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Structural bonding of European beech wood (*Fagus sylvatica* L.) with polyurethane adhesives

A study investigating various aspects of wood-adhesive interactions with a focus on wood extractives

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Dedicated to Helmut Pohland

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Friend and mentor

Abstract

Forest management plans in Central Europe will lead to an increasing hardwood harvest in the next decades. Until now, most of this harvest is being used for energy production. The bonding of hardwood can be a way to create more profitable products and bind carbon dioxide on a long-term. Simultaneously, adhesive manufacturers are searching for alternatives to standard formaldehyde-containing adhesives systems. Polyurethane adhesives can be a suitable alternative to bond hardwood or alternative wood species, but often show adhesion deficits when the wood-adhesive-bond is exposed to humid climate conditions. Especially the common standards such as EN 302, which have their origin in softwood bonding, strain hardwood to a higher degree due to its higher strength, as well as their higher swelling and shrinking coefficients. This requires further analysis on the wood-adhesive-interactions and is the motivation for the present thesis.

This study was performed on the base of an industrial research project that was mainly concerned to the development of a two-component polyurethane adhesive (2C PUR) system as an alternative for structural hardwood bonding. An experimental 2C PUR system was characterized and adjusted by various additives and fillers towards a proper hardwood bonding. This approach showed a certain capability of 2C PUR for structural hardwood bonding and sufficient performance in dry conditions, while the system still shows room for improvement in wet conditions.

In order to develop an adhesive system for structural hardwood bonding, deeper understanding of the interactions at the wood-adhesive interface and interphase are required. Therefore, main focus of this thesis was to better understand the possible influence of wood extractives and the performance of the interface at varying climate conditions. In the focus of the present research were polyurethane adhesives, but melamine-urea-formaldehyde and phenol-resorcinol-formaldehyde adhesives were also tested for comparison.

Main part of the investigation dealt with the influence of wood extractives on the curing behavior and mechanical performance on wood bonds in varying climate conditions. The findings show that all tested adhesive systems were negatively influenced by specific wood extractives. However, the adhesives were mainly influenced by those extractives which commonly occur in both, soft- and hardwoods. Henceforth it can be concluded that extractives specific for hardwood play a subordinated role in adhesion deficits.

Further studies within this thesis investigate the performance of wood-adhesive-bonds at the interface area under varying conditions. In addition, the influence of an adhesion promoting agent (primer) in combination with 1C PUR on the performance of beech wood bonds was tested. As a novelty, nanoindentation was successfully used to characterize the wood-adhesive interactions at the interface of water-stored bonds and extend possible application of this method. However, only minor effects of the primer on the local adhesion between adhesive and cell wall could be observed.

Zusammenfassung

Die Waldbewirtschaftungspläne in Mitteleuropa sehen einen steigenden Laubholzanteil in den nächsten Dekaden vor. Bisweilen wird der Laubholzeinschlag größtenteils zur Energiegewinnung genutzt. Das strukturelle Verkleben von Laubholz ist eine Möglichkeit ein profitableres Produkt zu schaffen und langfristig Kohlendioxid zu binden. Gleichzeitig suchen Klebstoffhersteller nach Alternativen zu klassischen formaldehydhaltigen Klebstoffsystemen. Polyurethanklebstoffe haben das Potential Laubholz und alternative Holzarten zu verkleben, zeigen aber oft Adhäsionsdefizite, wenn der Holz-Klebstoff-Verbund sich ändernden Klimata ausgesetzt ist. Zur erfolgreichen Modifizierung von Polyurethanklebstoffen sind weitere systematische Untersuchungen der Verklebungsschwachstellen und der Systematik dieser Defizite notwendig.

Die vorliegende Arbeit wurde auf Grundlage eines industriellen Forschungsprojektes durchgeführt, welches sich hauptsächlich mit der Entwicklung eines Zwei-Komponenten Polyurethanklebstoffsystems (2C PUR) beschäftigte. Zur Entwicklung des Klebstoffsystems sind weitere Kenntnisse über das Grenzflächenverhalten der Holzklebstoff-Interaktionen notwendig. Der Fokus der Arbeit lag auf Polyurethanklebstoffen. Zum Vergleich wurden ferner Melaminharnstoffharze und Phenol-Resorzin-Formaldehydklebstoffe untersucht. Ausgangspunkt war eine 2C PUR-Laborvariante, welche durch zahlreiche Additive und Füllstoffe zur Anpassung an die Laubholzverklebung modifiziert und anschließend charakterisiert wurde. Dieser Ansatz zeigte eine eingeschränkte Eignung von 2C PUR für die strukturelle Laubholzverklebung durch ausreichende Verklebungsfestigkeit in trockenem Klima. Jedoch führte Feuchteeintrag häufig zu Adhäsionsdefiziten an Buche.

Holzinhaltsstoffen wurde ein entscheidender Einfluss auf die strukturelle Vollholzverklebung und speziell die Verklebung von Laubholz zugesagt. Daher wurde in dieser Arbeit der Einfluss von Holzinhaltsstoffen auf die Aushärtung mehrerer Klebstoffsysteme, als auch auf die mechanische Festigkeit von Buchenverklebungen (*Fagus sylvatica* L.) in verschiedenen Klimata untersucht. Die Ergebnisse zeigen, dass alle Klebstofftypen durch einzelne Extrakte negativ beeinflusst wurden. Hierbei spielen die Extrakte, welche in Nadel- als auch Laubholz vorkommen, eine größere Rolle als die für Laubholz spezifischen Extrakte. Daher kann angenommen werden, dass die für Laubholz spezifischen Extrakte in den auftretenden Adhäsionsdefiziten, eine untergeordnete Rolle spielen.

Weitere Arbeiten untersuchten die Holz-Klebstoff-Eigenschaften an den Grenzflächen in variierenden Klimata. Ferner wurde der Einfluss eines Haftvermittlers (Primer) in Verbindung mit 1C PUR an Buchenholz geprüft. Erstmalig konnte Nanoindentierung erfolgreich zur Charakterisierung der Grenzfläche zwischen Holz und Klebstoff im nassen Zustand angewandt werden. Dies kann zu einer Erweiterung der bisherigen Anwendungsmöglichkeit der Methodik führen. Es konnte jedoch nur geringe Effekte des Primers auf die lokale Adhäsion zwischen Klebstoff und Holzzelle festgestellt werden.

Acknowledgements

This dissertation represents the work of my scientific studies at the Bern University of Applied Sciences (BFH) in Biel, Switzerland that were carried out within the frame of the research project “2K PUR Laub” (Project no. 18063.1). The project was funded by the Swiss Innovation Agency Innosuisse and I hereby want to thank for the financial support gratefully.

I wish to express my sincere thanks to my doctor father Univ. Prof. Dipl.-Ing. Dr. Johannes Konnerth from the University of Life Sciences in Vienna, Austria for his great support and encouragement during my PhD-studies. Further, I want to thank my supervisor at the BFH, Prof. Dr.-Ing. habil. Dr. h.c. Peter Niemz for his ambitious support and the establishing of various contacts to other research institutions.

Special thanks go to our industrial partner, the swiss adhesive manufacturer Collano AG. In particular I want to thank Dr. Steffen Harling for always having an open door to listen and his untiring continuing of the adhesive modification. Moreover, I want to thank Hans Stalder, Guntram Weiland and Daniela Odermatt for their contribution and support.

Furthermore, I want to thank Prof. Dr. Frédéric Pichelin, Head of Institute for Materials and Wood Technology (BFH) for his assistance in the project and Prof. Dr. Ingo Mayer for his expertise in the field of wood extractives. Next, I want to thank Nathalie Bieri for her practical support in the laboratory.

In addition, I want to thank the Institut für Holztechnologie gemeinnützige GmbH Dresden (IHD) and especially Prof. Dr. Mario Beyer and Dr. Christiane Swaboda for their advice during my work at their institute and the possibility to use their laboratory equipment.

In the end, I want to thank my wonderful wife Paula. Your endorsement and patience helped me a lot during this time and make you the wonderful person you are!

Specific research methods

The aim and methods of the specific studies are divided and explained followingly by their organization in manuscripts and listed by roman numbers:

Paper I demonstrates the characterization of experimental 2C PUR variants. Wetting properties on beech wood in terms of contact angle, free surface energy, surface tension as well as polar and non-polar compound were analyzed. Tensile strength and elastic modulus of the 2C PUR were determined following ISO 527-1. The mechanical performance on beech wood was investigated by lap-shear joints on beech wood (according to EN 302-1) and compared with a commercial 1C PUR and PRF adhesive.

Paper II shows an approach to determine the influence of eight selected wood extractives on curing and performance on wood bonding of an experimental 2C PUR system. Some of the chosen extractives commonly occur in both, hard- and softwoods while a few represent extractives that are characteristic for soft- or hardwood only. Their influence on the polyaddition reaction of 2C PUR was investigated by Attenuated total reflectance fourier-transform-infrared-spectroscopy and on the curing behavior in terms of gel point and storage modulus by rheology. Furthermore, extractives were blended into the adhesive and applied on European beech wood (*Fagus sylvatica L.*) to access lap-shear performance following EN 302-1.

Paper III While in paper II, 2C PUR was in focus, paper III shows the comparison to benchmark adhesives, namely 1C PUR, MUF and PRF. Furthermore, the setup in rheology and lap-shear tests was further changed. In particular, the extractives were not blended into the adhesives, but applied on the wood/veneer surface shortly before adhesive contact in both rheology and lap-shear experiments.

Paper IV investigates the wood-adhesive interactions of beech wood in wet condition to better understand common adhesion deficits with polyurethane. Therefore, nanoindentation was used to analyze a possible primer effect in combination with 1C PUR. PRF was further tested for comparison. Reduced E-Modulus and hardness of the bulk adhesive and of the wood cells were determined. Furthermore, the local adhesion between adhesive and wood cell was tested. Afterwards the results of nanoindentation were compared with micromechanical properties of lap-shear joints following EN 302-1. In addition, the influence of primer on the hydroxyl group accessibility of beech wood was determined by Dynamic vapor sorption analysis.

Declaration of authorship

Paper I. Bockel, Harling and Konnerth conceptualized the paper. Harling and Weiland prepared the adhesive system. Bockel carried out all experiments and evaluated the results with guidance of Harling and Konnerth. Niemz, Konnerth, Bockel and Pichelin jointly discussed the results and Bockel wrote the manuscript.

Paper II. Bockel and Mayer designed the structure of the study. Harling and Weiland prepared and developed the used adhesive. Bockel performed the ATR-FTIR, rheology and lap-shear joint experiments. The results of the ATR-FTIR experiments were jointly evaluated by Bockel and Bieri, the rheology experiments in agreement with Swaboda and Beyer. Results were discussed jointly by all authors and Bockel wrote the manuscript.

Paper III. Bockel designed the experimental setup of the paper. Harling and Weiland prepared a part of the used adhesives. Mayer supervised the selection of wood extractives and the interpretation of the results. Bockel evaluated the results of the ATR-FTIR experiments with guidance of Bieri. Bockel further discussed the rheology experiments with Swaboda and Beyer. The results were evaluated and discussed with all authors and Bockel wrote the manuscript.

Paper IV. Bockel and Konnerth planed the study. Harling and Weiland prepared a part of the used adhesives. Bockel carried out the nanoindentation experiments under the supervision of Konnerth. Bockel further performed the lap-shear joint experiments. Grönquist executed the DVS experiments. Pichelin, Niemz, Konnerth and Bockel jointly evaluated the results and Bockel wrote the manuscript.

Preface

Frame for this thesis was the research project “2K PUR Laub” (project no. 18063.1) funded by the Swiss Innovation Agency Innosuisse (Bern, Switzerland) which was carried out at the Bern University of Applied Sciences (Biel, Switzerland) in cooperation with the adhesive manufacturer Collano AG (Sempach Station, Switzerland). The research project was mainly concerned with the development of an 2C PUR adhesive for structural hardwood bonding. The dissertation was performed at the University of Natural Resources and Life Sciences (BOKU) in Vienna (Austria) in the Department of Material Sciences and Process Engineering (MAP) at the Institute of Wood Technology and Renewable Materials. The thesis was supervised by Univ. Prof. Dipl.-Ing. Dr. Johannes Konnerth of BOKU and Prof. Dr.-Ing. habil. Dr. h.c. Peter Niemz (BFH). Some experiments were carried out at the Institute of Wood Technology and Renewable Materials in Tulln (Austria). Another part of this thesis was realized at the Technical University Vienna (Vienna, Austria) in July 2018. Further studies were conducted at the Institut für Holztechnologie gemeinnützige GmbH Dresden (Dresden, Germany) in the Department of Chemistry within December 2016 and December 2017. In addition, few experiments were undertaken by Philippe Grönquist at the Swiss Federal Institute of Technology in Zurich (ETH), Switzerland in the Institute for Building Materials.

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List of abbreviations

1C PUR	One-component polyurethane adhesive
2C PUR	Two-component polyurethane adhesive
ATR-FTIR	Attenuated total reflectance fourier-transform-infrared-spectroscopy
A1	Treatment according to EN 302-1. Testing in standard climate.
A2	Treatment according to EN 302-1. Testing of water-immersed samples.
A4	Treatment according to EN 302-1. Testing of boiled and water-stored samples.
A5	Treatment according to EN 302-1. Boiling and water-storing samples. Testing of re-condition samples in standard climate
CLT	Cross-laminated timber
DVS	Dynamic vapor sorption analysis
EMC	Equilibrium wood moisture content
EN	European standard
E_r	Reduced elastic modulus (GPa)
G ‘	Storage modulus [Pa]
G ‘‘	Loss modulus [Pa]
Gel point	G ‘‘ = G ‘
Glulam	Glued laminated timber
H	Hardness (GPa)
LVL	Laminated veneer lumber
MOE	Modulus of elasticity [MPa]
MF	Melamine formaldehyde adhesive
MUF	Melamine urea formaldehyde adhesive
NI	Nanoindentation
η^*	Complex shear modulus [Pa]
NCO	Functional group of isocyanate
PF	Phenol formaldehyde adhesive
PVAc	Polyvinyl acetate adhesive
PRF	Phenol resorcinol formaldehyde adhesive
RH	Relative humidity of the ambient air [%]
Tan delta	G ‘/G ‘‘

TS	Tensile strength [GPa]
TSS	Tensile shear strength τ [MPa]
WFP	Wood failure percentage [%]
WMC	Wood moisture content [%]
W_{total}	Specific work of indentation (J/mm^2)

1. Introduction

1.1. Motivation and research gap

The use of timber as an engineering material has been known for thousands of years. Nowadays wood is increasingly used due to its positive influence on the carbon dioxide footprint of constructions and its better ecological performance in comparison to cement and steel [1]. Furthermore, recent forest inventory data evidence a rising amount of hardwood harvest for the next decades in Central Europe [2]. Predominant in this development is the species European beech wood (*Fagus sylvatica* L.) followed by European ash wood (*Fraxinus excelsior* L.), maple (*Acer*), oak (*Quercus*) and others [2]. The sales market is yet not prepared for the size of this trend and most hardwood until now is used thermally for energy production. One way to use hardwood more sustainable and efficient is the bonding to structural elements such as glue laminated timber (glulam), cross-laminated timber (CLT), laminated veneer lumber (LVL), hybrid composites or local enforcements [3].

Bonding of wood components is the most common connection technique in modern timber engineering and the processing of engineered wood products has the potential to overcome the challenges that arise with hardwood processing, such a higher tapering, higher swelling- and shrinking coefficients etc. [4]. The hardwoods often higher density and mechanical strength has the potential to produce solid wood products with smaller dimensions, but higher strengths.

Nowadays, only few manufactures in Central Europe process hardwood for structural bonding in a larger amount. The company Pollmeier Massivholz GmbH & Co.KG in Creuzburg/ Germany and Abalon Hardwood GmbH in Heiligenkreuz/ Austria show that is possible to process hardwood on a large scale. Pollmeier for example processes around 500.000 m^3 of European beech wood to high-quality assortments [2] annually. Furthermore, its innovative LVL product “Baubuche” from 3 mm thick beech veneer, bonded with phenolic adhesives, found its market entry in 2014. Another new producer is Fagus Suisse in Les Breuleux, Switzerland, who produces blockboards, block laminated lumber, block cross-laminated lumber and lamellas from European beech wood with melamine-formaldehyde adhesive.

A survey of Ohnesorge et al. [5] showed that the majority of the laminated wood manufactures in German speaking Europe use melamine-urea-formaldehyde (MUF) or melamine-formaldehyde (MF) adhesives with a share of 51%, while polyurethane adhesives were used by around 35% and resorcinol-based adhesives such as phenol-resorcinol-formaldehyde (PRF) and phenol-formaldehyde (PF) by about 9% of the manufacturers. Beside facing a new raw material mix on the market, industry and science are searching for adhesive systems that emit low or no formaldehyde. This trend was aggravated by the enlisting of the World Health Organization of formaldehyde as carcinogenic [6].

An interesting alternative to formaldehyde-containing adhesives is presented by polyurethane adhesives, which have been increasingly used in the field of structural wood bonding or finger jointing applications [7]. Polyurethane adhesive is mainly found as one-component polyurethane (1C PUR) adhesive, but also a few two-component polyurethane (2C PUR) adhesives are available. Main difference between both systems is the curing character and the process steps. While 1C PUR adhesive cures with the humidity of the adherend and environment, 2C PUR is able to cure without need of humidity from the adherend but by its own components (polyol and isocyanate). Therefore, the use of 1C PUR can be critical when bonding in environments of very low moisture contents [8]. 2C PUR comes with polyol and isocyanate separated and requires their blending shortly before application. Until now, 2C PUR is mostly being used for the bonding of rod threads into glulam. Another new approach is the face-butt bonding of softwood for structural purposes [9]. However, only few studies have been investigating the suitability of 2C PUR for structural wood bonding [10] [11].

Polyurethane adhesive in general can be characterized as light-colored, formaldehyde- and solvent-free and are of ductile character with having a high cohesive strength. They are known to bond softwood, especially spruce wood, well, while its use on hardwood often leads to adhesion deficits. These deficits could be mechanical weak points at the interface of adhesive and wood which lead to adhesion failure, especially when moisture is induced.

Some manufacturers therefore use an adhesion promoting agent (primer) to overcome adhesion deficits when the adherend is exposed to varying climate conditions. However, the window for optimal primer application is quite narrow [12] and small deviations can eliminate the positive effect.

The adhesion deficits of polyurethane adhesive on hardwood require a further understanding of the wood-adhesive-interactions as well as a mechanical-chemical modification of the adhesive system. 2C PUR systems are predestinated for such modification due to their separate components and blending only shortly before application. The hardness, a mechanical parameter used as a synonym for mechanical properties in general, was postulated as the main tweaking point by Clauß et al. [13]. It was concluded in their study, that with an increasing hardness of 1C PUR adhesive, a higher bonding performance on hardwood can be reached. Further, Na et al. [14] stated that high amounts of hard segment proportion and high cross-linking density yielded in better 1C PUR adhesive performance.

Later Harling et al. [10] used this approach to decrease the delamination of 2C PUR on beech wood from 100 to 30% by adding high filler contents to the polyol (60%) component.

Therefore, the initial variant of the 2C PUR tested in this thesis was modified with calcium carbonate as a filler and further additives. Next to an expected increase in tensile shear strength and delamination resistance, it was further aimed to achieve optimum wetting properties as well as a higher E-Modulus of the polymer in comparison to standard 1C PUR adhesives.

- Hypothesis (**No.1**) is that the modification of 2C PUR by filler and additives to increase the E-modulus can overcome bond strength deficits on hardwood and surpass requirements following EN 302 - 1 in dry and wet conditions. This is assuming that the adhesive is the weak point and adhesive modification by increasing the cohesive strength of the adhesive itself should result in better bond strength.

Research on polyurethane adhesives and in general structural adhesives for hardwood offers many starting points. Knowledge of the wood-adhesive-interactions can further help understanding the complex process of hardwood bonding. In recent studies on hardwood bonding [15] [16], it was expected that wood extractives can play a role in the occurring adhesion deficits on hardwood due to the formation of a chemical weak boundary layer.

Few studies and reviews have been dealing with the influence of extractives on wood bonding [17] [18] [19] [20]. The different surface chemistry of hardwood in comparison with softwood can lead to a lower surface energy and therefore influence the bonding with acid-curing adhesives [21], as well as the wetting performance in general. The influence of extractives was often assumed by determining extractive contents in wood [22] [23] or the bonding of extracted wood [24]. However, detailed knowledge is missing on the influence of various extractives on the curing and mechanical performance of relevant structural wood adhesives. Therefore, different methods were considered that could demonstrate a possible influence of extractives on the bulk adhesive such as Attenuated total reflectance fourier-transform-infrared-spectroscopy (ATR-FTIR) and rheology investigations. In addition, the performance of wood-adhesive bonds with applied extractives can reveal new insights towards the composite. Aim of this study was to evaluate a possible influence of wood extractives on the curing behavior and the mechanical performance on structural adhesives in glue joints, exposed to varying climate conditions. In addition, the question arises whether extractives that commonly occur in hardwoods impact the bonding to a higher degree than extractives that are common to softwoods.

- Hypothesis (**No.2**) is that wood extractives influence the curing behavior of structural adhesives as well as the performance of the bonded wood.

The bonding of hardwood with polyurethane in various climate conditions by means of lap-shear or delamination test has been topic to various studies [12] [4] [25] [26]. However, the function of the primer used in combination with 1C PUR adhesives is not fully understood yet. Testing single and pure adhesive films might not be able to display the real conditions in a bond line, since the surrounding wood affects the curing, mechanical relaxation and morphology as found by Ren et al. [27]. Therefore, investigations on wood-polymer-interactions are preferably conducted in a real joint. Few information is further available on the influence of primer on the micromechanical properties of the adhesive bond in various climate conditions. The primer is expected to improve the wetting of the adhesive and stabilize the wood cell walls at the interface and interphase [28] [29]. According to Frihart [29], the term “interface” is defined as the direct (local) boundary between the wood cell wall and the adhesive. The term “interphase” is being used for the region within an adhesive bond where the adhesive penetrates the pores of the wood substrate. Within this interphase multiple local “interfaces” are present.

In comparison to standardized testing methods, which often analyze the composite, nanoindentation (NI) can be used to precisely analyze local micromechanical properties. It was first applied on wood cell walls by Wimmer et al. [30]. Various studies on wood cell walls, bulk adhesives and their interactions followed to better understand the joint performance [31] [32]. Studies in this field mainly addressed the interphase region of wood-adhesive-bonds in dry conditions or the influence of moisture on thin adhesive films. Only few investigations have been carried out including the influence of different climate conditions [33] [34]. Hence, information is missing on how the primer functions at the interface between wood and adhesive. The interface should be tested by NI in water-stored conditions, where composites of wood and polyurethane adhesive often fail and where the primer can prevent adhesion deficits on hardwood. One possible approach to test interface performance by nanoindentation (NI) was proposed by Obersriebnig et al. [32]. This approach can reveal further insight in the wood-adhesive interaction in water-stored conditions as well as showing influence of the primer. Aim is to determine the influence of primer on the properties of wood cell walls at the interface and interphase.

- Hypothesis (**No.3**) is, that the application of primer increases the adhesion between wood cell wall and adhesive in wet conditions.

1.2. Selected methods

An overview of selected experimental methods are found in Table 1.

Table 1 Experimental methods, their standards and assignment to the papers.

Tested material	**Method**	**Standards and methods**	**Paper**
Wood-adhesive-bond	Tensile shear strength	EN 302-1 [35]	I, II, III, IV
	Rheology	-	II, III
	Nanoindentation	Obersriebnig et al. [32]	IV
Bulk wood	Dynamical vapor sorption analysis	Thybring et al. [36]	IV
	Contact angle measurement	DIN 55660-2 [37]	I
	Free surface energy	DIN 55660-2 [37]	I
	Tensile shear strength	EN 302-1 [35]	I, II, III, IV
	Nanoindentation	Obersriebnig et al. [32]	IV
Bulk adhesive	ATR-FTIR spectroscopy	-	II, III
	Contact angle	DIN 55660-2 [37]	I
	Surface tension	DIN 55660-3 [38]	I
	Rheology	-	II, III
	Tensile strength	EN ISO 527-1 [39]	I
	Nanoindentation	Obersriebnig et al. [32]	IV

A first step in adhesive characterization is often in determining the wetting properties on the adherend wood. Typically, the contact angle on the adherend wood as well as the free surface energy of the adherend is determined following DIN 55660-2. The adhesives surface tension can be characterized by the method if pendant drop (DIN 55660-3) and is used to describe the wetting performance. These methods can be primarily used to evaluate one adhesive system since adhesive properties are mainly influenced by formulation and viscosity. However, limitations are given for comparison in-between different adhesive systems. In addition, it can only describe a narrow window of time-related wetting.

