mainly influenced by the rheological properties of plastics rather than interfacial tensions at the wood-polymer interface, and SFE does not play a determining role for interfacial bonding in wood plastic composites.

Content

Acknowledgement……3
Zusammenfassung……5
Abstract……7
Chapter 1 Introduction……11
1.1 Wood Plastic Composites……11
1.2 Wood Fibers……13
1.3 Thermoplastics……16
1.4 Wood-Plastic Interface……18
1.5 Chemical Treatment……20
1.6 Sanding……23
1.7 Wetting relations……24
1.8 Research problems and interfacial bonding approach……32
1.9 Research questions……34
1.10 The methodology of thesis……35
Chapter 2 Material and Methods……38
2.1 Wood preparation……38
2.1.1 Sanding……38
2.1.2 Chemical treatments……39
2.3 FTIR characterization……41
2.4 Surface roughness measurement……41
2.5 Calculation of surface free energy (SFE)……42
2.6 Plastic preparation……43
2.7 Rheometer……43
2.8 Contact angle measurement using hot dosing unit……45
2.9 Evaluation of shear strength by ABES……47
2.10 Microscopic analysis……48
2.11 Statistical analyses……49
Chapter 3 Result and Discussions……54
3.1 Effect of chemical treatments on the surface chemistry of wood veneers……54

3.1.1 Acetylation……………………………………………………………………………………54
3.1.2 Effect of acetylation on surface wetting using hot dosing units……………………….56
3.1.3 The effect of butyric anhydride and MAPE treatments on the surface chemistry of wood veneers…………………………………………………………………………………………59
3.2 Effect of sanding on the surface roughness of non-treated and chemical treated veneers……………………………………………………………………………………………………61
3.3 Analysis of wood anatomy by scanning electron microscopy (SEM)…………………...64
3.4 The interaction of sanding and chemical treatments on surface wetting……………66
3.4.1 Assessment of CA calculations by least square approach………………………………69
3.4.2 Dynamic contact angle measurements by hot melting plastic………………………..74
3.4.3 Determination of plastic penetration to the wood bulk by hot melting plastic droplet……………………………………………………………………………………………………77
3.5 Effect of constant viscosity and temperature on IFSS……………………………………82
3.5.1 Interactions of polymer types and wood treatments on IFSS……………………………85
3.5.2 Identification of plastic dispersion pattern on the interfacial bonding area……..87
3.6 Determining the correlation between physical bonding and shear strength at wood–polymer interface……………………………………………………………………………89
Chapter 4 General Conclusions………………………………………………………………………91
List of tables……………………………………………………………………………………………94
List of figures…………………………………………………………………………………………95
List of diagrams………………………………………………………………………………………98
List of abbreviations…………………………………………………………………………………...99
Declaration……………………………………………………………………………………………101
Research bibliography………………………………………………………………………………102

Chapter 1

Introduction

1.1 Wood plastic composites

The growth of the human population across the world has raised a lot of environmental concerns over the past century. In terms of natural resources, overexploitation of forests by wood-based industries has caused the depletion of natural resources and created a severe challenge with high demands being placed on dwindling supplies (Lata et al. 2016, Dong et al. 2017). As an alternative, manufacturers have tried to increase the application of natural based composites (Pickering et al. 2016).

The term 'composite' for wood, has for years been applied to any types of small wood particles, glued together from the beginning of production (Maloney 1996). Over the previous decades, wood-based composites have mainly been manufactured using formaldehyde-based adhesives, which are known to be a hazardous chemical, due to the emission of toxic free formaldehydes (Fang et al. 2013, Song et al. 2016). Furthermore, the poor water resistance of these adhesives made them vulnerable to the absorption of moisture from the air and the releasing of toxic gases, which limited their application for indoor products (Liu et al. 2018).

There are basically two main classes of adhesives that can be applied for processing the wood-based composites: thermoset and thermoplastic resins. Formaldehyde based adhesives are classified in the category of thermoset resins, which are liquid at room temperature, turning solid at higher temperatures and once cured, cannot be melted again (Kim 2008; Ashori 2008). Unlike thermoset resins, thermoplastics get softer at higher temperatures and shows better rheological properties than thermoset adhesives when heated (Wolcott and Englund 1999, Braun et al. 2007).

The abundance of the different types of plastics available – whether they were already consumed and recycled for new application or to be used as the virgin polymer for the first time – made them a promising raw material for compounding with wood/lignocellulosic materials (Fini et al. 2015, Najafi 2013). Wood plastic composites (WPC) are considered a fairly new generation of wood-based composites, wherein the combination of wood/lignocellulosic materials with thermoplastics has already paved the way for the application of these products in both indoor and outdoor (Figure1) (Yang et al. 2007, Yao et al. 2008). The birth of WPC has been reported to have occurred in Italy in 1970 (Pritchard 2004, Ashori 2008). However, it seems that it was not produced on an industrial scale until the mid-90s in the US, where a company named Woodstock started producing automotive interior substrates by applying the Italian extrusion technique (Clemons 2002).

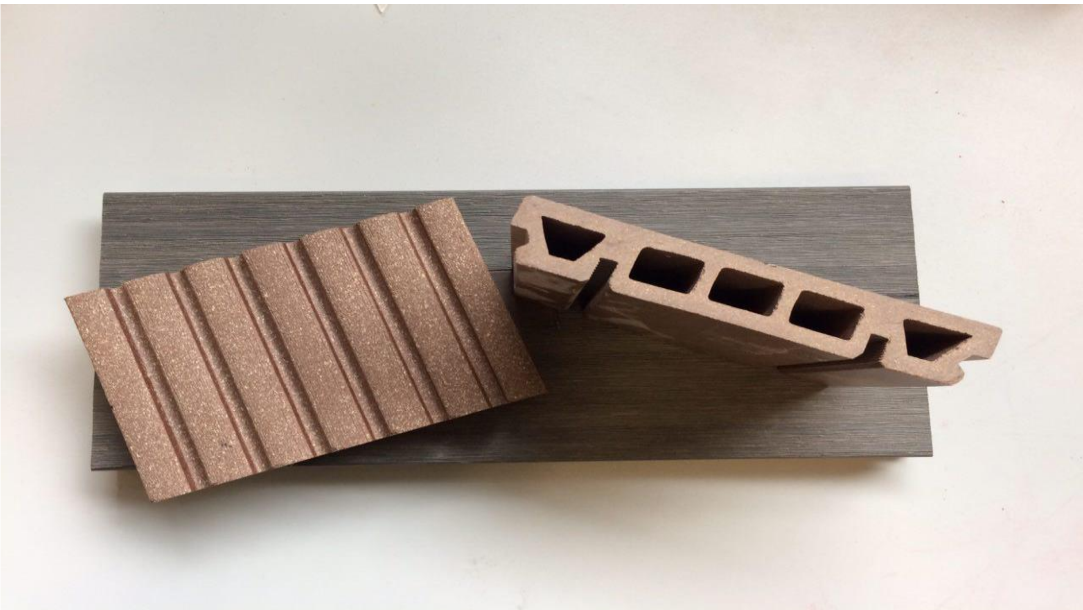


Fig1. Wood Plastic Composite (WPC) decking for outdoor flooring

From the outset, WPC faced two different industries that didn't have a lot of knowledge about each other. The previous reports show that plastic processors had a tendancy to react negatively towards using wood particles in the plastic industry in the past, due to some of the physical properties of woods being inherently inconsistent with plastics, such as its low bulk density, low thermal stability and its affinity to absorb moisture (Clemons 2002, Caulfield et al. 2005). Thanks to scholars and the increased expertise in both fields, it has since been proven, that the combination of wood and plastic holds a lot of advantages over using them purely as solid wood or pure thermoplastics (Yang et al. 2015).

The mixture of wood and plastic creates a composite that conveys the good properties of both phases together, including high strength, low density, dimensional stability, stiffness and water resistance (Cavdar et al. 2018, Kaboorani 2017, Hutyrova et al. 2016).

However, as previously mentioned, the lack of knowledge about any physical, chemical and mechanical properties of wood and plastics, can present the manufactures with some serious obstacles for processing WPC, that may keep them from producing a composite with those desirable properties. Thus, below we first give a brief explanation regarding the properties of each of the phases in WPC.

1.2. Wood fibers:

Wood based fillers contribute to the plastic matrix by reducing the cost of the manufacturing process as well as improving stiffness and resistance to both abrasion and shrinkage (Sewda et al. 2013, Schwarzkopf and Burnard 2016). The wood component in a WPC can be comprised of any types of natural fibres obtained from agricultural wastes; like wheat straw, cane bagasse or residues of wood industries like waste timber/woods or even other natural fibers like jute, knaf, jutes and rice husks (Patil et al. 2000). They contain some remarkable advantages including ecological features, biodegradability, low costs, nonabrasive nature, safe fiber handling, high possible filling levels, low energy consumption, high specific properties, low density and their renewable components which are environmentally friendly (Ashori 2008).

In terms of wood-based composites, one of the key roles of wood fibers is to bear the loaded stress on the composite that is transferred through the plastic matrix to the fibers at the interface region (Neagu et al. 2006; Huda et al. 2006). Previous studies have already proven that the final strength of a composite is greatly dependent on how well this stress transfer can be accomplished (Migneault et al. 2009, Ghanbari et al. 2014). Thus, there should be good interfacial bonding between the wood fibers and the plastic matrix to make that happen.

There are two common features among all kinds of wood fibers that usually hinder them from forming such a strong bond with a plastic phase; they usually have a lower allowable processing temperature and unlike hydrophobic plastic, have a hydrophilic structure which tends to absorb moisture, this factor may damage the final mechanical strength of the composite consequently (Chaharmahali et al. 2010, Faruk et al 2014). Furthermore, wood fiber is an anisotropic material, consisting of a cellular structure formed in a hierarchical levels (Tsuchikawa and Tsutsumi 2002; Trtik et al. 2007). It has three main axes, known as longitudinal, tangential and radial (figure 2). Depending on how the wood elements are oriented and/or which wood components have more concentration on each dimension, the mechanical properties of the fibers can differ in every mentioned direction (Green et al. 1999; Reiterer et al. 2002).

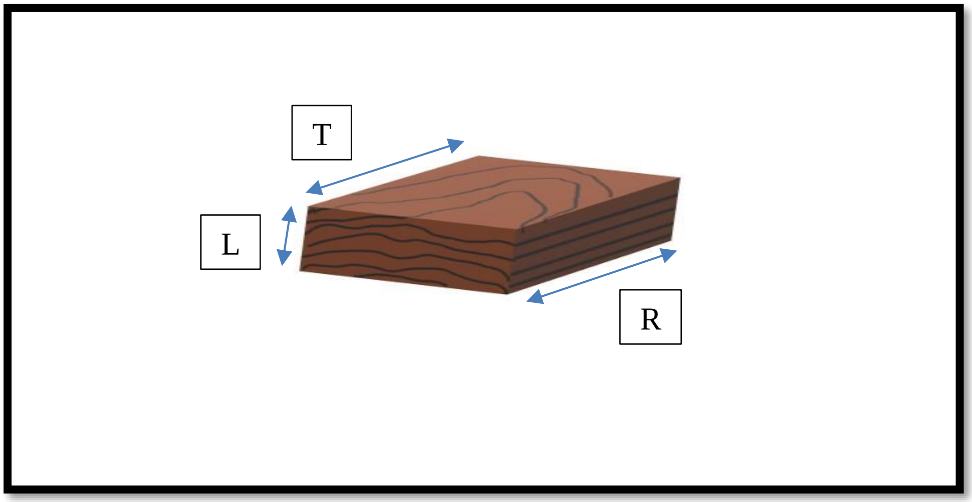


Fig2. Three principal directions of wood; (L) Longitudinal (T) Tangential (R) radial

Depending on the application of the final product, timber extracted from forests is mostly cut perpendicular to the wood grain, either in a regular direction or tangent to the growth rings, that are known as radial and tangential axes respectively (Slater and Ennos 2015). Previous studies have proven, that in general, the radial properties of wood species are significantly higher than the tangential directions (Reiterer et al. 2002, Beery and McLain 2007). This has been attributed to the presence of additional reinforcement wood cells in this direction known as ray parenchyma. The cellular structure of wood is mainly comprised of wood tracheids that are formed over the growth seasons of trees. They are principally divided into two categories of early wood and late wood. The early wood consists of thin cell walls with large lumens, whereas the late wood possesses thicker cell walls, usually with quite small lumens (Luostarinen et al. 2017) (figure3).

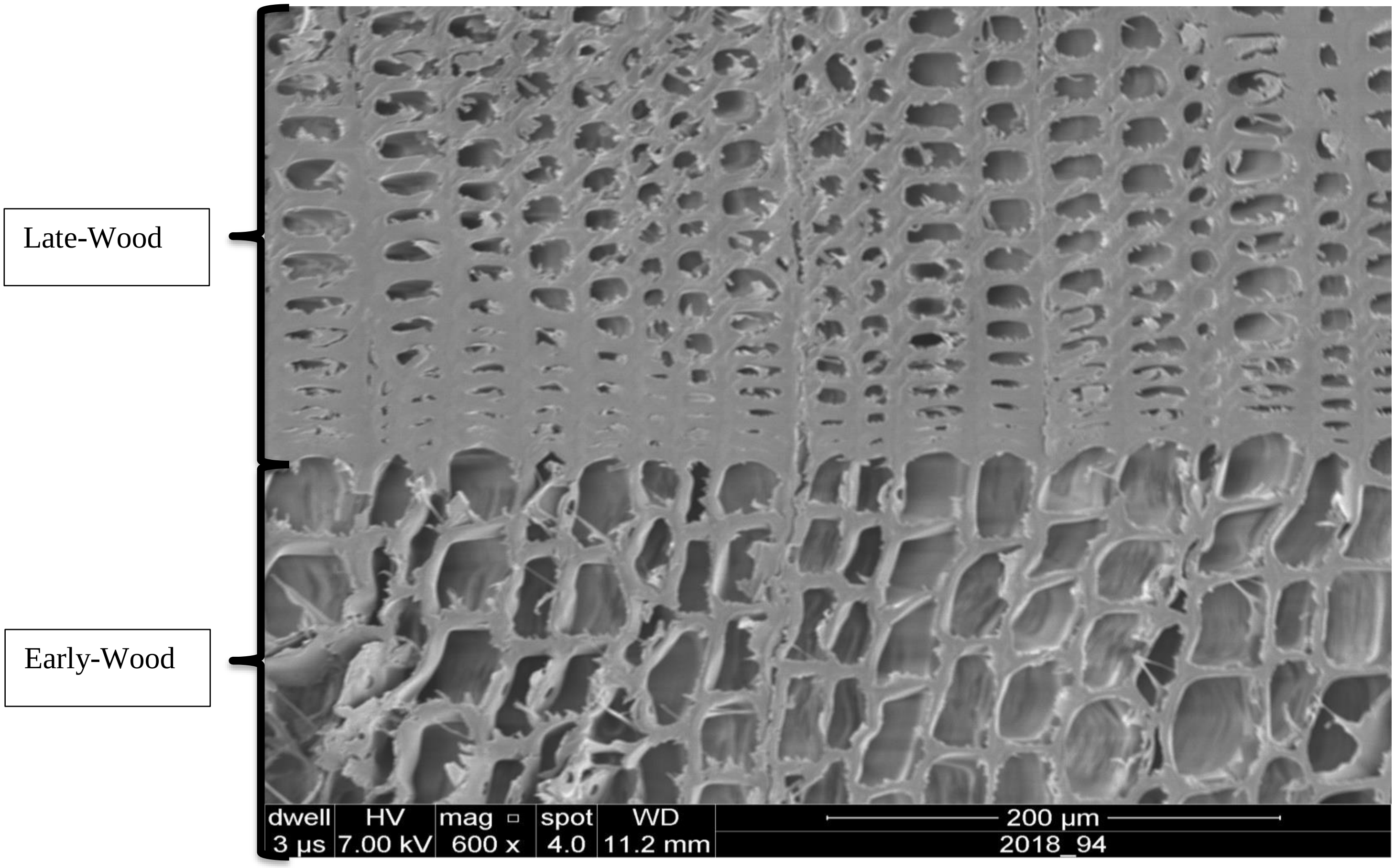


Fig3. SEM micrographs of wood spruce cross section

As can be seen in figure 3, all of the annual rings, comprising of early wood and late wood, together form a porous structure, which make wood more delicate against any loading stress on the wood surface. However, the thick walls of late wood, with its higher density compared to early wood, may contribute to the mechanical properties of wood fibers. Kučera and Bariska (1982) reported that in spruce, the late wood is more present in radial dimensions than tangential ones and this wood species contains ray parenchyma that are quite resistant to deforming. In the present study, spruce veneers were cut in a radial direction to optimize the mechanical properties of wood fibers and, to avoid the negative impact of the wood’s microstructure on the interfacial bonding between the wood and plastic interface.

1.3. Thermoplastic

There are basically two kinds of thermoplastic, known as oil-based and bio-based plastics. The traditional old plastics, which are provided from petroleum resources, are a big threat to the environment, as it takes a long time for decomposition once scrapped and their recycling leads to the release of toxic substances, with the addition of the high cost of the plastic purification itself (Galyavetdinov et al. 2016, Finkenstadt and Tisserat 2010, Álvarez-Chávez et al. 2012). WPCs have conventionally been manufactured by combining plant fibers with oil-based thermoplastics such as polyethylene families (PE) or polyvinyl chloride (PVC).

In recent years, as a result of increasing environmental concerns, there has been a huge interest in replacing petroleum-based plastics with bio-based plastics,which are derived from renewable resources (Su et al. 2015, Carus and Partanen 2018). Bio-based plastics are derived from renewable resources including corn, cellulosic, soy protein and starch, so they can be easily recycled back into the environment after use (Bajpai et al. 2014, Wool and Sun 2011).

Among the different bio-based plastics, Poly lactic Acid (PLA) has proven to have the highest potential for manufacturing with wood plastic composites (Qiang et al. 2012). As it is named, this polymer is produced by lactic acid, obtained from natural corn starch and sugar cane (Iwata T 2015, Qiang et al. 2012)(figure4). This polymer possesses favourable mechanical properties and can easily be processed using the injection moulding technique for making WPC (Qiang et al. 2014). That being said, there are still some serious obstacles regarding the development of this product on an industrial scale. According to Kühnert et al. (2017) Neat PLA has the following properties: high Yong's modulus, high scratch resistance, high transparency, certified composability, good printability, heat seal ability, high hydrophilicity, brittle, low impact strength, low heat resistance. It seems that the latter properties of PLA (especially its hydrophilic characteristic and brittleness) can be considered as some of the severe obstacles for using it with the wood phase.

.

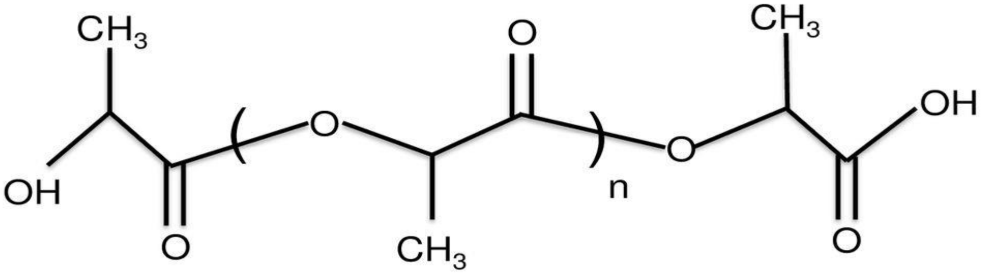


Fig4. Structure of poly lactic acid (PLA) containing both carboxylic (C=O) and hydroxyl

The polar or hydrophilic nature of wood itself causes an inherent incompatibility with hydrophobic plastics. This is due to the fact that there are many hydroxyl groups within the components of wood that are susceptible for receiving water molecules and thereby may result in poor wetting and inferior dispersion of wood particles in the matrix (Matuana and Stark 2015, Young et al. 2017). Consequently, it will lead to weak inter-facial interactions and give rise to mechanical failure in WPC (Teaca et al. 2018, Yang et al. 2010).

However, in terms of PLA, the question may arise as to whether such a hydrophilic characteristic of plastic can contribute to the interfacial bonding between wood and plastic. There are two opposing thoughts in this case: according to Joffre et al. (2017) using the lower hydrophobic plastics results in better stress transfer between the wood and plastic interface, whereas Lv et al. (2016) reported that it would only lead to poor compatibility with the wood phase, due to the large differences between the hydrophilic properties of wood and polymers.

On the other hand, the rheological properties of polymers may play a determining role in their bonding value with wood fibres. One of the most important properties of molten plastic is its shear viscosity and how it is influenced at higher temperatures (Sungsunti

2011). Previous reports show a meaningful difference between the viscosity of PLA and polyolefin plastics due to their amorphous and crystalline structures respectively.

In terms of PLA, the lower viscosity of this polymer may lead to the deeper glue line (Bakken and Taleyarkhan 2020). Thus, this property can be considered as a positive parameter helping interfacial bonding between the PLA and wood phases. Be that as it may, it is not still clear whether such a distinct property in PLA would cause a significant difference between the final mechanical properties of a composite made from this plastic and other variables of polyolefin.

To answer these questions and evaluate the effect of polarity and rheological properties of plastics on the interfacial bonding at wood-plastic interface, in the present study, a high density of polyethylene (HDPE), mixture of 3% MAPE with HDPE (coded as MHDPE) and Poly lactic acid (PLA), each containing hydrophobic, semi-hydrophobic semi-hydrophilic and hydrophilic chemical properties respectively, were separately administed to the wood surfaces of veneers, so that a true understanding of the formation of interfacial bonding between wood and plastic over the processing of the real composite could be achieved. Therefore, for better comprehension of this phenomenon, the main focus of the current study was on the interface area between wood and plastics.

1.4 Wood-Plastic Interface:

The optimization of this interfacial adhesion has always been one of the biggest challenges of previous studies (Balasuriya et al. 2002). There have been many attempts to improve the physical and the mechanical properties of the wood-plastic compound so that it can be more readily used by manufacturers in the industry (Mertens et al. 2018, Bekhta et al. 2017). It is already apparent that these properties are mostly influenced by an interface where two heterogeneous layers of wood and plastic meet each other (Matuana et al. 1998) (figure5). It has been proven that the interface between wood and plastic phases is the main area responsible for low stress transfer efficiency and inferior interfacial bonding in composites (chan et al. 2018). The performance of WPC is not only dependant on wood and plastic phases but also the effectiveness of load/stress transfer at the wood-polymer interface (Zhou et al. 2017, Fuqua et al. 2012).

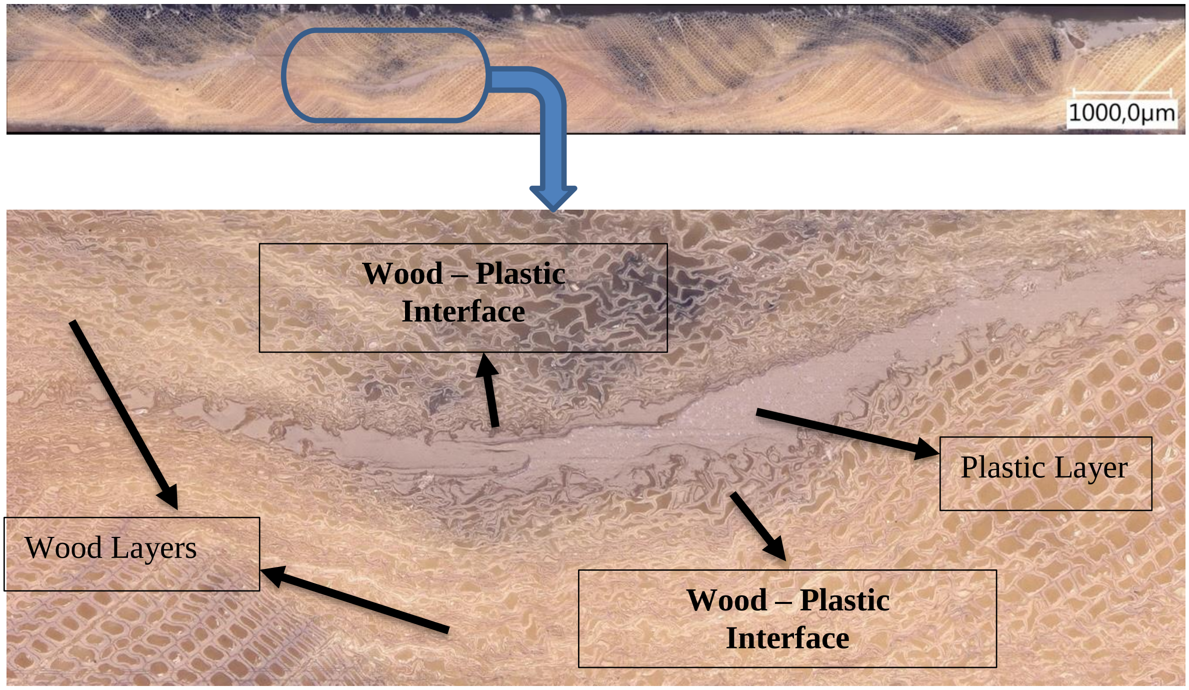


Fig5. Microscopic image of wood-plastic interfacial bonding region (VHX600)

Although there have already been several approaches presented by scientists in which they tried to improve the interfacial bonding at wood-polymer interfaces, these approaches could quite simply be divided into the two main classifications of physio-mechanical modification and chemical treatments, since interfacial bonding between wood fibres and polymers is only expected to be observed on occurrence of mechanical interlocking, chemical bonding and inter-diffusion bonding accordingly (Pickering et al. 2016, George et al. 2001).

As Pickering et al. (2016) reported, the mechanical interlocking is mainly fortified by factors like surface roughness, in which the morphological properties of the interface are mainly influenced, while chemical bonding needs a coupling agent that acts like a bridge between the wood and the matrix in order to form an interfacial bond between the two interphases. Such interactions can also happen simultaneously. However, since the mechanism of each modification and their impact on the composite is quite distinctive, it is still not clear whether or not there is a need to clarify the nature of each treatment; the most applicable methods for each type of modifications are briefly explained below.

1.5 Chemical Treatment

The incompatibility of wood and plastics are arise from the difference between the hydrophobic structure of plastics and the hydrophilic property of wood particles. This is a direct result of the presence of hydroxyl groups within the fibres, which make them susceptible to water absorption (Chang et al. 2009, Perisic et al. 2018). As previously mentioned, the entire arrangement of wood cells forms a porous structure on the surface that causes the penetration of water molecules and migration of moisture from the surface to the bulk of the wood fibres. To avoid this problem, there are two main approaches known as surface and bulk modifications, by which not only are the pores in the wood sealed but also the natural porosity of the fibers preserved (Hansmann et al. 2005).

Most of the chemical modifications were made, with a view on the reaction of a chemical reagent with the available cell wall hydroxyl; with the hope of blocking the OH free radicals and thereby reducing the hygroscopic properties of wood. This goal is normally achieved by formation of a single chemical bond with one OH group or cross-linking between two or more OH groups (Hill 2007).

Among the various methods, wood acetylation has received the most attention as a bulk modification process. The main aim of acetylation is to improve the dimensional stability of wood by the replacement of the wood hydroxyl groups with carbonyl groups of acetyl, so as to improve the dimensional stability and interfacial compatibility in wood reinforced composites (Hansmann et al. 2005, Hung et al. 2008, Stefke et al. 2016). There are various kinds of chemicals which are traditionally utilized for acetylation. Although acetic anhydride is known as the most applicable one among them, there are still some serious criticisms regarding the use of this chemical, two of which are outlined below:

1. The linear structure of Acetic Anhydride restricts the chemical reactions of this chemical with wood. As the anhydride chains get longer, there are fewer chances for carboxylic groups to react with the wood celluloses (Hill 2007).
2. The presence of acid by-products after the wood treatment can dilute the active anhydride reagents, which solely, would decrease the rate of reaction on wood (Rowell 2007).

$$\text{Fiber} + OH + CH_3 - C(=O) - O - C(=O) - CH_3 \rightarrow \text{Fiber} - OCOCH_3 + CH_3COOH$$

Formula1.The general reaction of acetic anhydride and wood cellulose

As an alternative Hill (2007) suggested cyclic anhydrides, which do not yield a by-product and which additionally, modify the wood polymers by formation of a covalently bonded carboxylic group. Rowell (2014) also reported that the product of acetic anhydride needs more of a separation process in order to recycle the acetic anhydride. Following that, Nuraishah et al (2017) concluded that using longer chain carboxylic acid anhydrides – such as butyric anhydrides – are needed to solve this problem. Another popular approach, which is mainly due to the improvement of interfacial adhesion between wood and polymer, is the application of maleic anhydride grafted with polypropylene (MAPP) or polyethylene (MAPE).

It has been reported that this coupling agent is able to react with the surface hydroxyl groups of wood by means of its anhydride groups of copolymers, whilst meshing with the plastic matrix using the other end of its copolymer at the same time (Rao et al. 2018). In another words, it can react chemically with wood and physically with the polymer sides of the composite (figure 6). That being said, the functionality of these coupling agents is mainly dependent on their molecular weight and the compatibility of their framework with the plastic interphase.

Consequently, it has already been observed that the application of MAPE has more advantages than MAPP, due to its higher molecular weight and framework being compatible with other polymer types (Teaca et al. 2018).