A method to analyze the adhesive-wood-composite is the testing in tensile shear-mode using lap-joint specimens following EN 302-1. This standard method can test the joint strength, where adherend and adhesive as well as their interactions can be analyzed. Further, the joint can be tested at various climate conditions with a considerably low wood usage. As this method is used for accreditation of adhesives intended for structural applications, an immense number of literature can be found [4] [15] [26].

The curing-behavior of adhesives is often analyzed chemically by ATR-FTIR-spectroscopy [40] [41]. The physical properties of curing can be observed by rheology [42] measurements. Hence, these methods are also predestinated to determine a possible influence of wood extractives on the behavior of adhesives.

To determine the mechanical bulk adhesive properties, usually tensile strength and E-Modulus of thin polymer films are determined. The method allows for an evaluation of mechanical properties of cured adhesives independent of the adherend wood. Comparative values can be found in the literature and the parameters were chosen as recommended by Kläusler et. al. [43].

Nanoindentation (NI) has been successfully used to characterize wood components and structural adhesives in dry and humid conditions [44] [45] [34].

Since the effect of primer is often determined macroscopically in mechanical composite performance by delamination or lap-joints [26] [12], the use of NI may help to determine the influence of primer on the micromechanics of wood cell walls and adhesive at the interface and interphase. In comparison with humid conditions, the storage in water should simulate the conditions applied in these standards and accounts for deeper insights of the primers function.

The accessibility of hydroxyl groups of wood shows the reaction potential with adhesives. It was assumed that the primer can influence the hydroxyl accessibility of hardwood which often shows a high degree of acetylation in comparison with softwood [46]. This can be analyzed by Dynamic vapor sorption analysis as shown in a prior study [36].

2. Fundamentals

2.1. Wood characteristics

Wood is a natural construction material and characterized by inhomogeneous, anisotropic and porous behavior. The benefits of wood for construction are its natural origin and low energy consumption and cost during production and transportation [47]. Furthermore, wood constructions can be built considerably fast and have high strength with a comparable low weight. In addition, they have a reduced carbon footprint in comparison with other established materials such as cement and steel [48].

The basic elements of wood are illustrated in Figure 1. From the outside of the trunk to the center are bark, cambium, sap wood, core wood and the pith (compare Figure 1).

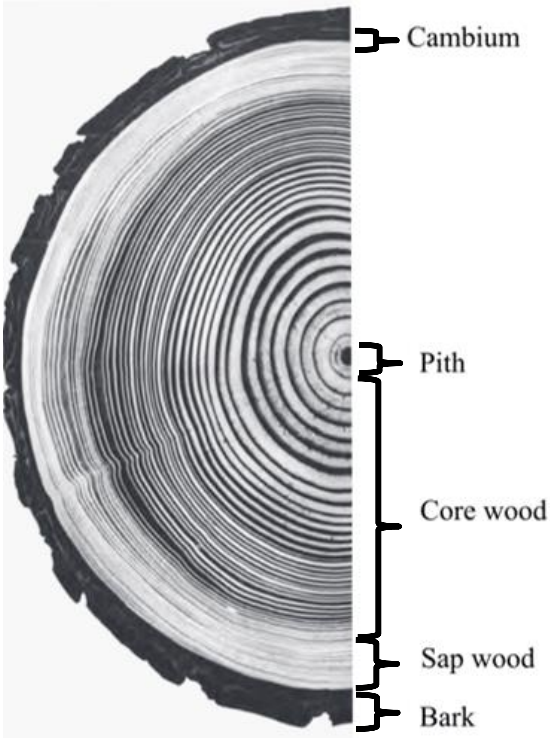

Figure 1 Basic overview of tree trunk at the example of softwood according to Grosser [49].

The outer bark provides mechanical protection for the softer inner parts of the tree. In the inner bark (phloem), the assimilates produced by photosynthesis in the leaves are transported to the roots and growing parts. The cambium layer produces wood to the inside secondary xylem and inner bark to the outside secondary phloem and is therefore responsible for the increasement. The sap wood is the living part of the tree and transports water from the roots to the leaves. Primary function of heart wood in the center of the trunk is mechanical strength for the trunk and storage of various nutrients. This part can be often easily visually differenced by the accumulation of mainly colorful chemicals that gives the heartwood a darker color for many species. The pith is the remnant of the first years of growth before the wood was formed.

The seasonal growth in temperate zones forms annual rings. The growth rate is highest in early spring, forming early wood, while it slows down during summer and autumn, producing latewood. Often the vessels are more wide-lumen with thinner cell walls in early wood (EW), while late wood (LW) is characterized by smaller lumen and proportionally more cell wall (compare Figure 2). The planes of a trunk can be divided as follows: the longitudinal (L) axis runs parallel to the fibers, the radial (R) shows the growing increments from the pith to the bark and the tangential (T) axis runs perpendicular to the fiber grain and tangential to the radial axis (compare Figure 2 and 3).

Density is one of the most important physical properties of wood and determined by the wood anatomical structure [48]. The density increases when the proportion of cells with thick cells walls rises. Therefore, hardwood often has a higher density, but also the amount of void spaces by vessels needs to be considered. The density is always related to the wood moisture content, which is another crucial properties of wood. Due to the woods high number of pores (in average 50-60% of the wood material), it has a high inner surface area [6]. This cavity system absorbs humidity from the air as well as other liquids such as adhesives.

Wood obtains a three-dimensional network of cells with different tasks such as conducting, storing and strengthening cells. The orientation and composition of these cells varies greatly for soft- and hardwood and further for individual species. Softwood contains a much simpler anatomical structure and has mainly tracheids (≥ 95%) [4] and parenchyma, but further wood rays, resin channels and pits as illustrated in Figure 2.

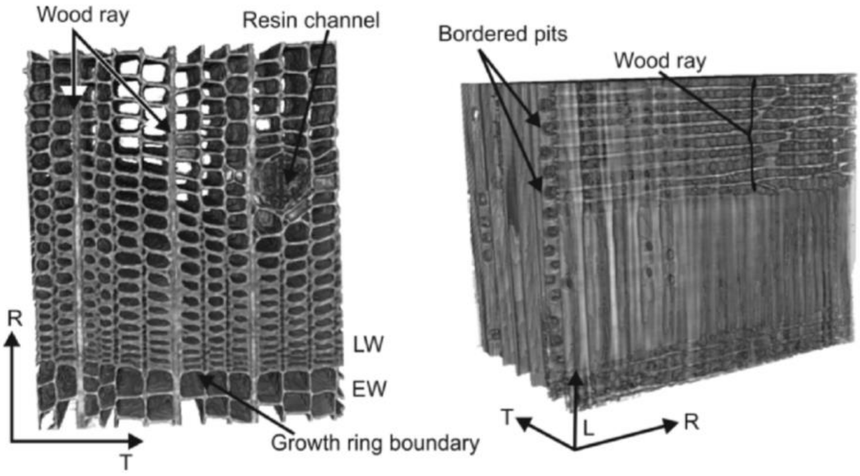

Figure 2 Anatomic of softwood at the example of Norway spruce (*Picea abies* Karst) [50].

Tracheids are very long cells often 100 times longer (1-10 mm) than wide and conduct mechanical and conductive needs to the three. The parenchyma mainly contains a storing function and the specialized parenchyma cells surround the resin channels to produce secretes. Wood rays are for the radial conduction of water and minerals from the center to the periphery. The flow of aqueous solution in-between the tracheids is controlled by the opening between the cells and named pits. These thin areas between two cells consist of a pit membrane, the pit aperture and the pit chamber.

In contrast to softwood, hardwood provides a higher amount of different cell types as illustrated in Figure 3. Hardwood contains various fibrous elements such as vessels and parenchyma in different patterns. Similar to softwood, pits are responsible for axial transport of aqueous solutions. Vessels are the water-leading elements in hardwood and connected by perforation plates. Tangentially, vessels can be connected with bordered pits. Parenchyma is mainly used for the storage of starch [47].

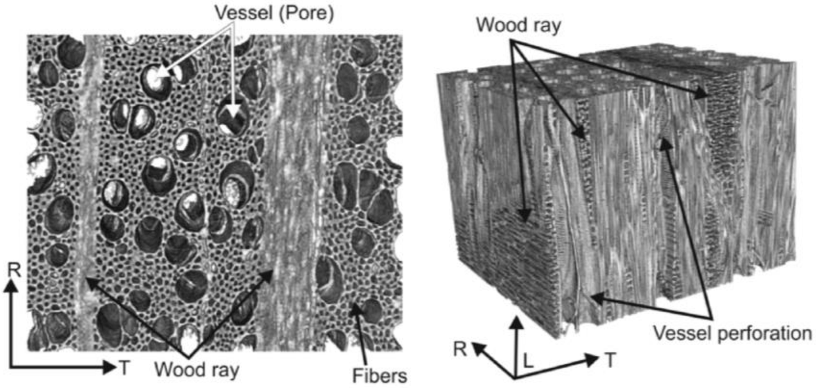

Figure 3 Anatomic of hardwood at the example of European beech wood (*Fagus sylvatica* L.) [50].

Understanding the woods properties in greater detail requires a view on the wood cells structure independent of its origin in hardwood or softwood as depicted in Figure 4.

In most wood cells, the cell walls and cell lumen dominate the visual appearance. The cell lumen is a void space. The cell wall consists of four wall layers which differ in their chemical composition as well as in their orientation of microfibrils. These microfibrils contain cellulose chains which are connected to thin macrofibrils of thickness of 10-25 nm [47]. Crystalline and amorphous parts are arrayed alternately. One macrofibril consist of 50-100 microfibrils and has around 0.5 µm thickness.

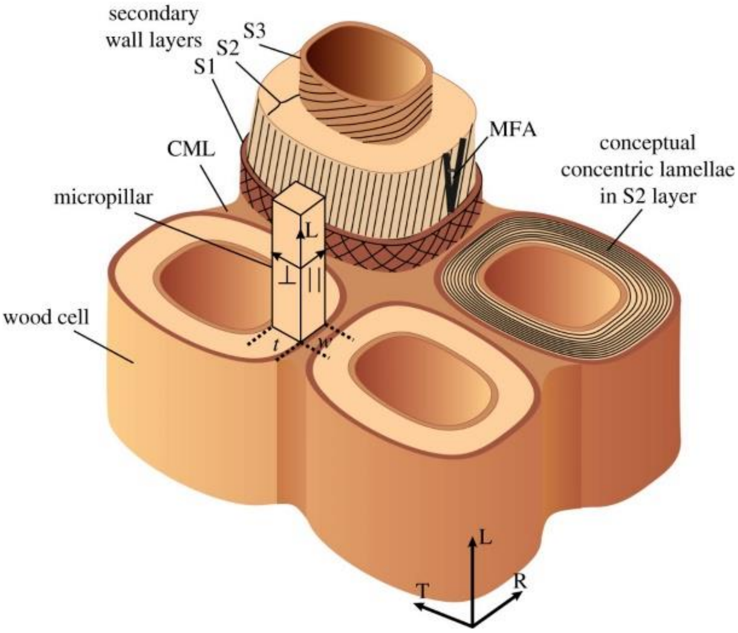

Figure 4 Wood cell overview [51].

The specific layers of the wood cell wall are the middle lamella (CML), the primary wall (S1), the secondary (S2) and the tertiary cell wall (S3). The middle lamella connects two neighbor cells and consists largely of lignin (90%), pectin and hemicellulose [52]. Due to the high lignification, this part is very stiff and has a high compression strength. The microfibril angle is around 0-50° for S2 and ca. 60-90° for the S1 and S3 layer [53]. The S2 layer is the widest component of the cell wall (80%) [47] and has therefore significant influence on the mechanical properties of wood [54]. Primary and tertiary wall only make up small amounts of the cell wall itself. In general, it can be said, that an increase in microfibril angle decreases the cell wall stiffness and increases the fracture strain.

Wood properties have to be seen as a conglomerate of different cell layers and types which lead to certain solid wood properties. In this thesis, only European beech wood (*Fagus sylvatica* L.) was used. Its anatomical, mechanical, physical and chemical properties are listed in Table 2. Norway spruce (*Picea abies*) was further listed for comparison since this species is still very abundant and commonly used in structurally wood bonding. More information about the chemical structure of wood can be found in the literature [48] [55]. Wood extractives are described specifically in chapter 2.4.

Table 2 Comparison of selected average properties of European beech wood and European spruce.

		European beech (*Fagus sylvatica* L.)	**European spruce** (*Picea abies* (L.) Karst.)
Chemical [4] [23]			
Cellulose [%]		39.4	41.7
Lignin [%]		24.8	27.4
Glucomannan [%]		1.3	16.3
Glucuronoxylan [%]		27.8	8.6
Other polysaccharides [%]		4.2	3.4
pH		5.3	4.7
Buffer capacity [mmol HCl/100g]		5.5	2.7
Extractive content [%] *		1.2	1.7
Physical and Mechanical** [55] [56]			
Density [kg/m^3]		660	420
Maximum swelling [%]	L	0.2	0.3
	R	7.7	4.2
	T	11.4	8.3
Tensile strength [N/mm^2]	L	110	90
	R	20	4
	T	9	3
Shear strength [N/mm^2]	L	10	10
Elastic Modulus [N/mm^2]	L	14.400	11.000
	R	2280	800
	T	1160	450
Compressive strength [N/mm^2]	L	45	40
	R	11	4
	T	6	4
Bending strength [N/mm^2]	L	120	80
Hardness Brinell [N/mm^2]	L	71	31
	R/T	35	12
*Extraction byCH_2CL_2 followed by C_2H_5OH **Measured at 12% RH Anatomical direction: L: longitudinal, R: radial, T: tangential			

2.2. Wood as an adherend

Adhesive bonding of wood is a complex process and differs to bonding of solid materials with its porous, inhomogeneous and orthotropic character. It involves many factors such as wood properties [57], surface preparation [58] [59], process parameters [59], adhesive type [26] and its reaction kinetics [57]. Therefore, one needs to consider multiple factors to understand the performance of an adhesive on wood.

While industry and science have plenty experience with the structural bonding of softwood, the bonding of hardwood in larger quantities is relatively new. Its manufacturing differs largely to the bonding of softwood, due to its different mechanical-physical and anatomical properties.

It’s often higher density as well as higher swelling and shrinking coefficients influences the performance of the bond line, especially when moisture is induced, to a higher degree [4]. Further, hardwood commonly has a lower free surface energy [21] than most softwood species which mainly contain hydrophobic substances such as unsaturated fatty acids and resins. Therefore, the bonding of acid-curing or pH-sensitive adhesives can be problematic with hardwood [21] as well as the wetting performance of adhesives in general.

Furthermore, isocyanate groups of polyurethane adhesives require the presence of hydroxyl groups to form urethane bonds [15]. It was shown that hardwood species such as European beech and European ash are lower in available hydroxyl groups than softwood species. Main reason for this is the higher degree of partly acetylated xylan-based hemicelluloses in hardwood [46]. In addition, the bonding process often must be adjusted towards hardwood. Manufactures therefore choose longer pressing times and higher pressure to bond hardwood. It is expected by the manufacturer that the anatomical structure as well as the higher density, require higher pressure, pressing time as well as a longer closed assembly time to form a reliable bonding line.

Bonding of wood is well described by the model of Mara [60] and depicted in Figure 5. The regions 1, 5 and 9 describe the bulk material. The interphase (2, 4, 6, 8) and the interface (3, 7) are most important in the wood bonding process. Similar to another reference [29] the term “interphase” is being referred as the region within an adhesive bond where the adhesive penetrates the pores of the wood substrate. Within this interphase multiple local “interfaces” are present. The latter is defined as the direct (local) boundary between the wood cell wall and the adhesive.

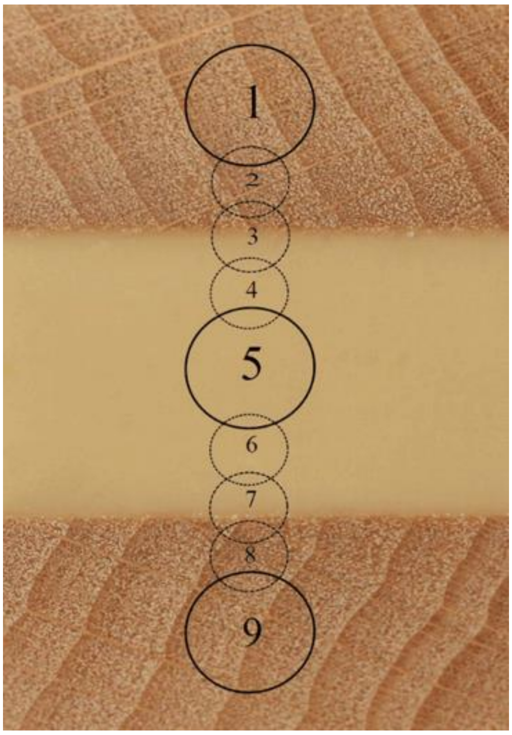

Figure 5 Model of wood bonding according to Mara [60].

Various theories on the interaction between adherend and adhesive are described in the literature [57] [21] and summarized as adhesion. While cohesion is summarized as the bonding forces in between atoms and molecules within the bulk adhesive, which lead to its strength.

Adhesion can be seen as the sum and interaction of many theories, which are described followingly. However, the individual theories shall not be seen exclusively but more occurring at the same time depending on the particular circumstances. The state-of-the-art according to Gardener et al. [21] categorizes adhesion theories into seven models:

Mechanical interlocking theory is based on geometrical factors such as an increase of surface and locking by friction and was proposed by MacBain and Hopkins in the 1990`s [21]. In wood bonding, this refers to the filling of pores and the substrate as a mechanical interlocking and is considered to contribute to some extent to the wood-adhesive bond strength. The mechanical interlocking provides higher resistance against shear forces than to normal forces [29].

Electronic or **electrostatic theory** was first proposed by Derjaguin in 1948 [61]. This theory is based on differences in electronegativity and the adherends interface can be seen as plates of an electrical condenser across which charge transfer from an electropositive to an electronegative material according to Gardener [51].

Adsorption or **wetting theory** refers to the interactions of adhesive and adherend at an atomic or molecular level. The free surface energy represents the force and is considered to be an important material property of both adherend and adhesive. According to Habenicht [42], an optimal wetting is given when the free surface energy is higher than the surface tension of the adherend and the contact angle of an adhesive drop is below 90°.

Diffusion theory bases on the concept that two materials can be solved in one another and create an interphase. According to Frihart [62] there are four scenarios for diffusion theory on wood (compare Figure 6) the occupation of free volume in the adherend, mechanical interlocking, the formation of interpenetrating polymer network, where crosslinks between the adhesives molecules and the wood cell wall are formed or where chemical crosslinks between the polymer and the wood cell wall occur.

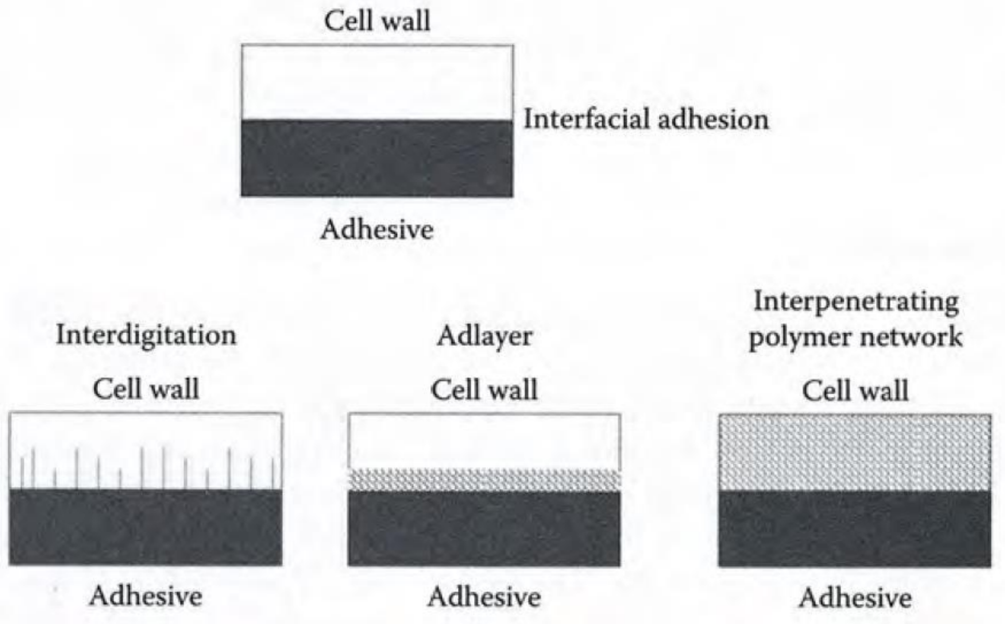

Figure 6 Models of adhesive-adherend interactions according to Frihart [62].

Chemical bonding theory or **covalent bonds** describe the state, when two atoms share an electron pair and improve the adhesion between adherends. Strong covalent bonds with dissociation energy of 60-700 kJ mol^{-1} are often discussed but can just be created under special circumstances and seem to be very unlikely to occur in solid wood bonding [21].

Acid-base theory is based on the concept where polar interactions are referred to as acid-base interactions. According to Gardener [21], an acid (electron-acceptor) is bonded to a base (electron-donor) by sharing the electron pair offered by the latter, which forms a coordinate bond.

Weak boundary layer is based on the theory that the bond cannot fail exactly at the interface between adhesive and adherend and was first mentioned by Bikermann in 1961 [63]. Later, Stehr and Johansson [64] distinguished this theory into chemical weak boundary layer and mechanical weak boundary layer. According to the authors, the chemical weak boundary layer is caused mainly by wood extractives migrating towards the surface an, while the mechanical weak boundary layer is caused by impurities, machining operation and degradation of the fibers by natural light radiation.

The bond strength itself is a sum of complex interactions. Often factors such as stress concentration, energy dissipation and deficits in surface layers have a greater influence on the bond strength than the adhesion itself [29]. The interaction forces and bond energies between adhesive and the adherend are shown in Table 3.

Table 3 Interaction forces and their bond energies following Frihart [29].

Type	Bond Energy (KJ mol^{-1})
Primary bonds	
Ionic	600 - 1100
Covalent	60 - 700
Metallic, coordination	110 - 350
Donor-accepted bonds	
Bronsted acid-base	up to 1000
Lewis acid-base	up to 80
Secondary bonds	
Hydrogen bonds	1 - 25
Van der Waals bonds	4 - 20
Dipole-induced dipole interaction	less than 2
Dispersion (London) forces	0.08 - 40

2.3. Structural wood adhesives and relevant standards

Various adhesives systems exist for the bonding of wood and wood composites. Detailed information can be found in the literature [65] [42] [57]. Adhesives used in constructions usually have a long setting time and cure at room temperature [29]. Focus of this thesis are mainly polyurethane adhesives (PUR), such as 1C PUR and 2C PUR adhesives. For comparison, a representative system of melamine-urea formaldehyde (MUF) and phenol-resorcinol formaldehyde adhesive (PRF) was used. All used adhesive systems show a chemical curing reaction (polyaddition or polycondensation), are cold-setting and create thermosetting polymers. Detailed mechanical information about the used or similar adhesive systems can be found in Table 4.

PRF adhesives can be described by forming a dark and brittle bonding line with a high resistance against humidity and changing climate conditions [66]. The curing reaction of the water-based two-component system is a polycondensation and resorcinol is used as a catalyzer to enable the cold-setting of the adhesive [29]. The adhesive systems requires basic conditions to perfectly cure [57]. Therefore, the bonding of acidic wood species such as oak, chestnut and birch can be problematic [66]. The alkali content in PRF leads to an increased water uptake and higher equilibrium moisture content [57]. This may further reduce tensions when the wood-adhesive composite is exposed to high moisture contents.

Also, phenol formaldehyde adhesives (**PF**) are being used in new structural hardwood products such as “BauBuche” but being cured by temperature. The bonding of the timber beams is afterwards carried out with PRF adhesive according to Pollmeier. While the formaldehyde emission during manufacturing require industrial safety measures, the subsequent emissions of the cured adhesive are very low [57].

MUF adhesives are a further modification of urea-formaldehyde adhesives (UF) towards better performance in humid conditions and water-based two-component adhesives. The addition of melamine increases the hydrolysis resistance due to its more stable peptide bond between melamine and formaldehyde [57]. MUF prefers acid conditions, but melamine as a good nucleophile can react with the electrophilic formaldehyde under varying pH-conditions [43].

This system has typically a light bonding line and a higher elastic modulus in comparison with PUR adhesives (compare Table 4). However, its elasticity can be adjusted by adding polyvinyl acetate (PVAc) adhesive according to Habenicht [42]. MUF is further characterized by comparingly higher formaldehyde emissions than PRF, but new adhesive systems with reduced formaldehyde content are now on the market.

PUR adhesives were introduced in the 1980s and 1990s for engineered wood products [7]. Their curing reaction is a polyaddition and the primary reaction occurs between the polyol's hydroxyl groups and the isocyanate groups of the hardener results in urethane formation. The secondary reaction takes place between the urethane and the excess of isocyanate which results in allophanate formation and cross-linking. Polyurethane adhesives are rather ductile and can be used to compensate or reduce occurring stresses in wood engineered products [67]. In wood bonding, PUR adhesives show a high cohesive strength but often adhesion deficits when bonding hardwood, which is exposed to changing climate conditions [15] [58].

According to Frihart [62], adhesive shall be grouped according to their chemistry and structure-property relationships. MUF and PRF adhesives belong to the in-situ adhesives which often infiltrate the wood cell walls and achieve a relatively rigid and highly cross-linked polymer after curing. PUR adhesives belong to the pre-polymerized adhesives which in general obtain a higher molecular weight than the in-situ adhesives. The pre-polymerized adhesives are not expected to penetrate wood cell walls and are therefore limited in developing an intermolecular network with the adherend.

Table 4 Selected properties (mean values) of different structural adhesives. Measurements are obtained from adhesive films, bond lines or bonded wood samples following EN 302-1 and EN 302-2 in standard climate conditions. The 1C PUR was applied in combination with primer.

Method	Material property	PRF	MUF	1C PUR	Reference
Adhesive film (TS)	MOE (GPa)	3.4	2.5	1.0	[43]
Adhesive film (NI)	MOE (GPa)	5.2	8.6	2.4	[45]
Bond line (NI)	MOE (GPa)	5.8 – 7.8	7.6 – 8.9	1.5 – 3.0	[68] [69] [70] [71]
Bond line dry (TSS on Beech wood, EN 302-1)	τ (MPa)	13.8	11.1	11.8	[26]
Bond line water-stored (TSS on Beech wood, EN 302-1)	τ (MPa)	7.2	7.5	6.6	
Bond line water-stored (delamination on Beech wood, EN 302-2)	Delamination (%)	2.7	6.4	8.2	

Few manufacturer of glulam’s use adhesion promoting agents (**primer**) in combination with 1C PUR adhesive to bond hardwood. In general, primer are divided into reactive and non-reactive types. The reactive primer are for example hydroxy methylated resorcinol (HMR), which has been investigated in various studies [72] [73] [28]. This primer is based on formaldehyde and requires long waiting times before manufacturing can be continued. Both characteristics yet prevented an industrial implementation. Richter [74] describes the constitution of these chemical-reactive primer in general as follows (compare Figure 7): A wetting promoting part faces the liquid adhesive. The bulk material of the primer is the hydrophobic part which further functions as a spacer grid. Facing the bulk material wood, the primer has a polar, absorbent part.

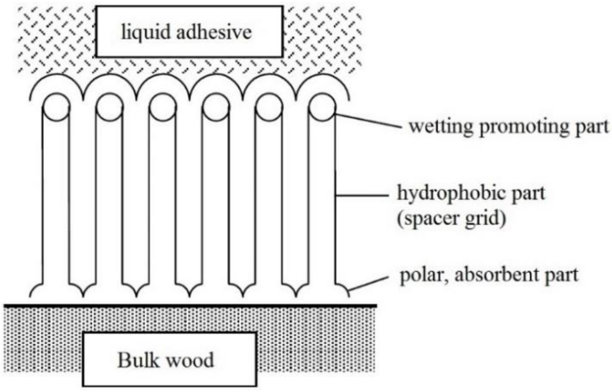

Figure 7 Adhesion promoting agent function according to Richter [74].

Non-reactive primers are often water-soluble polyol solutions and topic to this thesis. The function of the primer was topic to few studies, but often analyzed by its influence on the bonded joint in terms of tensile shear strength or delamination resistance following EN 302.

Konnerth et al. [26] showed that the application of primer can result in promising delamination resistance but does not work with every wood species similar. Robinia and ash for example showed only poor results despite primer application. In another study, Clerc et al. [12] were able to reduce delamination resistance on ash wood significantly. However, their study showed that the window of optimal primer application is quite narrow and the application weight as well as the concentration of the solved primer has to be considered carefully. Lüdtke et al. [59] investigated the influence of different combined surface treatments, such as face milling and peripheral planing with priming on different wood species. Priming in general lead to better glue joint performance in wet conditions, however, the ring-porous ash and oak wood showed lesser influence of primer, when being peripherally planed before primer and adhesive application. Therefore, the function of the primer is also influenced by the prior surface treatment of the adherend.

Research on water-based primer and 1C PUR by high resolution imaging techniques such as atomic force microscopy and confocal raman spectroscopy was performed by Casdorff et al. [75]. The atomic force microscopy showed a penetration of primer into the cell wall, however the confocal raman spectroscopy indicated, that 1C PUR did not penetrate the cell wall.

Other authors expect the primer to stabilize the woods surface mechanically [28] [62], but its exact function on the interface of wood-adhesive composite yet remains unclear.

Further experiments by high resolution imaging techniques are needed to analyze the primer function at the interface of the composite in wet conditions. This could help to address each wood species with its own primer application ratio and concentration.

In general, structural wood composites must bear various loading conditions. Next to physical-mechanical stresses, they are exposed to changing climate conditions, weathering and radiation [57]. These factors often occur together and create a complex load system that can reduce the performance of the wood-adhesive bond. In order to be approved for structural wood bonding in Europe, adhesive must fulfil requirements that are defined in standards.

An overview of tested and approved adhesive systems can be found in the literature [76]. Tensile shear strength and delamination resistance following EN 302 are standard testing to evaluate adhesive systems and provide various comparative values. This thesis uses the tensile shear lap-joints according to EN 302-1, inter alia, as a standard method to evaluate the adhesive performance. Further reference values can be found in the literature [68] [26] [4].

The production of structural wood products such as glued laminated timber, veneer laminated timber or composites is regulated by the standard EN 14080 [77]. The standards for structural adhesives are EN 301 for amino plastic adhesives [78] and EN 15425 for 1C PUR adhesives [79]. The accreditation of the components and products is performed by recognized institutions.

2.4. Wood extractives and their influence on bonding

Wood extractives or accessory compounds are non-structural components that can be extracted from wood by solvents. The components usually make up 2-5% of the dry wood mass of species native to Central Europe [55]. Furthermore, their amount and constitution can vary within tree species, location site, stem position, season, extraction method etc. [47]. On a cellular scale, extractives are concentrated in resin channels, parenchyma as well as in the middle lamellae, intercellular and cell walls of tracheids and fibers [55]. The occurrence of extractive classes is also depended on hard- or softwood. Following these extractive groups are described briefly:

- **Terpenes** mainly occur in conifers [80] and are major component of the trees resin. The most common monoterpenes of all softwood are α- and β-pinene and limonene [80]. Since these components do not contain functional groups, their influence can be expected as local hinderer of the adhesives cross-linking as described by the chemical weak boundary layer.
- **Phenolic components** are present in hard- and softwood but make up a larger part of the extractives in hardwood [55]. Most common phenolic components are phenols, tannins, stilbenes, lignans, tannins, flavonoids and isoflavone. These extractives are often characterized by some hydroxyl groups as functional groups.
- **Tannins** are phenolic components, can be found in soft- and hardwood and are in general water-soluble [55] and therefore a good solubility in water-based adhesives can be expected. They can be found in wood, bark and leaves and are classified into hydrolysable and condensed tannins [52]. Hydrolyzed tannins are built upon glucose and gallic acid and can be further hydrolyzed into these components [55], which can be transformed to acid components and influence the curing of adhesives. Condensed tannins are flavonoid-based oligomers and present an alternative phenol source to

synthetic adhesives [81]. Most promising species for phenolic sources in Europe are larch and pine [82]. Typically, tannins obtain various hydroxyl groups.

- **Carbohydrates** are produced by photosynthesis and found in hard- and softwood and used to store energy. They only make up a small part of the extractives but have an important physiological function for the plant. Further they have a technological relevance, e.g. for some cement-based wood engineered products [83] and have many hydroxyl groups as functional groups.
- Similar to softwood, hardwood contains a large number of **fats, waxes, fatty acids** and **alcohols**. Most of the fatty acids are bounded as triglycerides and mainly consist of linoleic acid [80]. In general, these extractives obtain long chains with a hydroxyl group at the end. Fats protect the woods tissue against the intrusion of water and are similar to carbohydrates, a relevant storage material. Table 5 shows the differences in linoleic acid and oleic acid for tree species native to Europe.
- **Organic acids** occur in hard- and softwood (compare Table 5). In general, they are weak acids, that do not fully dissociate in water, but therefore in organic solvents. Their functional groups are a hydroxyl group and an oxygen double bond.
- **Aldehydes** are volatile components of wood, which often dissolve in water and can originate from cleavage and oxidation of double bonds of other extractives [84]. They have one oxygen double bond as a functional group which is assumed to react with formaldehyde temporarily.

Inorganic components, such as calcium, kalium, magnesium, phosphor etc. are not topic of this thesis and further described in the literature [55]. Followingly in Table 5, selected extractives and wood properties are listed as an example for soft- and hardwoods native to Central Europe. These results show the variance of extractives and wood properties within relevant wood species for the timber industry.

It was proven that wood extractives influence various wood properties such as odor and color [55], equilibrium moisture content (EMC) at fiber saturation [85] or the dimension stability and durability[55]. Wood extractives are also known to influence various areas of wood and wood product manufacturing [86] [19].

Various extractives are expected to influence adhesives and the wood-adhesive-compound in a negative matter. Strong or medium strong acids may act as catalysts for the reaction of isocyanates with wood surfaces. Therefore, the distinctly higher concentration of acetic acids and the resulting lower pH value can serve as an explanation for the generally good adhesion performance of spruce wood [20].

Table 5 Selected wood species and some of their extractive contents [15].

Extractive	European beech	Norway spruce	European ash
	Fagus sylvatica L.	*Picea abies* (L.) Karst.	*Fraxinus excelsior* L.
Acetic acid [mg/kg]	114	423	227
Formic acid [mg/kg]	10	13	51
Linoleic acid [mg/kg]	66	235	303
Oleic acid [mg/kg]	15	113	80
Saturated fatty acids [mg/kg]	88	192	88
Unsaturated fatty acids [mg/kg]	81	499	517
Extractives pH	5.18	4.74	5.18
Surface pH	5.39	4.97	5.26

For structural wood bonding, some extractives are expected to play a negative role in this process [20]. The chemical composition of wood and especially the wood extractives mainly influence the pH-content and buffer capacity of the wood surface [87]. Therefore, wood extractives can influence the bonding by surface contamination [88], change in wettability and penetration [89] as well as the curing of the adhesive [90].

Only few studies have been conducted in the field of wood extractives on wood bonding in the last decades. This topic was primarily concerned with the import and usage of tropical wood species [20]. Later this question also arose for the usage of hardwood such as European beech wood (*Fagus sylvatica* L.), European ash (*Fraxinus excelsior* L.), Robinia (*Robinia pseudoacacia* L.) and Oak (*Quercus* L.) as well as alternative wood species e.g. European larch wood (*Larix decidua* Mill.) for structural wood bonding. The amount of extractive in European beech can also vary by the formation of heart wood. Schmidt [23] investigated the influence of formatted heartwood on the number of extractives and followingly its performance on bonding with various adhesives. He determined the extractive amount for red heart beech wood lower than for normal wood. However, no influence of heartwood was shown on its performance in bonding. On the other hand, European beech contains more extractives in the sap wood than in the heart wood – in contrast to most other species [47].

Different approaches were conducted to determine the influence of wood extractives such as surficial extractive removal [24], the artificial application on the adherend’s surface before bonding [91], the influence of extractives on bonded wooden products [18] [92] or blending of extractives into the adhesive [93]. Especially surficial extractions have to be considered carefully, when their effectiveness is not proofed and possible migration towards the surface occur [94]. Other studies determined the extractive content of wood specimen and compared it to mechanical strength of untreated samples [15] [23].

In general, the great variety and polarity of wood extractives can be seen problematic in this research question. Further information about the interactions of wood extractives and adhesives can be found in the literature [17] [20] [19] [95].

3. Main investigations

List of peer-reviewed papers and manuscripts:

Paper I
Modifying elastic modulus of two-component polyurethane adhesive for structural hardwood bonding.
S. Bockel, S. Harling, J. Konnerth, P. Niemz, G. Weiland, F. Pichelin
(Currently under revision).

Paper II
Influence of wood extractives on two-component polyurethane adhesives for structural hardwood bonding.
S. Bockel, I. Mayer, J. Konnerth, P. Niemz, C. Swaboda, M. Beyer, S. Harling, G. Weiland, N. Bieri, F. Pichelin
The Journal of Adhesion (2018), Vol. 94, Issue 10, pp: 829-845.

Paper III
The role of wood extractives in structural hardwood bonding and their influence on different adhesive systems.
S. Bockel, I. Mayer, J. Konnerth, S. Harling, P. Niemz, C. Swaboda, M. Beyer, N. Bieri, G. Weiland, F. Pichelin
International Journal of Adhesion and Adhesives (2019), Vol. 91, pp: 43-53.

Paper IV
Characterization of wood-adhesive bonds in wet conditions by means of nanoindentation and tensile shear strength.
S. Bockel, S. Harling, P. Grönquist, P. Niemz, F. Pichelin, G. Weiland, J. Konnerth
European Journal of Wood and Wood Products (2020).

3.1. Paper I

Manuscript currently under revision

Modifying elastic modulus of two-component polyurethane adhesive for structural hardwood bonding

S. Bockel[1,3], S. Harling[2], J. Konnerth[3], P. Niemz[1], G. Weiland[2], F. Pichelin[1]

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Abstract

Subject to this study is the modification of an experimental two-component polyurethane (2C PUR) as an alternative adhesive for structural hardwood bonding. The 2C PUR has been adapted by calcium carbonate as filler to increase its modulus of elasticity with the aim of increasing the modulus analogue to the ones typically observed for classic amino- and phenol based adhesives. The 2C PUR system was compared with a commercial one-component polyurethane (1C PUR) and a phenol resorcinol formaldehyde (PRF) adhesive. The wetting properties of the adhesives were tested in terms of surface tension, polar and dispersive part and contact angle on European beech wood (*Fagus sylvatica* L.). In addition, adhesive polymer films of 2C PUR were tested for tensile strength and E-Modulus following ISO 527-1. The adhesives bond performance on beech wood was determined by lap-joints according to EN 302-1 in various climate conditions.

The results show that 2C PUR has proper wettability properties on beech wood. Adding 60% wt filler to the polyol component increased the E-Modulus from 2.3 GPa (0%) to 4.4 GPa. The tensile strength of the modified 2C PUR polymer films was comparable with the industrial 1C PUR. Tensile shear strength and wood failure percentage of 2C PUR lap-joints were increased by adding filler and met requirements in dry and re-dried conditions according to EN 302-1. However, the addition of filler did not result in an improvement in wet conditions. The present study shows sufficient performance for bonding hardwood with 2C PUR in dry conditions, while the system still needs to be improvement regarding its performance in humid conditions.

Key words: adhesives for wood, polyurethane, contact angles, lap-joint, hardwood

1. Introduction

Polyurethane adhesives can be characterized as formaldehyde- and solvent-free and fast bonding at room temperature. Typically, they have a ductile character and a light-colored bonding line. Polyurethanes are created by reaction with different isocyanate and polyol types. Characteristic is the polar urethane-group that enables the adhesion on many adherends [1]. Their crosslinking reaction is a polyaddition, where the hydroxyl groups of the polyol and isocyanate groups lead to urethane formation. The secondary reaction results in allophanate formation and cross-linking which is controlled by the isocyanate excess. The reaction itself depends to a high degree on the stochiometric ratio between available hydroxyl groups of the polyol and NCO-groups (ISO-Index).

On the search for adhesives with low or no formaldehyde-emission, polyurethane adhesives lead to the continuous replacement of conventional adhesive systems, e.g. in the production of finger jointed solid timber or glulam. Furthermore, cross-laminated timber is nowadays almost exclusively produced with 1C PUR in Europe [2].

In general, polyurethane adhesive systems are available in one-component (1C PUR) and two-component (2C PUR) systems. 1C PUR contains prepolymers with reactive isocyanate groups and the curing process takes place by reaction with moisture from the adherend and ambient air. One drawback of the moisture induced curing behavior is insufficient curing when surpassing certain wood moisture content levels 8% [3]. For bonding of structural hardwood elements, few manufacturers are using 1C PUR in combination with an adhesion promoting agent (primer) to enhance the bonding performance, especially for joints exposed to humid conditions. This additional process step often requires a flashing-off time of the water-based primer solution. Recent studies showed that the spread rate of primer application and its concentration are very critical in hardwood bonding and small variations can reduce the primer’s effectiveness [4]. Furthermore, the choice of surface preparation can significantly change the bonding performance [5] as well as the primer’s efficiency [6].

The 2C PUR system comes with both components separately and is blended only shortly prior to application. This has the great advantage that the resin component can be modified to a higher degree in terms of viscosity, cross-linking density, reaction speed or polarity and the curing process becomes less dependent on the adherend’s moisture content. Furthermore, the higher flexibility in modifying the polyol component may substitute the process step of primer application, as needed for 1C PUR. Until now, the use of 2C PUR is mainly limited to the use of bonding thread rods into solid wood beams. One new application is the butt joint gluing of cross-laminated timber from softwood [7]. Only few studies have been dealing with 2C PUR in structural surface bonding, but with the restriction of testing only mechanical performance in dry conditions [8]. Own studies have been investigating the influence of extractives on the curing properties and performance of 2C PUR [9] [10].

However, polyurethane adhesives still tend to show deficits when bonding wood species different from Norway spruce, especially when bonding some hardwoods [11] [12] and when the bond is exposed to high moisture contents. An obvious difference to classical structural adhesives such as PRF and MUF [13] seems to be the significantly lower E-Modulus of PUR adhesives. Therefore, a mechanical modification aiming for an increase of modulus analogue to these classic amino- and phenol based adhesives seems to be one strategy.

The mechanical properties of polyurethane adhesives are mainly determined by the prepolymer composition, but bonding performance is often influenced by additives and fillers [14]. Very critical in polyurethane modification is the coordination of isocyanate content and functionality [15]. Shear strength of bonded wood was increased by a higher number of hard segments in polyurethane. Therefore, Clauß et al. [16] postulated hardness as the main-tweaking point in adhesive development. Harling et al. [17] was able to select suitable polyol components based on their hardness to increase mechanical performance of experimental polyurethane adhesives. Hypothesis to this study is, that the modification of 2C PUR by a filler results increased E-Modulus of the adhesive and therefore enables the adhesive to surpass standard requirements following EN 302-1 on beech wood in dry and wet conditions.

Following experiments were undertaken in this study:

1) Comparison of wetting properties of the adhesives in terms of surface tension and polarity on European beech wood by means of free surface energy and contact angle between different adhesive systems
2) Investigation of the effect of filler content in the resin component (0-60% wt) on the mechanical properties of thin 2C PUR films by means of tensile strength and E-Modulus in comparison to PRF
3) Influence of filler content in the resin component (0-60% wt) on the mechanical performance of lap-joints on beech wood following EN 302-1
4) Comparison of tensile shear strength and wood failure percentage of beech wood bonds using different adhesives in different climate conditions (EN 302-1)

2. Material and methods

2.1. Wood

Lamellas of European beech wood [*Fagus sylvatica* L.] with an average density of 689 ± 46 kg/m^3 were selected from one lot without any irregularities. The lamellas were planed for lap-joint manufacture to 10 mm thickness and subsequently conditioned in standard climate (20°C/ 65% RH) until an approximate equilibrium moisture content of 12% was reached. The determination of free surface energy of beech wood and contact angle of adhesives was carried out on one selected lamella at its radial plane with a freshly planed surface.

2.2. Adhesives

The selected adhesives for this study and some of their properties and process parameters are shown in Table 1. All polyurethane adhesives were provided by the adhesive manufacturer Collano AG (Sempach Station, Switzerland). The resin component of the 2C PUR was an experimental type polyester-polyether polyol (molecular weight 3000g/mol). Calcium carbonate was used as a filler with variants of 0, 15, 30 and 60% wt filler content.

The isocyanate component was Desmodur VK 10 from Covestro AG (Leverkusen, Germany), a mixture of diphenylmethane-4,4’-diisocyanate (MDI) with isomers and higher functional homologues (PMDI) with free reactive isocyanate groups of 31.5% (NCO).

The ISO index, describing the ratio between the isocyanate groups of the isocyanate component and hydroxyl groups of the polyol obtained 110 and should ensure saturation with isocyanate and a high crosslinking density.

The used type and amount of filler is a result of a previous selection process (not reported here), where different filler types, and amounts have been investigated in order to control the even adhesive flow into the interphase of wood and prevent a starvation of the bond line. To further support the adhesive in the bonding line, fumed silica was added to increase the surface area of the adhesive and prevent a deposition of the adhesive in the interphase. Other additives such as chain extender of low molecular weight were used to improve adhesion performance.

A commercial 1C PUR adhesive for structural wood bonding and accredited according to EN 15425:2017 (Type I) on spruce, fir and pine was chosen to evaluate and compare the 2C PUR performance. In addition, the PRF Aerodux 185 provided by Dynea AS (Krems, Austria) was selected as an established reference for structural wood bonding [1].

Table 6 Overview of adhesives, selected properties and processing parameters.

Adhesive	2C PUR	1C PUR	PRF
	Collano experimental type	Collano RP 2760	Dynea Aerodux 185 RL/HRP 155
Ratio weight (resin/hardener)	2.45: 1	-	1: 0.2
Viscosity (mPas) @ 20°C	40’000	20’000 - 30’000	8’000 - 10’000
Max. open time (min) @ 20°C	60	< 60	8-10
Application (g/m^2) one side	200	160	450
Closed assembly time (min)	0	0	30
Pressure (MPa)	0.8	0.8	0.8
Press time (h)	10	10	10

Due to the fact, that the 2C PUR variant is an experimental type, the adhesive application was selected more conservative with a spread rate of 200 g/m^2, while the spread rate of the established adhesives was selected according to the manufacturers recommendations.

Further detailed information of the adhesive systems obtained by attenuated total-reflection fourier transform spectroscopy and rheology can be found in a prior study [10].

2.3. Determining wetting properties

All measurements for determining wetting properties were carried out with the device Krüss Drop Shave Analyzer DSA 30 (Hamburg, Germany) at ambient temperature. The method following Owens, Wendt, Rabel and Kaelbe (OWRK) [18] was used to calculate the free surface energy of a solid from its contact angle with different liquids. This method further divides free surface energy into a polar and dispersive part.