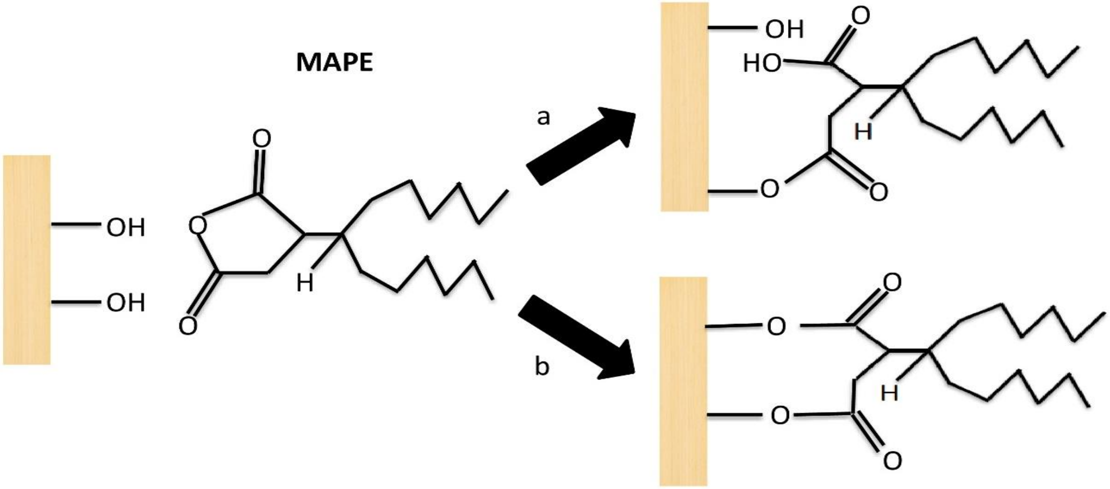


Fig6. Possible reactions of MAPE with wood fibers forming a. Mono-ester b. Di-ester bonding

In comparison to Acetylation, MAPE treatment yields a different method of reaction with wood fibers; the acetylation approach is known as a single site reaction, wherein one acetyl group is added per reacted hydroxyl groups with no further polymerization on the wood surface (Papadopoulos et al. 2019), whilst the reaction of MAPE with the OH groups of wood fibers leads to a graft polymerization structure, which may comprise of both a single site reaction and a copolymer reaction (Lu et al. 2005, Bouafif et al. 2008).

In the current thesis, in order to characterize the real influence of both treatments on the wood surface, acetic anhydride (AC) and maleic anhydride (MA) were chosen for acetylation purposes, each consisting of linear and cyclic anhydrides respectively, so that the real difference between the effect of linear and cyclic anhydride could be determined. Following the result of this experiment, Butyric Anhydride was then selected, as it contained longer linear chains of anhydrides for reacting with wood surfaces. Additionally, a pre-coating of MAPE was applied to veneer surfaces, with a view to analyzing the effect of these chemicals on the physio-mechanical and morphological properties of wood.

1.6 Sanding

Unlike real solid materials that mostly have uniform morphological properties on the surface, wood has many cavities inside (vessels, cell lumens), which are influenced by different underlying factors including: moisture content and the density of the structural properties (Magoss 2008, Chang et al. 2015). These factors can totally change the physio-mechanical properties of wood during cutting process which in turn cause irregularities on the wood surface after machine processing, resulting in the formation of uneven surfaces (Gurau et al. 2013, Thoma et al. 2015).

To solve this problem, the implementation of physical approaches is recommended, requiring the calculation of roughness parameters, which can be derived from the primary wood surface texture or obtained by surface treatment (Kúdela et al. 2018). It is already evident that the natural roughness of the wood surface improves the penetration of an adhesive throughout the wood, since rougher surfaces pose more peaks and valleys and thereby increases the glue line by forming a groove shape at the interface (Hiziroglu and Rabiej 2005, Shida and Hiziroglu 2010).

Sanding is one of the most widely used methods for fortifying the positive effect of surface roughness on wood interfacial bonding. However, according to Gurau (2010) it is still ambiguous how exactly it is that sanding can accelerate the bonding mechanism; this being a direct result of the lack of knowledge about the parameters influencing this type of modification. As the result, most of the previous investigations over the characterization of sanding and the way in which surface morphology is being influenced by this treatment are contradictory.

Whilst surface roughening has been recognized as a positive machining process used to improve surface bonding, there were some reports claiming the opposite.

Demirkir et al. (2014) claimed that higher surface roughness leads to the reduction of the contact area between wood and substrate and consequently causes a weak glue line. Ugulino and Hernández (2018) consequently noted that a good finish ended with lower roughness after sanding. Nevertheless, as these authors have also mentioned, almost all scholars agree on the cell-wall fibrillation up to a specific point in order to improve surface coating potential on the wood surface. In fact, mechanical treatments like sanding not only changes the morphological properties of the wood surface but also its chemical structure, wetting and its thermodynamic characteristic (Kúdela et al. 2018, Hubbe et al. 2015).

Sinn et al. (2004) and Papp and Csilla (2017) measured the values of the surface energy on different wood species after being were sanded with P400, P180, P100 and P60 sandpapers. They reported an increase in surface energy when increasing the surface roughness up to a certain point and the reduction of this parameter by using P100 and P60 grit sizes subsequently.

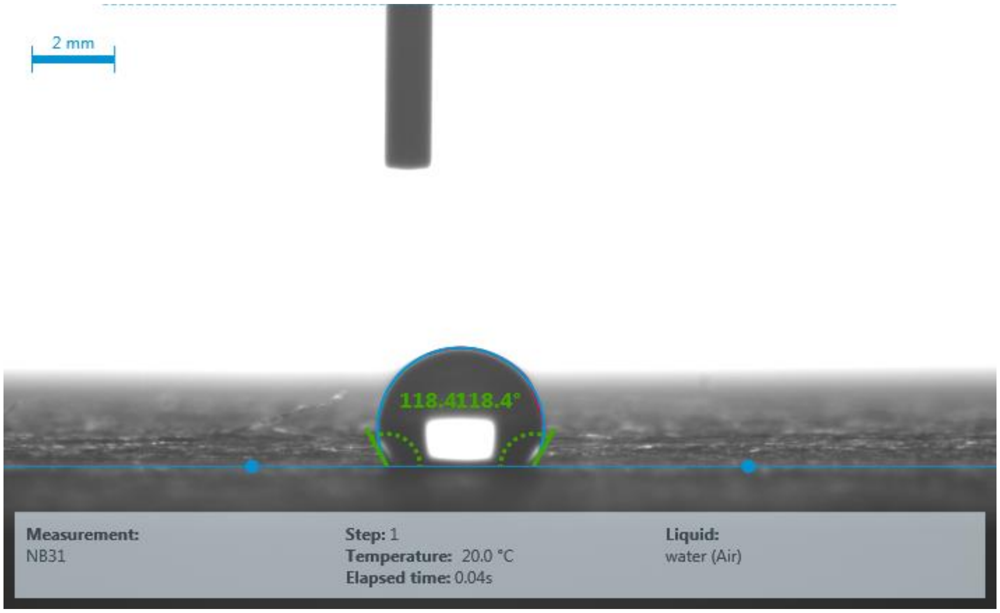
Based on these results, it can be deducted that the final functionality of the surface roughness parameter is quite dependent on the role it plays in changing the wetting properties of the wood; additionally in forming a surface area with both new physical and mechanical properties respectively. Therefore, in our current investigations, the characterization of surface wetting was marked as one of the highest priorities, in order to find out the interaction of both sanding and chemical treatments on the physical interactions between wood and plastic.

1.7 Wetting relations

Surface free energy (SFE) is defined as the energy required to produce a new surface of material (Schuster et al. 2015). From a chemical viewpoint, it can be interpreted as a linear combination of the total energies of all functional groups existing on a wetted surface (Janssen et al. 2006). There are several advantages to measuring surface free energy, such as the identification of the physical and chemical properties of a surface, characterization of wettability and the ability thereby to interpret the adhesion phenomenon occurring between the solid and the liquid surface (Cappelletti et al. 2013).

On the other hand, SFE is a standard scale used to evaluate the hydrophobicity of polymers. As is expected, polymers have very low SFE due to their stable structure (Kaczmarek et al. 2008). Consequently, most of the wood treatment methods have been elaborated, with a view to reducing the high SFE of the wood surface, thereby making it more compatible for a reaction with the low SFE surface of the plastic interphase.

Contact angle measurement (CA) has proven to be the most common and practical method for wetting evaluation and calculation of the surface free energy on solid surfaces. Law and Zhao (2015) announced that wettability and adhesion are the most common properties of a surface, both of which can be characterized by contact angle measurements. The contact angle is the angle when a liquid droplet wets a solid surface, and the angle between the liquid and the solid surface is measured to determine the adhesion property of the solid (Figure7).



Measurement: NB31

Step: 1

Temperature: 20.0 °C

Elapsed time: 0.04s

Liquid: water (Air)

Fig7. The Contact angle (CA) of water droplet on the wood surface

This experiment is usually carried out using several different liquids i.e. water, glycol and diiodomethane. Theoretically, each liquid is selected to represent the features of a polar or non-polar liquid. Regardless of how the approach is carried out, the principal of all methods is always based on the prominent Young equation (Young 1805), in which a static liquid droplet forming on a solid surface is described as follows;

$$\sigma_s = \sigma_{sl} + \sigma_l \times cos\theta \qquad (1)$$

Where σ_s is known as solid surface tension, $\sigma_l$is the liquid surface tension, σ_{sl} is referred to as solid-liquid interfacial tension and θ is the tangential contact angle formed at the liquid-solid-air interface. However σ_{sl} and σ_s are still two unknown values in these formulas, which require further calculation after experimental laboratory tests have been conducted. To solve this problem, Dupre (1869) devised a connection between the liquid droplet profile and the thermodynamic expression of work of adhesion as follows:

$$W_A = \sigma_l + \sigma_s - \sigma_{sl} \qquad (2)$$

Where the work of adhesion (W_A) is the work, which needs to be done so that liquid droplet can be separated from the solid surface. Finally, formula (3) is formed from the combination of formula (1) and (2) as follows:

$$\mathrm{Wad} = \sigma_l\ (1 + \mathrm{Cos}\theta) \qquad (3)$$

This simple formula enabled scientists to calculate surface free energy (SFE) through the work of adhesion in next step. Therefore, in the most advanced methods of SFE calculations, this equation is always applied as the basis for reducing unknown values in the main mathematical formula (Law and Hong 2016). That being said, wetting on the wood surface is solely a complex phenomenon, which requires a precise approach, due to the heterogeneous structure of wood.

Gindl et al. (2001) previously compared the different methods of SFE calculation on a wood surface and concluded that the Acid-Base method provides the maximum information about the chemical composition of wood's natural polymer surface. Interestingly, this method is actually the latest and most detailed approach of surface tension component methods, in which surface tension is assumed to be partitioned into different components, with every component illustrating its own individual intermolecular interactions (Vann Oss et al. 1986).

In 1969, Owens and Wendt divided the surface tensions of a solid and a liquid into dispersion and hydrogen components. At approximately the same time, Rabel (1971) and Kaelbe (1970) have publicized a similar attempt in partitioning the solid surface tension into dispersion and polar sides. As the result, this method is known as the OWRK method, in which the relations between liquid and solid surface tensions is formulated as

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^D \sigma_l^D} + \sqrt{\sigma_s^P \sigma_l^P} \qquad (4)$$

Whereσ_s^P, σ_s^D are the polar and dispersive parts of a solid andσ_l^p,$\sigma_l^D$are the polar and dispersive parts of a liquid respectively.

Vann Oss, Chaudhury, and Good (vOCG) developed the Acid- Base theory (1989, 2006). In the vOCG model, surface tension is assumed to be the sum of the two main parts. Consisting of the Lifshitz van der Waals component (σ^{LW}) or apolar side, in which the physical forces on a surface are to be determined, and the Lewis acid-base component (σ^{AB}) or polar side, where chemical forces are the focus (including hydrogen bonding interactions). The acid base component is also subdivided into electron-donor and electron-acceptor. Therefore, the final mathematical approach by vOCG which describes interfacial tension between Solid and Liquid surfaces is formulated as follows:

$$\sigma_l\ (1 + \mathrm{Cos}\theta) = 2\sqrt{\sigma_s^{LW} \sigma_l^{LW}} + 2\sqrt{\sigma_l^{-\sigma_s^+}} + 2\sqrt{\sigma_s^{-\sigma_l^+}} \qquad (5)$$

Since both the OWRK and Acid-Base methods are principally based on the polarity and dispersive properties of the surface, for the purposes of this study, both calculations were carried out to ensure the accuracy of the values obtained from the CA and SFE calculations. This was achieved by comparing both approaches against each other and applying a regression analysis to the OWRK method.

Contact angle measurement had always been a challenging field of study for scientists and in the most cases they faced too many unsolved dilemmas. The main reason for this is probably due to this fact that each of the internal and/or external influencing factors, with regards to this experiment, can vary with the differences between the test conditions and the procedures used to conduct each measurements. In some cases the significance of one parameter is of more importance, while in others the role of the same parameter is not significant at all. This has unfortunately confronted the scholars with contradictions and, in some cases, misleading results. To avoid experiencing test errors, there are some key points, which all should be considered when a test liquid is to be distributed on the wood surface:

- The hydrophobic or hydrophilic characteristics of both the solid and liquid phases are usually known as the most important concepts in surface science:

In terms of wood reinforced composite components, wood is known as an anisotropic material, possessing free hydroxyl groups on its surface, which gives it its hydrophilic characteristic; on the other hand, plastic has an isotropic nature consisting of frequent carbon and hydrogen atoms, thus forming a hydrophobic structure. In some experiments, this feature is of less importance as there is merely a physical interaction between the droplet and the solid surface. Therefore, to assess the effectiveness of this parameter, different kinds of liquids are usually tested in the experiment.

These liquids are typically as follows: water (hydrophilic), ethylene glycol (Semi hydrophilic, semi hydrophobic) and diode methane (hydrophobic). However, such liquids cannot always be a good representative of all hydrophobic and hydrophilic materials, since each liquid has its own properties. Above all, we should not forget that regardless of the droplet type, wettability is always the main objective with regards to measurement. Therefore, our main point of view should always be focused on obtaining a lower contact angle and achieving better wettability consequently.

- Surface roughness, which influences the final droplet shape on the solid substrate:

There are several interpretations which try to describe the impact of surface roughness on a wetted surface. To our knowledge, the best theory, which has truly explained the impact of this factor on surfaces, is the one described by Wenzel (1949). Based on this theory, roughness increases hydrophilicity/hydrophobicity on hydrophilic and hydrophobic surfaces respectively. Therefore, for the interaction between wood and plastic, it is likely to be considered as a negative factor as regards interfacial bonding; thus, on one hand we should decrease hydrophobic properties of plastic and on another hand we should also reduce the hydrophilic properties of the wood phase.

Theoretically our attempts should be focused on making the solid surface as smooth as possible, in order to avoid surface roughness at all. However, we should not forget that our main objective is to increase wettability and with regard to the hydrophilic phase, roughness is expected to increase this characteristic. Furthermore, surface roughness should also be evaluated from a morphological aspect. In this case, surface roughness can be assessed as being a positive factor for both sides. This is due to the fact, that in physical interaction there is always the possibility that both surfaces will have a groove-like structure, and this solely, would help keep the materials tightly joined. Therefore, this factor should be precisely measured, in order to diagnose its true nature in wood-plastic interactions.

- Surface tension and surface free energy (SFE) between liquid-liquid, solid-solid and liquid-solid phases:

Over the past decade, a lot of work has been done to determine the true characteristic of surface free energy on the adhesion properties of materials. Having said that, a crucial question remained unanswered: Does this factor have any influence whatsoever in interfacial bonding and the mechanical properties of the final composite? Recent research has answered it. Unfortunately, there were some misleading definitions in the past on which some scholars made mistakes in distinguishing surface tension from surface free energy perception.

There is no doubt that the surface tension of liquid has an intermolecular nature, in which molecules prefer to stay beside each other. Therefore, this parameter has a negative effect on wettability and spreading of the liquid droplet on solid surface. Surface tension always changes in a perpendicular direction on a surface, while surface free energy is a scalar quantity which has no specific direction at all (Law and Zhao 2016). Additionally, in contrast to surface tension, surface free energy is recognized as a positive factor for interfacial bonding, as it activates functional groups on the solid surface and thereby theoretically increases the potential of a solid to react with a liquid phase. However, the mechanism of this parameter is still unclear in wood-composite materials. Since, on the one hand it is only dependent on the hydrophilic properties of wood and it does increase if this property increases on the wood surface, while on other hand it is expected to visibly lower the compatibility between wood and plastic where hydrophilicity is to be reinforced in the wood phase.

- Molecular interaction between liquid and the solid surface which can potentially result in a chemical interaction in some cases:

According to Fowkes (1963), interactions between two bulk phases can only occur between forces of the same type. There is no doubt that if two different phases have a similar molecular interaction, it is more likely that chemical reactions will occur between them. This can be achieved either by trying to have some chemical manipulation on a solid surface and closing the chemical structure of the wood phase to an unpolar phase or by polarization of the plastic phase to create some functional groups on both sides. It is true, that generally polar molecules are dissolved in water whilst unipolar molecules do not have this ability but, there are some polar molecules like ketones and esters which are hydro-neutral.

Therefore, we should distinguish our basic definitions between the hydrophilic/hydrophobic characteristic from the polar/unipolar one. In a wood-polymer composite, wood is considered to be the polar phase whereas plastic is unipolar. If our concept is to homogenize both phases in order to achieve compatibility, we should either polarise or depolarise both phases. Although if we expect to increase interfacial bonding, then polarity is of particular importance. Therefore, this factor can also be a determining factor, being primarily dependant on molecular interactions and the forces existing between the atoms of each substance. Polarity rankings of functional groups are generally classified as follows:

Amide > Acid > Alcohol > Ketone ~ Aldehyde > Amine > Ester > Ether > Alkane

- Thermodynamic factors include test temperature and liquid viscosity, which are both effective parameters when the dynamic contact angle is measured over a specific period of time (Avramidis et al. 2009):

In fact, adsorption theory is based on thermodynamic forces (George et al. 2001). However, there is no doubt that thermodynamic force is in direct relation to heat and temperature. At room temperature where water-like liquids are to be laid on surface, there is no thermodynamic affect at all. Conversely, for materials with a high viscosity – like plastics – which need to be heated in order to flow easier, there is a direct correlation between the temperature and the viscosity of the liquid on wetting dynamics (Allin 2004, Kamal et al. 2009).

Since both surface tension and viscosity are known to decrease as temperature increases (wu et al. 1974, Kamal et al. 1994), our first priority is to increase the temperature as much as possible with a view to decreasing the viscosity ratio and obtaining better wettability. On the other hand, there is a pivotal margin for obtaining the ideal viscous substance, as elevated temperature levels lead to polymer degradation. So, it is suggested to choose a polymer with lower viscosity characteristics than variable plastics in the fields of wood-plastic composites. Furthermore, mixing a compatible sub-material with the plastic matrix is advised, after which the final plastic compound would possess both lower viscosity as well as the desirable physical strength of plastic.

Theoretically, variable test liquids are selected to represent the features of a polar or non-polar liquid but in practice there is a discrepancy between the physical and chemical properties of such a liquid and the molten plastic, which is compounded together with wood (Rezaee Niaraki and Krause 2017). Up to now, there have not been a lot of published studies using melted plastic liquid to measure the contact angle directly on the wood surface.

In almost all cases in previous experiments, the effect of heating on the wetting properties of the adherent and the adhesive was neglected, and contact angle (CA) measurements were carried out at room temperature (Rezaee Niaraki and krause 2019). This was in spite of the fact that at higher temperatures, both the interfacial properties and surface tension of polymers are significantly influenced (Wu 1974). Duncan and Mera (2005) described the high viscosity of polymers as one of the biggest obstacles for utilizing polymer adhesive droplets directly in surface wetting characterization. Aside from that, there was no other operational device capable of easily carrying out the CA measurements over the conventional flow range of polymers (160–230 C) in the past.

In this study, a high temperature dosing unit was primarily employed to record both the advancing θ_A and receding θ_r CAs of melted plastic on a wood surface over a specific period of time.

1.8. Research Problem and interfacial bonding approach

Fiber-matrix interfaces have always been a complex subject, since the interface has distinctly different properties from bulk phases and its characteristics are mainly influenced by chemical, physical and mechanical interactions as well as processing techniques (sanadi et al.1993). This area of research could become more complicated if each of these influencing factors impact differently on wood-polymer interfacial bonding, while there is further variation in the thermodynamic parameters of a system, such as temperature and pressure.

There is no doubt that in terms of interfacial bonding characterization, interfacial shear strength (IFSS) is of main importance, due to the fact that the critical shear force of fibers is the sum of both the chemical and physical bonding at the wood-polymer interface (Ren et al. 2017, Shida and Hiziroglu 2010). However, calculation of this value may automatically raise this question as to whether there is any significant interaction between the physical and chemical properties of interphase on the mechanical strength of a composite or, if there is no meaningful correlation between these parameters at all.

Although there have previously been some indirect trials on this subject by scholars, there is still no certain answer to this question. Even the outcomes of those studies are in some cases totally contradictory. Lui et al. (1994) claimed that acetylation increased surface free energy (SFE) on wood and resulted in better fiber wettability and polymer dispersion on the wood surface, the IFSS being improved consequently (Liu et al. 1994) However, as Hill (2007) has also explained in his book, this result is completely against the consensual view that acetylation is expected to increase hydrophobicity and reduce SFE subsequently. It is generally believed that a high surface energy value is not as a result of dispersion but rather an occurrence of the aggregation phenomenon and, that fibres may not have dispersed well enough consequently (Danayadi et al. 2010).

In another attempt, Mautuna et al. (1998) tried to decrease the SFE of wood veneers to close to that of a polymer. However, they could not observe any improvement in the IFSS at the end. On the contrary, Schwarzkopf et al (2017) have recently rejected the general belief about interfaces, in which a weak physical bonding is usually expected between polar wood components and nonpolar thermoplastics, as the result of their chemical incompatibility. Instead, they reported a strong interfacial bonding at the wood-plastic interface and attributed that to the strong mechanical interlocking obtained from wood surface roughness in the interphase.

Based on previous studies, there is no doubt that the mechanical properties of a polymer depend directly on the temperature over which bonding development between adhesive and adherent is to be processed (Alcock et al. 2007). Therefore, choosing the correct bonding temperature could optimize the bonding strength of plastics. Meanwhile, it should be noted that the temperature setting varies according to the glass transition range and crystallization behaviour of each plastic (Zhuravlev et al. 2016).

Conversely, thermoplastics are mainly classified in the category of Non-Newtonian fluids, which implies the fact that their viscosities are not only under the control of temperature and system pressure but can also further be impacted by factors like the shear rate and shear viscosity of plastics consequently (Allin 2004). Therefore, using the correct device to record the adhesion development over a wide range of temperatures is a big advantage to defining adhesion strength in the composite correctly.

The Automated Bonding Evaluation System (ABES) has been specifically designed to evaluate the shear strength of adhesives during the curing period, being further integrated for continuous testing over the hot pressing of wood-based composites (Jost and Sernek 2009). Therefore, in our current study, this device was further developed to evaluate the shear strength between wood and polymer adhesives.

1.9 Research questions

Based on the current introduction, it seems that the interfacial bonding at the interface is not only influenced by the physical, chemical and morphological properties of wood and plastic interphases but also the thermodynamic factors underlying the adhesion phenomenon over the manufacturing process of the composite at higher temperatures. The previous investigations in this area were mostly incomplete, due to either focusing only on one of the surface characteristics or evaluating all types of interfacial bindings together at the same time without concerning influencing factors in a thermodynamic system. Therefore, the present thesis is principally divided into primary and secondary questions to be solved, which are listed as follows in order of importance:

1. Primary question (principle aim of research):

Is there any significant correlation between shear strength and the wetting property of wood-plastic composites and to be more specific, what is the effect of chemical composition and mechanical interlocking on the interfacial bonding strength at the wood-plastic interface?!

2. Secondary questions:

- How effective is this thought in which scientists tried to homogenize both wood and plastic phases for obtaining better compatibility between composite components? Is it better to make both sides polar or unipolar? Is it not better to focus on the polar characteristic since this feature helps surface activations in comparison to the unipolar side? If polarity is recognized as a positive factor for interfacial bonding in WPC, is there any practical surface modification method that on the one hand could reduce hydrophilic characteristic of wood and on the other increase polarity of that in reaction with plastic?

- What is the true nature of surface roughness in wood plastic composites? Is this true that a smooth surface makes both sides compatibles in a composite or does roughness on the hydrophilic side results in better results?

- What is the true effect of thermodynamic factors – including temperature and shear viscosity – on the rheological properties of plastics over the processing of a wood-plastic composite?

- Does SFE have any impact on interfacial bonding and the mechanical properties of composites? There is no doubt that SFE is increased by hydrophilic characteristics. Yet is this an advantage or a disadvantage when wood is to be compounded with a hydrophobic plastic or, based on new research studies, does it not have any meaningful effect on wettability, with CA measurements solely being of importance?

1.10 The methodology of thesis

The main objective of this study was to ascertain if there is any explicit interaction between surface wetting and the shear strength of a wood–polymer composite. To this end, the present thesis has been divided into two main research areas;

1. In the first step, the surface morphology of the wood surface was targeted to characterize surface wetting and the interaction of sanding and chemical treatments on a wood veneer, so that the potential compatibility between the two kinds of treatments on the wood surface could thereby be investigated.

2. In the second and final step, the focus was devoted to wood-polymer interphases and the influence of the rheological properties of plastics on interfacial bonding in wood-plastic composites.

Analysis of both sides of the research study finally enabled us to investigate the correlation between physical bonding and shear strength in wood-plastic composites. The present thesis includes both unpublished and published works (Appendixes 1-3).

In the first year of this study, the main aim was to find out which method of chemical treatment was most effective on the wood surface and to evaluate the effectiveness of the equipment chosen to evaluate the wood surface wetting and interfacial shear strength of the wood-plastic interface under higher temperatures. The results of this stage were presented at the Materials Characterisations conference (2017, Estonia) and published in the journal of WIT Transactions on Engineering Sciences (ISSN: 1743-3533) titled **evaluation of wood surface modification using hot melting plastic droplets for contact angle measurements.** (Niaraki and Krause 2017).

In the Second publication (Rezaee Niaraki and Krause 2019), the main attempt was to characterize the physical properties of the wood surface after chemo-mechanical treatments. The Manuscripts entitled **"The correlation between physical bonding and mechanical properties of wood plastic composites Part 1: the interaction of chemical and mechanical treatments on physical properties"** is the outcome of this stage.

In third publication (Rezaee Niaraki and Krause 2020) **"The correlation between physical bonding and mechanical properties of wood plastic composites Part 2: Effect of thermodynamic factors on interfacial bonding at wood/polymer interface"** the final objective of the current thesis was investigated by analysis of the underlying factors that determine the final mechanical properties of a wood-plastic interface.

As previously mentioned, there were principally wood and plastic sides that meet each other at an interface. Therefore, the physical, chemical and mechanical properties of the final compound should have been determined once in the plastic and wood interphases separately and, once in the scope of interfacial bonding at the wood-plastic interface. Figure 8 shows the principal scope of the current thesis along with the equipment employed for the current study, according to that classification in each scope.

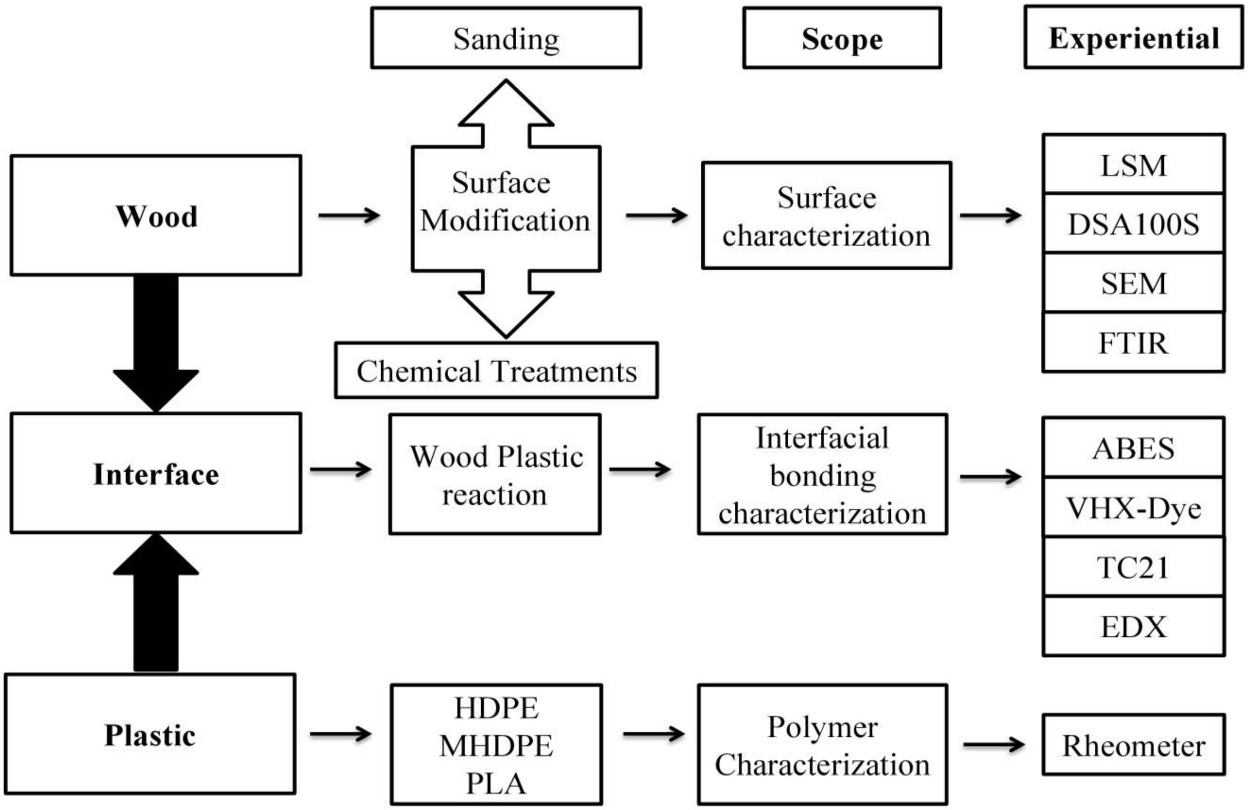


Fig8. General scope of thesis and the devices employed to serve each aim of study

Chapter 2

Materials and Methods

In this chapter, a list of all materials and methods used in the current study has been classified and noted, so that the aim of each experiment can thereby be clarified. Since the main focus of this study was on the interface site and interfacial bonding between wood and polymer, there were primarily two substrates that were separately prepared as follows:

1.1. Wood preparation

Based on introduction, spruce veneers were purchased and cut into longitudinal 117 x tangential 20 x radial 0.6 mm^3 dimensions. According to the available literature, there was no doubt that the presence of an extractive can disrupt the interfacial bonding by migration of the bulk to the surface and the changing of the wetting properties of the wood surface consequently (Wålinder and Gardner 2002). Therefore, in the first steps all cut veneers were extracted to avoid such a risk. The veneers were extracted via the soxhlet technique, using a mixture of ethanol-water (4:1) for 4 hours and then dried in an oven at 103°C for approximately 24h.

2.1.1 Sanding

To analyse the effect of surface roughening on both the physical-mechanical and chemical interactions of the wood surface with the plastic interphase, it was decided that sandpaper would be utilized for both smoothing and roughening purposes. An overview on previously done researches helped us to choose sandpaper with 100-grit size, so that both targets could be obtained at the same time. As the result, veneers were basically divided into sanded and unsanded.

2.1.2 Chemical treatments

To evaluate the efficiency of the acetylation process for wood modification, two of its most applicable chemicals known as Acetic Anhydride (AA) and Maleic Anhydride (MA) were first used to treat the veneers. For AA treatment, wood veneers were heated with a 1:1 part mixture of acetic anhydrides and pyridine solvent over 1h at 90°C. For MA treatment, the samples were also heated under the same conditions with a 1:2 part mixture of maleic anhydride and dimethylformamide (DMF) solvent, respectively. At the end of process, all treated veneers were dried at 103 °C for about 24 h.

After analysis of the test results obtained from this stage and further researches for finding a rather new generation of this technique, butyric anhydride was finally chosen to be used for esterification purposes, with the hope that this chemical, by possessing longer chains of anhydride within its framework, would be a good alternative for older chemicals commonly used for such a treatment. For each experiment, 500 ml of butyric anhydride was first poured into a glass flask and then put on the heater until its temperature reached 125°C.

For cooling purposes, a glass condenser was installed on the glass flask. Secondly, wood veneers (16 samples per test) were dropped into the solvent and were treated for 1 hour under the fume hood. After the treatment, samples were kept in the fume hood for 24 hours to erradicate the foul odour of butyric from the wood veneers. Finally, the samples were transferred to the dryer and dried at 105°C, before being prepared for tests.

Another method of surface chemical modification that was applied in the present study was the use of maleic anhydride grafted with polyethylene (MAPE) for pre-coating of the wood surface with the coupling agent, which has a similar structure to the plastic matrix. This allowed it to interact both chemically and physically with the wood and plastic interphases respectively and improve the interfacial bonding, by forming covalent bonding across the interface consequently.

The main obstacle for this method was to find the best approach for melting the MAPE in a way, which allowed it to be uniformly spread out on the veneers, without destroying the natural structure at higher temperatures. Biagiotti et al. (2017) recommended the usage of Xylene as a solvent for that purpose. They used a fiber-solvent ratio of 1:25 (wt/V) to treat the samples. In our experiment, having learned from that attempt, we first did some pre-experiments, starting from a rather dramatic temperature of 100°C and feeding the solvent slightly in order to observe the amount of solution; this was done by weighing both xylene and MAPE simultaneously.

We started by solving 20 gr MAPE in 500 ml Xylene and steadily increased the amount of coupling agent as well as the temperature in order to obtain the maximum solution. As a result, we finally succeeded in melting 50 gr MAPE in 500 ml Xylene at 140°C. This was recognized as a suitable solution for feeding a specific amount of wood veneers (16 veneers per treatment) to obtain an approximate WPG of 14 % at the end of the total chemical process. For all chemical treatments, the average weight percentage gains (WPG) of veneers were calculated and recorded according to eq 5;

$$WPG = \frac{M_t - M_{ov}}{M_{ov}} \qquad (5)$$

Where M_{ov} is the mass of oven-dried veneers and M_t the mass of oven-dried veneers after the chemical treatments. According to the wood preparation stage, there were a total of 1340 veneers, which were provided in six types of classification as follows:

- Unsanded, non chemically treated veneers
- Sanded, non chemically treated veneers
- Unsanded veneers, treated with MAPE
- Sanded veneers, treated with MAPE
- Unsanded veneers, treated with Butyric anhydride
- Sanded veneers, treated with Butyric anhydride

2.3 FTIR characterization

The Fourier transform infrared was performed on a Bruker Vector 33 FTIR-spectrometer. The spectra were recorded at between 3600 and 600 cm^{-1} on a DTGS detector, using analysis software OPUS 6.5 (Bruker, Germany) to detect available functional groups on the wood surfaces.

2.4 Surface roughness measurement

A 3D laser-Scanning-Microscope (Keyence-VK-X100, Osaka, Japan) was utilised to evaluate the surface roughness both before and after sanding and chemical treatments on the wood veneers. For surface analysis, each sample was placed under the microscope's red laser beam (658nm, 10x magnification) and scanned in an inspection area of 1350*1012 μm^2. For each measurement, 130 images were taken of the mentioned area and then merged together in order to form final single dataset. To increase clarity, images were fitted with an automated linear correction of plane inclination (SF surface, F operator) and were further processed by L Filter (double Gaussian filter).

The morphological datasets were all analysed according to standard EN ISO 25178. Lastly, the most important functional parameters of surface roughness were calculated and analysed as follows: Sa (roughness average), Sdr (developed interfacial area ratio), Spk (reduced peak height), Sk (core roughness depth) and Svk (reduced valley depth).

2. 5 Calculation of surface free energy (SFE)

A Data shape analyser (DSA 100, Krüss, Hamburg, Germany) was employed to measure the contact angle on the wood surface. For each sample, four sets of test liquids (water, diiodomethane, ethylene glycol and glycerol) were deposited on the wood veneer surface to form a visible advancing contact angle between the liquids and the wood surface.

Depending on the properties of the test liquid, the volumes of the droplets were selected in a range between 2 to 4 µl, so that external factors like gravity could not distort the droplet from its static state. All measurements were carried out 2 seconds after the sessile droplets were formed on the surface, in order to stabilize droplet shape and avoid any negative impact of the needles during their contact with the test liquids.

An acid-base model was simultaneously applied to determine the surface free energy of the wood surfaces according to the aforementioned wetting ratios (section 2). Test liquid databases were principally derived from the VOCG model and the ratio of the acid base parameters were further modified according to Della Volpe et al. (1997) (table 1).

Liquids	Surface free energy parameters (mN/m)				
	σ_l	$\sigma_{\mathrm{l}}^{\mathrm{LW}}$	$\sigma_{\mathrm{l}}^{\mathrm{AB}}$	σ_{l}^{+}	σ_{l}^{-}
water	72.8	21.8	51	65	10
Glycerol	64	34.4	29.5	16.9	12.9
Ethylene glycol	48	35.6	22.6	1.95	65.7
Diiodomethane	50.8	50.8	-	-	-

Table1. Test liquid database of acid-base model according to Della Volpe modification

2.6 Plastic preparation

Based on the hydrophilic and hydrophobic properties, Poly lactic acid (PLA) and a high density of polyethylene (HDPE) were provided respectively. In order to have a range inbetween (semi-hydrophobic, semi-hydrophilic), HDPE was separately melted together with 3% of MAPE at 150°C using a Haake Rheomex 600 OS mixer (Thermo Scientific, Germany).

To further utilise the plastics as plastic adhesive films for shear strength testing with wood veneers, each of the aforementioned plastics were placed within a metal frame (frame size 180 x 200 x 4 mm) and heated using a Siempelkamp press, the press temperature being set at 160°C for melting plastics. As the result, three types of thermoplastic adhesives were prepared for shear testing with veneers:

1. High density of polyethylene (HDPE- cc3054) purchased from SABIC,
2. poly lactic acid (4060D) sourced from Nature works Co, USA
3. the mixture of HDPE- cc3054 with 3% Maleic anhydride grafted with polyethylene(MAPE), coded as HDMAPE

2.7 Rheometer

In order to determine the shear viscosity (η0) of each polymer, frequency sweep tests were carried out by rheometer: Using a Discovery HR-2 (TA-Instruments, New Castle, USA), which was equipped with a plate-plate configuration (D = 25 mm, gap = 1mm), a constant strain (5%) was applied, while the frequency spanned from 0.1 rad/s to 100.0 rad/s. A comparison of the shear viscosity curves of the polymers (figure 9), value of η0 = 732 (pas) was calculated, to present the constant viscosity among PLA, HDPE and HDMAPE under 200°C, 158°C and 147°C respectively.

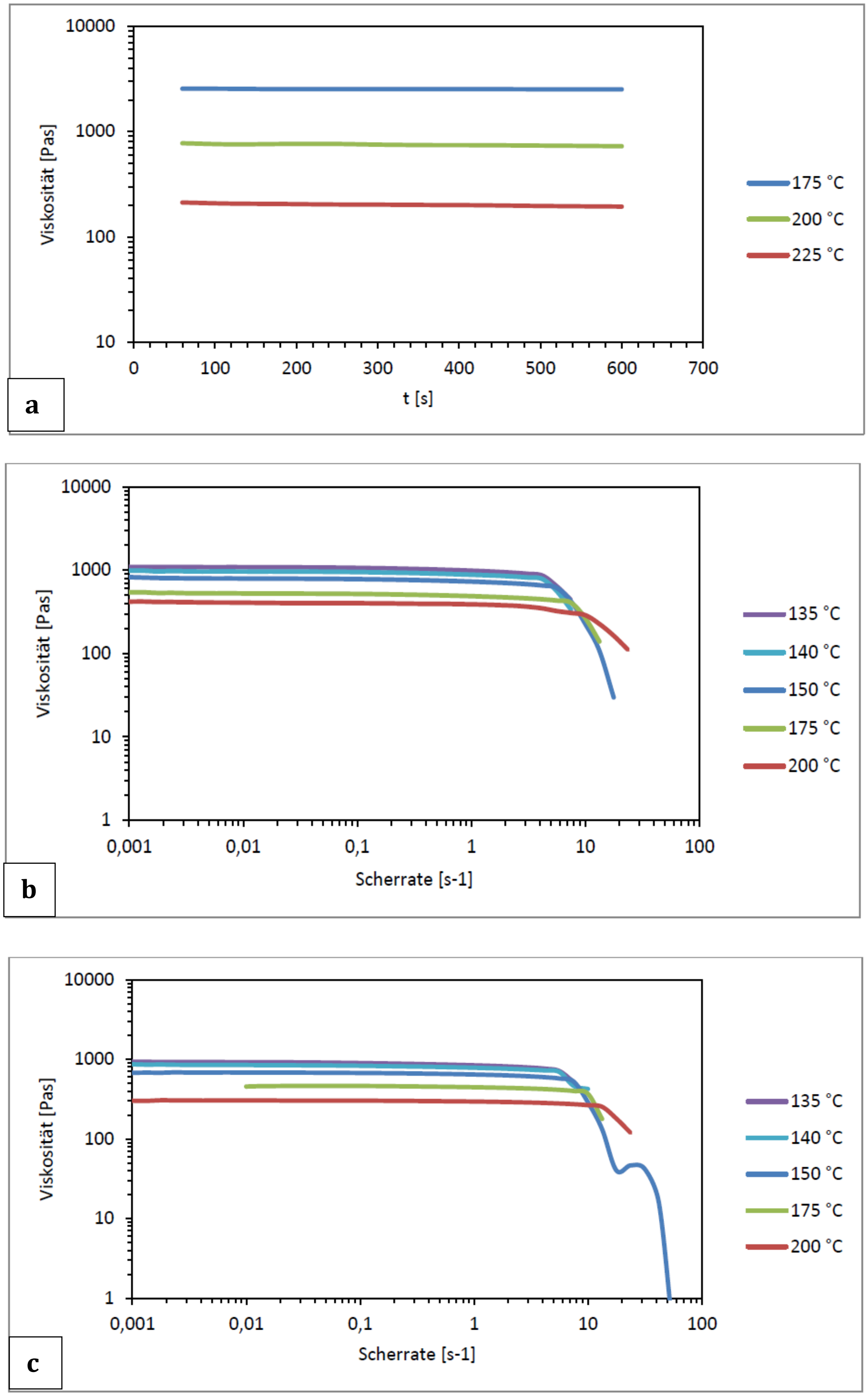


Fig9. Viscosity curves for HDPE (a), PLA (b) HDMAPE (c): rotation, plate-plate 25mm, 1000 ηm splat

2.8 Contact angle measurement using hot dosing unit

A hot dosing unit (DO3241) was purchased from Krüss GmbH (Hamburg, Germany). This device is a new generation of data shape analyzer (DSA100), which is able to form a sessile droplet from the plastic and measure the contact angle between the surface and hot melting droplet dynamically. Both the melting cylinder and temperature control chamber (TC21) are connected to temperature controllers, which are able to rapidly raise the temperature of both sides up to 400°C concurrently (figure 2). Therefore, all measurements were carried out under isothermal conditions.

Three types of polymers (PLA, HDPE and HDMAPE) were heated to 180°C in order for them to reach a desirable melt viscosity for this experiment. The volume of all plastic droplets was set between 4 and 6 μl in order to avoid the possible influence of external factors, including gravity. To ensure the correct measurements were obtained, melting droplets were deposited on the wood surface and the separation of the needle from the plastic droplets was immediately performed, to inhibit droplet distortion as the result of its contact with the needle nozzle.

Afterwards, the plastic droplets were allowed to rest on the surface for some seconds, being simultaneously monitored using Advance Software (Krüss GmbH) and the automatic height-width technique, until they formed an exact sessile droplet shape. At this moment, the measurement started and the first recorded contact angle was defined as the advancing contact angle (θ_A); all calculations were done over a period of 100s and the final measurement was recorded as the receding contact angle). Finally, the hysteresis phenomenon (CAH) was evaluated from the discrepancy between the two obtained values of contact angles on the wood surfaces.

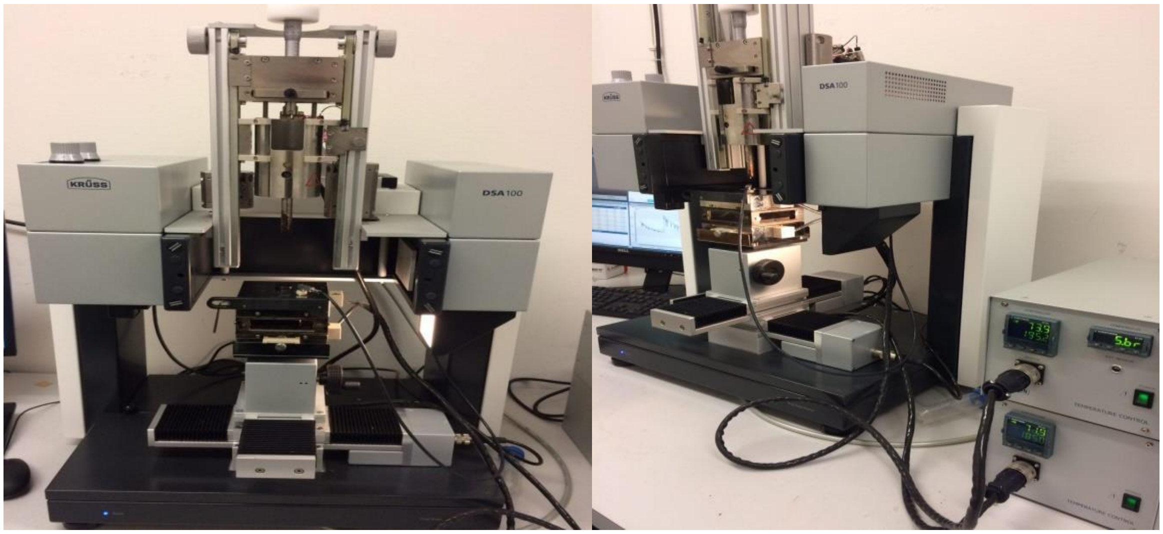


Fig10. Hot dosing unit (DO3241) and its temperature controllers on the right side

In a parallel experiment and in order to calculate the depth of plastic penetration into the wood cells from different directions, solid spruce was sliced into tangential, radial and transverse sections, each with dimensions of 30 x 15 x 2mm^3 (longitudinal x tangential x radial). According to the viscosity values obtained by rheometer (section, 2.7), the HDPE and PLA hot droplets were dispensed onto the wood surfaces at 158°C and 200°C respectively, so that the receding contact angle) of each plastic could be measured under constant viscosity, 100s from the moment the droplets were deposited onto the wood surfaces.

The samples were all cooled to room temperature and the plastic droplets then detached from the wood surfaces (figure 27, chapter 3), so that the average radius of the wood cells could be measured by using the scalar function of a digital microscope (VHX-6000 Keyence). The pendant drop method was employed using Advance Software (Krüss GmbH) to calculate the surface tension of the plastic liquids at the previously mentioned temperatures (figure 11).

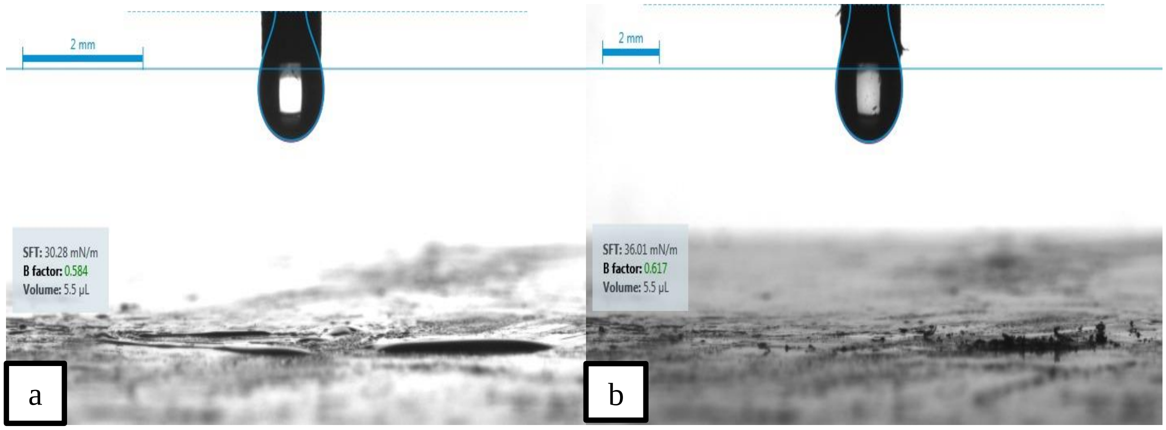


Fig11. The measured surface tensions of HDPE (a) and PLA (b) by using pendant drop method

Lastly, the results were entered into the following formula – known as the Washburn equation – that has been elaborated for the determination of the depth of capillary penetration into the early wood cells (Meijer 2007);

Washburn's equation ; $$L = \sqrt{\frac{\sigma_l \cos\theta\, r\, t}{2\eta}} \quad (6)$$

Where, σ_l was the surface tension of the plastic, θ was measured as the receding contact angle (θ_R), r was the average radius of the early wood cells, t was time of dynamic contact angle spreading on the surface (in this case: 100 s for all measurements carried out) and η was the plastic viscosity (in this case was set to 732 Pa.s for both plastics according to the temperature used).

2.9 Evaluation of shear strength by ABES

The Automated Bonding Evaluation System (ABES) was utilised to evaluate the bonding performance between the plastic adhesives (HDPE, PLA and HDMAPE) and one pairs from each of the veneer categories. In every experiment, two veneers were secured to the pneumatic pulling cylinder, which could induce up to 125N shear force and load a maximum pressing pressure of 20 MPa (figure12).

The bond area was defined between the two veneer strips with an overlap length of 5mm; a plastic film with a thickness of 0.5 mm had been embedded within the overlapping area and held together with the veneers using small hot press jigs, so that the bond strength development could be formed under the desired temperature conditions. Depending on the plastic types, all samples were tested once under a constant temperature (200°C) and once over the same aforementioned temperatures, in which the amount of viscosity reaches the same value for all polymers ($\eta 0 = 732$). After hot pressing for 20 s, samples were cooled down to room temperature by use of compressed air for 150s, so that adhesive curing occured completely. Finally shear force was applied by the system and monitored by the software for the calculation of interfacial shear strength (IFSS).

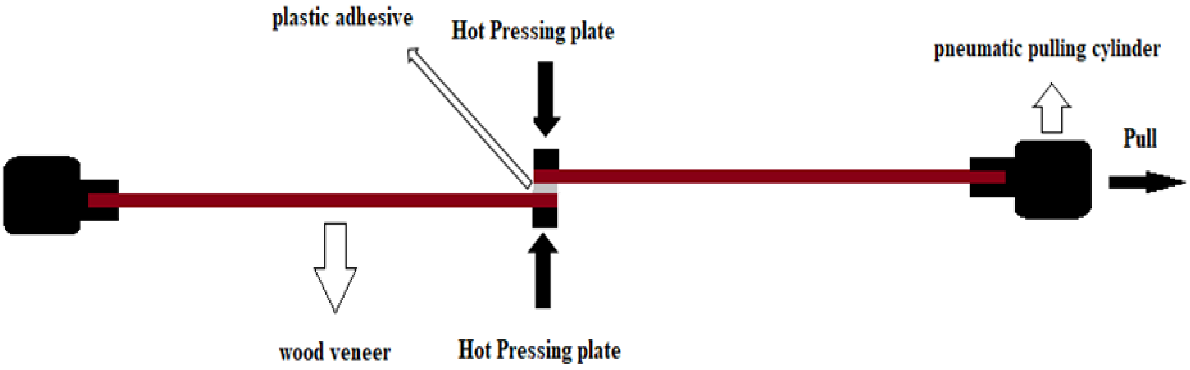


Fig12. Schematic description of shear test by the ABES

2.10 Microscopic analysis

In order to observe the morphological properties of the wood veneers, a field scanning electron microscope (FESEM using Quanta FEG Type 250, FEI Electron Optics SN: D9122, Netherlands.) was employed at an acceleration voltage of 7 kV and at 50x and 200x and 400x magnification. Test samples were cut perpendicularly and glued on to the stubs. Veneers were subsequently coated with gold prior to microscopic characterization. To further analyze the failure mechanism at the wood-polymer interface, a VHX-6000 digital microscope was employed to inspect the bond area after the bond strength test had been carried out by the ABES.

To further analyze plastics dispersion on the wood surface, Energy-dispersive X-ray spectroscopy (EDX) was employed via a scanning electron microscope (SEM), to observe the bonding areas of the tested veneers after evaluation of the shear strengths by ABES. The application of EDX was based on the analysis of the Electron-dispersive X-ray spectra from elements available on the surface. It can determine the values of the carbon and oxygen elements on the wood surface and, since the plastic framework contains only carbon atoms, it was employed with the hope of distinguishing the plastic element from the wood structure after shear strength testing by the ABES.

2.11 statistical analyses

In order to conduct the project with the least amount of risk and ensure the final outcomes from the testing devices had significant meaning, this study was devised and analysed using the Design of Experiment model (DOE). Unlike most other statistical analysis models, DOE allowed us to evaluate the effect of each influencing factors simultaneously, without needing to keep a parameter fixed for calculation. This solely, helped us to reach a higher level of accuracy and understand the important value of each factor in comparison to the other affective values at any one time.

A D-Optimal design type was selected to form the initial design, followed by a coordinate exchange algorithm with a view to obtaining precise model points. According to the principal aim of this study, there were three main devices, listed as the automated bonding evaluation system (ABES), DS100S (data shape analyser at room temperature) and TC21 (Hot dosing unit for measuring plastic contact angle at higher temperatures); which in comparison to the sub-devices, played the main role in investigating the correlation between wetting and shear strength of the wood-plastic interface. The operation of these devices were all programmed and controlled by DOE.

Tables 2-6 show the experimental plan obtained from DOE software. Each experiment was replicated ten times. Therefore, 860 experiments were carried out altogether in order to achieve the main data for further analysis. According to the factor combinations, which were randomly chosen by software, it was decided that the design scope would consist of 24 runs per testing condition (fixed temperature and fixed viscosity) for ABES and 19 runs for the DSA100S, so that a power calculation value would be close to 98 % for both experiments. The degrees of freedom for both testing conditions for ABES were identical again and had a total value of 23, including 13 model, 6 pure errors and 4 lack of fit and, for the CA measurements consisted of a total of 18 degree of freedoms, including 5 model and 13 pure errors respectively. The significance of all experiments was further determined by analysis of variance (ANOVA).

Factor	Name	Type	Minimum	Maximum	Levels
A	Mechanical treatment	Categoric	Unsanded	sanded	2
B	Chemical treatment	Categoric	Non-treated	BA	3

Table2. Factor coded groups designed by DOE for DSA100S

Factor	Name	Type	Minimum	Maximum	Levels
A	Mechanical treatment	Categoric	unsanded	sanded	2
B	Polymer	Categoric	HDPE	PLA	3
C	Chemical treatment	Categoric	Non-treated	BA	3

Table3. Factor coded groups designed by DOE for ABES

	Factor 1	Factor 2	Factor 3
Run	A:veneer treatment	B:polymer	C:chemical treatment
1	untreated	HDPE	untreated
2	untreated	MAPE-HDPE	untreated
3	untreated	PLA	untreated
4	untreated	HDPE	MAPP
5	untreated	PLA	MAPP
6	sanded	PLA	untreated
7	untreated	MAPE-HDPE	MAPP
8	sanded	HDPE	untreated
9	untreated	HDPE	MAPP
10	sanded	MAPE-HDPE	untreated
11	sanded	PLA	BA
12	sanded	MAPE-HDPE	MAPP
13	sanded	HDPE	untreated
14	sanded	HDPE	MAPP
15	sanded	MAPE-HDPE	MAPP
16	untreated	PLA	BA
17	sanded	PLA	untreated
18	sanded	HDPE	BA
19	untreated	HDPE	BA
20	sanded	PLA	BA
21	sanded	PLA	MAPP
22	sanded	MAPE-HDPE	BA
23	sanded	MAPE-HDPE	BA
24	untreated	MAPE-HDPE	BA

Table4. DOE plan set for shear strength testing by ABES (Constant Temperature)

	Factor 1	Factor 2	Factor 3
Run	A:veneer treatment	B:polymer	C:chemical treatment
1	untreated	MAPE-HDPE	BA
2	untreated	HDPE	untreated
3	untreated	MAPE-HDPE	untreated
4	sanded	PLA	MAPP
5	sanded	PLA	untreated
6	untreated	PLA	untreated
7	sanded	PLA	BA
8	sanded	MAPE-HDPE	BA
9	sanded	MAPE-HDPE	BA
10	sanded	HDPE	untreated
11	sanded	MAPE-HDPE	untreated
12	sanded	PLA	untreated
13	untreated	HDPE	untreated
14	untreated	HDPE	MAPP
15	sanded	MAPE-HDPE	MAPP
16	untreated	PLA	MAPP
17	untreated	MAPE-HDPE	MAPP
18	sanded	HDPE	BA
19	untreated	MAPE-HDPE	MAPP
20	untreated	HDPE	BA
21	sanded	HDPE	MAPP
22	untreated	PLA	MAPP
23	untreated	PLA	BA
24	sanded	HDPE	BA

Table5. DOE plan set for shear strength testing by ABES (Constant viscosity)

Run	Veneer Treatment	Chemical treatment
1	untreated	BA
2	Sanded	BA
3	Sanded	Untreated
4	Sanded	MAPP
5	Sanded	Untreated
6	untreated	Untreated
7	untreated	MAPP
8	Sanded	MAPP
9	Sanded	BA
10	untreated	Untreated
11	untreated	MAPP
12	Sanded	Untreated
13	untreated	Untreated
14	untreated	BA
15	Sanded	MAPP
16	untreated	Untreated
17	untreated	MAPP
18	untreated	BA
19	Sanded	BA

Table6. DOE plan used once by DS100S and once by TC21 devices for measuring contact angles of normal test liquids and melting plastic droplets on the wood surface respectively

Chapter 3

Results and discussion

As has previously been explained in introduction, in the current thesis, two kinds of surface modification methods were carried out on the spruce veneers, which were principally classified in the categories of sanding and chemical treatments. In the first part of this chapter, we first focused on the effect of each conducted treatments on the surface chemistry and the interaction of both treatments on the morphological properties of wood surfaces as follows:

3.1 Effect of chemical treatments on the surface chemistry of wood veneers

3.1.1 Acetylation

Figure 13 shows the FTIR spectra analysis obtained from the treated veneers with acetic anhydride (AA) and maleic anhydride (MA). The calculation of WPG (formula 5 – chapter2) proved that veneers were successfully treated with AA and MA, each group conveying a WPG of 20% and 17% at the end of treatment process respectively. As can be seen, in comparison to non-treated veneers, there are remarkable peaks within the region 1600 - 1800 cm^{-1} for both treated categories, which according to the Infrared Spectroscopy Absorption Table, is associated with the presence of carbonyl groups on the wood surface (Naumann et al. 2007).