The free surface energy and contact angle of European beech (*Fagus sylvatica* L.) was determined according to DIN 55660-2 [19] using static procedure. Prior experiments (results not shown) only revealed a minor difference in contact angle between tangential and radial plane of beech wood. Hence, experiments were conducted on the radial plane only. The contact angle of the adhesives on beech wood was tested by the same procedure as for the individual test liquids. For all testing liquids and adhesives, a minimum of 10 drops were tested. Purified water (Milli-Q ®) was obtained by the device Q-Gard 2 (Merck & Cie, Darmstadt, Germany). The remaining testing liquids shown in Table 2 were obtained from Sigma Aldrich in analytical grades (Buchs, Switzerland). As required by the standard, they obtain a wide range of polarity and one of the liquids obtained a polar part of 0. The drops were analyzed by ten measurements within two seconds when forming a stable drop. A total amount of 10 drops was measured for each adhesive type with a total amount of 10 measurements for each drop. In case of PRF, the drops were measured 10 minutes after initial blending to prevent the formation of bubbles during testing.

Table 2 Surface tension and its polar and disperse part of liquids to determine the wetting properties of surfaces according to DIN 55660-2 [19].

Chemicals	Surface tension σ_l (mN/m)	Disperse part σ_l^d (mN/m)	Polar part σ_l^p (mN/m)	Purity (%)
Distilled water	72.8	21.8	51.0	-
Diiodomethane	50.8	50.8	0.0	99.9
Ethylene glycol	47.7	30.9	16.8	99.5
Glycerin	64.0	34.0	30.0	98.0

Surface tension of adhesives was analyzed by the pendant drop method according to DIN 55600-3 [20]. Disposable syringes with steel cannula (1.8 mm Ø) were used to ensure proper drop formation. When the drop was stable, 10 measurements were taken within one second. To obtain the polar and dispersive part of the surface tension, the free surface energy of a reference sample without polar compound, in this study silicone (σ_l = 8.28 mN/m), was determined. The contact angle is determined and the disperse component calculated following the method of OWRK:

Eq. 1 $$\sigma_l^d = \frac{(1+cos\theta)^2 * \sigma_l^2}{4\sigma_s}$$

θ	mean value of contact angle between the liquid and the reference solid
σ_l	surface tension of the liquid
σ_s	free surface tension of the reference solid

With the disperse part of the surface tension known, the polar part is calculated as follows:

Eq. 2 $$\sigma_l^p = \sigma_l - \sigma_l^d$$

σ_l	surface tension of the liquid
σ_l^d	dispersive part of the surface tension of the tested liquid

2.4. Longitudinal tensile shear strength and wood failure on beech wood

Conditioned beech wood lamellas of 10 mm thickness were planed with fresh knives to 5 mm thickness within 30 min prior to bonding, cut to the required size and cleaned with compressed air. The adhesives were applied manually by a metal spatula in accordance with the manufactures recommendation as shown in Table 1. The application quantity of the adhesive was controlled by a scale. To ensure precise pressure distribution, the lamella pairs were stacked into a holding device before entering the hydraulic press (Lindenberg, Altendorf, Switzerland). The lamellas were pressed for 10 h with 0.8 MPa pressure at ambient temperature. After pressing, samples were stored in standard climate (20°C, 65% RH) for three weeks to ensure full curing and sample conditioning. Then, samples were cut to size and treated according to EN 302-1 [21] using the conditions described in Table 3. Subsequently, they were tested in tensile shear mode in a universal testing machine Zwick/Roell 30 kN (Ulm, Germany). Load was applied in load-controlled mode using a rate of 2 kN/min. The wood failure percentage were determined visually in 10%-steps.

Statistical analysis was preceded with a single factor variance analysis (ANOVA with 95% confidence interval) and a post hoc least significant difference to enable statistical comparison of the variants.

Table 3 Definitions of sample treatment for tensile shear strength according to EN 302-1 [21].

Treatment	Sample conditioning
A1	Testing after 7 days conditioning in standard climate 20°C/65% relative humidity
A2	4 days storage in cold water (20 ± 5)°C, testing in wet state
A4	6 h storage in boiling water, 2 h submerged in cold water (20 ± 5)°C
A5	6 h storage in boiling water, 2 h submerged in cold water (20 ± 5)°C, reconditioning until reaching initial mass, testing in dry state

2.5. Polymer films

The filler content was introduced by mixing different amounts into the polyol by a Vollrath Mixer (Hürth, Germany) at 750 rpm for 15 minutes followed by 15 minutes at 300 rpm and 50 mbar for evacuation of air. Variants with around 60%, 30% and 15% wt. were produced as well as a variant with no filler for comparison.

Cast films were prepared at ambient temperature. The liquid adhesives were applied on polyethylene foil with a defined thickness of ca. 150 µm by a film application device. For comparison, adhesive films of PRF were tested as well. Before the films were fully cured, samples were cut out using a bone-shaped punch-cutter after 3-4 hours to a specimen size of 120 mm length with 25 mm wide holders at the end. The gauge area obtained a width of 6.3 mm and a length of 35 mm. Specimens with inconsistent thickness, cracks, bubbles or other irregularities were sorted out. Films were subsequently stored in standard climate for three weeks to ensure full curing. Afterwards, they were tested in a universal testing machine Zwick/Roell 30 kN (Ulm, Germany) with a 500 N load cell following EN ISO 527-1 [22]. The strain in longitudinal and transversal direction was measured with a Videoextensometer (Zwick Roell, Ulm, Germany). Test speed was set to 0.75 mm/min between 0.05-0.25% strain, representing the region to determine the E-Modulus. After that, the test speed was increased to 5 mm/min until failure was reached and the tensile strength was obtained for the 2C PUR films. Due to the brittle character of PRF, a test speed to failure of 2 mm/min was chosen as proposed by Kläusler. et al [23].

3. Results and discussion

3.1. Wetting properties of beech wood and adhesives

The wetting properties on the radial plane of European beech wood (*Fagus sylvatica* L.) were characterized by contact angle, free surface energy and its polar and disperse part. For water, the contact angle directly after planing was 56.1 ± 4.5° and changed only insignificantly for 24 h old surfaces to 56.8 ± 4.8°. The calculated free surface energy, considering contact angle results of all four test liquids using the model of OWRK, resulted in 50.25 ± 12.7 mJ/m^2 for fresh beech and 52.8 ± 6.8 mJ/m^2 after 24 h. Due to the high standard deviation of the surface energy, the small increase in surface energy does not seem to be meaningful. Although the magnitude of the surface free energy is in the range of earlier measurements, typically ageing of wood surfaces results in decreasing surface energy [24]. The polar part of the beech surface directly after planing obtained 8.65 mJ/m^2 and the disperse part 41.6 mJ/m^2. After 24 h, the disperse part increased to 45.27 mJ/m^2 and the polar part decreased slightly to 7.53 mJ/m^2.

The surface tension and the disperse and polar part of the tested adhesives are shown in Figure 1.

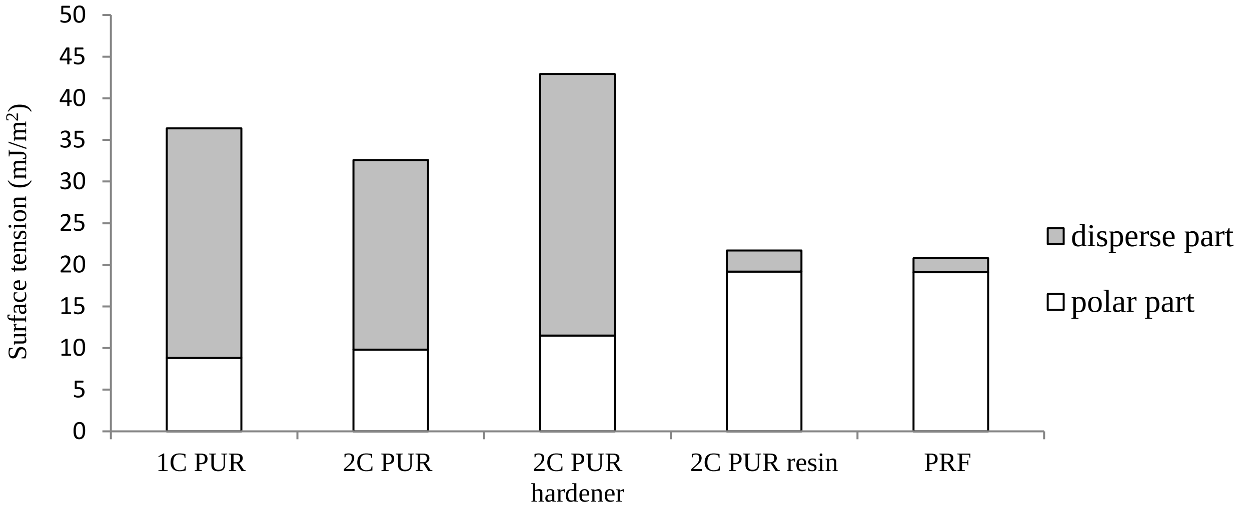

Figure 1 Disperse and polar parts of surface free energy of different adhesive systems and adhesive components (n=10) according to OWRK method at room temperature in liquid state.

The surface tension of the 1C PUR was slightly higher than for the 2C PUR. The 2C PUR system obtained a surface tension of 32.7 mJ/m^2 with a polar part of 9.8 mJ/m^2 and a disperse part of 22.8 mJ/m^2. However, the proportion of polar and disperse parts were relatively similar for both polyurethane adhesives. Analyzing the 2C PUR components it becomes evident, that the hardener contains a much larger disperse part than the resin component. The water-based PRF obtained a low surface tension together with a high polar part, which can possibly be explained by its low solid content of 55-61%, with water as solvent.

To determine the wetting of the used adhesives on beech wood, contact angles were measured. The contact angle of adhesives applied on beech wood are depicted in Figure 2. The direct comparison of adhesive systems should be considered with care, as additionally to the chemical nature different technological properties of the adhesive e.g. viscosity or density may bias the values measured on the porous wood substrate.

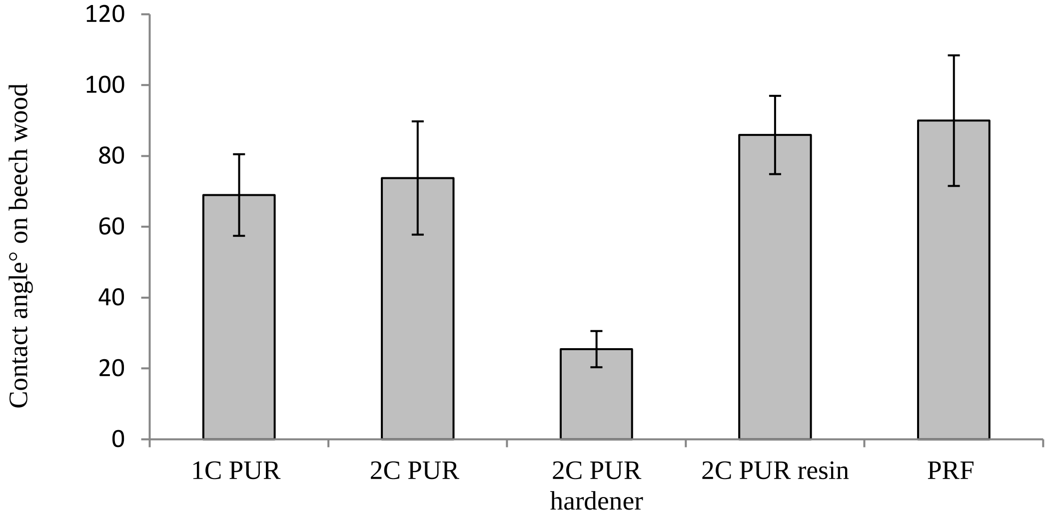

Figure 2 Mean value and standard deviation of contact angle of adhesives and adhesive components on fresh planed beech wood on its radial plane (n=10) at room temperature in liquid state.

In comparison, the modified 2C PUR system ranged similar to the 1C PUR. Furthermore, the contribution of both components of the 2C PUR system were tested separately. While the resin revealed a contact angle of 86°, the hardener obtained only 26°. Noticeable was the high contact angle of PRF on beech wood with ca. 90°, while having a low surface tension of only 20.8 mJ/m^2. The higher contact angle of PRF on the wood surface may be explained by the phenyl rings presented in its structure [25]. According to Habenicht [26] a contact angle ≥ 90° is characterized with incomplete wetting performance. However, a study of Stehr et al. [27] attested a decrease in contact angle after a short while.

3.2. Mechanical properties of adhesive films

The results of tensile strength opposed to E-Modulus for adhesive films are depicted in Figure 3.

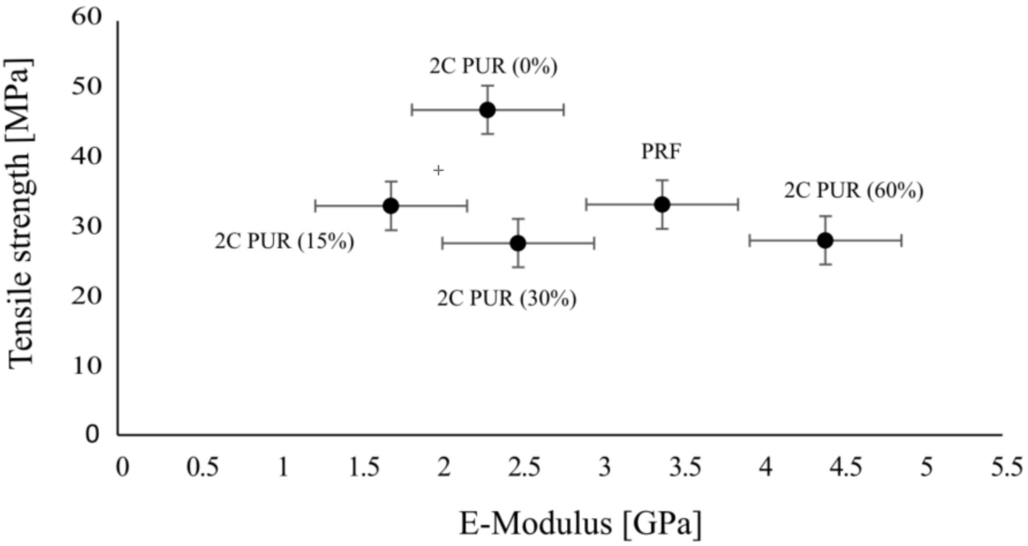

Figure 3 Tensile strength and E-Modulus of adhesive films in standard climate (n=10). For 2C PUR the amount of filler in the resin component is shown in wt %.

The 2C PUR variant without filler content demonstrated a high tensile strength of 47 MPa and a corresponding E-Modulus of 2.3 GPa. Adding 15% filler to the adhesive reduced the tensile strength considerably to 33 MPa and the E-Modulus to 1.7 GPa. A filler content of 30% showed a slightly lower tensile strength of 28 MPa and an increase in E-Modulus 2.5 GPa. The variant with 60% filler content revealed 28 MPa tensile strength and a significantly increased E-Modulus, compared to the unmodified reference, of 4.4 GPa. Noticeable was the high standard deviation for the various variants. Prior investigations by scanning electron microscopy showed a homogenous distribution of the filler in the glue line (results not shown). Hence, the observed deviation may not be explained by a local agglomeration or uneven distribution of the filler. In comparison, the PRF obtained a tensile strength of 33 MPa and an E-Modulus of 3.4 GPa which was in accordance with findings of the literature (Kläusler et al. 2013) and similar to the 2C PUR variants with 60% wt filler content.

Kläusler et al. [23] further reported for commercial 1C PUR systems tensile shear strength between 24 and 27 MPa and an E-Modulus from 1.0 to 1.1 GPa at 20°C and 65% RH. Therefore, commercial 1C PUR systems obtained a lower E-Modulus and tensile strength than the present experimental 2C PUR.

3.3. Tensile shear strength and wood failure percentage

The results of tensile shear strength (TSS) and wood failure percentage (WFP) of the 2C PUR variants with different filler contents (0-60% wt) in their resin component can be seen in Figure 4. Testing in dry conditions (A1) revealed that the variants with 0 and 60% filler content surpassed the standards requirement of 10 MPa, while the variants with 15% and 30% filler content slightly fell below it. Within the tested variants, the variant with 60% showed the highest TSS with a mean value of 14.5 MPa, while the WFP was slightly higher than the other variants with around 30%. In wet conditions (A4), no variant was able to surpass the standards requirement of 6 MPa. In-between the variants different deviations were observed. All variants showed a complete absence of WFP.

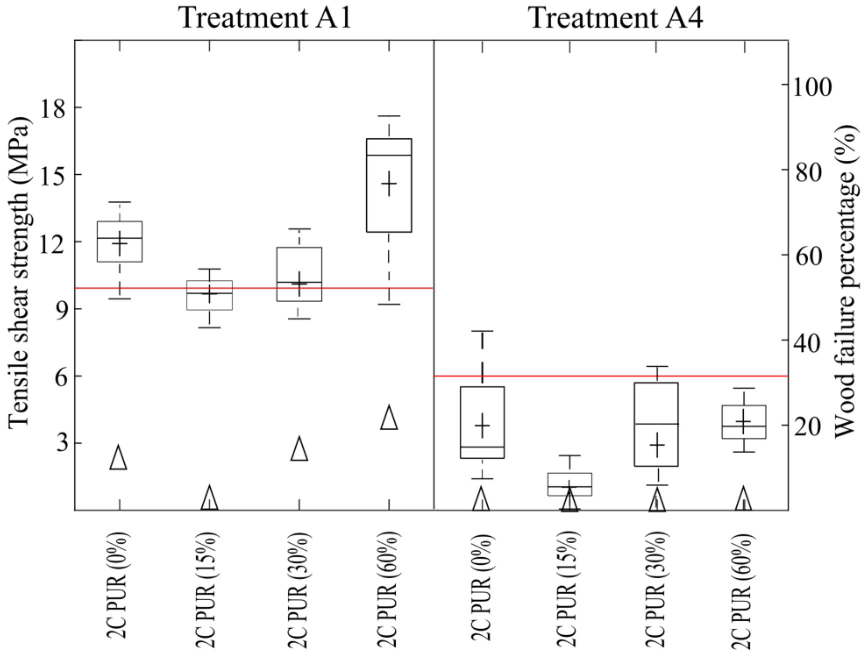

Figure 4 Boxplots of tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A1 and A4 for 2C PUR with different amounts of filler in the resin component (0, 15, 30, 60%). Boxplots indicate median, interquartile range and minimum and maximum are shown as whiskers. Red line marks standards requirement for each treatment according to EN 302-1.

The results of TSS and wood WFP of lap joints bonded with different adhesives and solid beech wood of similar geometry as a reference are shown in Figure 5. For the commercial 1C PUR Collano RP 2760, the test results of the accreditation of the Material Testing Institute of the University of Stuttgart [28] were used. The accreditation was carried out with the same parameters as in the present study. Testing in dry conditions (treatment A1) revealed, that all variants surpassed the standards requirement of 10 MPa. Between the three adhesives, no significant difference in TSS was found.

While the 2C PUR including 60% of filler showed only low WFP, 1C PUR and PRF obtained high WFP of around 80%. After storing specimens in water for four days (treatment A2), a considerable reduction in both, tensile shear strength and WFP was observed for all adhesive systems including the solid wood reference. 1C PUR and PRF were able to exceed the standards requirement of 6 MPa, while the 2C PUR performed significantly lower. Both polyurethane adhesives (1C and 2C) demonstrated a lack of WFP, while it was reduced to 50% for the PRF bonded joints. After treatment A4, the solid wood reference was further reduced in comparison to treatment A2. A significant difference was found between the two polyurethane adhesives, while PRF and 1C PUR could pass the standard requirement. Similar to treatment A2, both PUR versions revealed a total absence of WFP, while PRF maintained again a high WFP of 90%. When comparing PUR and PRF, it has to be mentioned that molecules of low molecular weight of the PRF are typically expected to penetrate the cell wall and are therefore typically able to stabilize the interphase region [29]. In addition, PRF and PUR adhesives are typically very different in their mechanical properties.

All samples re-gained their original dry strength after treatment A5. While all adhesives surpassed the standard requirements, especially the values for WFP differed significantly from each other. In terms of tensile shear strength, the beech wood lap-joints revealed an adequate performance of the 2C PUR system in dry (A1) and re-dried (A5) conditions and achieved standard requirements for these treatments according to EN 302-1. Both tested polyurethane adhesives revealed a lack of WFP, but only 2C PUR showed adhesion deficits when tested in wet conditions (A2 and A4). In contrast the 1C PUR passed the standards requirements in wet conditions.

While the WFP of PRF changed only slightly for the different treatments, the 1C PUR showed slight elevated WFP in dry conditions only. In contrast, the 2C PUR showed comparably low WFP values also in both dry conditions (A1, A5).

The absence of WFP in wet conditions for the tested polyurethane adhesives and especially the 2C PUR indicates an adhesion failure at the interface of the adherend. The lower performance of polyurethane adhesives on hardwood in comparison to PRF was also observed for a range of other polyurethane based systems when no primer was applied [6].

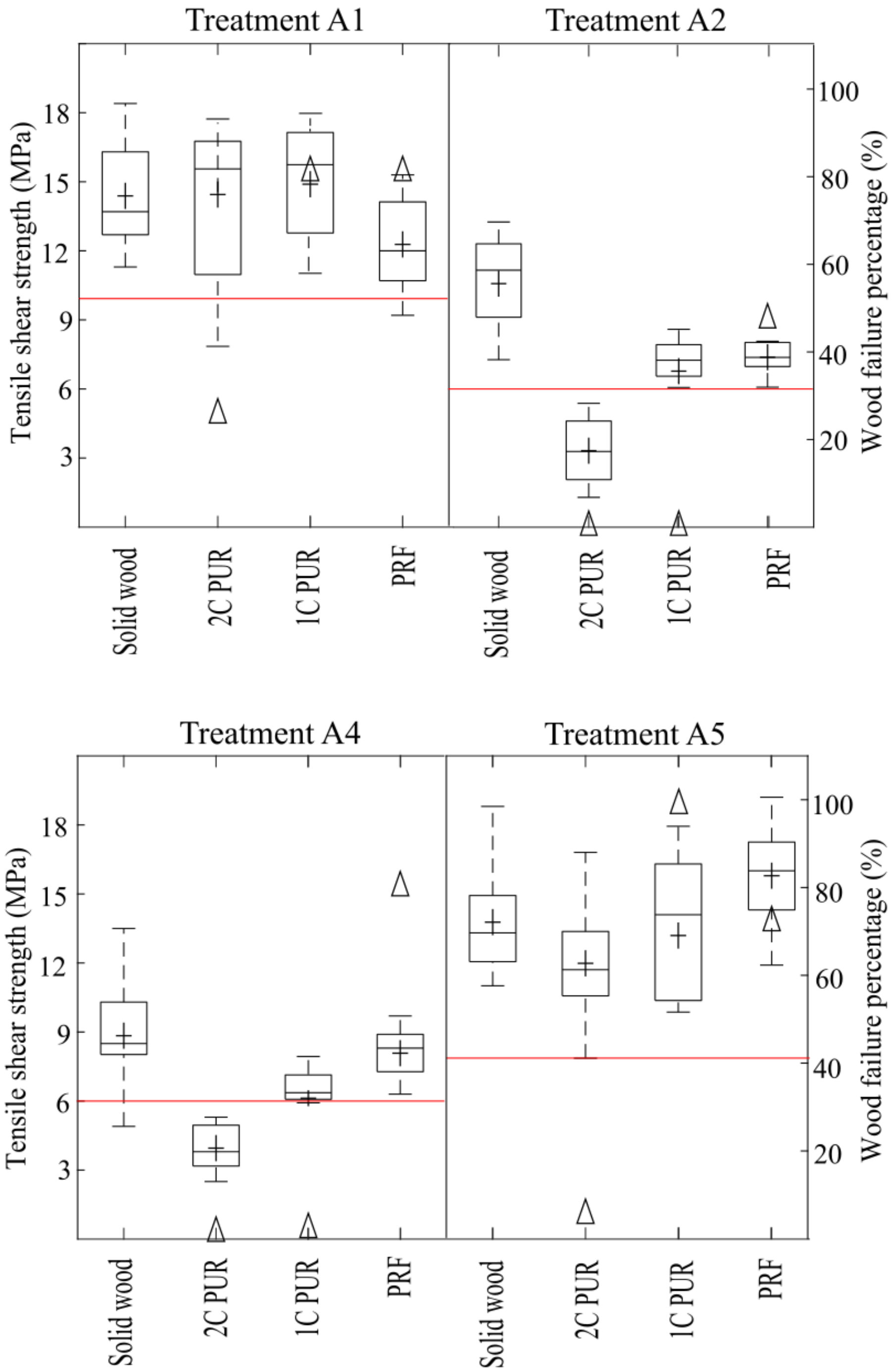

Figure 5 Boxplots of tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A1, A2, A4 and A5 for the adhesives 2C PUR modified with 60% filler, 1C PUR, PRF and the solid wood reference (n=15). Boxplots indicate median, interquartile range and minimum and maximum are shown as whiskers. Red line marks standards requirement for each treatment according to EN 302-1.