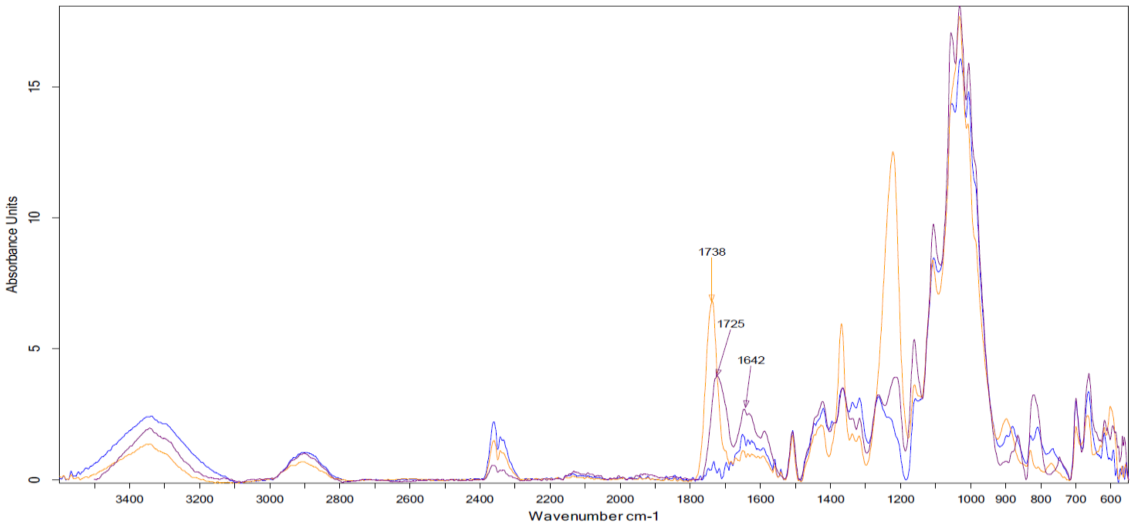


Fig13. FTIR spectra of REF (yellow color), MA (blue color) and AA (pink color) treated samples

Comparing AA and MA treatments, AA treatment resulted in an almost intense peak at 1738 cm^{-1}, whilst the spectra analysis on the MA treated veneers indicated the presence of two moderate peaks at 1642 cm^{-1}, 1725 cm^{-1} on the wood surface. In response to that it should be noted here, that in chemistry, there are basically two types of conjugated and unconjugated systems in which carbonyls are separated by one or more than one bonds from each other respectively (Mitsui 2010, Windono et al. 2012).

When the treatment is carried out by acetic anhydride, there are always more carboxylic compounds at one’s disposal but, due to the unstable structure of linear acetic anhydride and its incompatibility with wood chemical morphology, they are likely to form an unconjugated structure (Figure14).

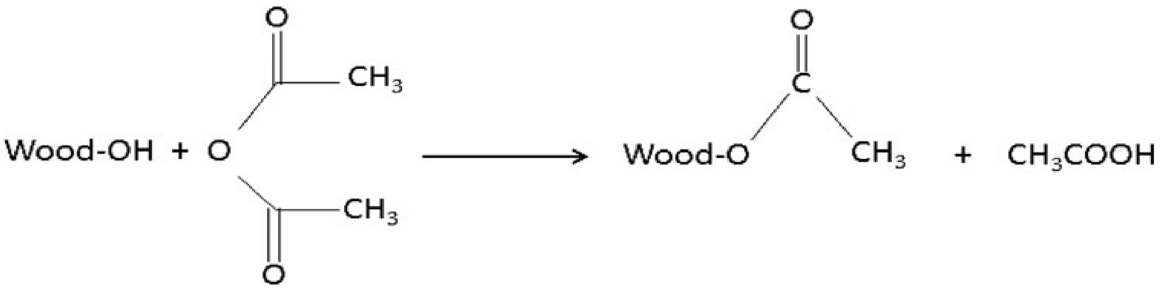


Fig14. Chemical reactions of acetic anhydride on the wood surface

Therefore, FTIR peak showed a 1738 cm^{-1} wave number after AA treatment, which is normally attributed to unconjugated carbonyl groups on the wood surface (Jahan et al. 2007). On the contrary, when maleic anhydride reacts with wood components, there is always one more carbonyl group per reaction (1642cm^{-1}), which is called a conjugated carbonyl group and forms a much more stable structure than acetic groups due its cyclic structure (figure15) (Naumann et al. 2007, Mitsui 2010).

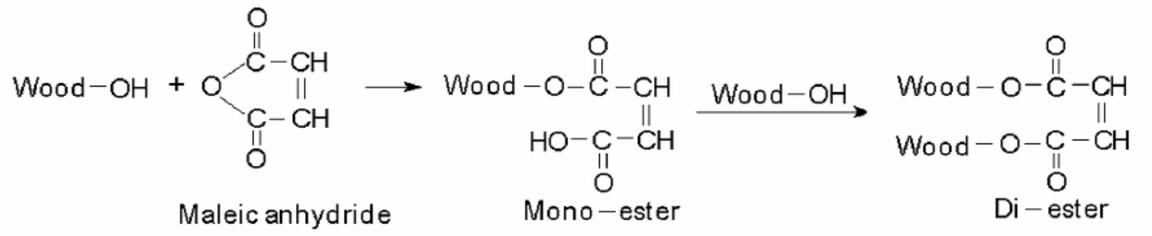


Fig15. Chemical reactions of maleic anhydride on the wood surface

3.1.2 Effect of acetylation on surface wetting using hot dosing units

The contact angle measurements were carried out by the deposition of hot melting plastic droplets of high density of polyethylene (HDPE) on the wood veneer surfaces. Diagram 1 shows the final calculations on the three groups of wood veneers; coded as REF (non-treated), AA (treated with Acetic anhydride) and MA (treated with Maleic anhydride) veneers.

As it is shown, AA treated samples had slighly more contact angles than both the REF and MA treated veneers. This is contradictory to conventional beliefs, where it would be expected for there to be a higher hydrophobic surface value after acetylation and consequently a lower contact angle of the hydrophobic HDPE droplet on the wood surface.

Conflictingly, the current observation showed, that AA makes the wood surface more resistant to reacting with a unipolar plastic droplet than the REF samples. This is in accordance with Liu et al. (1994) who stated that acetylation increases the surface free energy of wood specimens. They announced that by the replacement of hydroxyl groups in wood structure with acetyl groups, fiber surfaces are dominated by the ester configuration, which have a more polar characteristic than hydroxyls groups.

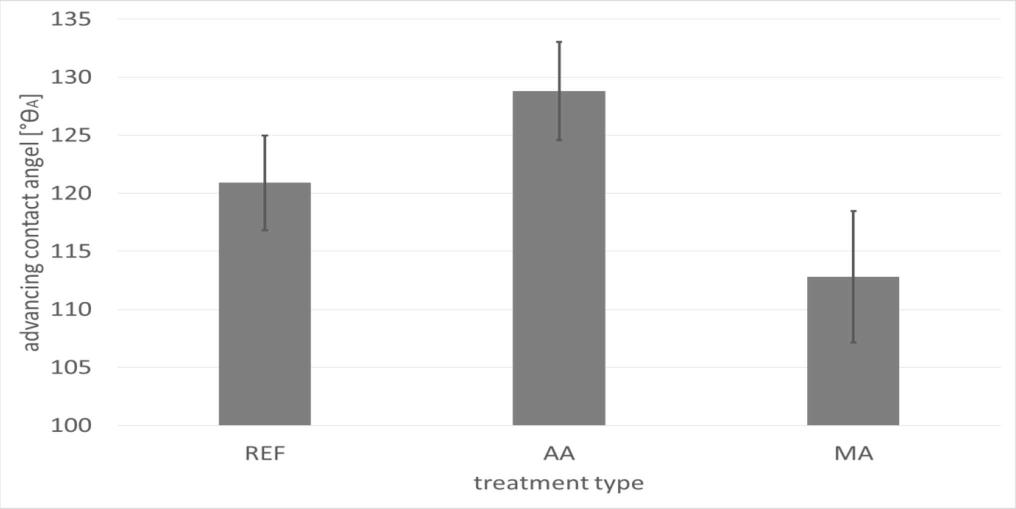


Diagram1. The contact angle measurements between wood surfaces and HDPE hot droplet

It was observed that the MA treatment presented the lowest contact angle. This is supported by the wide application of MA grafted on PE or PP as a coupling agent for wood plastic composites. This is also in accordance with Rowell and Clemons (1992) where they concluded, that the reaction of MA with wood made the wood characteristic similar to a thermoplastic matrix.

There are two main aspects in which the function of both acetic and maleic anhydrides can be distinct from each other. Under normal circumstances, the difference between the chemical structures of these two anhydrides is the main focus. Generally speaking, the application of chemicals that release acidic products (In this case acetic acid) over processing by catalyst is avoided. Since it may also degrade the polysaccharide components of wood (Rowell 1984, Hills 2007).

However, the presence of acid could dilute the active anhydride reagents, and this exclusively, may cause the reduction of the reaction rate of acetic anhydrides on a wood surface (Hills 2007).

There is a major difference between the types of structures on which these two chemicals are usually formed. There are some previous studies which suggested not to utilize the linear anhydrides like acetic anhydride on wood, as the longer chain anhydrides have less potential to bond with the cellulose components of the wood structure (Jahan et al. 2007, Hills 2007). However, according to Hassan et al. (2017) the unsuccessful treatment whilst using acetic anhydride may be just due to the presence of acetic acid after treatment and they even advised to use other families of acetyls instead, which convey higher carboxylic chains like Butyric and propionic anhydrides.

Surface interactions and the formation of the final chemical reactions between wood and chemical substances, are of more importance than the natural ability of the substance to increase the hydrophilicity or hydrophobicity of the wood surface. There is some new evidence showing that MA treatment does not hydrophobize wood fibres; rather, it increases the gluing ability of wood when reacting with other chemicals (Hundhausen et al. 2015). This is in accordance with our findings, since the utilization of the hydrophilic MA as chemical treatment resulted in a lower contact angle of hydrophobic HDPE on the wood surface (diagram 1).

Unlike general beliefs in which Acetylation is always considered as an efficient chemical for wood modification, our findings recommend the utilization of this chemical be restricted to its application and the objective of chemical treatment. Meanwhile, we strongly suggest choosing the optimal chemical process for this treatment, depending on the chemicals chosen from the acetyl family for wood’s modification.

In terms of surface wetting, we observed no significant improvement on the plastic wetted veneers treated with AA. To our understanding, this can be attributed to the basic distinction between the definition of hydrophilicity-hydrophobicity and polarity-un-polarity. In wood science, as the concentration of chemical treatments is mostly focused on the resistance of wood cells against the moisture absorption in order to increase the dimensional stability of wood, these two terms usually make use of the same definition. However, as Liu et al. (1994) quite rightly stated, acetylation blocks the hydroxyl access for reaction with water molecules, by forming carbonyl bonding on the wood surface, yet the ester groups are considered as polar components themselves and the polarity of the wood surface may even increase as a consequence of this treatment.

Therefore, it seems that the final aim of the chemical treatments, which was to obtain a hydrophobic surface in order to reduce the inherent interactive incompatibility between hydrophilic wood and hydrophobic plastics, was not achieved in this experiment. Based on the results and practices learned from this experiment, we then continued the chemical process on the wood surfaces using butyric anhydrides and Maleic anhydride grafted with polyethylene (MAPE).

3.1.3 The effect of butyric anhydride and MAPE treatments on the surface chemistry of wood veneers

The average weight percentage gains (WPG) of veneers were calculated and recorded as 17% and 10 % for both treated veneers with BA and MAPE respectively. Figure 16 presents the FTIR spectra of all wood veneer types in the range around 3600 and 600 cm^{-1}. As can be seen, there were two main peaks in which we could quite obviously distinguish the MAPE treated veneers from the others; these were the peaks 2849 cm^{-1} and 2924 cm^{-1}, which according to previous references, refer to the C-H stretching vibration of wood and plastic (Bulasuriya et al. 2002, Kupstsov and Zhizhin 1998).

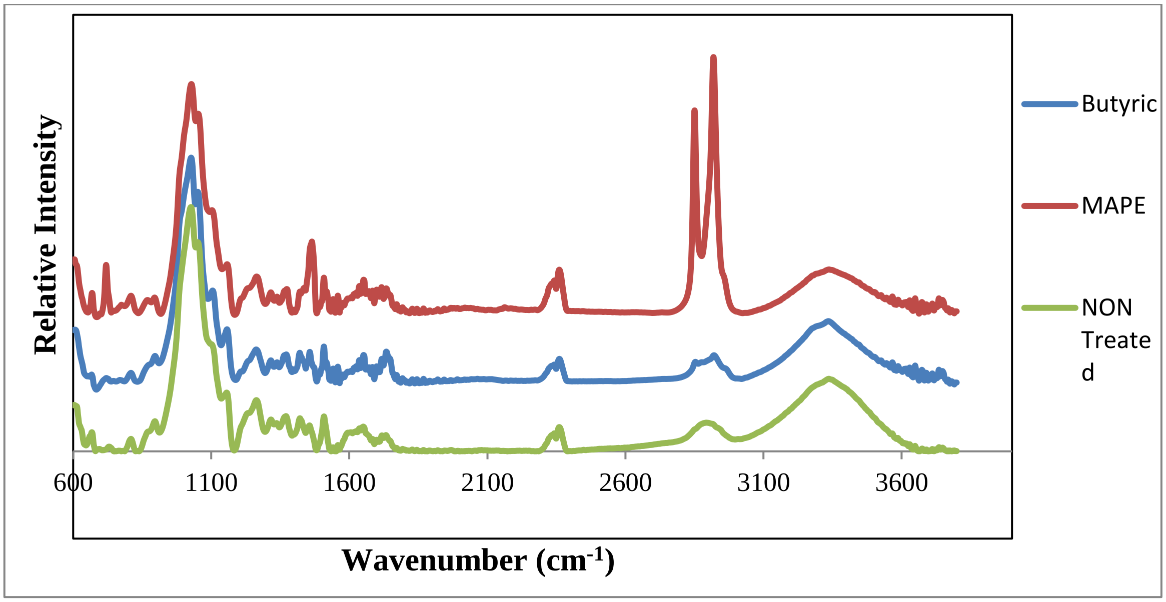


Fig16. FTIR spectra of wood veneers in the range of 3600-600 cm-1; Non Treated (green), BA treated (Blue) MAPE treated (Red) veneers

Unexpectedly, the analysis of fundamental molecular vibrations on the surface of Butyric anhydride (BA) treated veneers, showed no evidence for the presence of anhydride carbonyl adsorption on the surface; this can usually be observed in the region of 1904-1770 cm^{-1} as the result of esterification by such chemical treatments (Matuana 2001, Zhang et al. 2017, Lifen et al. 2015). This again verifies that this chemical alone, could not form a strong chemical bond with the available functional groups on the wood surface, without the mobility of a catalyst or use of grafting methods.

This is in accordance with the findings of Hills (2007) and Chang and Chang (2002), who reported the reduction of reactivity with wood cells when longer chain anhydrides were used for modification. To solve this problem, the use of a catalyst is highly advised; it increases the reactivity of linear anhydrides, by breaking down their longer chains, so that they can easier react with wood cells.

3.2. Effect of sanding on the surface roughness of non-treated and chemical treated veneers

Diagram 2 shows surface roughness parameters obtained from an areal material ratio curve. As can be seen, both core roughness (Sk) and reduced peak height (Spk) dramatically increased after the sanding process. However, this trend was reversed when chemical treatments were applied on the wood veneers. This is in accordance with Ugulino and Hernandez (2018) and Cool and Hernandez (2011), who also found a significant increase in Sk and Spk when P-100 grit sandpaper was applied during sanding and concluded, that the abrasive grains of this sand paper form the peaks heights, deep grooves and cell-wall fibrillation and it can thereby contribute to the spreading of liquids on the wood surface consequently.

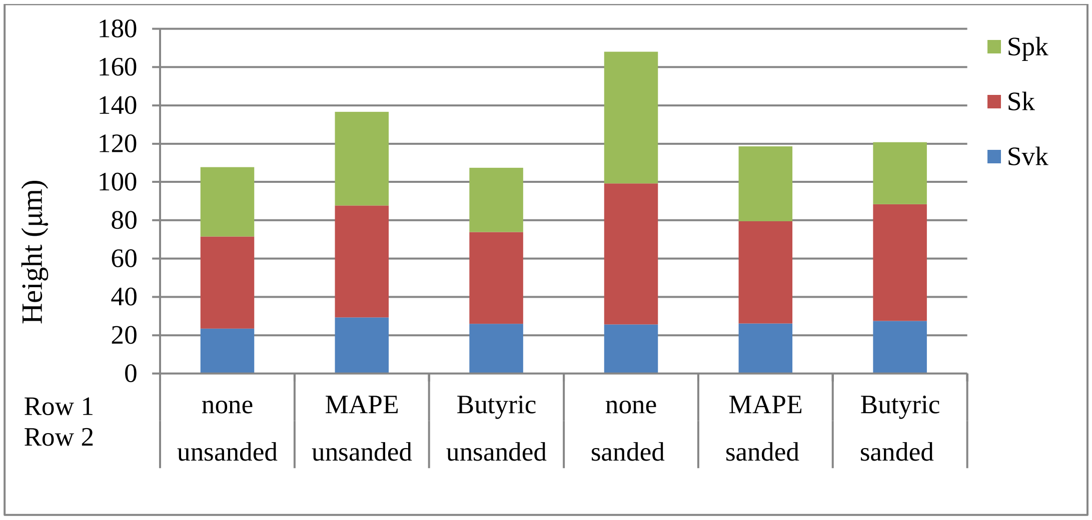


Diagram2. 3D functional parameters of surface roughness: (A) reduced valley depth (Svk), core roughness (Sk) and reduced peak height (Spk) (Row 1: chemical treatment, Row 2: mechanical treatment).

Developed interfacial area ratio (Sdr), which is known as an indicator for evaluating the percentage of additional surface area (Dai et al. 2016), confirmed that sanding partially increased the interfacial areas on wood veneer surfaces too (Diagram 3). As we observed in our research, MAPE treatment significantly decreased the Sdr from 3,41% to 2,98% for the sanded MAPE treated veneers.

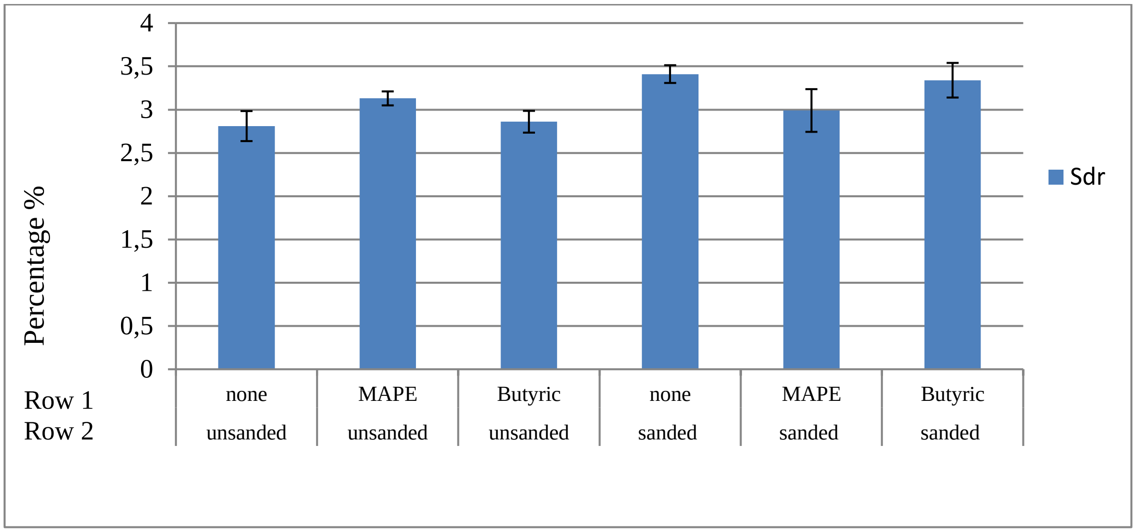


Diagram3. 3D functional parameters of developed interfacial area ratio (Sdr) (Row 1: chemical treatment, Row 2: mechanical treatment)

Based on current results, it can be assumed that surface roughness seemingly facilitated chemical penetration from the wood surface into its bulk. Therefore, the chemicals, which remained on surface, could better cover the wood surface and result in a smoother surface subsequently. On the contrary, in the unsanded samples, the chemicals mostly aggregated on the surface and caused an uneven surface after chemical treatments.

3D topographical images, obtained by a Laser-Scanning-Microscope (LSM-Keyence-VK-X100) revealed too, that the MAPE treatment formed a uniform, even surface on sanded veneers in comparison to the roughened surfaces of the sanded veneers (Figure17).

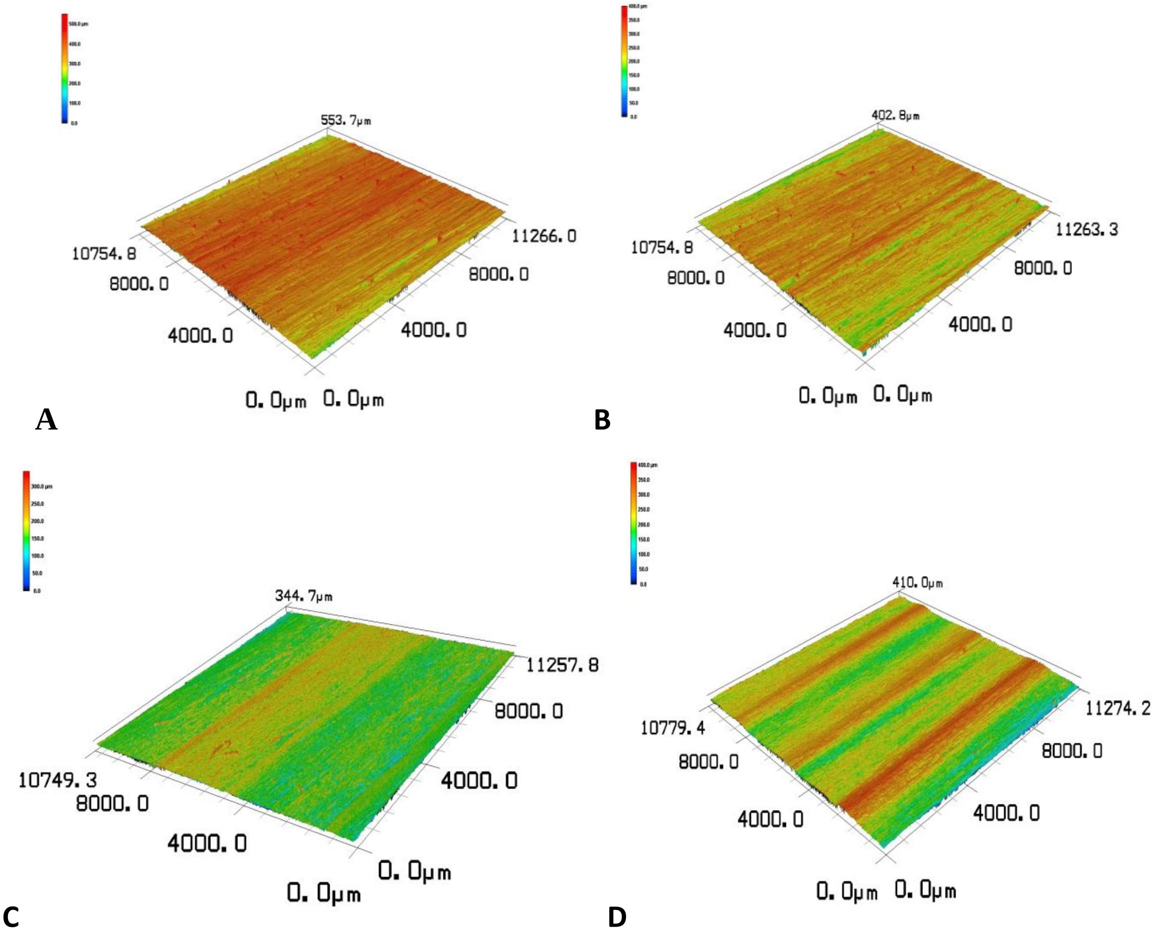


Fig17. 3D topographical images of wood veneers: (A) sanded, (B) sanded treated with MAPE, (C) unsanded, (D) unsanded treated with MAPE

Sa (arithmetical mean height) is considered another important functional parameter for characterization of a surface. This parameter is a roughness indicator, used to define the discrepancy in height of each point, compared to the arithmetical mean of the surface. Sa analysis also revealed this trend (diagram 4), as it was drastically increased after sanding, showing the increment of surface roughness by sanding. This value decreased once chemical treatment was performed on the sanded surfaces.

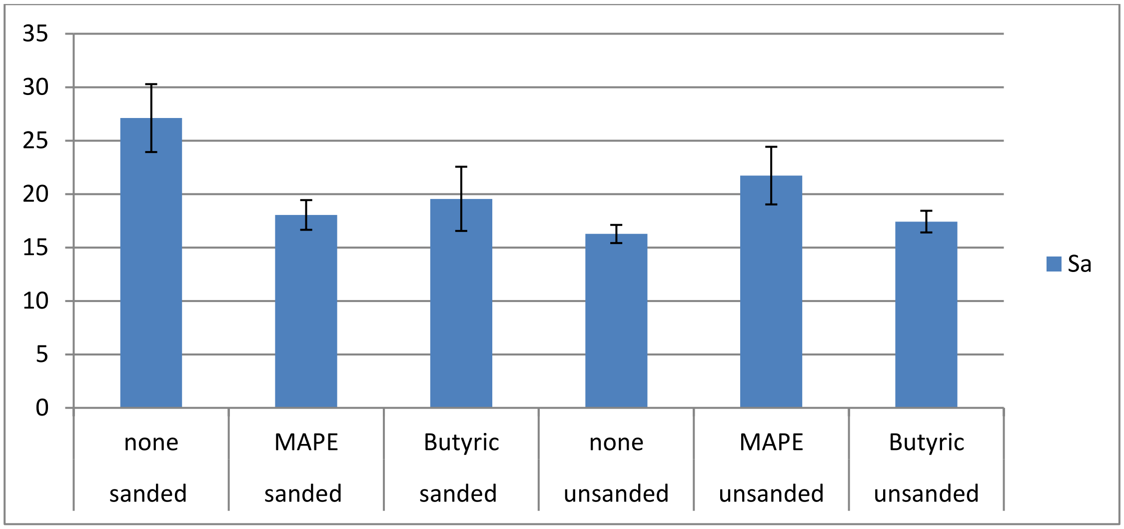


Diagram4. 3D functional parameter of Sa (arithmetical mean height)

3.2 Analysis of wood anatomy by scanning electron microscopy (SEM)

Scanning electron microscope images (SEM) over the cross-section of wood surfaces were conducted, in order to observe the effects of both sanding and chemical treatments. The wood cells were entirely filled with plastics after the chemical treatment with MAPE (figure 18a-c). SEM photographs of the longitudinal direction also showed the presence of MAPE on the surface of treated veneers, that was uniformly dispersed and which formed a fine layer on the wood surface (figure 18d-f).

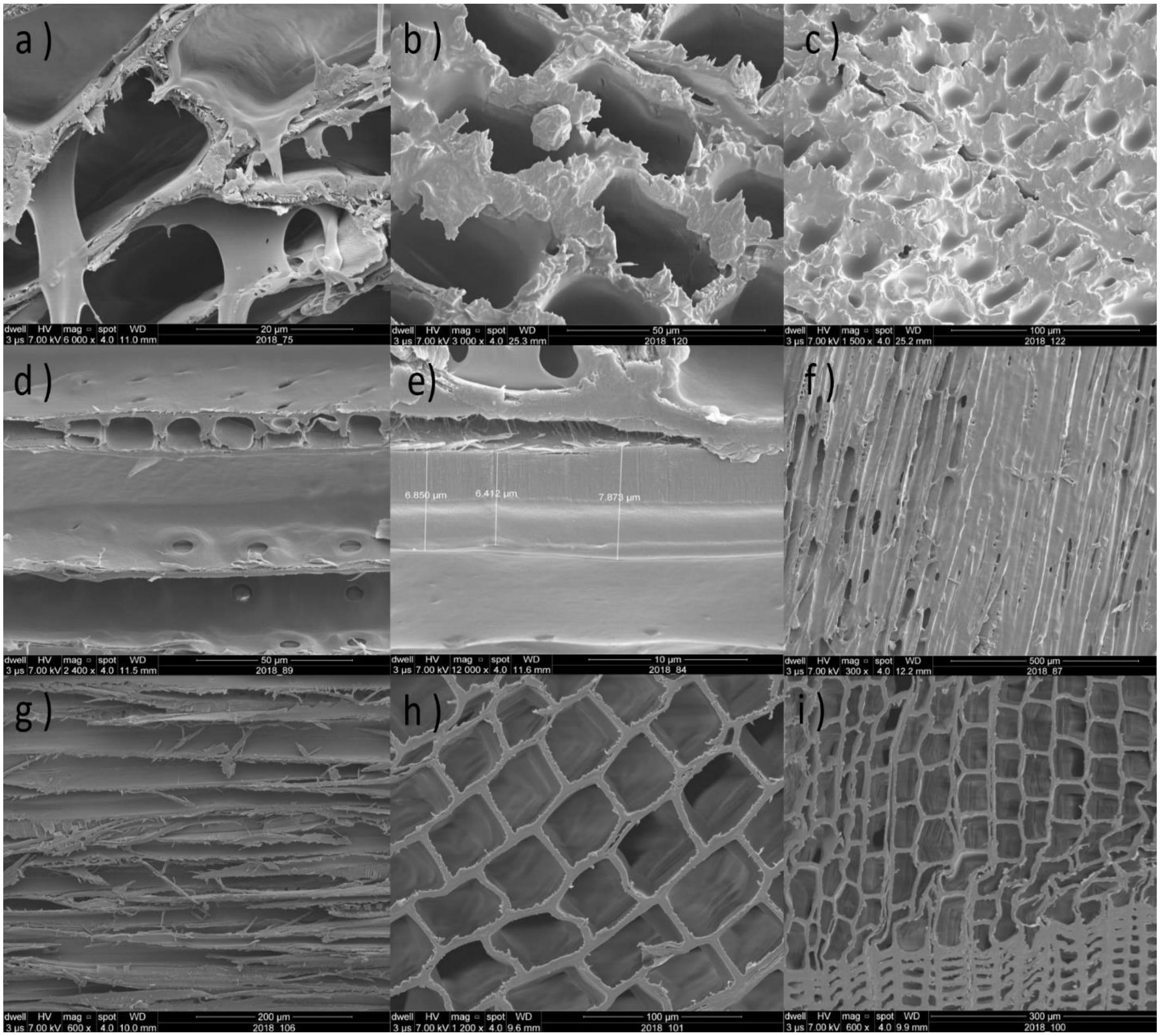


Fig18. SEM micrographs of treated veneers with MAPE (a-f) and non-treated veneers (g-i)

The surface of the treated veneers with butyric anhydride had already been damaged before any mechanical tests were performed on the samples (Figure 19). This too can be assumed a negative impact of the released acid by-products (in this case; butyric acid) whilst processing this chemical with the veneers at a high temperature, which may result in the degradation the wood structure itself (Risholm-Sundman et al. 1998).

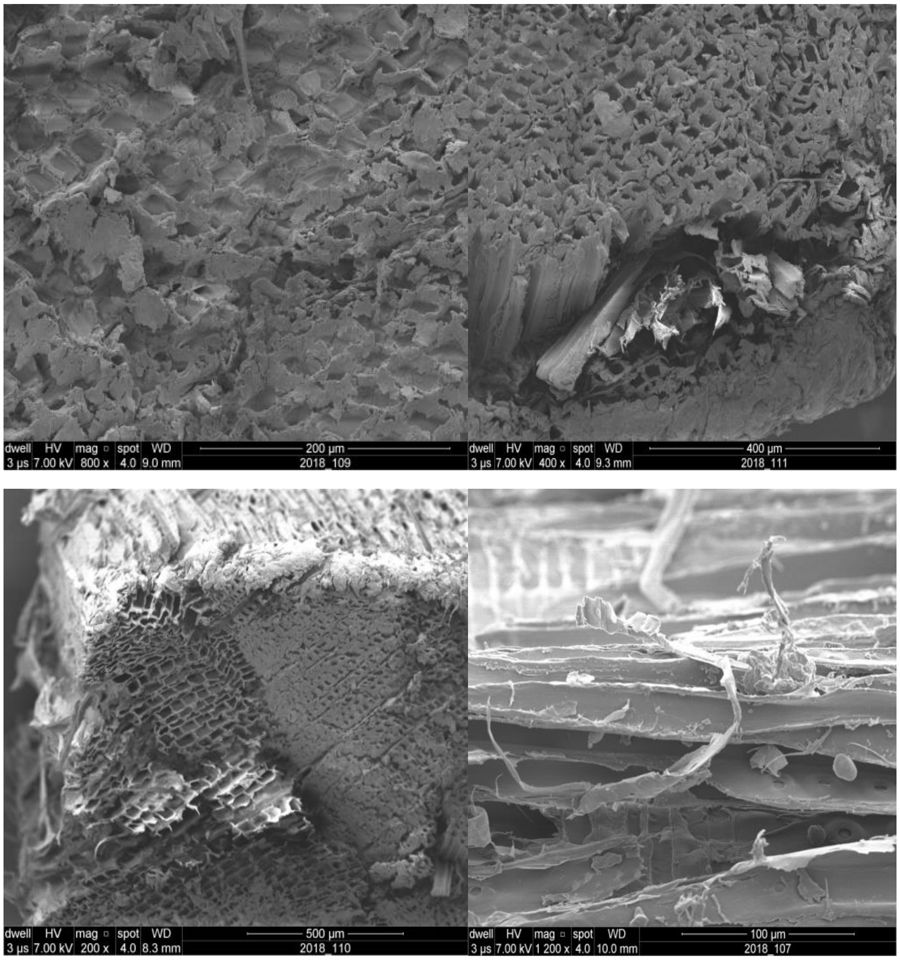


Fig19. SEM images obtained from cross-sections of treated veneers with Butyric anhydride

3.4 The interaction of sanding and chemical treatments on surface wetting

The results of contact angle measurements on the veneer surfaces are presented in table 7. All current data has been analysed using the Design of Experiment program (DOE), to investigate the effect of both mechanical and chemical treatments on the surface free energy components, obtained via the Acid-Base model. Both influencing factors were found to be highly significant ($p < 000.1$). The calculation of R^2 parameter also confirmed the above findings ($R^2= 0, 9924$, adjusted $R^2 = 0.9895$, predicted $R^2= 0.9837$).

sample		Contact Angle θ (degrees)				Surface free energy parameters (mN/m)				
Mechanical treatment	Chemical treatment	water	Ethylene glycol	Diiodomethane	Glycerol	σ_s	σ_s^{LW}	σ_s^{AB}	σ_s^{+}	σ_s^{-}
Unsanded	Non	75	18	15	64	53	49	4.5	4.1	1.22
Sanded	Non	86	29	25	70	47	46.15	1.31	1.31	0.33
Unsanded	MAPE	127	88	49	100	37	34.62	2.37	1.62	0.87
Sanded	MAPE	140	106	59	116	28	25.14	1.6	1.26	0.48
Unsanded	BA	118	50	17	102	50	48.06	2.01	5.34	0.19
Sanded	BA	90	28	16	84	49	49	0	0.79	0

Table7. Contact angles of different probe liquids on wood veneers and their surface free energies obtained by VOCG model

Both treatments noticeably decreased the surface free energy on the wood veneers. However, in terms of chemical treatment this reduction was highly remarkable, as the highest contact angles of test liquids and consequently lowest surface energies were obtained from samples chemically treated with MAPE (σ_s = 37 mN/m).

As a matter of fact, one of the main purposes of MAPE treatment is to reduce the hydrophilicity of wood, by replacing the hydroxyl groups of wood cells with the carboxylic groups of maleic anhydride, decreasing the surface energy of wood consequently (Biagiotti et al. 2004). In our current findings, the surface free energy of wood was also decreased by the addition of MAPE. This claim can be further verified by means of the surface tension component achieved from the Acid-Base Model (table 1). As can be seen, both the apolar σ_S^{LW} and polar σ_S^{AB} components of surface energy decreased after treatments, no matter whether the veneers were treated once or twice by MAPE and sanding simultaneously.

This reduction is more pronounced for $apolar\ part$ (σ_S^{LW}) specifically for samples treated with MAPE, where σ_S^{LW} decreased drastically from 49mN/m for non-treated veneers, to 37mN/m and 28mN/m for unsanded, MAPE-treated and sanded, MAPE-treated samples respectively. These differences demonstrated that MAPE had indeed, successfully covered the surface and decreased the surface energy after chemical treatment.

On the other hand, as with the previous findings described in section 4.1, it seems that roughening is once more quite compatible with chemical treatment. As it has not only reduced surface energy of veneers similarly to MAPE treatment but also helped MAPE to coat better on the wood surface, so too has the value of the developed interfacial area ratio (Sdr) been significantly decreased for sanded-MAPE treated samples (diagram 3).

This does imply that the sanded veneers, which already had more accessible areas on their surface (Sdr=3.41%), could more efficiently be covered by MAPE. As a result, sanded samples treated with MAPE showed the lowest surface energy = 28 mN/m) and smoothest surface subsequently (Spk=39.186μm). This is consistent with previous studies that had already confirmed the increase of surface area as the result of sanding and wetting improvement consequently (Ryan et al. 2008, Heydari et al. 2016)

3.4.1 Assessment of CA calculations by least square approach

To further evaluate the validity of the measured CAs on the wood surfaces as regards the testing liquids, the regressive approach of OWRK was employed to certify the significant coefficient between the effect of sanding and chemical treatments and, the obtained values of polar and disperse surface energy of the wood surfaces. According to formula 4 in the introduction, the surface energy of all 6 veneer categories was measured and recorded in Diagram 5. As was shown, the SFE values obtained by employing OWRK approach were almost the same as the Acid-Base method (Table7), which alone could be taken as proof of the accuracy of the measurements taken on the wood surfaces.

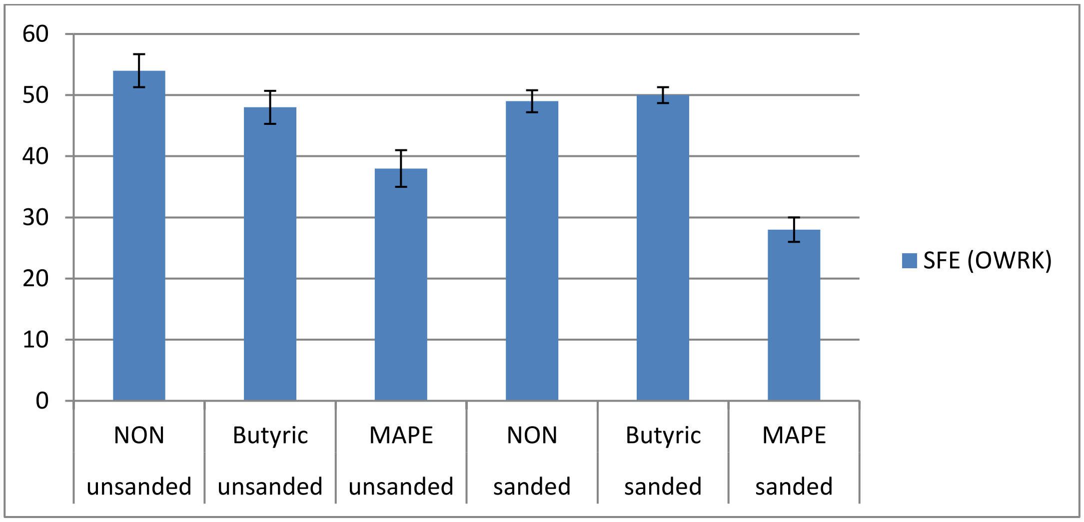


Diagram5. Surface Free energy values of wood veneers according to OWRK approach

The standard least squares approach as regards the veneers was entirely plotted according to the combinations of formulas 2 and 4 (chapter1) with the standard linear equation as follows:

$$y = mx + b$$

$$\frac{(1+\cos\theta)\sigma_l}{2\sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p}\sqrt{\frac{\sigma_l^p}{\sigma_l^d}} + \sqrt{\sigma_s^d} \qquad (1)$$

Where the slope $\left(\sqrt{\sigma_s^p}\right)$ and y-intercept $\left(\sqrt{\sigma_s^d}\right)$ are associated with the square roots of the polar and disperse components respectively, and thereby two unknown values of solid surface energy can be statistically analysed (Rabel 1971, Rossi et al. 2012). Figures 20 -22 show the final measured regression lines among the CAs of testing liquids on 6 veneer groups. As is shown, in almost all calculations, the average final values of R^2 are more than 0.80 including: non-treated veneers (R^2=0,96), sanded veneers (R^2=0,81), non-sanded MAPE treated veneers (R^2 =0,96) and sanded MAPE treated veneers (R^2=0,98). These results confirm once more that there is a significant correlation between veneers modification and the final surface energy of the wood surface accordingly.

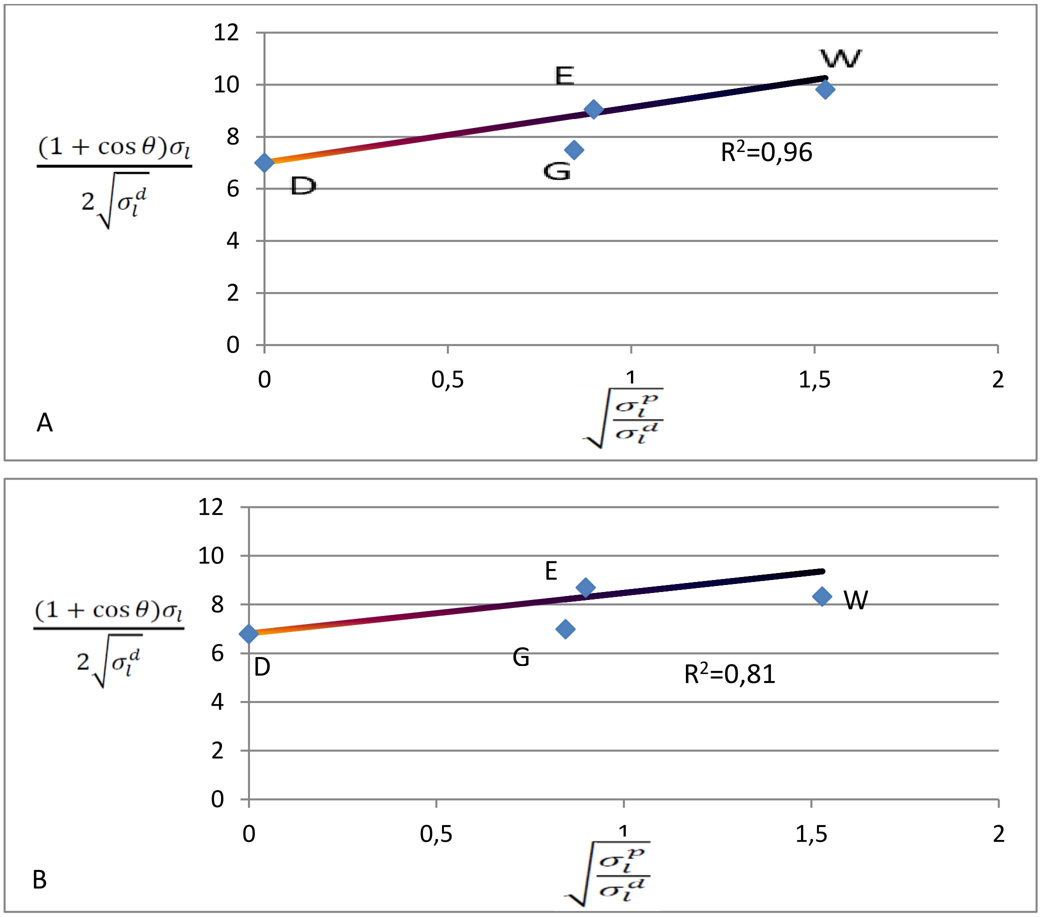


Fig20. OWRK plots of tested liquids (D: Diiodomethane, G: Glycerol, E: Ethylene glycol and W: Water) on A) non-sanded and B) sanded veneers

Analysis of the regression plots from the OWRK on the chemically treated veneers, revealed another interesting fact, which could be applicable for future studies aiming to characterize the physical properties of low surface energies by this method: in the case of almost all chemically treated veneers, the slope of best fit linear regression, which represents the polar property of a solid surface $\left(\sqrt{\sigma_s^p}\right)$, was negative (figure9).

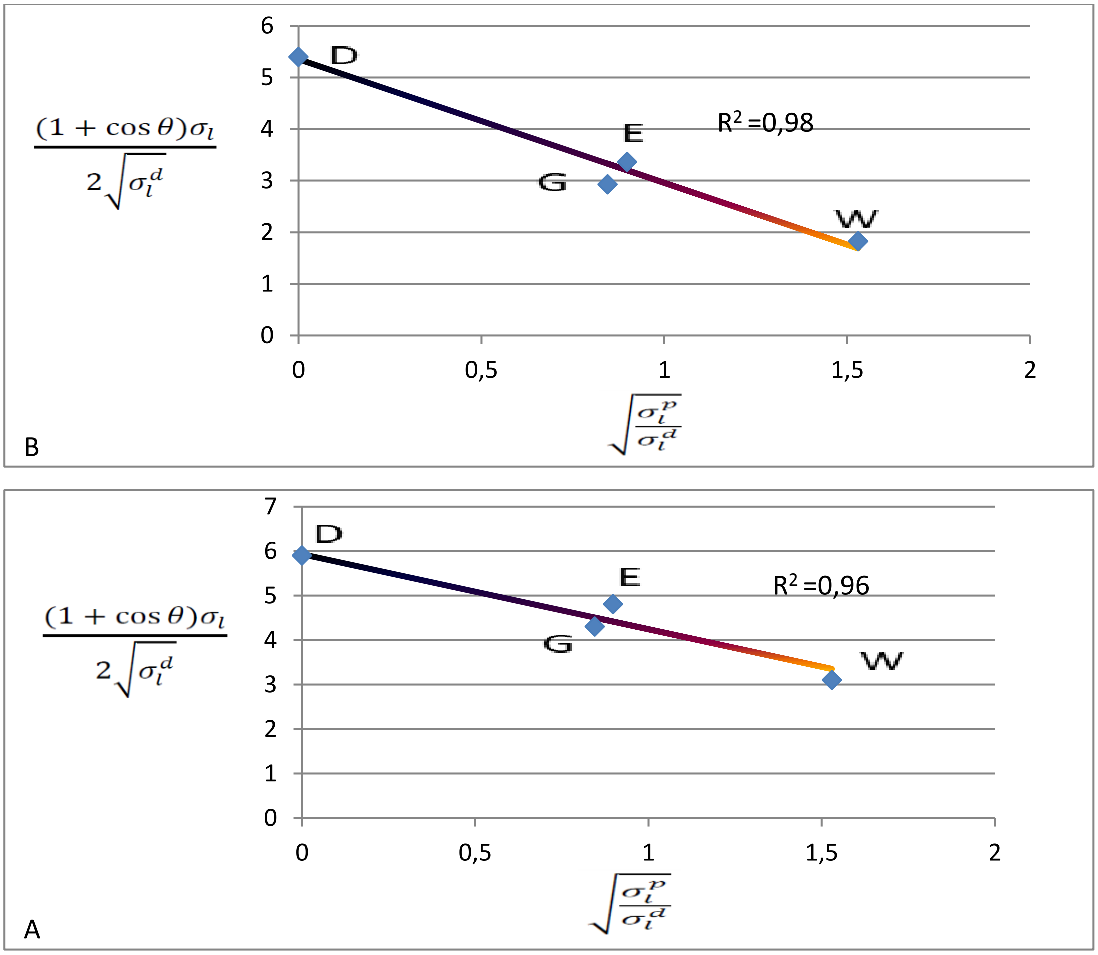


Fig21. OWRK plots of tested liquids (D: Diiodomethane, G: Glycerol, E: Ethylene glycol and W: Water) on A) non-sanded MAPE treated and B) sanded MAPE treated veneers

Figure 22 plotted the CAs measurements on the wood surfaces treated with butyric anhydride. As demonstrated, the values of R^2 showed its lowest level compared to the other types of tested veneers in this experiment, showing a high fluctuation among the morphological properties of veneers treated with this chemical. Such a big uncertainty was more tangible in the terms of the sanded butyric treated veneers, where the slope of polar components changed to a positive trend, showing no specific influence by this chemical on the wood surfaces. This is in accordance with the previous calculations of surface free energy (SFE) on this group of veneers (Table 7) in which butyric treatment caused no comprehensive change on the SFEs values of veneers in comparison to non-treated samples.

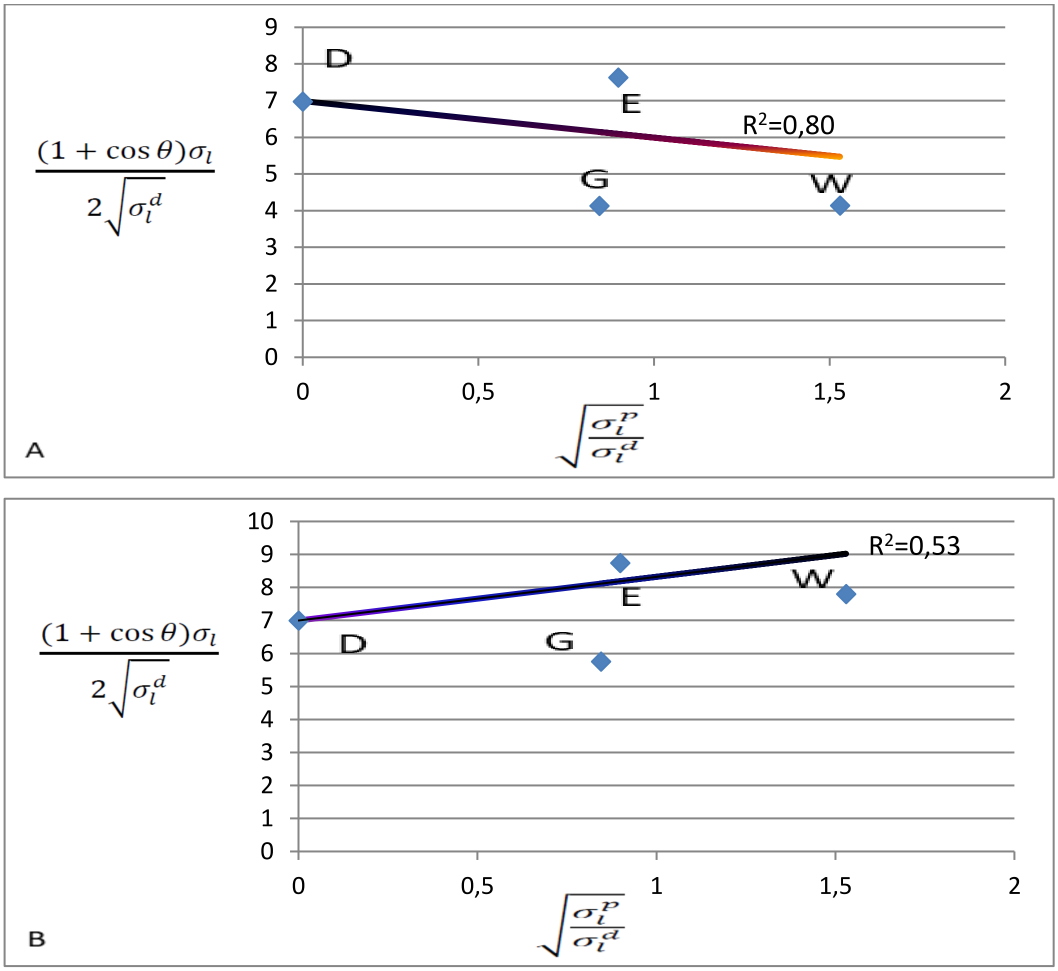


Fig22. OWRK plots of tested liquids (D: Diiodomethane, G: Glycerol, E: Ethylene glycol and W: Water) on A) non-sanded butyric treated and B) sanded butyric treated veneers

Unlike MAPE treatment, the impact of BA treatment on solid surface energy was negligible. Figure 23 shows the result of a comparison between all treatments according to statistical analysis software (DOE). It is obvious that BA treatment had no significant influence on the surface free energies of unsanded and sanded veneers. Veneers, which had merely been sanded, had a partially lower surface energy (47 mN/m) than veneers sanded and treated with BA (49 mN/m).

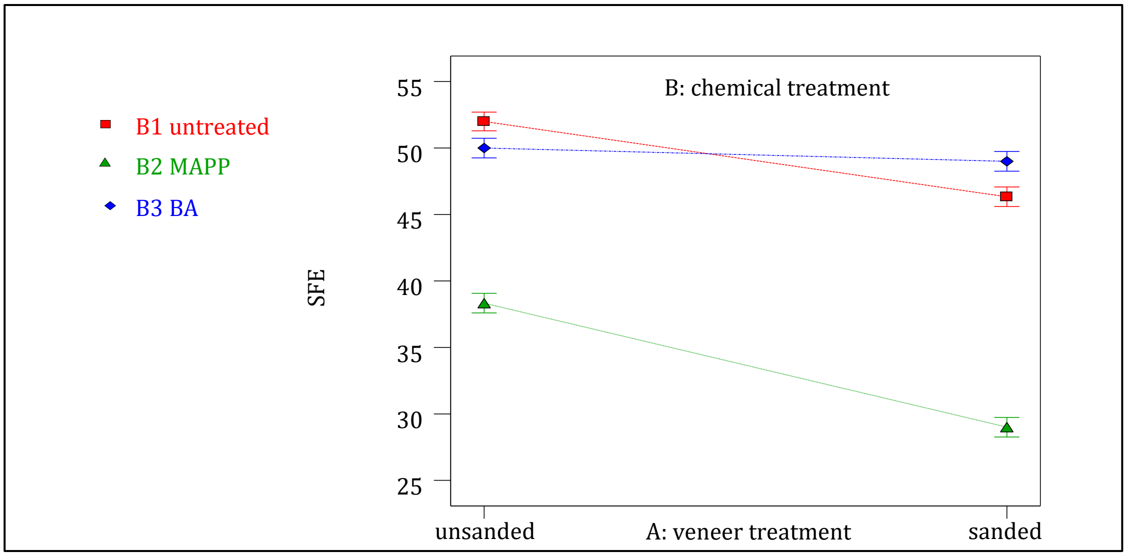


Fig23. Interaction of sanding and chemical treatments on wood surface energy by DOE program

Such a clear distinction between the performances of each chemical treatment on the wood surface, can only be detected in the function and nature of applied chemicals. Butyric anhydride belongs to the linear anhydride family and, like most members of the Acetic anhydride family, is usually applied to increase the dimensional stability of wood, by substitution of the hydroxyl groups in the wood cells with the carboxylic groups of anhydrides (figure24) (hill 2007). However, in reality, the majority of reactive OH sites are located inside the wood structure (Papadopoulos et al. 2002).

This specifically, can be considered as a serious obstacle for longer chain anhydrides with a higher molecular weight than butyric anhydride ($C_8H_{14}O_3$), which according to previous scientific findings, are potentially less reactive with wood than shorter chain anhydrides (Hill and Jonathan 1999).

Over the past decade, scientists have attempted to get over this problem by using catalysts, so that longer chains of anhydride could break down and better react with wood. Papadopoulas and Hill (2002) used pyridine as a catalyst to solute butyric and propionic anhydrides in wood. On the contrary, Li et al. (2000) hinted at avoiding catalysts, which are harmful to the wood structure and wood treated with Acetic, butyric and propionic anhydrides without the presence of catalyst. This concept was further supported by Chang et al. (2002), who could achieve a 16% WPG (weight percent gain) in wood after butyric treatment without reactors.

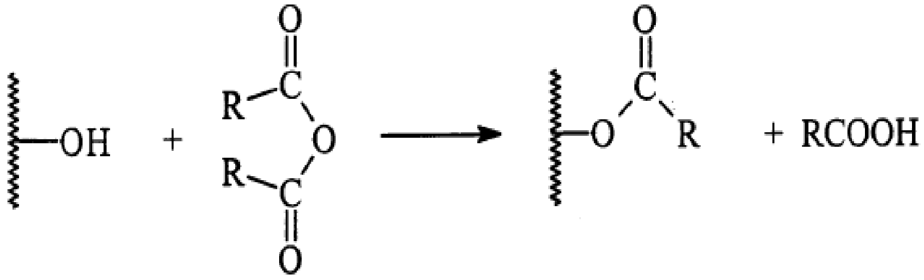


Fig24. Anhydride modification scheme on wood surface, where R=CH_3 (acetic anhydride), R = C_3H_7 (butyric anhydride)

In this study with respect to the environmental aspect, butyric treatment was also carried out without the use of hazardous chemicals. Although the chemical process seemed completely successful after the treatment (WPG of 17 %), our continuous observation later showed that the butyric started to evaporate after a period at room temperature, some of treated samples losing up to 7% of their weight. Therefore, our current findings could also be evidence supporting the first procedure, in which using a catalyst is a necessity when long chain anhydrides are to be used for chemical treatments on the wood surface.