4. Discussion

The wetting properties of the experimental 2C PUR system were similar to the tested 1C PUR adhesive in terms of surface tension, polar and disperse part as well as contact angle on beech wood. It can be concluded that 2C PUR fulfils requirements for spontaneous wetting according to Habenicht [26] with the adhesive having a lower surface tension than the surface free energy of the adherend beech wood. The good wetting properties of 2C PUR enable a surface-wide and close contact on beech wood in combination with the development of a consistent bonding line. Interestingly the sufficient wetting in liquid state could not be sufficiently transferred to the cured state, as evident from the complete absence of WFP for this adhesive.

Studies of Obersriebnig et al. [30] showed that polyurethane adhesives have a higher adhesion on more hydrophobic wooden surfaces, while a water-based adhesive obtained higher adhesion on more hydrophilic surfaces. Subsequently, the 2C PUR might have some disadvantages in general with his, in comparison to PRF, lower polarity of the adhesive system. It remains questionable if a modification of the PUR towards higher polarity and consequently reduced wettability would result in improved bonding performance – similar to the PRF – or other factors dominate the superior performance of the PRF adhesive.

The modification of 2C PUR by a high amount of filler led to an increase in E-Modulus, going along with a reduction in tensile strength of adhesive films close to the level of PRF. Similar to other studies, film properties of the 2C PUR didn’t perform linear with the addition of filler content as shown in other studies [31] [32].

The modification by filler further showed an increase of TSS in dry conditions, which was in accordance with findings of Clauß et al. [14]. However, this improvement was not transferred to the performance in wet conditions (A4). In contrast Harling et al. [17], were able to reduce the delamination resistance of 2C PUR on beech wood according to EN 14080 [33] from 100% to 30% by varying polyol and hardness. This was mainly explained by the reduction of adhesive flow into the cell lumina of the interphase, as observed in a study of Clauß et al. [14]. The latter authors also showed that the positive effect of filler on the bond can be reduced with an increasing moisture content. This appeared to be more important for the tensile shear strength than for the delamination test. In addition, the wood failure percentage of the 2C PUR variant was noticeable high in comparison with PRF and the commercial 1C PUR system.

The recent modifications of the experimental 2C PUR showed to be partly successful in comparison with bonding properties of commercial 1C PUR when no adhesion promoting agent (primer) was used [6]. As the mechanical properties of the adhesive polymer itself can be modified by filler addition to similar magnitude as for a conventional adhesive, the low performance in wet conditions together with the absence of WFP is assumed to have its origin in adhesion deficits.

The approach to increase the E-Modulus of 2C PUR by using a filler was successful, while its effect on wood-bond performance was limited. It can be expected that especially when moisture is induced, the performance of the 2C PUR at the interface lacks in adhesion and therefore reduces the WFP. Hence the E-Modulus of the system cannot be considered the most critical factor in adhesive formulation.

While the process parameters have already been tested sufficiently, following studies shall focus on the selection of pre-polymers as well as a wide range of additives and fillers to address this problem. One possible continuation of further research may be the implementation of the function of the primer into the polyol component of the 2C PUR in order to enhance the adhesion, especially in wet state.

5. Conclusion

The results of the present study show that the modified 2C PUR system has proper wetting properties on beech wood. The tensile strength of the bulk adhesive of the 2C PUR variant with 60% wt filler content is well in range of common PRF adhesives, while due to modification by filler a significantly higher E-Modulus could be reached with the 2C PUR. The modified 2C PUR with 60% filler was improved in comparison to lower filler contents and surpassed standard requirements of lap-joints in dry (A1) and re-dried (A5) conditions according to EN 302-1, but not in wet conditions (treatment A2 & A4).

As the mechanical properties of the adhesive polymer itself can be modified by filler addition to a wide range, the low performance in wet conditions together with the absence of WFP is assumed to have its origin in adhesion deficits. Further studies have to address the adhesion deficits to adjust the 2C PUR system accordingly.

List of abbreviations

1C PUR	One-component polyurethane adhesive
2C PUR	Two-component polyurethane adhesives
PRF	Phenol resorcinol formaldehyde adhesive
TSS	Tensile shear strength
WFP	Wood failure percentage

Declarations:

Availability of data and materials

The data generated or analyzed during this study are available from the corresponding author upon request.

Competing interests

On behalf of all authors, the corresponding author states there is no conflict of interest.

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Authors´ contributions

SB carried out all experiments and wrote the manuscript. SH and GW produced and modified the adhesive. JK supervised a part of the experiments and revised the manuscript. PN and FP discussed the results with SB and revised the manuscript.

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3.2. Paper II

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Influence of wood extractives on two-component polyurethane adhesives for structural hardwood bonding

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Abstract

When bonding wood for structural applications, the wood-adhesive-bond is influenced by a variety of factors. Next to the physical and mechanical properties of wood species, their chemical composition e.g. wood extractives can play a role in bonding wooden surfaces. A two-component polyurethane system (2C PUR) was chosen to better adapt to the current adhesion problem. The influence of extractives on the cross-linking was determined by Attenuated total reflection fourier-transform-infrared-spectrometry (ATR-FTIR) and on the rheological behavior in terms of gel point and storage modulus. Therefore, 2C PUR was mixed with 10% of eight common wood extractives separately. Furthermore, mechanical properties of beech wood (*Fagus sylvatica* L.) bonded with extractive enriched adhesive were tested by means of tensile shear strength tests and evaluation of wood failure. These results of ATR-FTIR clearly show that the majority of cross-linking was terminated after 12 h. Acetic acid and linoleic acid expedited the isocyanate conversion during the first 2.5 h. The curing in terms of gel point and storage modulus of 2C PUR was accelerated by starch, gallic acid, linoleic acid and acetic acid. Heptanal, pentanal, 3-carene and limonene decelerated the curing. All extractives lowered the storage modulus determined after 12 h. The bonding of beech wood with extractive-adhesive-blends showed slightly decreasing of mechanical properties, with the exception of marginal increasing in case of linoleic acid and pentanal.

In summary it can be said, that 2C PUR is sensitive to the influence of wood extractives and can therefore be partly hold responsible for adhesion problems occurring when extractives in surface-wide and higher contents are available.

Key words: adhesives for wood, polyurethane, infrared spectroscopy, rheology

1. Introduction

The existence of wood extractives can pose serious problems in numerous processes in the wood industry such as lumber drying [1], pulp production [2] [3] [4], finishing [5] [6], wood composites [7] [8] [9] and bonding of wood [10] [11].

Bonding of wood is a complex process that involves many factors such as wood properties, surface preparation and process parameters. For structural bonding e.g. glulam, a dependable adhesion between adhesive and the adherend wood is indispensable. The physiochemical interactions implicated in this process between the curing adhesive and wood are mainly acid-base, electro-static and van-der-Waals type [12]. These in turn are directly dependent on the physiochemical properties of the adherend wood. Wood extractives influence the chemical, biological, physical, and optical properties of this adherend [4].

High extractive contents can effectuate low equilibrium moisture content at fiber saturation [13]. In addition, extractives like lipophilic resins (e.g. terpenes) increase the dimension stability and durability, while swelling and biodegradability is significantly reduced [4].

The pH content and buffer capacity of wood is mainly depended on the chemical composition and concentration of extractives [14] and take high influence in chemical-technological processes such as bonding [15].

Wood extractives are suspected to hinder the bonding with some wood species and adhesive types [11]. Their influence can be summarized as follows: [16]:

Surface contamination: Wood extractives can, due to their occurrence or migration to the surface, effect the surface properties of wood such as pH-content and chemical constitution. This thin contamination can be described as “weak boundary layer” and can act as a barrier [17]. **Change in polarity and wettability:** Secondly, reducing the polarity also decreases the wettability of wood with most of adhesive types. This can hinder the permeability of the wood surface, e.g. vessels, tracheid etc., with adhesive and the development of an interlocking between adhesive and the adherend wood [18].

Curing and setting of adhesive: Thirdly, the wood extractives and the adhesive itself can interact chemically such as catalyst/ retardants. Different methods can be used to temporarily reduce the influence of extractives prior to gluing such as sanding and planing [18]. Sanding revealed positive delamination resistance for beech and ash wood using one-component polyurethane adhesive [19]. When removing extractives by solvent-extraction, the unknown migration of these compounds to the surface subsequent to the treatment could be seen as a critical point. This treatment might therefore also lead to an increase in surficial extractive concentration [20].

In order to demonstrate the different areas in wood bonding, where extractives can affect the wood bonding, a model referring to Mara [21] is illustrated in Figure 1.

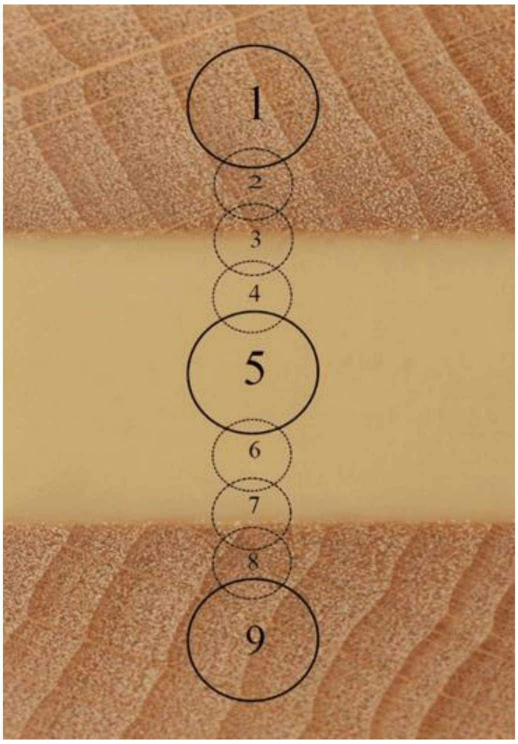

Figure 1 Model of wood bonding representing bulk material (1, 5, and 9), interface (3, 7) and interphase region (2, 4, 6, and 8).

While 1, 5 and 9 describe layers of the wood bound which represent the bulk material, the remaining zones describe the interphase (2, 4, 6, and 8) and the interface (3, 7) regions, which effect the adhesive-wood interactions.

Polyurethane has a wide range of applications e.g. wood bonding. Some one-component polyurethane systems (1C PUR) are successfully used in the field of wood bonding for structural applications, but the prior application of adhesion promotor requires long open primer time in the bonding process. Two-component polyurethane systems (2C PUR) do not require adhesion promotor and have the potential for structural bonding with high cohesive strength, but still present adhesion problems with hardwood and are not accredited for structural application yet [22]. The crosslinking-reaction of 2C PUR is a polyaddition. The primary reactions following mixing of the system are between the hydroxyl groups of the polyol and isocyanate groups, resulting in urethane formation. The degree of cross-linking is controlled by the isocyanate-group (NCO) of the pre-polymer and by the hydroxyl of the polyol [23]. The secondary reaction is between urethane and the excess of isocyanate which results in allophanate formation and cross-linking. An NCO-Index above 110, which was chosen for the present study, could ensure saturation with isocyanate as well as a relatively high cross-linking-density and an enhanced adhesion according to literature [24].

Few works have examined the influence of wood extractives on the cross-linking or curing of adhesives. In order to understand the effect of extractives, most works have focused on the influence of extractive removal [10], the artificial application on the adherends surface prior to bonding [25] or the influence of extractives on wooden products [7] [8].

Wood extractives of high acidity are known to accelerate the curing of acid-curing urea-formaldehyde-resins and decelerate bonding with alkaline hardening phenol-formaldehyde-resins [26]. Polyphenolic extractives such as tannins are even used as binders in the wood based industry [26] and therefore could also work as a further polyol component.

To our knowledge, no published word has considered the exclusive effect of different wood extractives on the physiochemical properties of 2C PUR and the manner in which they can be hold responsible for common adhesion deficits.

The variety and plurality of wood extractives make it difficult to investigate their influence/ interactions. Hence, eight representative extractives for hardwood and softwood were chosen namely heptanal, pentanal, 3-carene, limonene, starch, gallic acid, linoleic acid, acetic acid and different methods selected to investigate their influence on 2C PUR as well on the bonding with beech wood (*Fagus sylvatica* L.). This part should simulate the bulk material adhesive in contact with the interface, merging with extractives.

It is assumed that various wood extractives influence the cross-linking and rheology of 2C PUR and consequently affect the processing behaviour and performance of 2C PUR beech wood adhesive bonds.

Therefore, the following items were investigated in the present study:

1) Comparison of the influence of wood extractives on the isocyanate conversion of 2C PUR via Attenuated total reflection fourier-transform-infrared-spectroscopy (ATR-FTIR).
2) Determination of the influence of extractives on the process of curing of 2C PUR by rheology
3) Effect of extractives on the performance in tensile shear strength of beech lap joints bonded with 2C PUR

2. Materials and methods

2.1. Wood

European beech wood boards [*Fagus sylvatica* L.] was used for tensile shear test were prepared according to EN 302-1 [27]. The boards were conditioned in the climate 20°C/65% relative humidity (RH) until equilibrium moisture content (EMC) and approximate moisture content (MC) of 12% was reached. The average specific densities of the lamellas were determined to be around 700 ± 46 kg/m^3. All wood material was used from the same lot. Boards with knots, portions of heart wood, discolorations or any type of irregularities were not used. Subsequent to conditioning the material was cut to lamellas of 10 mm thickness according to the standard. Freshly planed European beech wood has a slight acid pH-content of around 4.75 [28], its extractive content was measured to be fewer than 2% for cold water- and organic solvent-extractions [28].

2.2. Adhesive

A 2C PUR adhesive system was used for the present study, consisting of a polyol and an isocyanate component. As polyol component, an experimental type provided by Collano AG (Sempach Station, Switzerland) was used which is filled with 60% calcium carbonate (defined on a unit weight basis) and 0.5% wetting agent [29] as standard setting. The isocyanate component is Desmodur VK 10 from Covestro AG (Leverkusen, Germany), a mixture of Diphenylmethan-4,4 `-diisocyanate (MDI) with isomers and higher functional homologues (PMDI) [30] . Both components are mixed manually in a ratio of 2.44 to 1 (polyol to isocyanate, based on a unit weight basis) within 3 min shortly before application or by Speedmixer (3 min at 2400 rpm). When the polyol and isocyanate were mixed, 10% of extractive (weight-related volume) was added and has been mixed for 1 min. Samples without extractives as reference and extractives were measured directly using ATR-FTIR and rheology or used to glue beech wood samples.

2.3. Wood extractives

The wood extractives analogues and some of their properties are listed concisely with their international Chemical Abstract Service number (CAS), substance class and purity in Table 1. They were purchased by Sigma Aldrich (Buchs, Switzerland) representing a synthetically produced wood extractive analogue. Thus, the concentration of extractives in wood is considerably much lower; a high concentration of 10% (defined on a unit weight basis) was chosen in order to verify the influence of extractives on 2C PUR in extreme conditions. The range of chosen extractives represents many common extractives in hard- and softwood as determined in previous work [19]. A unit weight basis was chosen to compare with common literature statements, those mainly present extractives in % to the dry mass. However, this led partly to different additions in molar masses. Starch and gallic acid were present in powder form, all other extractives in liquid form.

Table 1 Classification and purity of selected extractives.

Extractive	CAS	Substance class	Purity [%]
Heptanal	111-71-7	Aldehyde	95
n-Pentanal	110-62-3	Aldehyde	97
3-carene	13466-78-9	Bicyclic terpene	90
(R)-(+)-Limonene	5989-27-5	Monocyclic terpene	97
Potato Starch	9005-28-8	Polymeric carbohydrate	97
Gallic acid	149-91-7	Phenolic acid	≥ 97.5
Linoleic acid (Oleic acid as major impurity)	60-33-3	Fatty acid	60-74 (18-32)
Acetic acid	64-19-7	Organic acid	≥ 99.7

2.4. Measurement of isocyanate conversion

The measurement of isocyanate conversion of liquid 2C PUR with and without extractives was done by ATR-FTIR. This device collects high spectral resolution data over a wide spectral range of solids, liquids or gases and is a common tool to indicate the cross-linking of polymers in a quantitative manner [31]. Using a Perkin Elmer Spectrum 100 (Schwerzenbach, Switzerland) equipped with an attenuated-total-reflectance (ATR) unit using a diamond-crystal with a window size of approximately 1 mm^2 and a measuring depth of 4.4 µm spectra were acquired from 4000 cm^{-1} to 650 cm^{-1}. ATR-FTIR measurements were conducted at room temperature (20°C) with a resolution of 4 cm^{-1} and 10 scans each. When the adhesive and the adhesive-extractive-blend were spread on the crystal, spectra were taken every 30 min during the first three hours, then after 6, 12 and 24 h. During the measuring period, the blend stayed on the crystal. Next to multiple measurements of the check plot, three repetitions were determined in every variant

2.5. Rheological measurements

Rheological investigations were conducted on an Anton Paar rheometer MCR-302 (Buchs, Switzerland) under isothermal conditions at 20°C. All materials were measured with plate-geometry (25 mm, sample thickness 0.5 mm) with a deformation of 0.05 % and a frequency of 1 rad/s for 12 h. Amplitude sweep and frequency sweeps before and after curing showed that the curing measurement was measured within the linear viscoelastic range (results not shown).

2.6. Tensile shear strength and wood failure on beech wood

For bonding of the beech wood lamellas as adhesives isocyanate and the polyol component were mixed manually for 2 min; afterwards the extractive was added and blended for another minute. This blend was spread on one side of the freshly planed lamella and distributed equally with a toothed lath. The specific adhesive load per glue line was 200 g/m^2 when using pure adhesive and 220 g/m^2 for the adhesive-extractive blend to ensure the same amount of active adhesive polymer for all variants. After gluing, the lamella with adhesive was put together with its counterpart lamella. Six pairs were stacked at the same time in an apparatus to ensure proper pressing in the hydraulic press Lindenberg (Altendorf, Switzerland) at a pressure of 0.8 MPa for 10 hours. Prior to cutting to final size, lamellas were stored in the climate 20 °C/ 65% RH for three weeks. Samples were tested in tensile shear mode until failure in a universal testing machine Zwick 30 kN (Ulm, Germany) in two conditions (A1 and A4). According to EN 302 – 1, A1 treatment requires dry samples acclimatized in standard conditions of 20°C/65 % RH, whereas A4 treatments includes 6 h sample storage in boiling water, 2 h storage in cold water (20 ± 5 °C) and finally testing in wet state. For testing a load controlled speed of 2 kN/min was selected. The tensile shear strength was obtained by dividing the recorded tensile load from the testing machine by the overlapping shear area. The latter was determined using a caliper Mitutoyo (Urdorf, Switzerland). The wood failure amount was visually determined in 10%-steps.

3. Results

3.1. Measurement of isocyanate conversion

The FTIR-ATR-measurements showed several representative peaks in the spectra. Two peaks of the methylene group (CH_2), the asymmetric stretch vibration at 2927 cm^{-1} and the symmetric stretch vibration at 2855 cm^{-1} form a double wave band which does not alternate during polyaddition as can be seen in Figure 2. Hence, these peaks were used as a reference for the conversion of the isocyanate peak (NCO) at approximately 2263 cm^{-1}.

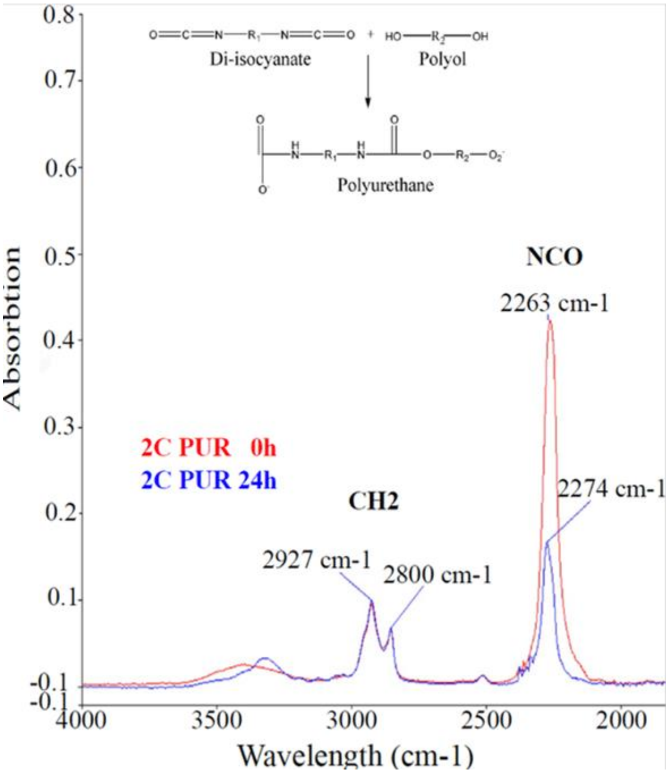

Figure 2 ATR-FTIR Spectra representing CH_2 and NCO wave bands of 2C PUR after 0 h and 24 h.

The area of the selected peaks was measured for each variant. Assuming that the chemical reaction took place homogenously, the following formula [31] was used for the isocyanate conversion as an approach to determinate the degree of polyaddition:

$$Degree\ of\ isocyanate\ conversion\ \alpha = 1 - \frac{(Area\ Isocyanate_t / Area\ Isocyanate_0)}{(Area\ Methyl_t / Area\ Methyl_0)}$$

t = peak surface after a defined time

0 = peak surface at the first measurement

The majority of the isocyanate conversion was completed after 12 h. Figure 3 displays the mean values of the isocyanate conversion of all variants in % between 0.5 and 24 h. All variants deliver high standard deviations through the process of polyaddition as can be seen in Table 10, which also shows the numeric values of the mean values. The blends with linoleic acid and acetic lead to an accelerating of the conversion during the first 2.5 h. The blend with pentanal slightly lowered the conversion within the first three hours of measurement. The remaining blends do have a similar trend as the 2C PUR reference.

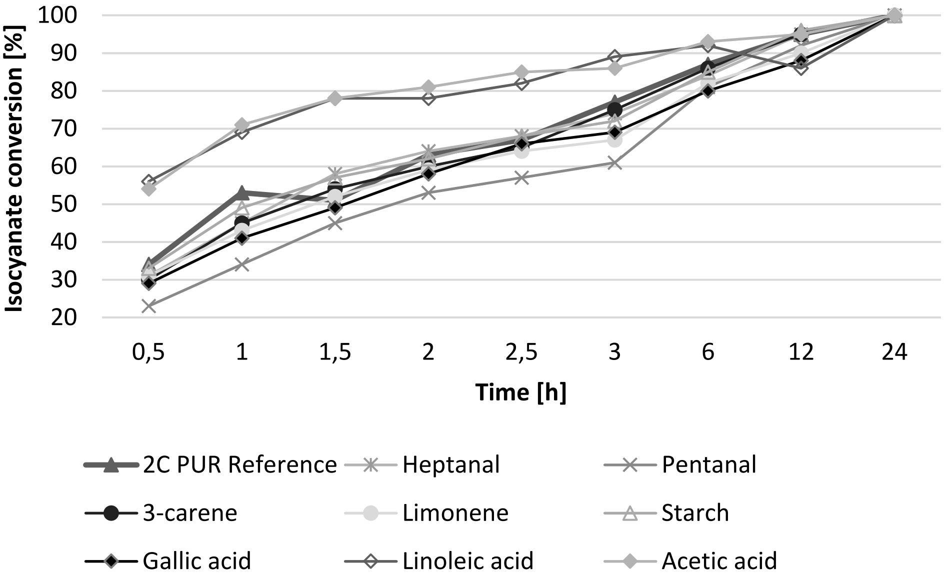

Figure 3 Isocyanate conversion determined by ATR-FTIR.