3.4.2 Dynamic contact angle measurements by hot melting plastic

Table 8 exhibited the results of both advancingθ_A and receding θ_R contact angles obtained by dispensing hot melting plastic droplets on the wood veneer surfaces. Regardless of veneer types, PLA showed the lowest contact angle in comparison to the other adhesive droplets used (CAH°~ 57). This is consistent with Duncan et al. (2005), who claimed that the wetting behavior of hot melt adhesives is more influenced by their visco-elastic properties than surface tension. At higher temperatures, the molecular interactions become weaker and weaker compared with the kinetic energy of molecular motion, which results in reduction of liquid surface tension (Bormashenko and Edward 2018).

Mechanical Treatment	Chemical Treatment	Adhesive	Advancing contact angle (θ_A)	Receding contact angle (θ_R)	CAH°
Non-sanded	untreated	PLA	103	45	58
Non-sanded	MAPE treated	PLA	98	41	57
Non-sanded	Butyric treated	PLA	107	52	55
sanded	untreated	PLA	94	37	57
sanded	MAPE treated	PLA	96	39	57
sanded	Butyric treated	PLA	105	49	56
Non-sanded	untreated	HDMAPE	116	88	28
Non-sanded	MAPE treated	HDMAPE	107	78	29
Non-sanded	Butyric treated	HDMAPE	114	88	26
sanded	untreated	HDMAPE	110	81	29
sanded	MAPE treated	HDMAPE	103	72	31
sanded	Butyric treated	HDMAPE	117	90	27
Non-sanded	untreated	HDPE	120	94	26
Non-sanded	MAPE treated	HDPE	110	87	23
Non-sanded	Butyric treated	HDPE	118	90	28
sanded	untreated	HDPE	116	89	27
sanded	MAPE treated	HDPE	100	82	18
sanded	Butyric treated	HDPE	117	91	26

Table 8. Advancing θ_A and receding θ_R contact angles on veneer surfaces using hot melted plastics

Unlike crystalline plastics, which resist against shearing by stretching their crystal structure, PLA consists of more viscous properties than elastic features due to its amorphous structure and, when a shear force is applied to the PLA droplet, its static resistance is lower than other adhesives. This does lead to stronger shear thinning behavior in the polymer, in which plastic viscosity is drastically decreased while the shear rate is increased (Awal et al. 2015, Fried 2014). As the result, the PLA could stick to the wood surface easier than other polymers.

In terms of veneer treatments, sanding also decreased the plastics' receding contact angles) on the wood surface. This phenomenon was already expected since, according to previous studies, surface roughness would normally result in the pinning phenomenon that contributes to polymer droplets being able to easily adhere to the surface (Eral and Oh 2013, Yasuda et al. 1981). As a consequence, the $\theta_R$value, which represents the surface adhesion, is significantly decreased, suggesting a stronger adhesion interaction between wood and polymer droplets (Law et al. 2016).

With regards to the chemical treatment, MAPE treated veneers once again showed better wettability when HDPE and HDMAPE plastics were deposited on the wood surfaces, as the discrepancy between θ_A and θ_R had a notable reduction in comparison to non-treated veneers. These results are in accordance with lam et al. (2002), who reported in their comprehensive research that, using homologous liquids on a hydrophobic surface results in the reduction of the hysteresis phenomenon (CAH°) and a slight increment of sorption between the liquid droplet and the solid surface subsequently (Lam et al. 2012).

In terms of chemical treatments with butyric anhydride (BA), there was also no significant change in the CA values of the different plastic types on the wood surfaces compared to the other veneer categories. However, this may not only be associated with the visco-elastic properties of the used plastics (independent from veneers kinds), but also the ineffectiveness of this chemical in regards to reacting with wood cells for chemical modification.

Whether the final results of the hot dosing unit are satisfactory or not, this approach, like other surface characterization methods, gives us a general overview of plastic penetration into the axial direction of the wood surface. In other words, to achieve a true image of the plastic penetration pattern on the wood surface, applying a quantitative technique that can exactly clarify the depth of plastic penetration from the wood surface into bulk is quite necessary. Therefore, in the following step, attempts were made to determine the depth of penetration for dynamic plastic droplets on the wood surface using the quantitative measurement approach.

3.4.3 Determination of plastic penetration to the wood bulk by hot melting plastic droplet

In almost all previous studies, measuring the contact angles on the wood surface led mostly to differing results. This does automatically create a sense of uncertainty regarding the integrity of the methods employed for calculations; whereas such variations actually originally derived from the complex nature of the wood structure itself. Unlike most solid surfaces that have usually a fine surface, wood has inherent porosity on its surface, which causes capillary penetration into its structure.

Furthermore, the inherent roughness of the wood surface gives rise to the spreading of liquid in a direction perpendicular to the wood cells rather than parallel (Meijer 2004). The effect of surface roughness of wood on liquid dispersion has been already explained (Section 3.2).

In this experiment, the depth of plastic penetration from the wood surface to its bulk was characterized by measuring the height of capillary rise in the longitudinal tracheids of solid wood. For this purpose, solid spruce was cut in longitudinal, radial and tangential directions, so that the effect of wood cutting on plastic penetration could be evaluated at the same time. The average sample dimensions were 29 x 16 x 3 mm^3.

Based on the plastic viscosity values that were already measured by rheometer in chapter 2, two kinds of PLA and HDPE plastics were once more deposited by the hot dosing unit onto the wood surface at a constant viscosity. After the plastic droplets were cooled to room temperatures, the interfacial bonding areas between the wood and plastic droplets were detected by a Keyence VHX-6000 digital microscope. To diagnose the penetrated plastic phase from the wood cells, polar filters were applied to the light beam of the microscope.

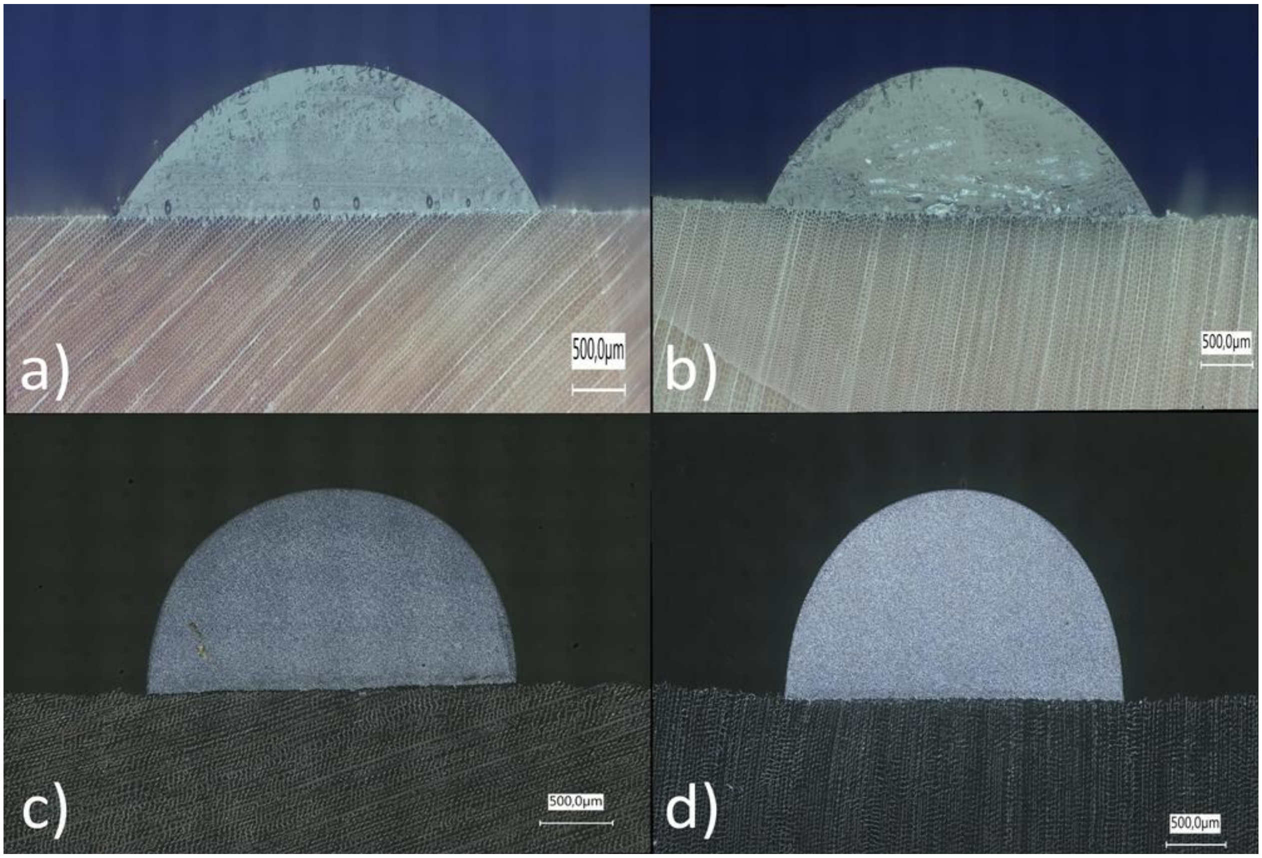


Fig25. VHX-6000 digital microscopic images of a-b) PLA and c-d) HDPE droplet on radial and tangential sections of massive spruce surface

The results revealed that almost for both plastic types, when deposited on the radial or tangential sections of the spruce, showed no comprehensive plastic penetration able to be detected by microscope observation (Figure 25). This was expected since in these directions, only the ray parenchymes and the ray tracheids are close to the surface, which may cause the penetration of the high-viscous plastics into the wood cells; longitudinal tracheids, visible from the cross-section view, are actually closed canals over the radial and tangential directions that need the presence of ray tracheids and the pits there between to make flow penetration possible (Flynn 2007). Therefore, it was almost impossible to view the plastics' penetration from the transverse direction. On the contrary, when the plastics were deposited on the cross-sections and the samples examined under a light microscope from the radial and/or tangential directions, the penetration of the plastics in the wood cells was quite apparent (figure 26). These results are consistent with Meijer et al. (2001) and Meijer (2004), who reported the coating penetration of fluids through the ray tracheids in spruce.

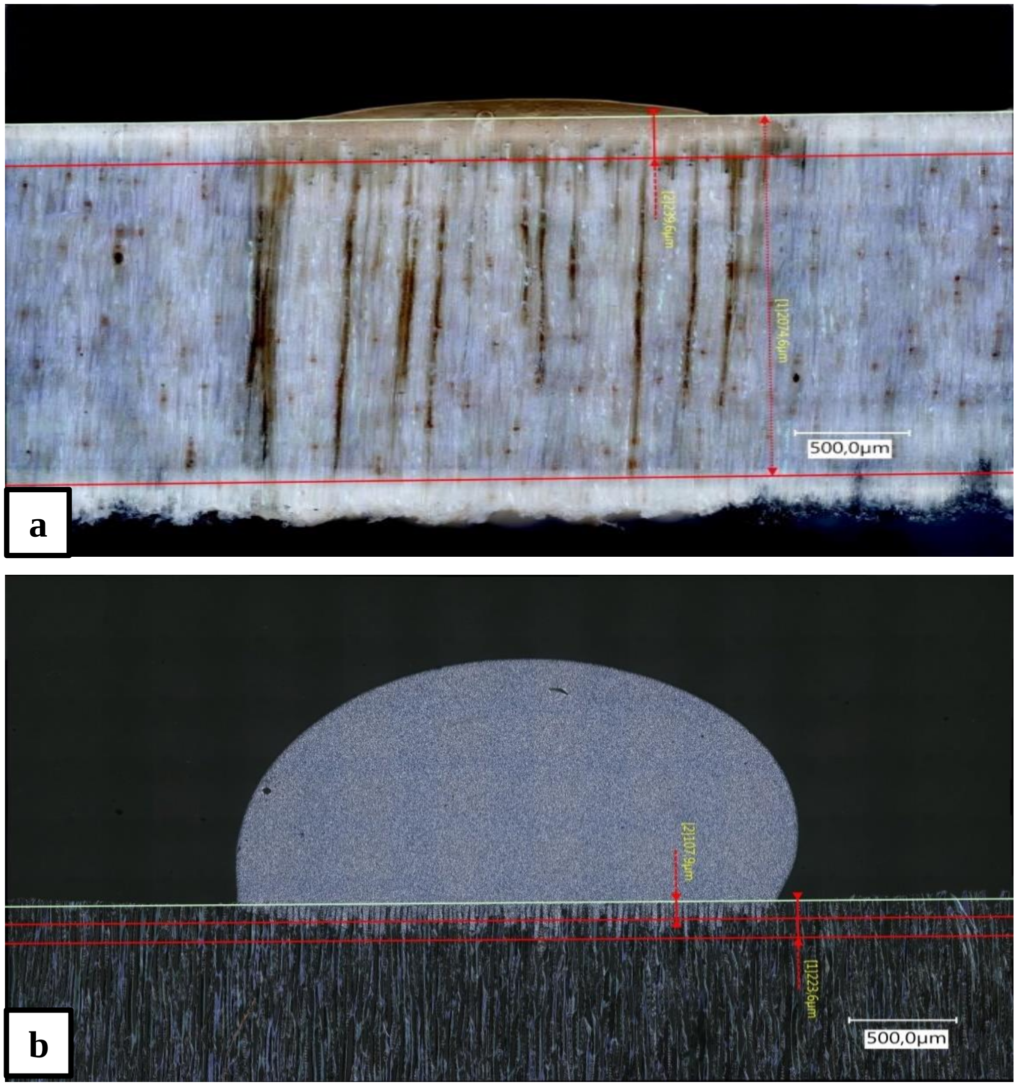


Fig26. VHX-6000 digital microscopic images of PLA (a) and HDPE (b) droplets on the cross sections of spruce veneers

Our microscopic observations on the wood-plastic interface after detaching the plastic droplets from the wood surface also revealed that in comparison to HDPE, PLA more uniformly wet the entire interfacial area over the cross sections of both early and late woods (figure 27). Nevertheless, there were still some wood cells on the interfacial areas that remained unfilled after being coated by both plastics. Instead, microscopic images exhibited that some other wood cells that were far away from the interfacial bonding area between wood and plastics were also filled with the plastics.

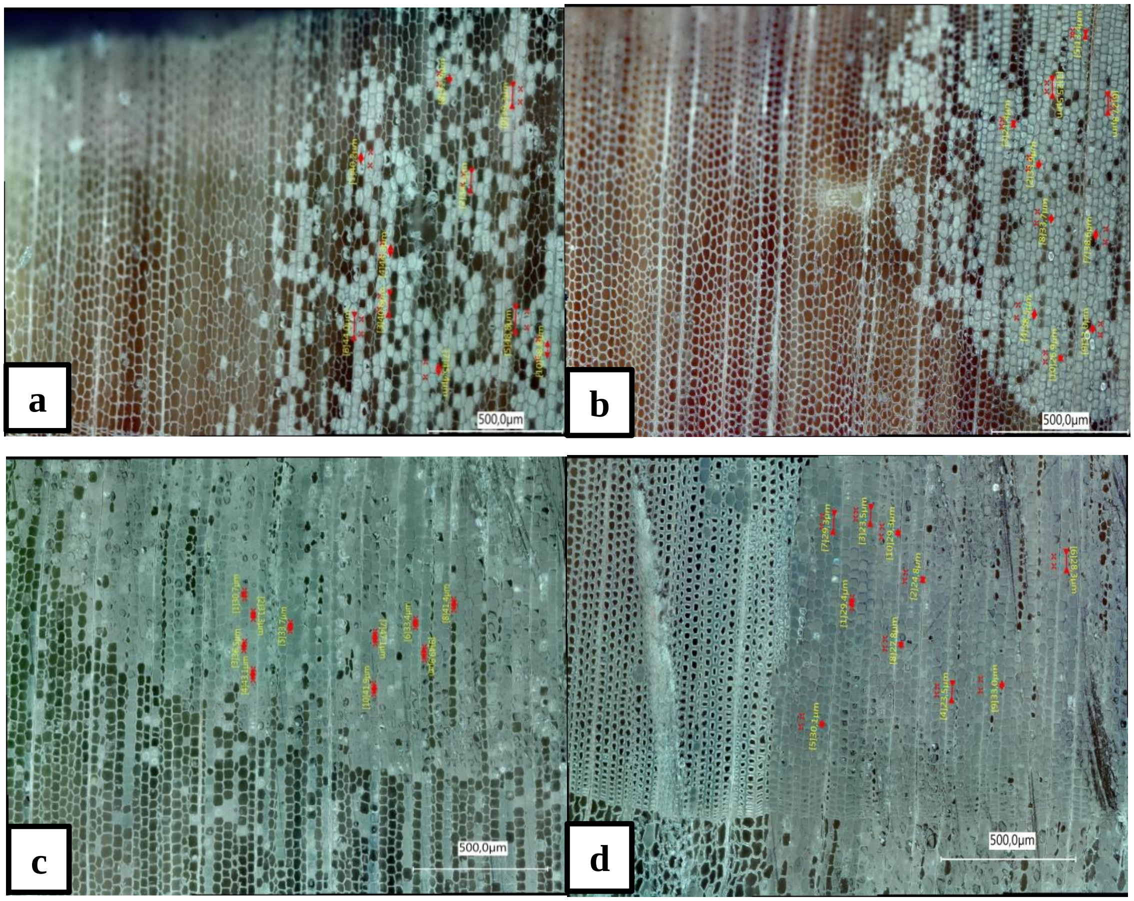


Fig27. Interfacial bonding are between HDPE (a-b), PLA (c-d) and earlywood (a,c), latewood (b,d) of spruce veneers over cross-sections

This can be also associated with the roles of the ray tracheid on the tangential/radial directions of spruce that transfer the fluids horizontally by means of bordered pits between adjacent cells.

As is shown in figure 26, we subsequently observed two different patterns of penetrations depending on the plastic type. In comparision to HDPE, PLA could penetrate into the wood cells more thoroughly. The calculation of the height of capillary rise by Washburn´s equation (equation 6: chapter 2), resulted in values similar to those measured by the scalar function of a digital microscope, confirming a significant difference between the depths of penetration for the two plastics under constant viscosity (table 9).

Plastic Type	Length of penetration (μm) (VHX600-Keyence)	Length of penetration (μm) (Washburn´s Equation)	Advancing Contact Angle (θ_A°)	Receding Contact Angle (θ_R°)	Testing Temperature (°C)	Viscosity (Pa.s)	Surface tension ($\frac{mN}{m}$)
HDPE	107	93	127	101	158	732	30
PLA	191	239	103	45	200	732	36

Table9. The length of plastics penetration on the cross-section of massive spruce at constant viscosity

From these results, it can be assumed that there is no tangible difference between testing the samples under constant temperature and constant viscosity. As is listed in table 3, although both plastics were tested using the same viscosity value, the length of penetrations showed a significant change independent from this property.

One can also deduce, that other features of plastics including molecular weight and molecular structure may play a key role for polymer penetration in wood rather than viscosity itself. Furthermore, according to Teuber et al. (2016), since the viscosity of plastic is considered a non-newton fluid, it is mainly influenced by its shear-thinning behavior and will never stay constant.

Thus, when confronted with the wood interphase, its viscosity may also be reduced consequently. Contrarily, unlike the general conclusions, which opine that lower surface tensions of liquids at higher temperatures contribute to the better wettability of said fluids, our observation showed that lower values of the receding contact angle) were not directly influenced by this parameter, as PLAwith rather higher values of surface tension (36 mN/m) than HDPE (30 mN/m) in the same viscosity value, had significantly lower contact angles than HDPE on the wood surfaces.

The reason for this can be detected in the hydrophilic nature of PLA, that on the one hand may contribute to the increase of its surface tension due to the mobility among its polar components and, on the other hand facilitates the penetration of this polymer into the wood cells, due to the affinity of this polar plastic to react with hydrophilic fillers like wood (Kühnert et al. 2017).

Another influencing factor is the molecular structure of plastic itself. PE has the high crystalline structure, that lowers the penetration rate or even inhibits this plastic from forming a physio-mechanical interaction with the wood interphase compared to amorphous PLA, due to the high mobility among the crystalline molecules of PE and its resistance against shearing by stretching of their crystalline framework (McKeen et al. 2014). Therefore, to our understanding, the factors known as molecular structure and molecular weight determine the final penetration pattern of plastics to the wood bulk.

3.5 Effect of constant viscosity and temperature on IFSS

Table 10 shows the average of interfacial shear strengths (IFSS) between the wood and plastic interphases which were tested by ABES: once under isothermal condition and once using a constant viscosity. As can be seen, regardless of polymer type, choosing a higher pressing temperature resulted in a slightly better IFSS at the wood-polymer interface than testing the plastics at their constant viscosity values. This can be attributed to the fact that, at lower temperature, the melt viscosity of polymers is still high and plastic films can not be well dispersed on wood surfaces (Takase et al. 1989). A high hot-pressing temperature could have a positive impact on the penetration of the polymers into the wood and make the veneer surfaces well encapsulated with plastic (Song et al. 2016).

Veneer types		Polymer Type	Average Interfacial Shear Strength N/mm2 (Std. Dev.)	
Mechanical treatment	Chemical treatment		Constant Temperature(°C)	Constant Viscosity (η0)
Unsanded	Non	PLA	7.14 (0.3)	7.06 (0.33)
Sanded	Non	PLA	8.19 (0.44)	8.1 (0.47)
Unsanded	MAPE	PLA	7.61 (0.37)	7.57 (0.42)
Sanded	MAPE	PLA	7.22 (0.45)	7.2 (0.52)
Unsanded	BA	PLA	6.75 (0.5)	6.69(0.56)
Sanded	BA	PLA	6.4 (0.69)	6.61 (0.63)
Unsanded	Non	HDPE	2.82 (0.29)	2.43 (0.46)
Sanded	Non	HDPE	3.51 (0.43)	3.28 (0.48)
Unsanded	MAPE	HDPE	7.62 (0.54)	7.52 (0.41)
Sanded	MAPE	HDPE	8.53 (0.47)	7.81 (0.46)
Unsanded	BA	HDPE	2.66 (0.19)	2.48 (0.18)
Sanded	BA	HDPE	3.07 (0.22)	3.54 (0.58)
Unsanded	Non	HDMAPE	4.25 (0.31)	3.38 (0.37)
Sanded	Non	HDMAPE	4.63 (0.42)	3.75 (0.44)
Unsanded	MAPE	HDMAPE	8.51 (0.43)	7.60 (0.43)
Sanded	MAPE	HDMAPE	8.23 (0.52)	7.17 (0.36)
Unsanded	BA	HDMAPE	4.38 (0.31)	4.12 (0.26)
Sanded	BA	HDMAPE	4.18 (0.46)	3.30 (0.4)

Table10. Average shear strength of wood-polymer interfaces once in constant temperature and once in constant viscosity value

This phenomenon was more pronounced when PLA was applied between the veneers, as it could not be further detected by the naked eye after shear testing (figure 28a). This could be related to the differing nature of this plastic compared to PE. Unlike crystalline PE which has a lower rate of penetration due to its higher crystallinity, PLA has an amorphous structure and can rapidly penetrate into the bulk due to both its lower molecular weights and lower melt viscosity at higher temperatures (McKeen et al. 2014, Yuan et al. 2008, Luedtke et al. 2019). This is why both the HDPE and HDMAPE adhesives could easily be distinguished from the wood surface by the naked eye (figure 28b and 28c).

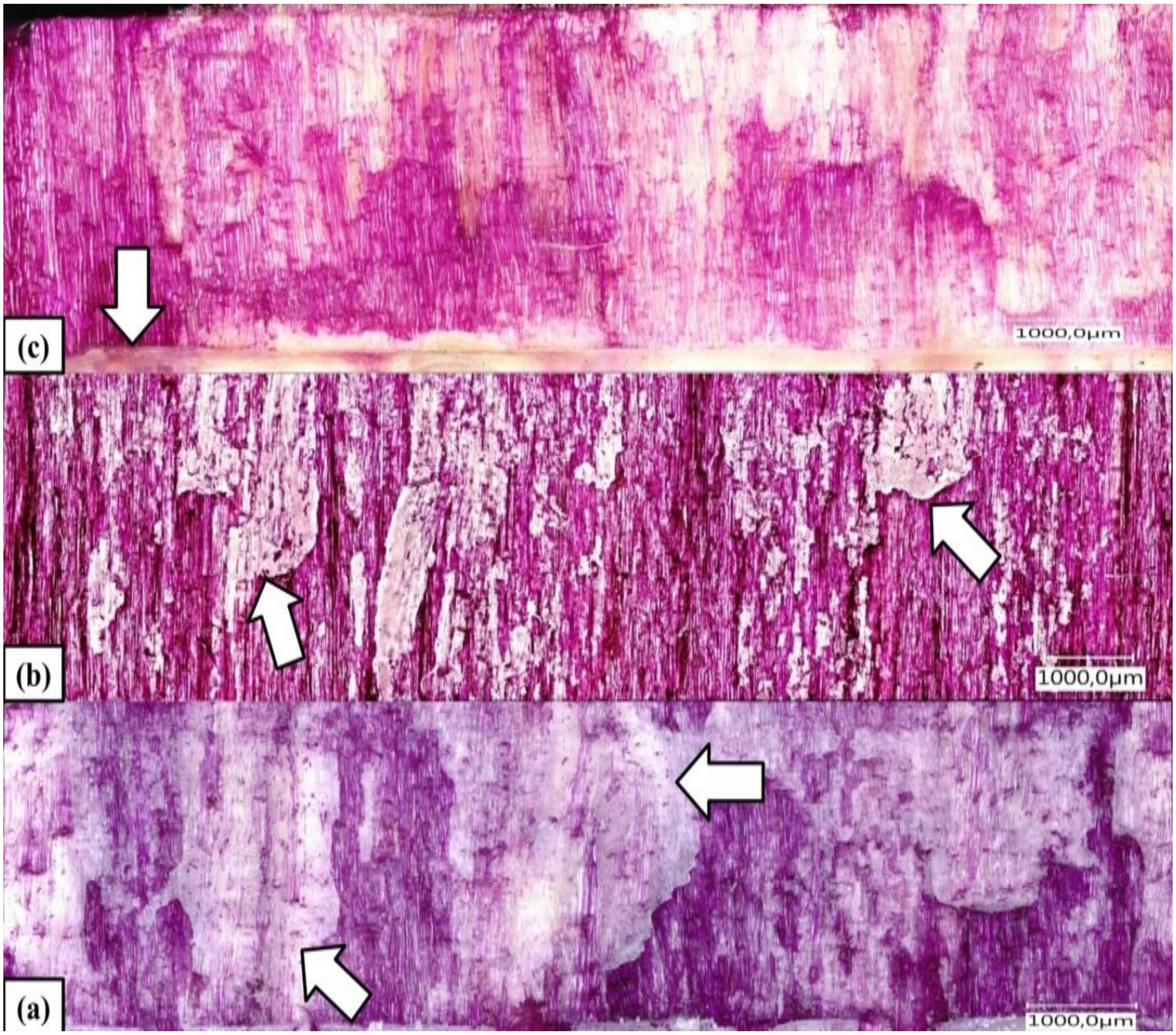


Fig28. Veneer bonding areas with, (a) HDPE and (b) HDMAPE and (c) PLA plastics after ABES testing (plastic remains were remarked by arrows

3.5.1 Interactions of polymer types and wood treatments on IFSS

To find out whether mechanical and chemical treatments had any comprehensive influence on IFSS as the different polymers were embedded into the bonding area, all the shown values in table 10 were further analyzed by Design of Experiment program (DOE). Both treatments were found to be highly significant ($p < 000.1$). The calculation of the R2 parameter also confirmed the current finding (R^2= 0, 9970, adjusted R^2 = 0.9932, predicted R^2= 0.9852). Figure 29 indicates the interaction between chemical and mechanical treatments on the shear forces at the wood-polymer interface. As is demonstrated, among the applied polymers, PLA had the highest shear force for both the untreated sanded and non-sanded veneers.