Table 7 Numeric values of isocyanate conversion for mean values and standard deviation.

MV/ STD [%]	0.5 h	1 h	1.5 h	2 h	2.5 h	3 h	6 h	12 h	24 h
2C PUR	34±2	53±7	51±5	63±3	67±2	77±9	87±7	95±0	100
Heptanal	31±6	45±5	58±6	64±3	68±5	74±7	84±4	95±2	100
Pentanal	23±3	34±6	45±4	53±2	57±2	61±3	81±3	92±3	100
3-carene	30±3	45±3	54±3	60±4	65±5	75±10	86±4	95±1	100
Limonene	31±2	43±3	52±5	59±4	64±5	67±6	82±2	90±3	100
Starch	33±10	49±11	57±8	62±5	68±2	72±4	85±4	96±3	100
Gallic acid	29±2	41±6	49±5	58±7	66±10	69±6	80±6	88±7	100
Linoleic acid	56±5	69±7	78±4	78±8	82±5	89±0	92±3	86±2	100
Acetic acid	54±10	71±2	78±3	81±1	85±2	86±1	93±1	95±2	100

3.2. Rheological measurement

The rheometer displays the storage modulus (G’), loss modulus (G’’) and dissipation factor tan δ = (G’’/G’) as a function of time in isothermal conditions (20°C) in the unit Pascal (Pa) as shown in Figure 4 for the used 2C PUR System. The crossing of storage modulus and loss modulus (tan δ = 1) describes the gel point, where the polymerization of the polymer leads to a gelation. The storage modulus was measured at 12 h, as after this time no further change in storage modulus was evident for the 2C PUR reference

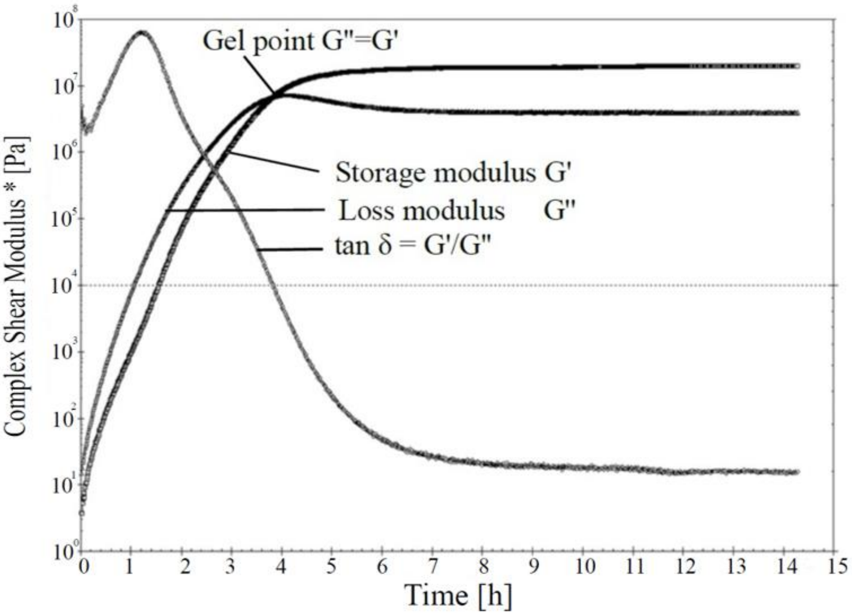

Figure 4 Measurement of storage modulus, loss modulus, gel point and tan δ by rheology of the 2C PUR reference.

The different extractives influence the curing in various ways. The occurrence of gel points of the reference and the blends are compared in Figure 5. All variants showed a significant deviation in comparing to the reference. The aldehydes heptanal and pentanal, as well as the terpenes limonene and 3-carene increased the timespan to reach the gel point, which is interpreted as a decelerating of the reaction speed. Limonene approximately redoubled the achievement of the gel point. Starch, gallic acid, linoleic acid and acetic acid increased the timespan to reach the gel point. This can be understood as an accelerating of the reaction. Linoleic acid and acetic acid obtained the gel point at an approximate fourth of the reference.

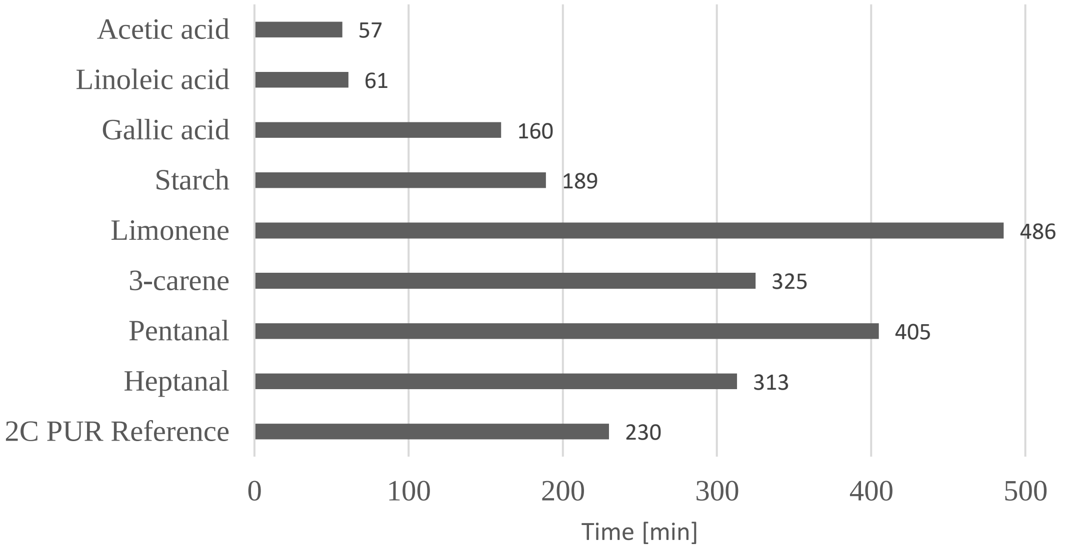

Figure 5 Occurrence of gel points measured as time (min) when G``=G`.

Secondly, the storage modulus at 12 h was compared as can be seen in Figure 6. The storage modulus G`of the 2C PUR reference after 12 h obtained 19.9 MPa. All extractives decreased the G` at 12 h significantly namely linoleic acid (-51%), acetic acid (-40%), gallic acid (-31%), 3-carene (-60%) and starch (-76 %). With distance, limonene reduced the G` at 12 h the most (-99%). However, values for limonene, heptanal and pentanal can be expected to further increase after the measuring area, since they did not complete curing within 12 h. All other blends and the reference were able to reach a constant G` within this time.

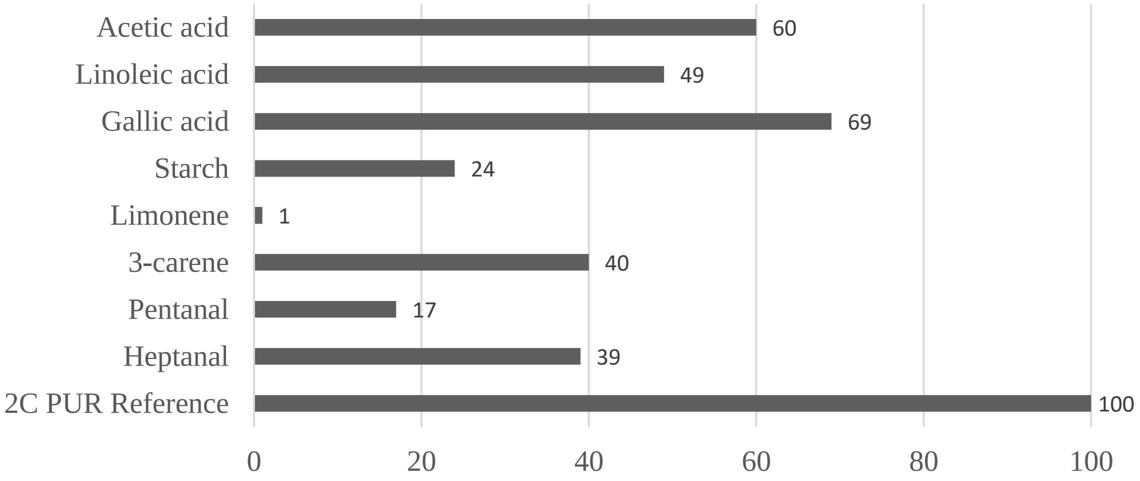

Figure 6 Relative storage modulus G` at 12 h [%].

3.3. Tensile shear strength and wood failure on beech wood

The results are displayed in Figure 7 and Figure 8. Testing samples in dry conditions (A1) showed that the mean tensile shear strength of the 2C PUR system is slightly lower than the one of solid wood (Figure 7). Linoleic acid and pentanal increased the mean value for tensile shear strength slightly. The remaining extractives delivered lower average values. The WFP of beech wood was lowered for most of the extractives in comparison with 2C PUR. Noticeable is the high WFP for 3-carene with 90% and linoleic acid with 80%. The testing in wet conditions A4 (Figure 8) lowered the tensile shear strength and WFP of 2C PUR and the extractive-blends, but the tendency of pentanal and linoleic acid remained up to a certain degree. The ongoing adhesion deficits of 2C PUR are reflected in the high decrease of WFP to 0 of all samples including the reference. When testing hardwood according to EN 302:1 standard, high standard deviations of tensile shear strength are commonly observed. In our opinion, this can be primarily explained through the wide definition of growth ring angle in the standard (30-90°) and the higher swelling of beech wood in comparison with soft wood [32]. Cooked and water stored beech wood samples additionally tend to deform, often leading to non-valid results. Additionally, differences in density could further explain variations, but in this case, density varied only up to 10 % within each variant and did not correlate with strength values. These effects aggravate further differentiation between the extractive classes.

The statistical analysis was preceded by a two-paired t-test ($\alpha > 0.05$) between the 2C PUR reference and each extractives-variant. For the treatment A1, all variants expect pentanal and linoleic acid, revealed significant lower tensile shear strength. Pentanal and Linoleic acid did not show significant differences to the reference. In case of the treatment A4, no significant differences were obtained between the 2C PUR reference and the extractives heptanal, 3-carene, limonene and starch. Significant improvements were obtained for pentanal and linoleic acid as well as a decline for gallic acid and acetic acid. Hence it could be proven, that the majority of extractives lowered the tensile shear strength of beech wood.

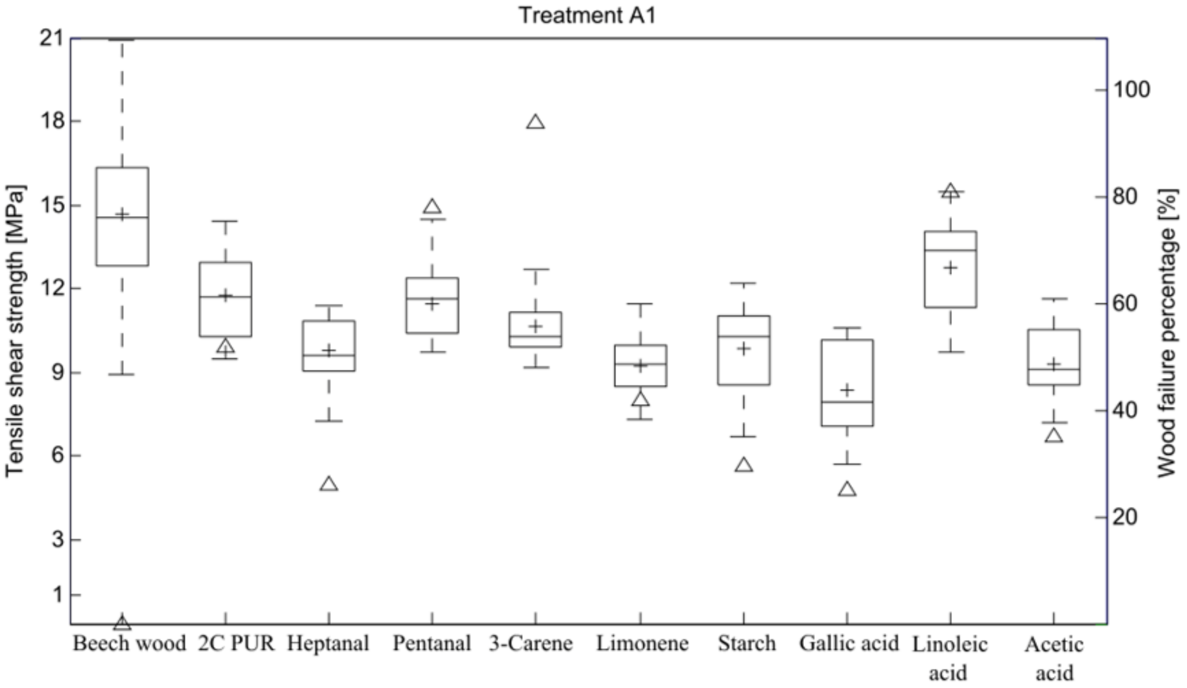

Figure 7 Boxplots refer to tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A1. Comparison of solid beech wood, the 2C PUR reference and the 2C PUR enriched with extractives. For each variant 20 samples were tested.

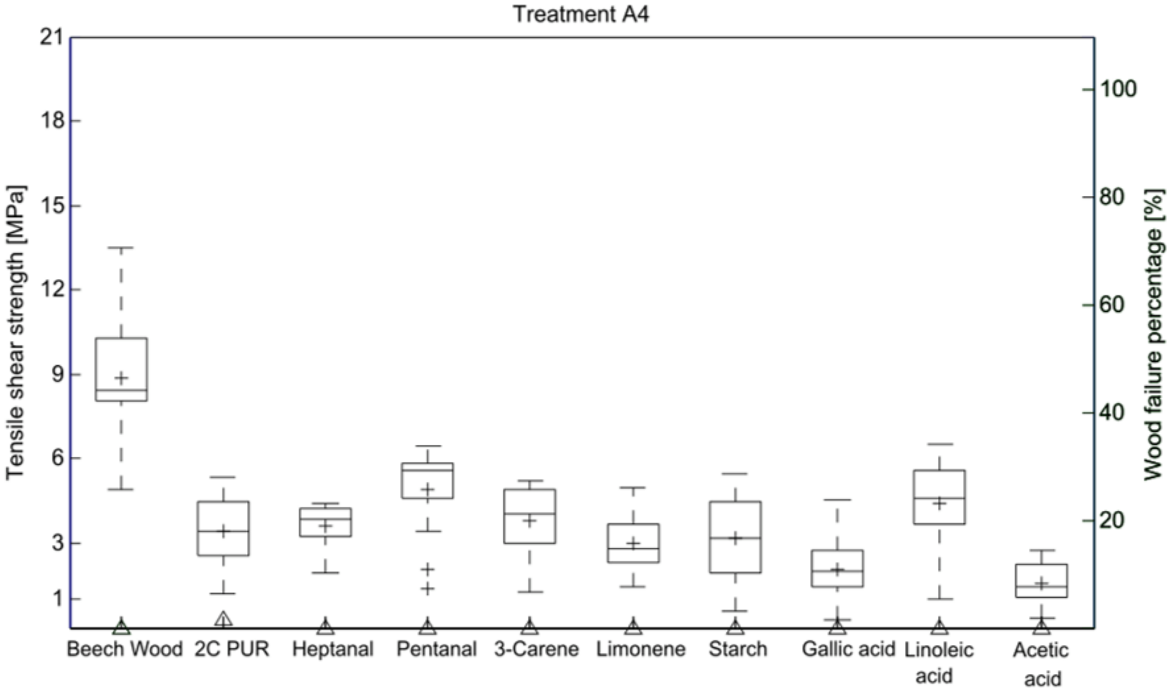

Figure 8 Boxplots refer to tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A4. Comparison of solid beech wood, the 2C PUR reference and the 2C PUR enriched with extractives. For each variant, 15 samples were tested.

4. Discussion

The influence of wood extractives on 2C PUR and bonds with European beech wood has been studied using different techniques. These methods characterized the influence of extractives on the fresh, cured and aged (three weeks old wood bond) polymer.

In the ATR-FTIR-measurements, few extractives showed a detectable influence on the isocyanate conversion. While linoleic acid and acetic acid accelerated the conversion at the beginning, a slight decelerating for pentanal was observed. The carboxylic acids most likely reacted with the isocyanate under the production of amine groups [33]. Further their acidity could have increased reaction speed, respectively isocyanate conversion. Pentanal is expected to decrease the conversion simply by its inert behavior. Thus, some extractives changed the isocyanate conversion during the first 2.5-3 h; all variants continued the conversion to 24 h. However, high standard deviations most likely reduced further differentiation in-between the extractives and the reference. This could be explained by low volume manual mixing of the adhesive-extractive blends and the restricted solubility of the extractives in 2C PUR. Furthermore, the presence of starch and gallic acid in powder form could most probably influence the reactivity with 2C PUR, but not in a detectable manner. However, the reaction of free hydroxyl groups from the polyose arabinogalactan (typical carbohydrate for larch wood) and free isocyanate has been proven to reduce the formation of cross-linking/ urethane formation in one-component polyurethane by FT-IR [25]. Another factor for the restricted differentiation of the extractives could have been the amount of impurities. Since these usually are not determinate by the provider, no further conclusion could be made.

The determination of the rheology revealed information on the fresh and cured polymer regarding gelation and storage modulus at 12 h. Key findings was that all extractives influenced the curing of 2C PUR significantly. The carboxylic acids (acetic acid, linoleic acid, gallic acid) do react with the isocyanate as explained before. Therefore, a reduction of the cross-linking-density can be expected since the amides do not support further chain formation. Similar observations have been made for alkaline phenolic adhesive and acid extractives that accelerated the curing of the adhesive prematurely while reducing its wettability and permeability into the wood [17]. The release of CO_2 within the amide synthesis can be expected to create bubbles inside the adhesive and its surface. Therefore, further reduction of its mechanical strength could be expected. The carbohydrate starch showed an accelerating of the gelation and the greatest reduction of storage modulus. Hence it can be concluded that starch is the extractive with the highest impact on the curing of 2C PUR. This can be explained through the reaction of isocyanate and the hydroxyl groups of the extractive up to the point; where there is no sufficient isocyanate remained to ensure a sufficient cross-linking density. This disproves the previous assumption, that carbohydrates do not influence the bonding with wood [11]. Nevertheless, this assumption could not be transferred to gallic acid, which also contains multiply hydroxyl groups. However, both could not enhance the cross-linking-density with a possible function as a polyol through their hydroxyl groups. The aldehydes pentanal and heptanal, as well as the terpenes 3-carene and limonene did influence the adhesive majorly by their non-reactive behavior. They can be understood as local blocker of the polyaddition, simply by separating polyol and isocyanate and therefore creating lesser urethane groups. During sample preparation of bonded beech wood, their odor after three weeks could still be noticed, which underlines this explanation. No literature was found with a similar approach in rheology, but prior works with 1C PUR showed that measurement by oscillation reveals difficulties due to the polycondensation and the expansion of the 1C PUR during the release of CO_2 within the measuring plates (results not shown).

The influence of extractive on wooden bonds showed minor effects and no correlation to the results of ATR-FTIR and rheometer. Still, linoleic acid and pentanal was able to increase the mean value for the tensile shear strength in dry conditions. Linoleic acid has the highest molar mass of the acids and could have catalyzed the polyaddition. Even so, no similar observation was made for the other acids.

Yet remarkable is the transfer of the slight increase in tensile shear strength to the results of the wet testing. However, it can be concluded that inferior effects on wooden bonds happen to the partly occurrence of extractives on the interface of the adherend. Furthermore, differentiation is expected to decline through high standard deviations of the standard test itself with European beech wood. In general, it was proven, that the majority of extractives has a significant negative influence on the bonding with European beech wood. Künniger et al. [25] demonstrated on fir wood bonds with one-component polyurethane, that arabinogalactan – if applied in high concentrations over 20% - influenced the bonds, especially in high humidity’s, in a negative matter.

Nussbaum & Stereley [17] revealed a correlation between the extractive content and the adhesion failure of test specimen, when exposed to water. A conclusion from this could be that the wood-adhesive-bond is reduced by the cleavage of hydroxyl bonds. The majority of these bonds are expected to re-bond, when the sample is acclimatized again to standard climate. This effect can be compared with the Velcro-effect [34] that describes the development of new bonds of bonds, when a prior applied stress is released. Own results with testing dry, wet and re-dried tensile shear strength samples proof this hypothesis (results not shown). Next to the cleavage of hydroxyl bonds through free water, the existence of extractives could hinder the bonding between wood and the adhesive system through a reduction of available hydroxyl groups and other functional groups. These hydroxyl bonds explain the high cohesive strength of polyurethane adhesives [12]. When applying the results of rheology to the wood-adhesive-bond, the influence of extractives can be reduced to their influence on adhesion, namely to the interface and interphase area. A migration to the bulk adhesive can be questioned due to their restricted solubility. The storage modulus characterizes the stiffness of the adhesive; therefore, a minor stiffness creates a local weakening at the interface and interphase region. Experiments which included the surface characterization and determination of extractive content of different wood species which were further bonded with different adhesive systems could not determinate direct connections [28]. Therefore, extractives can be seen as part of the adhesion failure, but further research is needed to understand the effect of each extractive class.

In order to overcome adhesion problems caused by extractives, an increase of the ISO-Index could compensate the negative effect, especially caused by the extractives that are rich in hydroxyl groups, e.g. starch, gallic acid. Furthermore, this excess of isocyanate could reduce the catalyzing effect of the acids. From an industrial point of view, a planing of solid wood surfaces prior to bonding is state of the art. A surface extraction with, e.g. hot water, to focus the removal of surficial carbohydrates, did not achieve positive effects in similar works [25].

In general, extractions are costly to implement in a process and their outcome is uncertain. The incomplete removal of defined extractives can lead to initiation of further extractive migration to the surface, and consequently to a change in surface chemistry as well as wettability and permeability. A different approach is the applications of an adhesion promotor such as “primer”. This led to enhancement in delamination-resistance of some extractive-rich species [35] [36]. Nevertheless, this application adds another process steps, the primer often require long flashing times and its function is not fully understood yet. To our opinion, a realistic approach would be the modification of the adhesive system in order to compensate the effects of the wood extractives. In the case of 2C PUR, this would be a modification of the polyol component which will be subject of a subsequent study. For this step of modification, further specific allocation of extractive classes and their influence on the adhesive system are necessary.

5. Conclusion

The results show that the used extractives influence the 2C PUR, independent of their chemical interactions with the adhesive, in a mostly negative manner. Key findings were that all extractives, especially the carbohydrate starch, influence the rheology of the 2C PUR regarding gel point and storage modulus at 12 h. Hence the influence of extractives has been so far underestimated as well as the range of influencing extractives. When extractive occur in a considerably high and surface-wide amount, adhesion problems can be expected. Reason for this can be seen in the interaction of extractives with the adhesive system, the change of surface chemistry and the blockage of functional groups by extractives. Therefore, wood extractives can be hold partly responsible for the adhesion deficits of 2C PUR. It is proposed to address this problem by modification of the adhesive system, e.g. the polyol component.