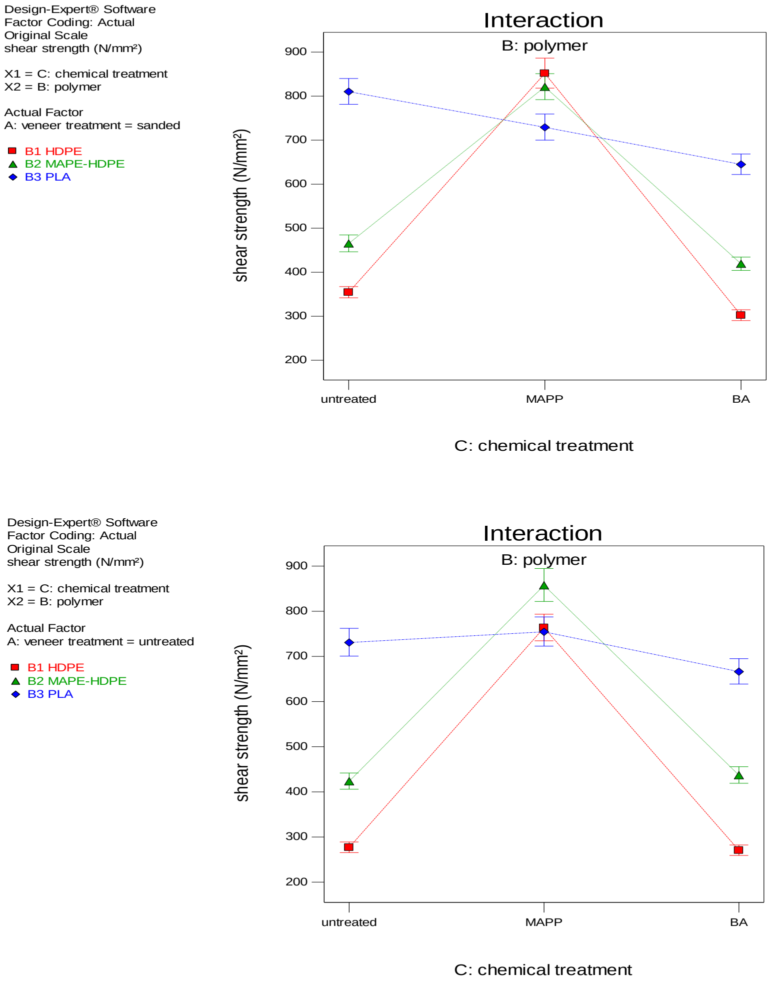


Fig29. DOE analysis of interaction between chemical and veneers treatment on IFSS

This could be explained by the hydrophilic characteristic of PLA, wherein lactic acids with an equimolar concentration of hydroxyl and carboxyl-end groups join to form a polymer (Garlotta 2001). This would intrinsically improve the interfacial bonding between the polar sides of a matrix and the hydroxyl groups of cellulose on the wood surface and, make plastic more compatible with wood veneers in comparison to other plastics (Takatani et al. 2008, Mihai et al. 2014).

On the contrary, chemically treating with MAPE only significantly increased IFSS when the hydrophobic plastics were applied as adhesives. This order of change was more tangible in terms of the veneers, which were sanded before MAPE treatments and, on which testing with both HDMAPE and HDPE adhesives resulted in much higher IFSS values than PLA. Such a clear-cut distinction between the test results could be evidence for the interference of more than one factor, which acted simultaneously to form the interfacial bonding at wood-polymer interface.

First and foremost, the inherent mechanism of MAPE treatment should be of main importance, in which esterification causes the reduction of the polarity and hydrophilic nature of wood fibers and thereby improves interfacial adhesion between wood and polymer matrix interphases (Chen et al. 2013, Cavdar et al. 2014).

Furthermore, pre-coating of the wood surface by polymer will increase the compatibility of the wood fibers and matrix, since coupling agents facilitate optimum stress transfer at the wood-polymer interface (George et al. 2001). Nevertheless, it is believed that pre-sanding forms a fresh surface, which contributes to the glue bonding of wood fibers and gives rise to the strong shear strength at the interface (Aydin 2004, Hiziroglu et al. 2014).

In our current study, sanded veneers treated with MAPE also showed the highest shear strength (8.53N/mm^2), which does certify the effectiveness of both treatments on plywood interfacial bonding. This concurs with the general belief that sanding can increase the adhesion properties of wood by increasing surface roughness, in which a brush-like grafting on the fibers is formed that helps interlocking and entanglements between the fibers and the polymer matrix (George et al. 2001, Sulaiman et al. 2009).

However, in terms of PLA adhesive, the combination of sanding and chemical treatment was not successful. This may be as a result of the hydrophilic nature of this polymer in reaction with the hydrophobized wood surface, creating an incompatibility between the wood adherent and plastic adhesive as a result.

Aside from that, PLA poses a lower molecular weight than other plastics and increasing the temperature could intensify this feature of the plastic (Garlotta 2001, George et al. 2001). Therefore, when the wood surface was already blocked by hydrophobic plastic, some amounts of PLA could easily seep out of the glue line and cause a lack of adhesives between two veneers, thereby lowering shear strength subsequently (Fig 28a).

In terms of chemically treating with butyric anhydride, not only was there no significant increment of ISS at the wood polymer bonding area, a substantial negative impact on this parameter was observed when PLA was applied as the adhesive. This is consistent with Vick and Rowell (1990), where a similar acetylation process resulted in the reduction of bond shear strength between wood and thermoplastics (Vick and Rowell 1990).

As Hill (2007) later explained in his book, it seems that this chemical treatment increases the risk of cell wall degradation as the consequence of the high temperature and generation of the acid by-product in the cell walls.

3.5.2 Identification of plastic dispersion pattern on the interfacial bonding area

In the previous section, the interfacial bonding between wood and plastic phases was characterized by testing two kinds of bio-based (PLA) and oil-based (HDPE) thermoplastics on the veneer overlap in the ABES. Based on the findings, it can be assumed that bio-based polymers have an inherent compatibility to positively react with natural wood surfaces compared with oil-based plastics.

Figure 30 shows EDX images captured from the remains of the PLA and HDPE plastics on the tested wood veneers. It seems that this technique is quite useful in diagnosing the remaining HDPE on the interfacial bonding area, as the carbon elements of plastics (pink color) are clearly distinguishable from the oxygen groups (green color) of wood. However, this approach was not successful for detection of PLA, as this polymer contains the same similar oxygen components that are normally present in the wood structure. Thus, there was no specific area on the interfacial bonding area after shear testing wherein plastic remains could be clearly identified from the wood surface.

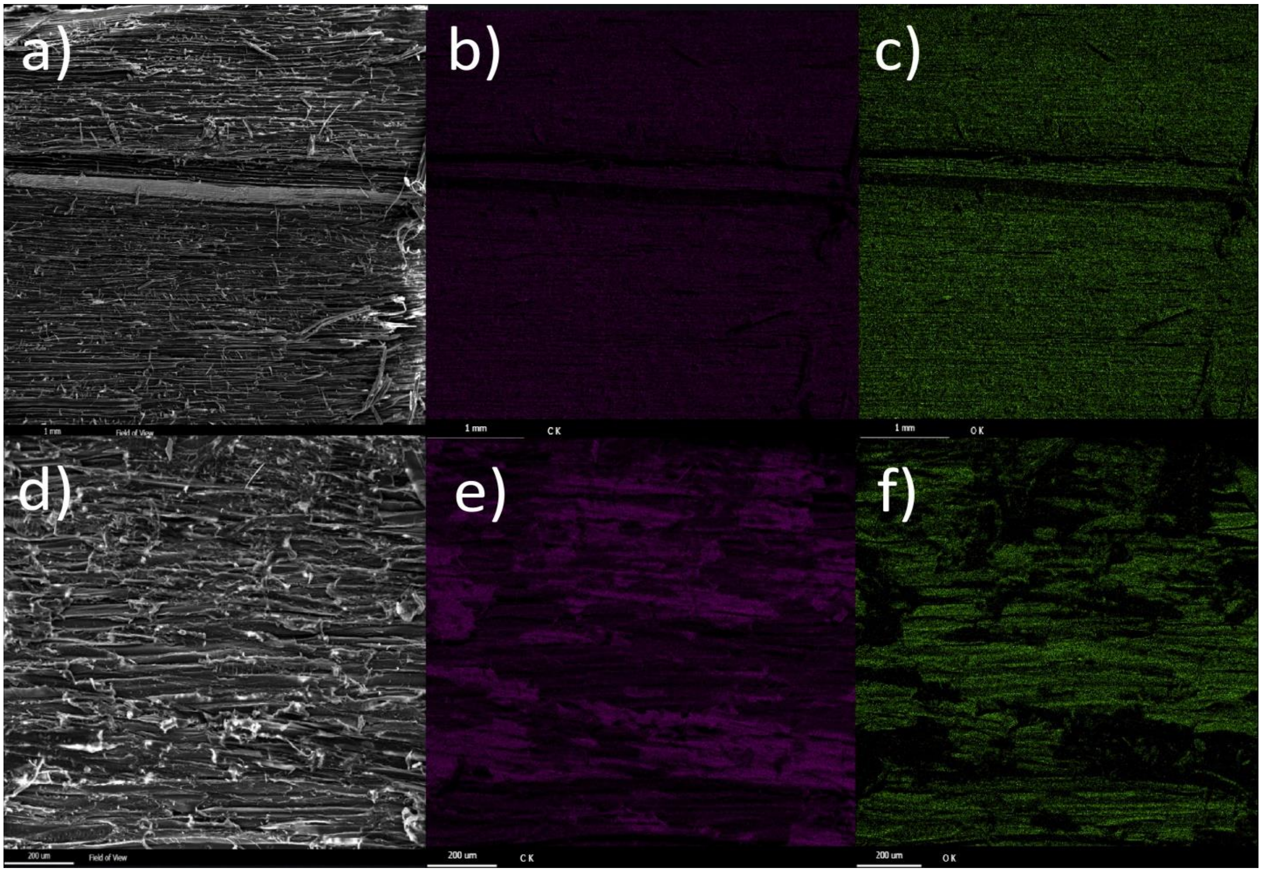


Fig30. EDX images of PLA (a-c) and HDPE (d-f) remains on wood surface after ABES testing

3.6 Determining the correlation between physical bonding and shear strength at wood–polymer interface

Diagram 6 shows the final results of both the shear strength (IFSS) and surface free energy (SFE) calculations (extracted from the first part of this work). From these findings, it can be said that there could be a predictable correlation between the physical properties and shear strength of wood surfaces. This is as a result of the reduction in SFE values from 49 mN/m for non-treated veneers to 28 mN/m for sanded, MAPE-treated veneers, resulting in a partial increment of IFSS for all tested adhesives.

These findings are in agreement with previous studies, in which the pre-treatment of a wood surface with plastic coupling agents improved the wetting and physio-mechanical properties of the wood–plastic composite (Cantero et al. 2003, Cisneros-López et al. 2017). However, it seems that SFE solely does not play a determining role, since there was no tangible enhancement in IFSS values as a result of a drastic decrease in SFE from non-sanded, MAPE-treated veneers (37 mN/m) to sanded MAPE-treated veneers (28 mN/m).

Meanwhile, as already explained in the previous section, the influence of this parameter is less at higher temperatures when the melted polymer is used as the liquid phase to wet the solid substrate. Mautuna et al. (1998) pointed out that the matching of fibers and surface tensions of plastic is an effective criterion for good adhesion. But as these authors also stated, this relationship is only valid for a few polyolefins, in which similar hydrocarbons are repeated throughout the polymer's entire framework.

Be that as it may, as was also mentioned, in the same research study, they found no meaningful correlation between the surface tensions of PVC and wood veneers. In fact, the present experiment also determined the compatibility among sanding, chemical treatments and the applied adhesives as key factors for IFSS increment, which can be fortified by improving wetting between the wood and polymer interphases.

Our final conclusion supports one of the recent studies by Law and Zhao (2016), wherein they concluded that the methodologies employed to calculate surface tension are a semiempirical rather than a straightforward technique. These authors also suggested using contact angle measurement as the main reference for surface and interfacial studies so that the wetting properties of materials can be diagnosed immediately.

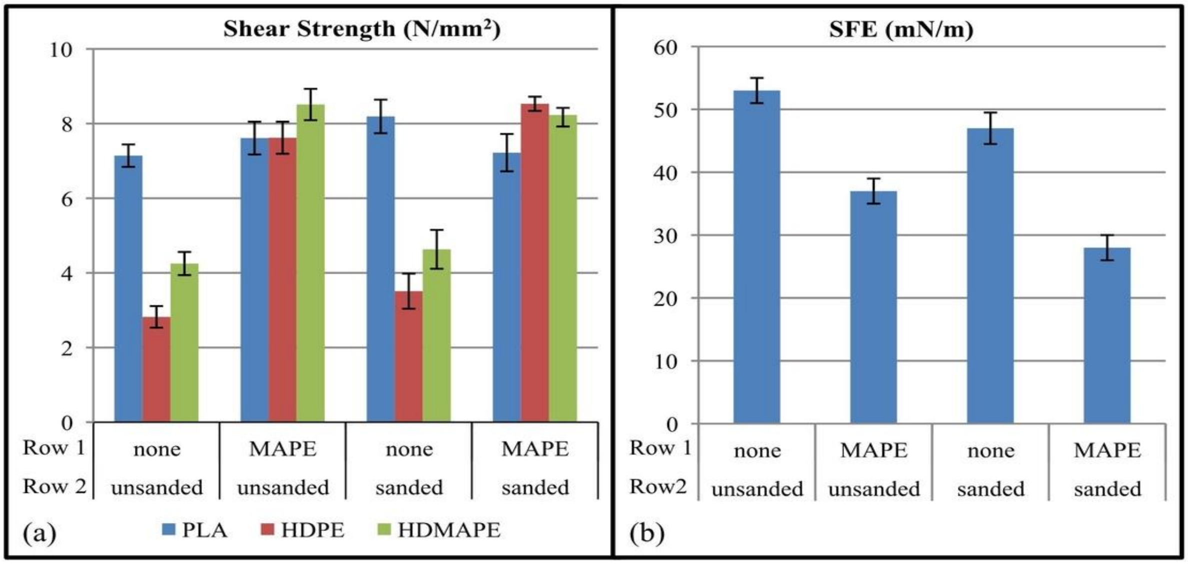


Diagram6. Average shear strengths (IFSS) (a) and surface free energy (SFE) calculations (b) on wood surfaces (Row 1: chemical treatment, Row 2: mechanical treatment)

Chapter 4

General Conclusions:

This thesis has been devoted to investigating the impact of chemo-mechanical treatments on the physio-mechanical interfacial-bonding between wood and plastic composites. To this end, two sorts of sanding and chemical treatments were first conducted on wood surfaces and the effect of these modifications on the surface morphology and chemical components of wood surface then characterized using surface evaluation techniques. Two main thermodynamic factors of temperature and viscosity, underlying the interfacial bonding at wood-polymer interface, were both evaluated. To sum up, the following conclusions have been summarized as its main outcomes:

- Although surface free energy (SFE) is an important parameter for surface characterization, it cannot be applied as a straightforward approach to predicting the interfacial bonding strength (IFSS) of the final composite before processing. Unlike Newtonian fluids, which tend to respond linearly against shearing stress, the surface tension of polymers is distinguished by their different viscose-elastic behaviours. In fact, the surface tension of polydisperse plastics tends to decrease dramatically at higher temperatures due to their lower molecular weight (like PLA), whilst monodispersed plastic behaves more elastically and its intermolecular interactions tend to keep their primary layout.

  We therefore concluded that plastic adhesion is more dominant by its fundamental property rather than the interfacial tension at the wood-polymer interface. For future experiments, we strongly recommend measuring the hot melting plastic contact angles on the wood surfaces directly, so that the wetting properties of the wood plastic composites can correctly be determined at the interface.

- PLA is more compatible with a solid wood structure, since it consists of a hydrophilic amorphous polymer that can easily penetrate to the bulk of the wood and form a strong interfacial bond; this is caused by its lower molecular weight, higher shearing thinning behaviour and its lower melt viscosity. Thus, we strongly recommend that in future studies, the achievement of optimum interfacial bonding in the wood plastic composites; both the polarity and the viscoelastic properties of the chosen plastic should be matched to the cellular structures of the wood fibers.

- The calculation of roughness parameters and the topographic analysis of samples by microscope, revealed that sanding helps the fine dispersion of the chemical treatment by increasing the interfacial areas on the wood surface. As a result, chemicals could easier penetrate to the depths of the wood and disperse more uniformly on the surface.

  Furthermore, sanding helps glue bonding by forming a fresh surface and improving wetting on wood veneers, on which plastics could easily spread out. Roughening causes mechanical interlocking between the wood and polymer surfaces. Analysis of hot melting plastic droplets on the sanded veneers has also revealed that θr partially decreased after sanding, which could be further evidence for the occurrence of the pinning activation phenomenon after sanding.

- High melt viscosity of polymers at lower temperatures could hinder the homogenous dispersion of the polymers on the wood surfaces, causing a weak stress transfer between the wood fibres and plastic interphases subsequently.

- It has been concluded that the pre-coating of a wood surface with MAPE is an effective approach to increasing the IFSS, by changing the chemical composition between the wood and plastic interface. In this case, surface roughening could pave the way for a more efficient coating of MAPE and the obtaining of a more hydrophobic surface consequently. As to the sanded samples treated with

MAPE, they resulted in the lowest dispersion of the component on the wood surface and lowest value of SFE subsequently.

- Although both apolar σ^{LW} and polar σ^{AB} components on the wood surface were both decreased after treatments, the decrease of the total value of surface energy was mainly due to the reduction on the dispersion side. This implies that physical bonding is predominantly determined by the dispersive forces on the wood surface. Our findings disagreed with the conventional belief in which the hydrophilic properties of wood are usually known to be responsible for weak physical bonding.

List of Tables

Table1. Test liquid database of acid-base model according to Della Volpe modification

Table2. Factor coded groups designed by DOE for DSA100S

Table3. Factor coded groups designed by DOE for ABES

Table4. DOE plan set for shear strength testing by ABES (Constant Temperature)

Table5. DOE plan set for shear strength testing by ABES (Constant viscosity)

Table6. DOE plan used once by DS100S and once by TC21 devices for measuring contact angles of normal test liquids and melting plastic droplets on the wood surface respectively

Table7. Contact angles of different probe liquids on wood veneers and their surface free energies obtained by VOCG model

Table8. Advancing θ_A and receding θ_R contact angles on veneer surfaces using hot melted plastics

Table9. The length of plastics penetration on the cross-section of massive spruce at constant viscosity

Table10. Average shear strength of wood-polymer interfaces once in constant temperature and once in constant viscosity value

List of Figures

Fig1. Wood Plastic Composite (WPC) decking for outdoor flooring

Fig2. Three principal directions of wood; (L) Longitudinal (T) Tangential (R) radial

Fig3. SEM micrographs of wood spruce cross section

Fig4. Structure of poly lactic acid (PLA) containing both carboxylic (C=O) and hydroxyl

Fig5. Microscopic image of wood-plastic interfacial bonding region (VHX600)

Fig6. Possible reactions of MAPE with wood fibers forming a. Mono-ester b. Di-ester bonding

Fig7. The Contact angle (CA) of water droplet on the wood surface

Fig8. General Scope of thesis and the devices employed to serve each aim of study

Fig9. Viscosity curves for HDPE (a), PLA (b) HDMAPE (c): rotation, plate-plate 25mm, 1000 ηm splat

Fig10. Hot dosing unit (DO3241) and its temperature controllers on the right side

Fig11. The measured surface tensions of HDPE (a) and PLA (b) by using pendant drop method

Fig12. Schematic description of shear test by the ABES

Fig13. FTIR spectra of REF (yellow color), MA (blue color) and AA (pink color) treated samples

Fig14. Chemical reactions of acetic anhydride on the wood surface

Fig15. Chemical reactions of maleic anhydride on the wood surface

Fig16. FTIR spectra of wood veneers in the range of 3600-600 cm^{-1}; Non Treated (green), BA treated (Blue) MAPE treated (Red) veneers

Fig17. 3D topographical images of wood veneers: (A) sanded, (B) sanded treated with MAPE, (C) unsanded, (D) unsanded treated with MAPE

Fig18. SEM micrographs of treated veneers with MAPE (a-f) and non-treated veneers (g-i)

Fig19. SEM images obtained from cross-sections of treated veneers with butyric anhydride

Fig20. OWRK plots of tested liquids (D: Diiodomethane, G: Glycerol, E: Ethylene glycol and W: Water) on A) non-sanded and B) sanded veneers

Fig21. OWRK plots of tested liquids (D: Diiodomethane, G: Glycerol, E: Ethylene glycol and W: Water) on A) non-sanded MAPE treated and B) sanded MAPE treated veneers

Fig22. OWRK plots of tested liquids (D: Diiodomethane, G: Glycerol, E: Ethylene glycol and W: Water) on A) non-sanded butyric treated and B) sanded butyric treated veneers

Fig23. Interaction of sanding and chemical treatments on wood surface energy by DOE program

Fig24. Anhydride modification scheme on wood surface, where R=CH_3 (acetic anhydride), R = C_3H_7 (butyric anhydride)

Fig25. VHX-6000 digital microscopic images of a-b) PLA and c-d) HDPE droplet on radial and tangential sections of massive spruce surface

Fig26. VHX-6000 digital microscopic images of PLA (a) and HDPE (b) droplets on the cross sections of spruce veneers

Fig27. Interfacial bonding are between HDPE (a-b), PLA (c-d) and earlywood (a,c), latewood (b,d) of spruce veneers over cross-sections

Fig28. Veneer bonding areas with, (a) HDPE and (b) HDMAPE and (c) PLA plastics after ABES testing (plastic remains were remarked by arrows

Fig29. DOE analysis of interaction between chemical and veneers treatment on IFSS

Fig30. EDX images of PLA (a-c) and HDPE (d-f) remains on wood surface after ABES testing

List of Diagrams

Diagram3.1. The contact angle measurements between wood surfaces and HDPE hot droplet

Diagram3.2. 3D functional parameters of surface roughness: (A) reduced valley depth (Svk), core roughness (Sk) and reduced peak height (Spk) (Row 1: chemical treatment, Row 2: mechanical treatment)

Diagram3.3. 3D functional parameters of developed interfacial area ratio (Sdr) (Row 1: chemical treatment, Row 2: mechanical treatment)

Diagram3.4. 3D functional parameter of Sa (arithmetical mean height)

Diagram3.5. Surface Free energy values of wood veneers according to OWRK approach

Diagram3.6. Average shear strengths (IFSS) (a) and surface free energy (SFE) calculations (b) on wood surfaces (Row 1: chemical treatment, Row 2: mechanical treatment)

List of Abbreviations

AA	Acetic Anhydride
ABES	Automated bonding evaluation systems
BA	Butyric Anhydride
CA	Contact Angle
DOE	Design Of Experiment
DSA	Data Shape Analyser
EDX	Energy Dispersive X-Ray
Fig	Figure
FTIR	Fourier Transform Infrared Spectroscopy
HDPE	High Density of Polyethylene
IFSS	Interfacial Shear Strength
LSM	Laser Scanning Microscope
MA	Maleic Anhydride
MAPE	Maleic Anhydride Grafted with Polyethylene
OWRK	Owens Wendt Rabel Kaelbe Method

PLA	Poly Lactic Acid
SEM	Scanning Electron Microscopy
SFE	Surface Free Energy
VOCG	Vann Oss Chaudhury Good Method
WPG	Weight Percentage Gain

Declaration

According to the regulations on dissertations of Department of Biology, University of Hamburg, hereby I would officially declare that the present study has been done by my own and I have never used previous published works without stating the sources and aids. I have listed all the contributions of third party and noted all used statement resources from the literatures.

Pouria Rezaee Niaraki

Research bibliography:

Alcock B, Cabrera NO, Barkoula NM, Reynolds CT., Govaert LE, Peijs T (2007) The effect of temperature and strain rate on the mechanical properties of highly oriented polypropylene tapes and all-polypropylene composites. Compos. Sci. Technol. 67:2061-2070.

Allin SB (2004) Polymer Science and Technology. 2nd Edition (Fried JR). Journal of Chemical Education. 81(6):809.

Álvarez-Chávez CR, Edwards S, Moure-Eraso R, Geiser K (2012) Sustainability of bio-based plastics: general comparative analysis and recommendations for improvement. Journal of Cleaner Production, 23(1):47-56.

Ashori A (2008) Wood–plastic composites as promising green-composites for automotive industries. Bioresource technology, 99(11):4661-7.

Avramidis G, Hauswald E, Lyapin A, Militz H, Viöl W, Wolkenhauer A (2009) Plasma treatment of wood and wood-based materials to generate hydrophilic or hydrophobic surface characteristics. Wood Material Science and Engineering, 4(1-2):52-60.

Awal A, Rana M, Sain M (2015). Thermorheological and mechanical properties of cellulose reinforced PLA bio-composites. Mech. Mater. 80:87-95.

Aydin I (2004) Activation of wood surfaces for glue bonds by mechanical pre-treatment and its effects on some properties of veneer surfaces and plywood panels. Appl. Surf. Sci. 233:268-74.

Bajpai PK, Singh I, Madaan J (2014) Development and characterization of PLA-based green composites: A review. Journal of Thermoplastic Composite Materials, 27(1):52-81.

Bakken AC, Taleyarkhan RP (2020) Plywood Wood Based Composites Using Crystalline/Amorphous PLA Polymer Adhesives. International Journal of Adhesion and Adhesives. 26:102-581.

Balasuriya, PW, Ye L, Mai YW, Wu J (2002) Mechanical properties of wood flake–polyethylene composites II Interface modification. J. Appl. Polym. Sci. 83:2505-2521.

Beery WH, Ifju G, McLain TE (2007)Quantitative wood anatomy—relating anatomy to transverse tensile strength. Wood and Fiber Science.15(4):395-407.

Bekhta P, Lyutyy P, Ortynska, G (2017) Properties of veneered flat pressed wood plastic composites by one-step process pressing. J. Polym. Environ. 25:1288-1295.

Biagiotti J, Puglia D, Torre L, Kenny JM, Arbelaiz A, Cantero G, ... & Mondragon I (2004). A systematic investigation on the influence of the chemical treatment of natural fibers on the properties of their polymer matrix composites. Polymer Composites, 25(5), 470-479.

Bingham NH, Fry JM (2010) Regression: Linear models in statistics. Springer Science & Business Media. pp. 7. Ch 1.

Bledzki AK, Reihmane SA, Gassan J (1998) Thermoplastics reinforced with wood fillers: a literature review. Polym. Plast. Technol. Eng. 37:451-468.

Bormashenko EY (2018) Wetting of real surfaces. Walter de Gruyter GmbH & Co KG.pp. 5-7.

Bouafif H, Koubaa A, Perré P, Cloutier A, Riedl B (2008) Analysis of among-species variability in wood fiber surface using DRIFTS and XPS: Effects on esterification efficiency. Journal of wood chemistry and technology, 28(4):296-315.

Braun J, Duretek I, Müller U, Friesenbichler W, Endesfelder A (2007) Investigations of the rheology and reactivity of extrudable wood-resin compounds. Monatshefte für Chemie-Chemical Monthly, 138(4):337-41.

Cantero G, Arbelaiz A, Llano-Ponte R, Mondragon I (2003) Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. Compos. Sci. Technol. 63:1247-1254.

Cappelletti G, Ardizzone, S, Meroni D, Soliveri G, Ceotto M, Biaggi C ... & Raimondi L.(2013) Wettability of bare and fluorinated silanes: a combined approach based on surface free energy evaluations and dipole moment calculations. Journal of colloid and interface science, 389(1):284-291.

Carus M, Partanen A (2018) Natural fibre-reinforced plastics: establishment and growth in niche markets. Location: Nova Institut.

Caulfield DF, Clemons C, Jacobson RE, Rowell RM (2005) 13 Wood Thermoplastic Composites. Handbook of wood chemistry and wood composites, 18:365.

Cavdar, AD, Mengeloglu F, Karakus K, Tomak ED (2014) Effect of chemical modification with maleic, propionic, and succinic anhydrides on some properties of wood flour filled HDPE composites. BioResources. 9:6490-6503.

Cavdar AD, Tomak ED, Mengeloglu F (2018) Long-term leaching effect on decay resistance of wood-plastic composites treated with boron compounds. J. Polym. Environ. 26:756-764.

Chaharmahali M, Mirbagheri J, Tajvidi M, Najafi SK, Mirbagheri Y (2010) Mechanical and physical properties of wood-plastic composite panels. Journal of Reinforced Plastics and Composites, 29(2):310-9.

Chan CM, Vandi LJ, Pratt S, Halley P, Richardson D, Werker A, Laycock B (2018) Composites of wood and biodegradable thermoplastics: A review. Polymer Reviews. 58: 444-494.

Chan CM, Vandi LJ, Pratt S, Halley P, Richardson D, Werker A, Laycock B (2018) Mechanical properties of poly (3-hydroxybutyrate-co-3hydroxyvalerate)/wood flour composites: Effect of interface modifiers. J. Appl. Polym. Sci. 135. p.46828.

Chang H, Tu K, Wang X, Liu J (2015) Fabrication of mechanically durable superhydrophobic wood surfaces using polydimethylsiloxane and silica nanoparticles. Rsc Advances, 5(39):30647-53.

Chang HT, Chang ST (2002) Moisture excluding efficiency and dimensional stability of wood improved by acylation. Bioresource technology, 85(2):201-4.

Chang WP, Kim KJ, Gupta RK (2009) Moisture absorption behavior of wood/plastic composites made with ultrasound-assisted alkali-treated wood particulates. Composite Interfaces, 16(7-9):937-51.

Chen J, Wang Y, Gu C, Liu J, Liu Y, Li M, Lu Y (2013) Enhancement of the mechanical properties of basalt fiber-wood-plastic composites via maleic anhydride grafted high-density polyethylene (MAPE) addition. Materials. 6:2483-2496.

Chen Z, Wang C, Cao Y, Zhang S, Song W (2018) Effect of adhesive content and modification method on physical and mechanical properties of eucalyptus veneer/poly-β-hydroxybutyrate film composites. Forest Products Journal. 68(4):419-429.

Cisneros-López EO, González-López ME, Pérez-Fonseca AA, González-Núñez R, Rodrigue D, & Robledo-Ortíz, JR (2017) Effect of fiber content and surface treatment on the mechanical properties of natural fiber composites produced by rotomolding. Compos Interface. 24:35-53.

Clemons C (2002) Wood-plastic composites in the United States: The interfacing of two industries. Forest Products Journal, Vol. 52, no. 6, Pages 10-18.

Cool J, Hernández, RE (2011) Improving the sanding process of black spruce wood for surface quality and water-based coating adhesion. Forest Products Journal. 61:372-380.

Dai Q, Li M, Khonsari MM, Huang W, Wang X (2018) The thermocapillary migration on rough surfaces. Lubrication Science. 31(5):163-170.

Dányádi L, Móczó J, Pukánszky B (2010) Effect of various surface modifications of wood flour on the properties of PP/wood composites. Compos. Pt. A. Appl. Sci. Manuf. 41:199-206.

de Meijer M, Thurich K, Militz H (2001) Quantitative measurements of capillary coating penetration in relation to wood and coating properties. Holz als Roh und Werkstoff. 59(1):35-45.

de Meijer M (2004). A review of interfacial aspects in wood coatings: wetting, surface energy, substrate penetration and adhesion. In COST E18 Final Seminar. pp. 26-27.

Della Volpe C, Siboni S (1997) Some reflections on acid–base solid surface free energy theories. J. Colloid. Interface. Sci. 195:121-136.

Demirkir C, Aydin I, Colak S, & ÇOLAKOĞLU G (2014) Effects of plasma treatment and sanding process on surface roughness of wood veneers. Turkish Journal of Agriculture and Forestry.38 (5):663-667.

Dong X, Zhuo X, Wei J, Zhang G, Li Y (2017) Wood-Based Nanocomposite Derived by in Situ Formation of Organic–Inorganic Hybrid Polymer within Wood via a Sol–Gel Method. ACS applied materials & interfaces, 9(10):9070-8

Duncan B, Mera R, Leatherdale D, Taylor M, Musgrove R (2005) Techniques for characterising the wetting, coating and spreading of adhesives on surfaces. UK: NPL Report DEPC MPR. 20:1-40.

Dupré A and Dupré P (1869) Théorie mécanique de la chaleur. Gauthier-Villars.

Eral HB, Oh JM (2013) Contact angle hysteresis: a review of fundamentals and applications. Colloid. Polym. Sci. 291:247-260.

Fang L, Chang L, Guo WJ, Ren YP, Wang, Z (2013) Preparation and characterization of wood-plastic plywood bonded with high density polyethylene film. Eur J Wood Prod 71(6):739-746

Fang L, Chang L., Guo WJ, Chen Y, Wang Z (2014) Influence of silane surface modification of veneer on interfacial adhesion of wood–plastic plywood. Appl. Surf. Sci. 288:682-689.

Faruk O, Bledzki AK, Fink HP, Sain M (2014) Progress report on natural fiber reinforced composites. Macromolecular Materials and Engineering, 299(1):9-26.

Fini SH, Farzaneh M, Erchiqui F (2013) Study of the elastic behaviour of wood–plastic composites at cold temperatures using artificial neural networks. Wood Science and Technology, 49(4):695-705.

Finkenstadt VL, Tisserat B. (2010) Poly (lactic acid) and Osage Orange wood fiber composites for agricultural mulch films. Industrial crops and products. ,31(2):316-20.

Flynn KA (2007) A review of the permeability, fluid flow, and anatomy of spruce (Picea spp.). Wood and Fiber Science. 27(3):278-84.

Fowkes FM (1963) Additivity of intermolecular forces at interfaces. i. determination of the contribution to surface and interfacial tensions of dispersion forces in various liquids1. The Journal of Physical Chemistry. 67(12):2538-2541.

Fox HW, Zisman WA (1952) The spreading of liquids on low-energy surfaces. III. Hydrocarbon surfaces. Journal of Colloid Science. 7(4):428-42.

Fuqua MA, Huo S, & Ulven CA (2012) Natural fiber reinforced composites. Polymer Reviews. 52(3):259-320.

Galyavetdinov NR, Safin RR, Voronin AE (2016) Analysis of physico-mechanical properties of composites based on polylactide and thermally modified wood fibers. InMaterials Science Forum. pp. 202-206.

Garlotta D (2001) A literature review of poly (lactic acid). J. Polym. Environ. 9:63-84.

Gaugler M, Luedtke J, Grigsby WJ, Krause A (2019) A new methodology for rapidly assessing interfacial bonding within fibre-reinforced thermoplastic composites. Int. J. Adhes. Adhes. 89:66-71.

George J, Sreekala MS, & Thomas S (2001) A review on interface modification and characterization of natural fiber reinforced plastic composites. Polymer Engineering & Science. 41(9): 1471-1485.

Ghanbari A, Madhoushi M, Ashori A. (2014) Wood plastic composite panels: Influence of the species, formulation variables and blending process on the density and withdrawal strength of fasteners. Journal of Polymers and the Environment. 22(2):260-6.

Gilbert Gedeon PE (1999) Wood Structure and its Physical Properties.

Gindl M, SinnG, Gindl W, Reiterer A, Tschegg S (2001) A comparison of different methods to calculate the surface free energy of wood using contact angle measurements. Colloids and Surfaces A. 181:279-287.

Green DW, Winandy JE, Kretschmann DE (1999) Mechanical properties of wood. Wood handbook: wood as an engineering material. Madison, WI: USDA Forest Service, Forest Products Laboratory, 1999. General technical report FPL; GTR-113: Pages 4.1-4.45.

Gurau L, Mansfield-Williams H, Irle M (2013) The influence of measuring resolution on the subsequent roughness parameters of sanded wood surfaces. European Journal of Wood and Wood Products, 71(1):5-11.

Gurau L (2010) An objective method to measure and evaluate the quality of sanded wood surfaces. In D. J. Ridley-Ellis and J. R. Moore (eds.) Cost Action E53: The Future of Quality Control for Wood and Wood Products (Edinburgh: Edinburgh Napier University). pp. 1–9.

Gurunathan T, Mohanty S, & Nayak SK (2015) A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Composites Part A: Applied Science and Manufacturing, 77: 1-25.

Haghdan S, Tannert T, Smith GD (2015) Wettability and impact performance of wood veneer/polyester composites. BioResources. 10:5633-5654.

Hansmann C, Weichslberger G, Gindl W (2005) A two-step modification treatment of solid wood by bulk modification and surface treatment. Wood science and technology. 39(6):502.

Hassan N, Hamid NH, Jawaid M, Tahir PM, & Ujang S (2017) Decay resistance of acetic, propionic, and butyric anhydrides modified rubberwood against brown rot (Coniophora puteana). BioResources. 12(3):4527-4546.

Heydari G, Moghaddam MS, Tuominen M, Fielden M, Haapanen J, Mäkelä JM, Claesson, PM (2016) Wetting hysteresis induced by temperature changes: Supercooled water on hydrophobic surfaces. J. Colloid. Interface. Sci. 468:21-33.

Hill CAS (2007) Wood modification: chemical, thermal and other processes Chichester, England: John Wiley & Sons.

Hill C S, Hillier J (1999) Studies of the reaction of carboxylic acid anhydrides with wood. Experimental determination and modelling of kinetic profiles. Physical Chemistry Chemical Physics, 1(7): 1569-1576.

Hiziroglu S, Rabiej R (2005) Factors affecting adhesive shear strength of overlaid composite panel. Am. J. Appl. Sci.(Special Issue). 1-4.

Hiziroglu S, Zhong ZW, Ong WK (2014) Evaluating of bonding strength of pine, oak and nyatoh wood species related to their surface roughness. Measurement. 49:397-400.

Hubbe, Martin A, Douglas J. Gardner, and Wei Shen. "Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies." BioResources 10.4 (2015): 8657-8749.

Huda MS, Drzal LT, Misra M, Mohanty AK (2006) Wood-fiber-reinforced poly (lactic acid) composites: evaluation of the physicomechanical and morphological properties. Journal of Applied Polymer Science.102(5):4856-69.

Hundhausen U, Kloeser L, & Mai C (2015) Usability of maleic anhydride as wood modification agent for the production of medium density fibreboards (MDF). European journal of wood and wood products.73 (3):283-288.

Hung KC, Wu TL, Chen YL, & Wu JH (2016) Assessing the effect of wood acetylation on mechanical properties and extended creep behavior of wood/recycled-polypropylene composites. Construction and Building Materials.108: 139-145

Hutyrová Z, Ščučka J, Hloch S, Hlaváček P, Zeleňák M (2016) Turning of wood plastic composites by water jet and abrasive water jet. Int J. Adv. Manuf. Tech. 84:1615-1623.

Iwata T (2015) Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. Angewandte Chemie International Edition.54 (11):3210-5.

Jahan MS, Chowdhury DN, Islam MK, Moeiz SI (2007) Characterization of lignin isolated from some nonwood available in Bangladesh. Bioresource technology.98(2):465-9.

Janssen D, De Palma R, Verlaak S, Heremans P, & Dehaen W (2006) Static solvent contact angle measurements, surface free energy and wettability determination of various self-assembled monolayers on silicon dioxide. Thin Solid Films. 515(4):1433-1438.

Joffre T, Segerholm K, Persson C, Bardage SL, Hendriks CL, Isaksson P (2017) Characterization of interfacial stress transfer ability in acetylation-treated wood fibre composites using X-ray microtomography. Industrial Crops and Products. 95:43-9.

Jost M, Sernek M (2009) Shear strength development of the phenol–formaldehyde adhesive bond during cure. Wood. Sci. Technol. 43.p.153.

Kaboorani A (2017) Characterizing water sorption and diffusion properties of wood/plastic composites as a function of formulation design. Constr. Build. Mater. 136:164-172.

Kaczmarek H, Felczak A, & Szalla A (2008) Studies of photochemical transformations in polystyrene and styrene–maleic anhydride copolymer. Polymer degradation and Stability. 93(7): 1259-1266.

Kaelble DH (1970) Dispersion-polar surface tension properties of organic solids. The Journal of Adhesion. 2(2):66-81.

Kamal MR, Calderon JU, Lennox BR (2009) Surface energy of modified nanoclays and its effect on polymer/clay nanocomposites. J. Adhes. Sci. Technol. 23:663-688.

Kim S (2009) Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission. Bioresource Technology. 100(2):744-8.

Kučera LJ, Bariska M (1982) On the fracture morphology in wood. Wood Science and Technology. 16(4):241-59.

Kúdela J, Mrenica L, & Javorek Ľ (2018) The influence of milling and sanding on wood surface morphology. Acta Facultatis Xylologiae Zvolen res Publica Slovaca. 60(1): 71-83.

Kühnert I, Spörer Y, Brünig H, Tran NHA and Rudolph N (2018) “Processing of poly(lactic acid),” in *industrial applications of poly(lactic acid)*. Cham: Springer International Publishing. 1–33.

Kuptsov AH, Zhizhin GN (1998) Handbook of Fourier Transforms Raman and Infrared Spectra of polymers. Elsevier, Amsterdam.

Kureli I, Doganay S (2015) The effects of surface roughness, adhesive type, and veneer species on pull-off strength of laminated medium density fibreboard. BioResources. 10:1293-1303.

Lam, C.N.C., Wu, R., Li, D., Hair, M.L., Neumann, A.W. (2002) Study of the advancing and receding contact angles: liquid sorption as a cause of contact angle hysteresis. Adv. Colloid. Interface. Sci. 96:169-191.

Lata K, Dubey B, Misra AK (2016) Modeling the effects of wood and non-wood based industries on forestry resources. Natural Resource Modeling.29 (4):559-580.

Law KY and Zhao H (2016) Surface wetting: characterization, contact angle, and fundamentals. Switzerland: Springer.

Li JZ, Furuno T, Katoh S, Uehara T (2000) Chemical modification of wood by anhydrides without solvents or catalysts. Journal of wood science. 46(3):215-221.

Li L, Hu Y, Cheng F (2015) Butyration of Lignosulfonate with Butyric Anhydride in the Presence of Choline Chloride. BioResources. 10(2):3181-3196.

Liu FP, Wolcott MP, Gardner DJ, Rials TG (1994). Characterization of the interface between cellulosic fibers and a thermoplastic matrix. Composite Interfaces. 2(6):419-432.

Liu M, Wang Y, Wu Y, He Z, Wan H (2018) "Greener" adhesives composed of urea-formaldehyde resin and cottonseed meal for wood-based composites. Journal of Cleaner Production.187:361-371.

Lu JZ, Negulescu II, Wu Q (2005) Maleated wood-fiber/high-density-polyethylene composites: Coupling mechanisms and interfacial characterization. Composite Interfaces.12 (1-2):125-40.

Luedtke, J, Gaugler M, Grigsby WJ, Krause A (2019) Understanding the development of interfacial bonding within PLA/wood-based thermoplastic sandwich composites. Ind. Crop. Prod. 127:129-134.

Luostarinen K, Pikkarainen L, Ikonen VP, Zubizarreta Gerendiain A, Pulkkinen P, Peltola H. (2017) Relationships of wood anatomy with growth and wood density in three Norway spruce clones of Finnish origin. Canadian Journal of Forest Research. 47(9):1184-92.

Lv S, Gu J, Tan H, Zhang Y (2016) Modification of wood flour/PLA composites by reactive extrusion with maleic anhydride. Journal of Applied Polymer Science,15;133(15).
M Rowell, R. (2014). Acetylation of wood–A review. International Journal of Lignocellulosic Products, 1(1), 1-27.

Magoss E (2008) General regularities of wood surface roughness. Acta Silvatica et Lignaria Hungarica,4:81-93.

Maloney TM (1996) The family of wood composite materials. Forest Products Journal, 46(2):19-26.

Matuana L M, Stark NM (2015) The use of wood fibers as reinforcements in composites. In Biofiber reinforcements in composite materials (pp. 648-688). Woodhead Publishing.

Matuana LM, Balatinecz JJ, Sodhi RNS, Park CB (2001) Surface characterization of esterified cellulosic fibers by XPS and FTIR spectroscopy. Wood Science and Technology.35(3): 191-201.

Matuana LM, Balatinecz JJ, Park CB (1998) Effect of surface properties on the adhesion between PVC and wood veneer laminates. Polym. Eng. Sci. 38:765-773.

McKeen LW (2014) The effect of temperature and other factors on plastics and elastomers. Elsevier Science, William MA, USA.

Mertens O, Benthien JT, Krause A (2018) Monitoring of fibre dimensions after a novel wood-plastic compounding approach. Eur. J. Wood. Prod. 76:801-804.

Migneault S, Koubaa A, Erchiqui F, Chaala A, Englund K, Wolcott MP (2009) Effects of processing method and fiber size on the structure and properties of wood–plastic composites. Composites Part A: Applied Science and Manufacturing. 40(1):80-5.

Mihai M, Legros N, Alemdar A (2014) Formulation-properties versatility of wood fiber biocomposites based on polylactide and polylactide/thermoplastic starch blends. Polym. Eng. Sci. 54:1325-1340.

Mitsui K (2010) Acetylation of wood causes photo bleaching. Journal of Photochemistry and Photobiology B: Biology. 101(3):210-214.

Mittal KL (2003) Contact Angle, Wettability and Adhesion.3rd ed. VSPBV, Boston.

Najafi SK (2013) Use of recycled plastics in wood plastic composites–A review. Waste management.33(9):1898-905.

Naumann A, Peddireddi S, Kües U, Polle A (2007) 10. Fourier Transform Infrared Microscopy in Wood Analysis. Wood production, wood technology, and biotechnological impacts, 179.

Neagu RC, Gamstedt EK, Berthold F (2006) Stiffness contribution of various wood fibers to composite materials. Journal of composite materials. 40(8):663-99.

Nussbaum RM (1999) Natural surface inactivation of Scots pine and Norway spruce evaluated by contact angle measurements. Eur. J. Wood. Prod. 57:419-424.

Owens DK, Wendt RC (1969) Estimation of the surface free energy of polymers. Journal of applied polymer science. 13(8): 1741-1747.

Papadopoulos AN, Bikiaris DN, Mitropoulos AC, Kyzas GZ (2019) Nanomaterials and chemical modifications for enhanced key wood properties: A review. Nanomaterials.9 (4):607.

Papadopoulos AN, Hill CAS (2002) The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against Coniophora puteana. Holz als Roh-und Werkstoff. 60(5):329-332.

Papp EA, Csiha C (2017) Contact angle as function of surface roughness of different wood species. Surfaces and Interfaces. 8: 54-59.

Patil YP, Gajre B, Dusane D, Chavan S, Mishra S (2000) Effect of maleic anhydride treatment on steam and water absorption of wood polymer composites prepared from wheat straw, cane bagasse, and teak wood sawdust using novolac as matrix. Journal of Applied Polymer Science. 77(13):2963-7.

Perisic SD, Radovic I, Petrovic M, Marinkovic A, Stojanovic D, Uskokovic P, Radojevic V (2018) Processing of hybrid wood plastic composite reinforced with short PET fibers. Materials and Manufacturing Processes.33 (5):572-9.

Pickering KL, Efendy MA, Le TM (2016) A review of recent developments in natural fibre composites and their mechanical performance. Composites Part A: Applied Science and Manufacturing. 83:98-112.

Pritchard G (2004) Two technologies merge: wood plastic composites. Plastics, Additives and Compounding. 6(4):18-21.

Qiang T, Yu D, Gao H, Wang Y (2012) Polylactide-based wood plastic composites toughened with SBS. Polymer-Plastics Technology and Engineering. 51(2):193-8.

Qiang T, Yu D, Zhang A, Gao H, Li Z, Liu Z, Chen W, Han Z (2014) Life cycle assessment on polylactide-based wood plastic composites toughened with polyhydroxyalkanoates. Journal of cleaner production.66:139-45.

Rabel W (1971) Einige Aspekte der Benetzungstheorie und ihre Anwendung auf die Untersuchung und Veränderung der Oberflächeneigenschaften von Polymeren. Farbe und Lack.77 (10):997-1005.

Rao J, Zhou Y, Fan M (2018) Revealing the interface structure and bonding mechanism of coupling agent treated WPC. Polymers. 10(3):266.

Reiterer A, Burgert I, Sinn G, Tschegg S (2002) The radial reinforcement of the wood structure and its implication on mechanical and fracture mechanical properties—a comparison between two tree species. Journal of materials science. 37(5):935-40.

Ren D, Yu Z, Zhang X, Wang H, Wang H, Yu Y (2017) Quantitative characterization of the interface between bamboo fiber and polypropylene with pull-out test and nanomechanical imaging. J. Mater. Sci. 52:1296-1307.

Niaraki PR, Krause A (2017) Evaluation of wood surface modifications using hot melting plastic droplet for contact angle measurements. WIT Transactions on Engineering Sciences. pp.31-36.

Rezaee Niaraki P, Krause A (2019) Correlation between physical bonding and mechanical properties of wood plastic composites: Part 1: interaction of chemical and mechanical treatments on physical properties. Journal of Adhesion Science and Technology. 31:1-2.

Rezaee Niaraki P, Krause A (2020) Correlation between physical bonding and mechanical properties of wood–plastic composites: part 2: effect of thermodynamic factors on interfacial bonding at wood–polymer interface. Journal of Adhesion Science and Technology. 34(7):756-68.

Risholm-Sundman MA, Lundgren M, Vestin E, Herder P (1998) Emissions of acetic acid and other volatile organic compounds from different species of solid wood. Holz als Roh-und Werkstoff. 56(2):125-9.

Rossi D, Rossi S, Morin H, Bettero A (2012) Within-tree variations in the surface free energy of wood assessed by contact angle analysis. Wood science and technology.46:287-98.

Rowell RM (2007) Chemical modification of wood. Handbook of engineering biopolymers, homopolymers, blends, and composites. Cincinnati, OH: Hanser Gardner Publications, Inc., Pages 673-691.

Rowell RM (1984) Penetration and reactivity of cell wall components. The Chemistry of Solid Wood. 207:175-210.

Rowell RM, Clemons CM (1992). Chemical modification of wood fiber for thermoplasticity, compatibilization with plastics, and dimensional stability. In Proceedings of Washington State University International Particleboard/Composite Materials Symposium (USA).

Ryan BJ, Poduska KM (2008) Roughness effects on contact angle measurements. Am. J. Phys. 76:1074-1077.

Sanadi AR, Rowell RM, Young RA (1993) Evaluation of wood-thermoplastic-interphase shear strengths. J. Mater. Sci. 28:6347-6352.

Schuster JM, Schvezov CE, Rosenberger MR (2015). Analysis of the results of surface free energy measurement of Ti6Al4V by different methods. Procedia Materials Science. 8: 732-741.

Schwarzkopf MJ, Burnard MD (2016) Wood-plastic composites—Performance and environmental impacts. InEnvironmental Impacts of Traditional and Innovative Forest-based Bioproducts (pp. 19-43). Springer, Singapore.

Schwarzkopf M, Muszyński L, Hammerquist CC, Nairn JA (2017) Micromechanics of the internal bond in wood plastic composites: integrating measurement and modeling. Wood. Sci. Technol. 51:997-1014.

Sewda K, Maiti SN (2013) Dynamic mechanical properties of high density polyethylene and teak wood flour composites. Polymer bulletin.70 (10):2657-74.

Shida S, Hiziroglu S (2010) Evaluation of shear strength of Japanese wood species as a function of surface roughness. Forest products journal.60(4), 400-404.

Sinn G, Gindl M, Reiterer A, & Stanzl-Tschegg S (2004) Changes in the surface properties of wood due to sanding. Holzforschung. 58(3): 246-251.

Slater D, Ennos R (2015) Interlocking wood grain patterns provide improved wood strength properties in forks of hazel (Corylus avellana L.). Arboricultural Journal: The International Journal of Urban Forestry. 37(1):21-32.

Song W, Wei W, Li X , Zhang S (2016) Utilization of polypropylene film as an adhesive to prepare formaldehyde-free, weather-resistant plywood-like composites: Process optimization, performance evaluation and interface modification. BioResources. 12(1):228-254.

Song W, Wei W, Li X, Zhang S (2017) Utilization of polypropylene film as an adhesive to prepare formaldehyde-free, weather-resistant plywood-like composites: Process optimization, performance evaluation, and interface modification. BioResources. 12:228-254.

Stark NM, Cai Z, Carll C (2010) Wood-based composite materials: Panel products, glued-laminated timber, structural composite lumber and wood-nonwood composite materials. In: wood as an engineering material: chapter 11. Centennial ed. General technical report FPL; GTR-190. Madison, WI: US Dept. of Agriculture, Forest Service, Forest Products Laboratory. pp.11-1.

Stefke B, Windeisen E, Schwanninger M, Hinterstoisser B (2008) Determination of the weight percentage gain and of the acetyl group content of acetylated wood by means of different infrared spectroscopic methods. Analytical chemistry.80 (4): 1272-1279.

Su M, Chen J, Pan Z, Li X, Xu A, Hong J (2015) Study on the preparation and mechanical properties of injection-moulded wood-based plastics. Journal of Applied Polymer Science.132 (5).

Sulaiman O, Hashim R, Subari K, Liang CK (2009) Effect of sanding on surface roughness of rubberwood. J. Mater. Process. Technol. 209:3949-3955.

Sungsanit K (2011) Rheological and mechanical behaviour of poly (lactic acid)/polyethylene glycol blends, PhD thesis, RMIT University, Melbourne.

Takase S, Shiraishi N (1989) Studies on composites from wood and polypropylenes. II. J. Appl. Polym. Sci. 37:645-659.

Takatani M, Ikeda K, Sakamoto K, Okamoto T (2008) Cellulose esters as compatibilizers in wood/poly (lactic acid) composite. J. Wood. Sci. 54:54-61.

Teaca CA, Tanasa F, Zanoaga M (2018) Multi-component Polymer Systems Comprising Wood as Bio-based Component and Thermoplastic Polymer Matrices–An Overview. BioResources, 13(2). 4728-4769.

Teuber L, Militz H, Krause A (2016) Processing of wood plastic composites: the influence of feeding method and polymer melt flow rate on particle degradation. Journal of Applied Polymer Science. 133(13).

Thoma H, Peri L, Lato E (2015) Evaluation of wood surface roughness depending on species characteristics. Maderas. Ciencia y tecnología. 17(2):285-92.

Trtik P, Dual J, Keunecke D, Mannes D, Niemz P, Stähli P, Kaestner A, Groso A, Stampanoni M (2007) 3D imaging of microstructure of spruce wood. Journal of structural biology. 159(1):46-55.

Tsuchikawa S, Tsutsumi S (2002) Application of time-of-flight near-infrared spectroscopy to wood with anisotropic cellular structure. Applied spectroscopy. 56(7):869-76.

Ugulino B, Hernández RE (2018). Analysis of sanding parameters on surface properties and coating performance of red oak wood. Wood Material Science & Engineering, 13(2):64-72.

Ugulino B, Hernández RE (2018) Analysis of sanding parameters on surface properties and coating performance of red oak wood. Wood. Mater. Sci. Eng. 13:64-72.

Van Oss CJ, Good RJ, Chaudhury MK (1986) The role of van der Waals forces and hydrogen bonds in "hydrophobic interactions" between biopolymers and low energy surfaces. Journal of colloid and Interface Science. 111(2), 378-390.

Van Oss CJ, Ju L, Chaudhury MK, Good RJ (1989) Estimation of the polar parameters of the surface tension of liquids by contact angle measurements on gels. Journal of Colloid and Interface Science, 128(2), 313-319.

Van Oss CJ (1995) Interfacial Forces in Aqueous Media; CRC Press: Boca Raton, FL, USA. Volume 26. ISBN 1420015761.

Vick CB, Rowell RM (1990) Adhesive bonding of acetylated wood. International Journal of Adhesion and Adhesives.10: 263-272.

Wålinder ME, Gardner DJ (2002) Acid–base characterization of wood and selected thermoplastics. Journal of Adhesion Science and Technology. 16(12):1625-1649.

Wenzel RN (1949). Surface roughness and contact angle. The Journal of Physical Chemistry. 53(9):1466-1467.

Windono T, Jenie UA, Kardono LB (2012) Isolation and Elucidation of Pyrrolizidine alkaloids from tuber of Gynura pseudo-china (L.) DC. Journal of Applied Pharmaceutical Science. 2(5):5.

Wolcott MP, Englund K (1999) A technology review of wood-plastic composites. In33rd international particleboard/composite materials symposium proceedings pp. 103-111.

Wool R, Sun XS (2011) Bio-based polymers and composites, Elsevier.

Wu S (1974) Interfacial and surface tensions of polymers. J. Macromol. Sci. Rev. in Macromol. Chem. 10:1-73.

Yang HS, Wolcott MP, Kim HS, Kim S, Kim HJ (2007) Effect of different compatibilizing agents on the mechanical properties of lignocellulosic material filled polyethylene bio-composites. Composite Structures. 79(3):369-75.

Yang L, Li Hi, Zhong ZY (2010) Study on mechanical properties of PP/wood powder composite." Plastics Science and Technology. 38(2): 36-39.

Yang TC, Chien YC, Wu TL, Hung KC, Wu JH (2017). Effects of heat-treated wood particles on the physico-mechanical properties and extended creep behavior of wood/recycled-hdpe composites using the time–temperature superposition principle. Materials.10 (4): 365.

Yang TH, Yang TH, Chao WC, Leu SY (2015) Characterization of the property changes of extruded wood–plastic composites during year round subtropical weathering. Constr. Build. Mater. 88:159-168.

Yao F, Wu Q, Lei Y, Xu Y (2008) Rice straw fiber-reinforced high-density polyethylene composite: Effect of fiber type and loading. Industrial Crops and Products, 28(1):63-72.

Yasuda H, Sharma AK, Yasuda T (1981) Effect of orientation and mobility of polymer molecules at surfaces on contact angle and its hysteresis. J. Polym. Sci. Ed. 19:1285-1291.

Young Thomas (1805) "III. An essay on the cohesion of fluids." Philosophical transactions of the royal society of London 95: 65-87.

Yuan Q, Wu D, Gotama J, Bateman S (2008) Wood fiber reinforced polyethylene and polypropylene composites with high modulus and impact strength. J. Thermoplast. Compos. Mater. 21:195-208.

Zhang Z, Zhang Y, Lin Z, Mulyadi A, Mu W, Deng Y (2017) Butyric anhydride modified lignin and its oil-water interfacial properties. Chemical Engineering Science. 165:55-64.

Zhou Y, Fan M, Lin L (2017). Investigation of bulk and in situ mechanical properties of coupling agents treated wood plastic composites. Polymer Testing.58: 292-299.

Zhuravlev E, Madhavi V, Lustiger A, Androsch R, Schick C (2016) Crystallization of polyethylene at large undercooling. ACS Macro Letters. 5:365-370.

Zivkovic I, Pavlovic A, Fragassa C (2016) Improvements in wood thermoplastic matrix composite materials properties by physical and chemical treatments. International Journal for Quality Research. 10 (1).

Vicki Marais
Dorfstr. 31
23881 Koberg
Germany

12.12.2020

Letter of confirmation

I, Vicki Marais, being an English teacher at the Berlitz Language school, located in Hamburg, Germany; hereby confirm that I have assisted Pouria Rezaee Niaraki with her dissertation *Correlation of physical bonding and shear strength in wood plastic composite*.

Having grown up and resided in South Africa for twenty one years with English as my home language, after which I spent 14 years in England, I can confirm that I am a native speaker of the English language. Additionally, all of the my schooling and further studies were completed in English.

I assisted Pouria by correcting the language of her dissertation, in order to clarify her thoughts and the results of her study. I reviewed the complete dissertation, from the index to the conclusion.

Marais

Vicki Marais