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3.3. Paper III

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The role of wood extractives in structural hardwood bonding and their influence on different adhesive systems

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Abstract

Bonding of hardwood for structural applications is a complex process. Various factors influence the bond performance and the interface area is considered the most crucial part. The chemical composition of the interface, e.g. wood extractives, is expected to influence the bonding of hardwoods. The subject of this study was to determine the influence of seven model substances that represent common wood extractives on different adhesive systems namely one-component polyurethane, two-component polyurethane, melamine urea formaldehyde and phenol resorcinol formaldehyde. The influence of the model substances on the cross-linking behavior of the adhesives was determined by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and on the rheological properties in terms of gel point and storage modulus. In addition, model substances characteristic for selected wood extractives were applied to the surface of European beech wood [*Fagus sylvatica* L.] before bonding and consequently tested in tensile shear mode according to EN 302-1. The ATR-FTIR spectra showed an influence of some substances on the crosslinking for all adhesive systems. Further, the curing process was mostly accelerated for phenol resorcinol formaldehyde, while melamine urea formaldehyde and polyurethane showed a less negative change in rheological behavior. The mechanical strength of beech wood bonds at room climate indicated only minor influence of model substances, but samples tested in wet conditions demonstrated a significant effect on some adhesive systems. It was concluded that polyurethane adhesives degrade by acid substances and melamine urea formaldehyde by starch and gallic acid. Phenol resorcinol formaldehyde system was influenced negatively by starch and acids.

Key words: wood extractives, adhesives for wood, polyurethane, interfaces, infrared spectroscopy, rheology, lap-shear

1. Introduction

Within the next decades, the hardwood harvest in Central Europe is going to increase significantly without the sales market being prepared yet. Until now most of the hardwood in this region is used for energetic purposes. One way to use hardwoods in a sustainable and more profitable way and to adapt to future markets can be its bonding to structural elements such as glue laminated timber, laminated veneer lumber, hybrid composites or local enforcements. Furthermore, these processes do not require much energy and lower the carbon footprint of constructions. While the wood working industry has experience with the bonding of many types of softwood, the processing of hardwood and certain softwood species still lacks knowledge, accreditation for structural application and appropriate adhesive systems. Hardwood in general has a lower cutting yield than softwood which aggravates the production of timber with big dimensions. In addition, it has different wood properties such as a more heterogenic cell structure, often a larger deviation in fiber angle, higher strength, density and higher swelling and shrinking coefficients. In combination, these properties impact the bonding performance - especially when moisture is inducted - to a higher degree. This makes it difficult for hardwoods to be processed for bonded structural products, but also present potential for applications with smaller diameter and higher strength. Still the bonding of many hardwood species reveals adhesion problems. In comparison with softwood, different chemical composition, e.g. wood extractives, could influence the adhesive-adherend-interaction at the interface through changing surface polarity, wettability and permeability as well as a different curing and setting of the adhesive system. It was stated by Nussbaum and Sterley that especially fatty acids and triglycerides increase the wood hydrophobicity with time [1]. Further, water-soluble polymeric saccharides have a negative effect on bond quality with phenol formaldehyde resins and oak wood according to Wang [2]. In addition, it was declared by Roffael that extractives of high acidity decelerate the bonding with alkaline-hardening phenol formaldehyde resins [3]. Studies by Bockel et al. [4] showed a high influence of acids on two-component polyurethane adhesives. Beside their influence in wood bonding, extractives are known to create problems in many fields of the wood working industry such as lumber drying, pulp production, finishing and manufacturing of wood composites. The allocation of adhesion deficits by wood extractives is further aggravated by the diverse occurrence in tree species, growing condition, season, trunk length and diameter. The extractive`s influence on bonding has been investigated with a few experiments but there is a lack of research regarding the influence of common wood extractives for industrially used adhesives in the field of solid wood bonding. In the present study, a selection of representative extractives for quantitively important European soft- and hardwood were chosen to determine their influence and possible differences that may help to better understand adhesion deficits. For hardwoods, Risholm-Sunman et al. ascertained the aldehyde pentanal for beech wood [5]. Gallic acid can be found in oak as summarized by Hillis [6]. The monoterpene fraction of softwoods varies among species – therefore 3-carene and limonene were chosen to represent compounds of volatile wood oil (turpentine). Subsequently extractives that occur for soft- and hardwoods in different amounts in compliance with Hillis [6] were chosen such as starch as a polysaccharide, linoleic acid as a fatty acid and acetic acid as an organic acid.

Regarding adhesives used for load bearing timber structures, surveys performed in German-speaking Europe by Ohnesorge [7] showed that most ~~of~~ glue laminated timber producers use melamine formaldehyde or melamine urea formaldehyde systems (51%), followed by polyurethane adhesives (35%) and resorcinol based adhesives (9%). Therefore, the adhesives in this work were chosen accordingly with the focus on polyurethane adhesive. These have the advantage of not containing formaldehyde or solvents, the development of a light bonding line and the potential for structural hardwood bonding. These polyurethane adhesives are available in two systems as one-component polyurethane (1C PUR) or two-component polyurethane (2C PUR) adhesives. 1C PUR requires a certain minimum moisture content available in the adherend and is often used in combination with an adhesion promoter (primer) prior to bonding. 2C PUR has the advantage of reacting through both components, the polyol and the isocyanate. Furthermore, the polyol component can be modified up to a high degree, since it ~~is~~ does not react-prior to blending. Hence, 2C PUR represents an interesting alternative to formaldehyde-free adhesive systems in hardwood constructions. Phenol resorcinol formaldehyde (PRF) systems have been increasingly used in structural wood bonding since the Second World War. Typical for PRF is the formation of a dark-brown bond line and high bonding strength, even under humid conditions. Since the World-Health-Organization listed formaldehyde as cancer-causing [8], the usage of formaldehyde-containing adhesive systems is under pressure. Therefore, the industry is actively searching for formaldehyde-free adhesive systems, or ones with a reduced formaldehyde content, like modern melamine urea formaldehyde systems (MUF).

The understanding of the interaction between the adherend wood, its extractives and different adhesive system still reveals research gaps. Hypothesis of this study is that wood extractives influence all selected adhesive systems for structural applications. While our prior study [4] focused on the extractives influence on the curing behavior of bulk 2C PUR adhesives and the resulting bond strength, we have selected the following methods to observe the effect of extractive model substances applied at the interface on the curing behavior of different adhesive systems typically used for structural applications:

1) Influence of model substances on the cross-linking reaction of 1C PUR, MUF and PRF by Attenuated total reflection fourier transform infrared-spectroscopy (ATR-FTIR)
2) Effect of model substances on the curing of adhesive systems in terms of gel point and storage modulus by rheology of 2C PUR, MUF and PRF
3) Consequence of applied model substances on European beech wood for bonded lap joint tensile shear strength with 1C PUR, 2C PUR, MUF and PRF

2. Materials and methods

2.1. Wood

European beech wood lamellas [*Fagus sylvatica* L.] for tensile shear tests were prepared according to EN 302-1 with acclimatization in standard climate (20°C/65% relative humidity) until they reached an approximate moisture content of 12%. The average density of the lamellas was 700 ± 46 kg/m^3. The wood was used from the same lot and all types of irregularities were sorted out such as knots, heart wood or discoloration. After conditioning, the material was planed to 5 mm thickness, cleaned by compressed air and bonded within one hour. For the rheology experiments, European beech wood veneers of 0.9 mm thickness and tangential cut were used.

2.2. Adhesives

An overview of the selected adhesives is listed in Table 1. The MUF Grip Pro® Design from Akzo Nobel Coatings GmbH (Elixhausen, Austria) and the PRF Aerodux 185 from Dynea AS (Krems, Austria) are accredited for structural applications according to EN 301. The two polyurethane adhesives were obtained from Collano AG (Sempach-Station, Switzerland) and do not hold this accreditation yet. Pressure and pressing time were chosen according to authors own experiences with hardwood and recommendations of the adhesive producers. The ISO index for the polyurethane adhesives obtained 110 and could ensure saturation with isocyanate as well as high cross-linking density.

Table 8 Overview of different adhesive systems, some of their properties and their processing parameters.

Adhesive	**1C PUR**	**2C PUR**	**MUF**	**PRF**
	Collano RP 2860	Collano experimental type	Akzo Nobel Grip Pro® Design	Dynea Aerodux 185 RL/ HRP 155
Ratio weight [resin/hardener]	-	2.45:1	1:0.5	1:0.2
Viscosity [mPas] @ 20°C	25’000	40’000	Resin 10'000 - 25’000 Hardener 1'700 - 3’500	8’000-10’000
Max open time [min.] @ 20°C	60	12	10	8-10
Application [g/m^2] one side	200	200	450	450
Closed Assembling time [min.]	-	-	30	30
Pressure [N/mm^2]	0.8	0.8	0.8	0.8
Press time [h]	10	10	10	10

2.3. Model substances

The model substances were selected with the aim of representing a range of common wood extractives. Some of their properties are listed in Table 2. These synthetically produced extractives were purchased from Sigma Aldrich (Buchs, Switzerland) and were used at 10% loading based on the wet weight of the adhesive. The concentration of extractives occurring in native woods is typically significantly lower; a higher concentration was chosen to lead to significant differences and to overcome typically expected high standard deviations, especially when testing hardwood lap-joints in tensile shear mode. However, this leads partly to different additions in molar mass, but most of the quantities in the literature are based on a percentage of the wood mass. Potato starch and gallic acid were present in powder form, all other substances in liquid form. For linoleic acid the major impurity with 18 - 32% was oleic acid. No data was available for the remaining impurities of the substances, since the producer does not investigate them.

Table 9 Classification, Chemical Abstract Service number, substance class and purity of selected model substances.

Substance	CAS no.	Substance class	Purity [%]
n-Pentanal	110-62-3	Aldehyde	97
3-Carene	13466-78-9	Bicyclic terpene	90
(R)-(+)-Limonene	5989-27-5	Monocyclic terpene	97
Potato starch	9005-28-8	Polysaccharide	97
Gallic acid	149-91-7	Phenolic acid	≥ 97.5
Linoleic acid	60-33-3	Fatty acid	60-74
Acetic acid	64-19-7	Organic acid	≥ 99.7

2.4. Measurement of cross-linking

A Fourier-transform-infrared-spectrometer Perkin Elmer Spectrum 100 (Schwerzenbach, Switzerland) equipped with an attenuated-total-reflectance (ATR) unit and a diamond crystal was used to determine the influence of model substances on the polymerization of the adhesive. The contact size of the crystal was approximately 1 mm x 1 mm with a possible measuring depth of 4.4 µm. Spectra were taken in the range from 4000 cm^{-1} to 500 cm^{-1}. Measurements were conducted at 20°C with a resolution of 4 cm^{-1} and 10 scans each. To simplify the experiment, the samples were kept after blending on microscope slides and cutouts of ca. 0.5 g were used for the measurement. For each variant, three repetitions at 0, 1, 3, 6 and 24 h were made to ensure validity.

2.5. Rheological measurements

Rheological measurements were carried out with a Haake Mars III (Darmstadt, Germany) rheometer with plate to plate in oscillation mode to determine the gel point (G´ = G´´) and storage modulus (G´). The aluminum plates were 35 mm in diameter with a measuring gap of 0.5 mm. The upper stamp was covered with a thin Beech veneer (described in 2.1.) bonded with epoxy resin Araldite Ultra Standard (Basel, Switzerland) and subsequently pressed with screw clamps. Approximately 2 g of adhesive was used for each measurement. The adhesive itself was always prepared in contents of around 30 g to ensure correct blending of resin and hardener. The model substances were applied with a thin brush on the veneers surface shortly before starting the rheometer in a ratio to the adhesive of 1:10 (w/w). Weight measurements ensured that volatile substances did not evaporate prior to the measurement. Gallic acid and potato starch were diluted in distilled water and applied on the surface of the beech veneer. The experiment was started when the distilled water was evaporated. For all adhesives, a frequency of 1 Hz and a deformation rate of 0.5% was selected. To accelerate the experiment speed, 2C PUR and PRF adhesive were measured at 40°C while the fast-reactive MUF was measured at 20°C to ensure differentiation of the substances influence within a reasonable timespan. The storage modulus was determined 2 h after the adhesive and the substances were blended.

2.6. Tensile shear strength and wood failure on beech wood

For beech wood bonding, the substances were applied on one side of the lamella by a thin brush to create a model compound. The substances in powder form (gallic acid and potato starch) were diluted in water and the solution was applied on the surface as described in section 2.5. The substances were applied in a ratio of 1:10 (w/w) to the adhesive system. After adhesive application, the lamellas were put together with its counterpart and stacked into an apparatus to ensure regular pressure distribution. A Lindenberg (Altendorf, Switzerland) hydraulic press was used at a pressure of 0.8 MPa for 10 h. After pressing, the lamellas were stored in a standard climate for three weeks to ensure full polymerization. Samples were then cut to size and subsequently tested in tensile shear mode according to EN 302-1 until failure using a universal testing machine Zwick 30 kN (Ulm, Germany) in two conditions (A1 and A4). According to the standard, A1 treatment is the testing of dry samples in a standard climate, whereas A4 samples are cooked for 6 h and stored in cold water (20 ± 5°C) for a further 2 h. Specimen are finally tested in wet state. The testing force was applied in load controlled mode at 2kN/min. For the tensile shear test, ten values were collected for each variant and treatment. Wood failure was determined visually in 10%-steps. Subsequently statistical analysis was preceded by analysis of variance ($\alpha > 0.05$) between all adhesives and treatments. In addition, solid beech wood samples for tensile shear strength test were prepared for comparison with the other variants.

3. Results and discussion

3.1. Measurement of cross-linking

For comparison, 1C PUR without addition of a model substance at 0 and 24 h is displayed in Figure 1. The peak at ~3330 cm^{-1} is the stretching vibration of NH that was created after 24 h. The spectra further showed a shoulder peak at ~2925 cm^{-1} and ~2854 cm^{-1} corresponding to the stretching vibration of CH_2 and CH_3, which showed a slightly higher intensity after 24 h. Most important for the polyurethane spectra is the NCO peak at ~2226 cm^{-1}, which shows the conversion of isocyanate. Furthermore, stretching vibration of C=O was found at ~1729 cm^{-1}. Deformation vibration at ~1522 cm^{-1} interfered with NH. Deformation vibration of C-H-N at ~1411 cm^{-1} proved further cross-linking after 24 h. The urethane formation was found by amid bands at ~1670 cm^{-1} and ~1522 cm^{-1} and C-O stretching vibration at ~1230 cm^{-1} and ~1061 cm^{-1}. Subsequently, C-O was found at ~1061 cm^{-1} and did not show alteration. This peak determination agreed with the studies of Malucelli et al. [9].

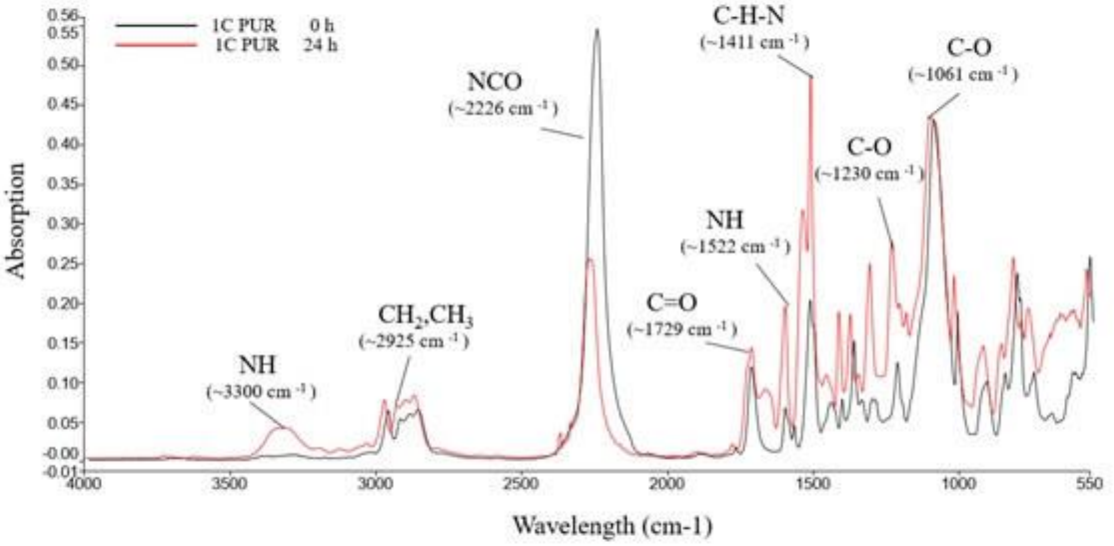

Figure 1 Spectra of 1C PUR reference at 0 h and 24 h.

After 24 h, the adhesive-substance blends of 1C PUR in Figure 2 showed a minor influence in comparison with the reference. While starch and linoleic acid slightly increased the isocyanate conversion, the terpenes as well as acetic acid decreased the conversion marginally. The remaining substances were close to the reference; thus, no statement could be made.

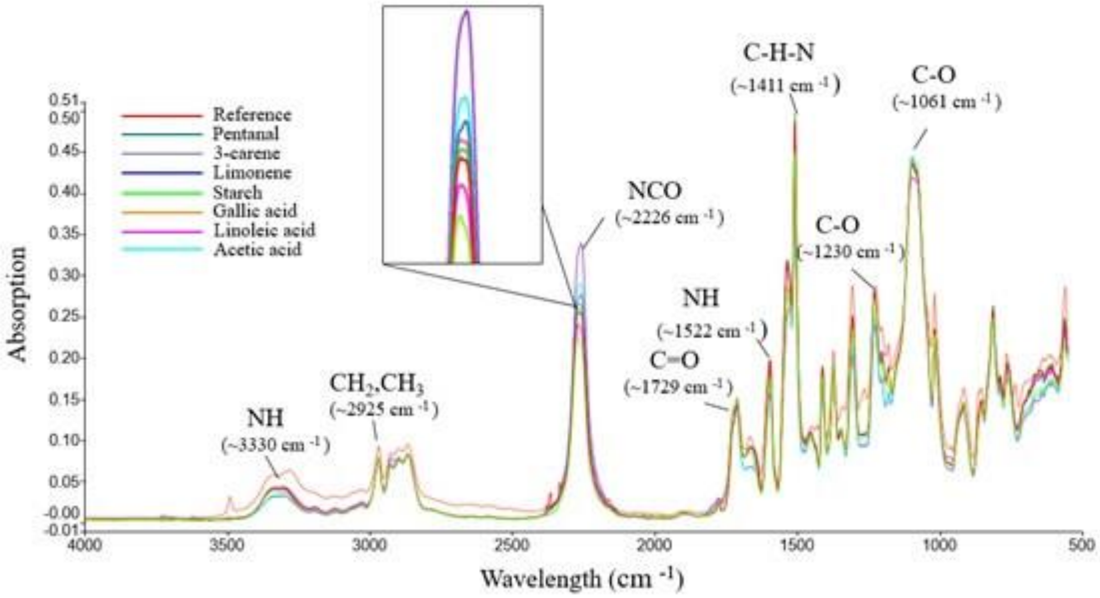

Figure 2 Spectra of 1C PUR reference and extractive-blends at 24 h.

The spectra of MUF obtained by ATR-FTIR are depicted in Figure 3 and were in accordance with Merline et al. [10]. At ~3304 cm^{-1}, the OH-peak decrease shows the process of water evaporation. The shoulder peak at 2931 cm^{-1} is the stretching vibration of CH_2-groups. The peak observed at ~2353 cm^{-1} corresponds to CO_2. At 1703 cm $^{-1}$ a shoulder peak for C=O was discovered. Primary amines (NH) were found at ~1629 cm^{-1} and were reduced during the polycondensation. Ring vibration at ~1543 cm^{-1} revealed C=N. Stretching vibration of bridged CH_2 at ~1348 cm^{-1} gave evidence for methylene bridge formation. Subsequently the peak at ~990 cm^{-1} interfered with CH and the melamine triazine ring ($(HCN)_3$) with ~812 cm $^{-1}$.

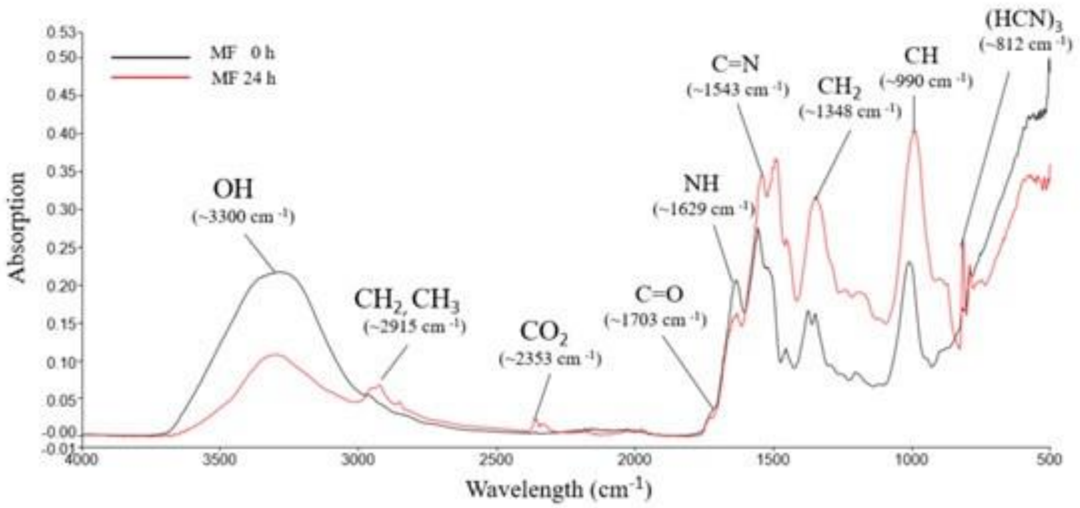

Figure 3 Spectra of MUF reference at 0 h and 24 h.

Comparing the reference spectra of MUF with the model substance blends after 24 h in Figure 4, an exact interpretation of the model substance influence is difficult. However, pentanal and linoleic acid increased the intensity. Acetic acid on the other hand increased the intensity of the bands which represents the polymerization process.

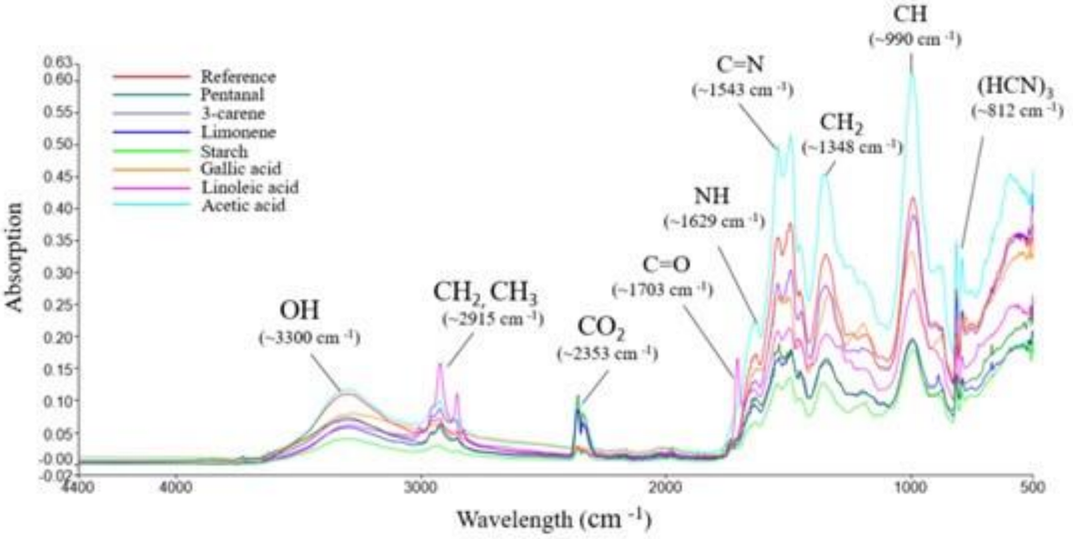

Figure 4 Spectra of MUF reference and extractive-blends at 24 h.

Figure 5 demonstrates the polycondensation of PRF between 0 and 24 h. The determined peaks were aligned with Poljansek and Krajnc [11]. The peak at ~3223 cm^{-1} marks the OH-group of the resin and its reaction after 24 h. At ~2973 cm^{-1} peaks interfere with CH_3 and CH_2. The peak observed at ~2358 cm^{-1} corresponds to CO_2. The conversion of formaldehyde can be observed at 1703 cm $^{-1}$ with the reduction of C=O. The aromatic ring vibrations of C=C were found at ~1591 cm^{-1} and ~1498 cm^{-1}. Asymmetric stretch at ~1225 cm^{-1} revealed C-C-O and at ~1473 cm^{-1} CH in plane deformations. Formation of ether links at ~1168 cm^{-1} and ~1082 cm^{-1} clearly showed polymerization.

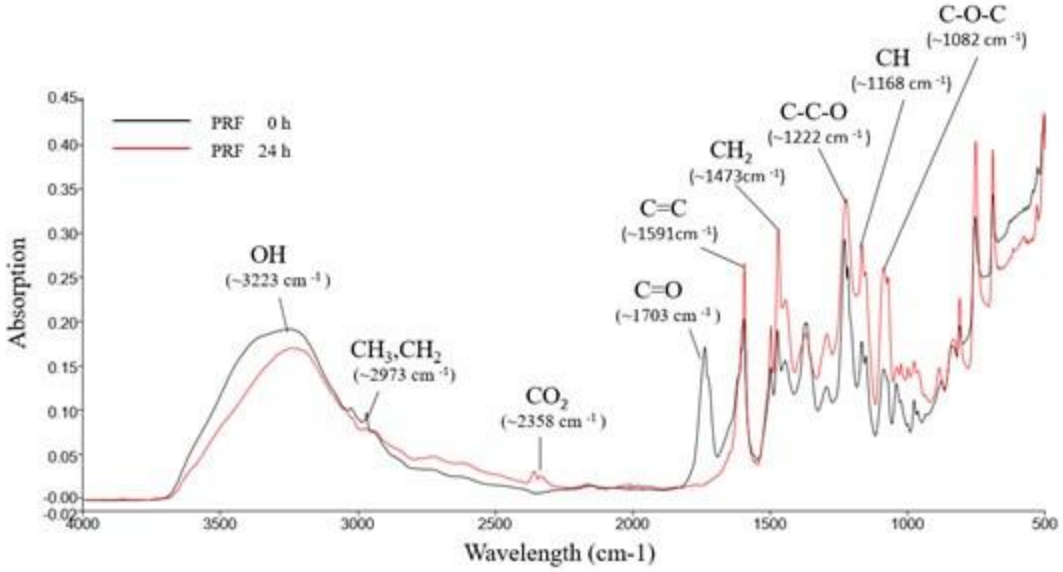

Figure 5 Spectra of PRF reference after 0h and 24 h.

In comparison to the reference, the substance blends showed minor deviation in Figure 6. Pentanal, linoleic acid and acetic acid show a slightly higher response for C=O at ~1591 cm^{-1} and linoleic acid an increase of CH_3, CH_2 at ~2973 cm^{-1}. These components possess carbonyl groups as well as CH_2, CH_3 which is why these intensities do not safely indicate changes in polycondensation.

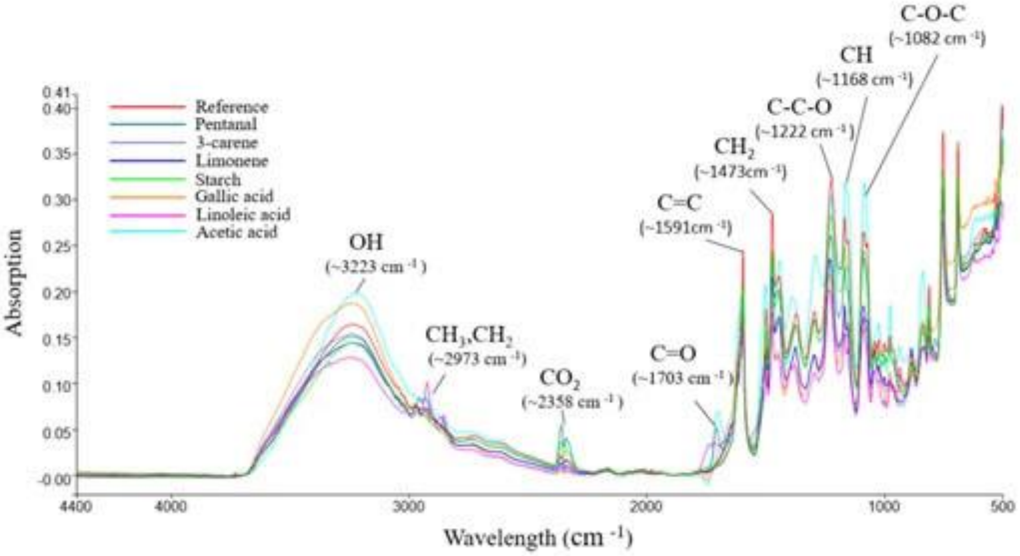

Figure 6 Spectra of PRF reference and extractive-blends at 24 h.

The ATR-FTIR measurements demonstrated an influence of some substances. For 2C PUR, prior works by Bockel et al. showed that mainly acetic acid and linoleic acid influenced the adhesive system by an acceleration of isocyanate conversion [4]. Contrary to this, the influence of model substances on the ATR-FTIR-spectra of 1C PUR in Figure 6 revealed a lower influence of these compounds which aggravated determining an influence. One possible explanation could be the delayed polymerization process through the ambient moisture. Additional measurements after 72 h still show clear peaks of isocyanate (results not shown). An influence for MUF and PRF adhesives was less clear to observe and to assign to specific substances. In general, acid substances and the aldehyde pentanal showed acceleration and partly hindering of the formaldehyde conversion. For MUF, a concrete way to analyze the polymerization can be the triazine ring at ~812 cm^{-1}. Since its overlapping with water does not enable a clear differentiation, no definitive conclusion about the polymerization process can be made based on the results reported here. It can be concluded that with the exception for polyurethane, the determination of the model substances influence on cross-linking behavior can be considered rather approximate.

3.2. Rheological measurement

Rheological behavior of the adhesive was determined in terms of gel point and on the cured adhesive in terms of storage modulus G´ after 2 h. Detailed explanations for rheological experiments can be found in the literature. Figure 7 shows the occurrence of gel points in percentage of the references for the adhesive-substance-blends. The gel point for the references obtained for 2C PUR (55 min.), MUF (38 min.) and for PRF (18 min.). When comparing the references with the adhesive-substance-blends the influence of the model substance on the gel point becomes evident. For 2C PUR basically two substances significantly influenced the gel point, acetic acid reduced it by 39% compared to the reference and linoleic acid by 85%. The gel points of the other adhesive-substance-blends ranged within the reference. The behavior of MUF was clearly influenced by all substances. The highest acceleration of the gel point was found for starch with a gel time of only 32% of the reference. The remaining substances were in the range of 54 – 76%. PRF showed the proportionally highest influence of model extractives on its gel point within the investigated adhesives. Most substances reduced the time span to the gel point, except for 3-carene with 94% of the reference. Highest acceleration of the gel point was measured for acetic acid with 17%. The remaining substances reduced the gelation for PRF in-between 22 – 39%.

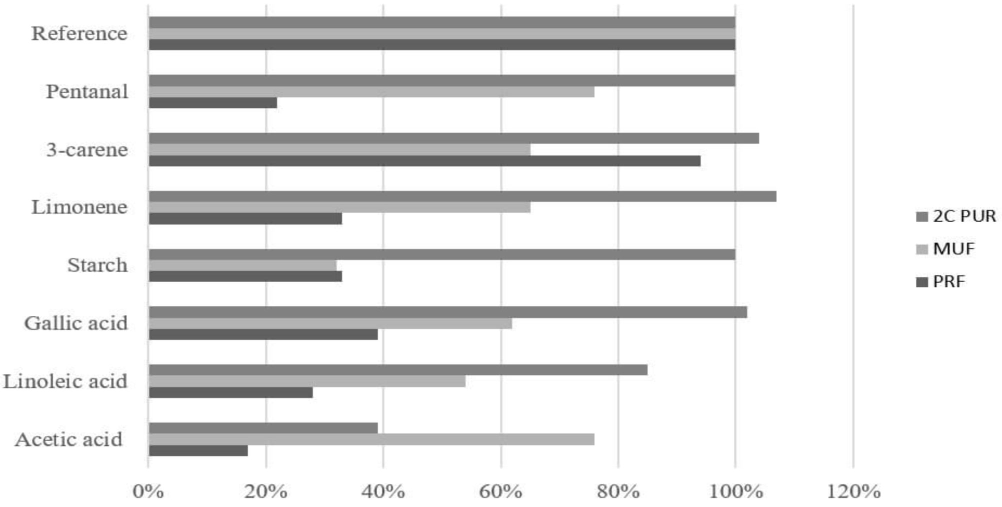

Figure 7 Gel points (G`=G``) of PRF and PUR at 40°C and MUF at 20°C in % of reference.

Two hours after blending, the storage modulus G´ obtained was 0.5 MPa for 2C PUR, 0.9 MPa for MUF and 2.85 MPa for PRF reference adhesives. In Figure 8 the storage modulus is displayed in percentage of the reference which was set to 100%. 2C PUR showed an overall reduction of G´ for all substances. The highest reduction of G´ was determined for acetic acid to be 23% of the reference. The remaining substances reduced G´ in-between 51 - 88%. MUF adhesive showed reductions for pentanal, 3-carene, gallic acid, linoleic acid and acetic acid. Starch increased G´ slightly and limonene almost obtained the same level. PRF obtained the highest reduction in G´ for acetic acid with less than 1%, followed by linoleic acid with 6 %. While starch increased G´ to 217% of the reference, the other substances reduced it between 68 – 80%.

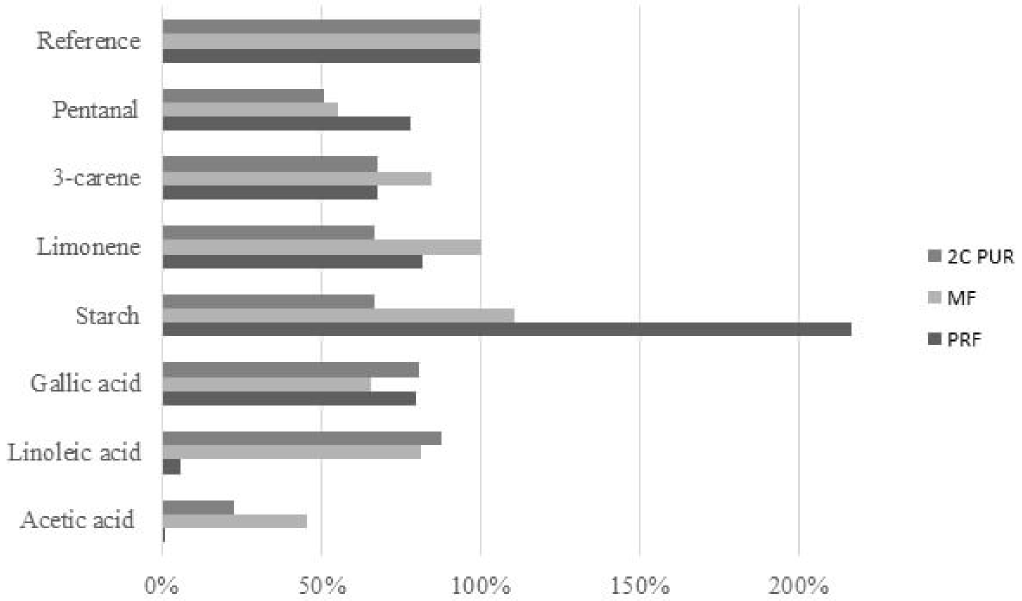

Figure 8 Storage moduli at 2 h for PRF, MUF and 2C PUR in % of reference.

For 1C PUR, no utilizable data could be obtained due to the expansion of the adhesive system and the pressure towards the oscillating plate. This can be explained with the release of CO_2, which is created during the degradation of the carbamic acid derivative. Gel points of 2C PUR were only influenced by linoleic acid and especially acetic acid. The latter acid can react with the isocyanate forming amine groups which may lead to an acceleration of the cross-linking. However, gallic acid did not show a remarkable influence, even though it has a higher acidity (pK_S, 3,3) than the other acids. Problem here could have been the low solubility of gallic acid at the interface of the beech veneer at the measuring stamp. While MUF showed a slight acceleration for all extractives, only starch reduced the gelation time strongly. Starch might have functioned as a thickener, following in acceleration of the cross-linking. PRF was influenced by all model substances. 3-carene reduced the gel point slightly, but the remaining substances accelerated the gelation to about half of the references speed. Especially these acids accelerated the alkali-hardening adhesive system. Conversely, other work of Roffael and Rauch revealed the prolonging of curing with tannin acids of resole type phenolic resins [12].

The G´ of 2C PUR is affected by all model substances, particularly by acetic acid. For MUF, starch led to a slight increase in G´ while the remaining substances reduced it. In comparison to the MUF molecules, starch has a higher molar mass. Therefore, an increase in storage modulus could be reasonable if the starch dissolves in the resin. The rheological behavior of MUF showed the highest resistance against acids. One explanation could be the difficult blending of the MUF systems with extractives or the segregation afterwards. For PRF, similar observations by Nussbaum and Sterley stated that acid extractives accelerate the curing [1]. In addition, it can be noticed, that starch, pentanal and 3-carene further accelerated the curing of PRF.

3.3. Tensile shear strength and wood failure on beech wood adherends

After conditioning in standard climate (A1), a significant difference between the variants was found for the model compound 1C PUR ($p=2.30E-02$) and PRF ($p=5.74E-08$). The application of pentanal, terpenes and starch led to a distinct increase in tensile shear strength for 1C PUR adhesive blends. Except for starch, these model substances also enhanced the wood failure. The remaining substances did not show an influence on the tensile shear strength, but gallic acid decreased and linoleic acid and acetic acid slightly increased wood failure percentage. 2C PUR revealed a considerable decrease in strength for pentanal. A decrease in wood failure was detected for pentanal, limonene, linoleic and acetic acid. Starch presented a strong increase in wood failure. Yet remarkable is the high variation of tensile strength for pentanal. MUF did not show significant influence on its tensile shear strength after treatment A1. Still, the substances pentanal and both terpenes lead to an increase of the wood failure, while the remaining were in a similar range of the reference. PRF reveals a significant reduction of tensile strength for gallic acid and increase for 3-carene. The wood failure was decreased for limonene, gallic acid, linoleic and acetic acid. An increase was observed for pentanal, 3-carene and starch. Except for the blend of gallic acid and PRF, all other variants after treatment A1 reached the required 10 MPa in tensile shear strength according to the standard EN 302-1 (compare Figure 9).

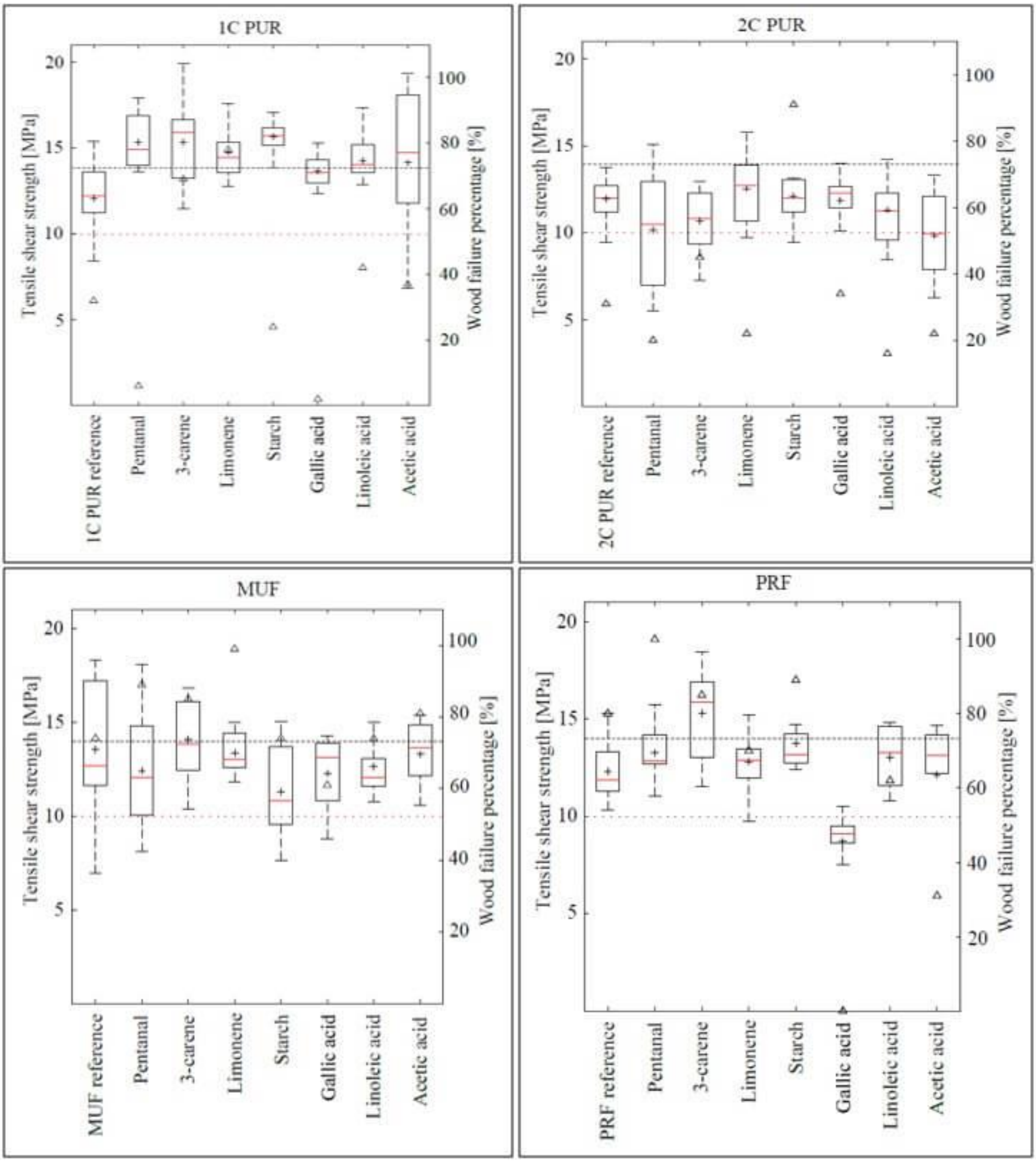

Figure 9 Boxplots refer to tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A1 for 1C PUR, 2C PUR, MUF and PRF. Comparison of reference and the model-substance-modifications (n=10). Dashed black line refers to mean tensile strength of solid beech wood and dotted red line the minimum requirement for lap-joints according to EN 302-1.

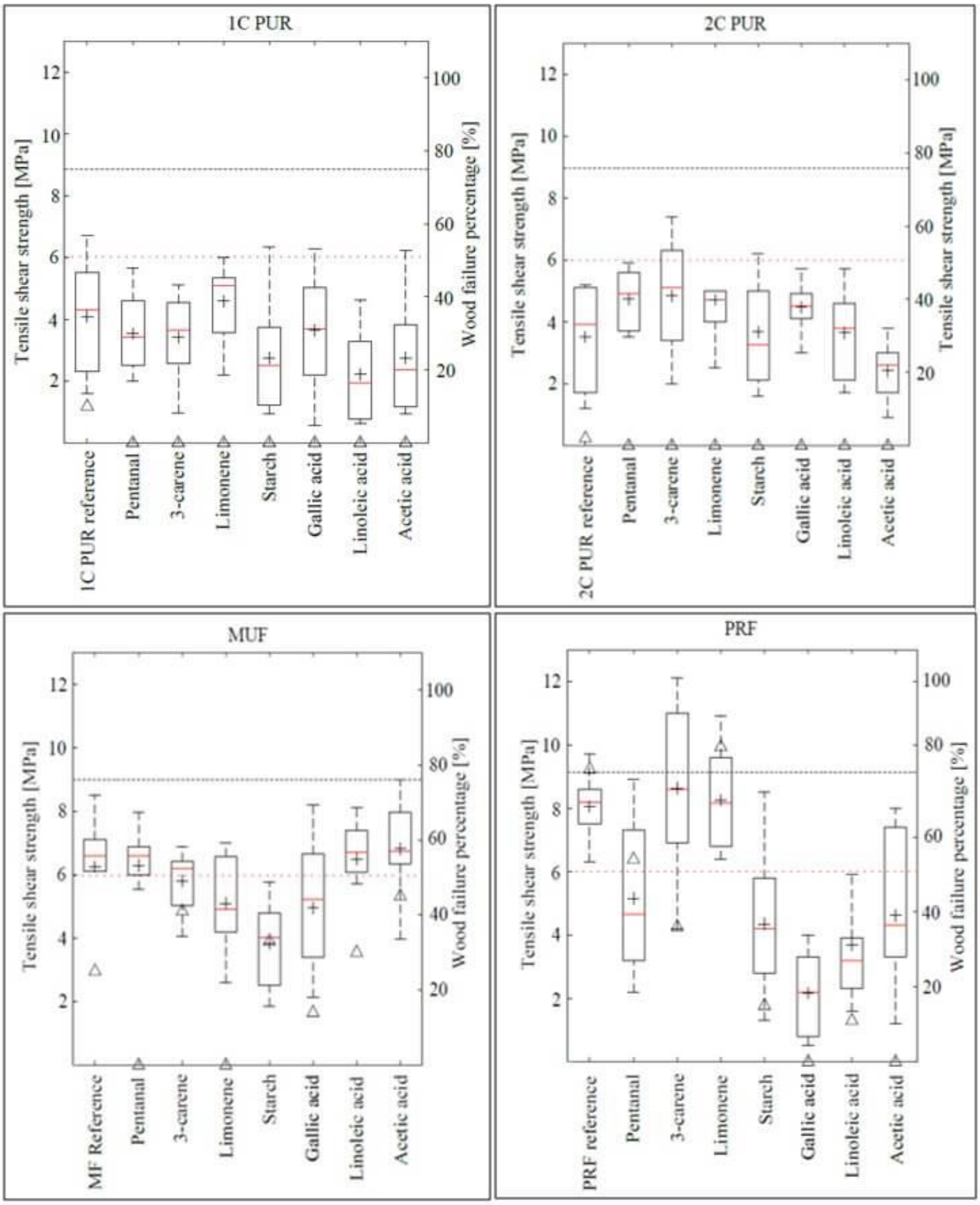

Figure 10 Boxplots refer to tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A4 for 1C PUR, 2C PUR, MUF and PRF. Comparison of reference and the model-substance-modifications (n=10). Dashed line refers to mean tensile strength of solid beech wood and dotted line the minimum requirement for lap-joints according to EN 302-1.

When testing lap-joints after A4 treatment (boiling and tested in wet conditions) as shown in Figure 10, a high reduction of mechanical strength and wood failure can often indicate some deficits in adhesion towards the adherend. The analysis of variance showed significant differences within the variants for 1C PUR (p=2.54E-02), 2C PUR (p=2.85E-03), MUF (p=2.59E-04) and PRF (p=2.15E-11). Most evident for both polyurethane adhesives is a reduction of wood failure to 0% indicating some deficits in adhesion towards the adherend. Simultaneously all values for both polyurethane adhesives clearly perform below standard requirements. When comparing the two polyurethane adhesives, they have in common that starch and the acids linoleic acid and acetic acid reduce the tensile shear strength, while the remaining model substances did not negatively influence these adhesives. A clear differentiation was difficult due to the low tensile shear strength and its wide scattering. MUF showed a great reduction in tensile strength for starch. The substances pentanal, limonene and gallic acid reduced the wood failure after A4 treatment. The highest influence of substances on tensile strength was observed for PRF. Pentanal, starch, gallic acid, linoleic acid and acetic acid reduced the tensile strength slightly. Except for limonene, all other model substances, especially starch and the acids, reduced the wood failure strongly. The strongest impact was determined for gallic acid with 28% of the reference mean value and a loss in wood failure to 0%.

An effect of model substances on wood bonding could also be observed. The references achieved tensile shear strength values in comparison with solid beech wood ranging between 82% and 91% in dry conditions. Standard deviations of the extractive blends were within the solid wood range. The dry testing A1 revealed only a minor and partly positive influence of substances on the tensile shear strength. The increase of wood failure for some variants might be associated with the degradation of the interface and interphase area. This assumption could not be proven for A1 conditions because the wood failure percentage is furthermore influenced by sample density and local fiber orientation. The inducting of moisture and high temperatures within the treatment A4 conversely led to partly significant influences of model substances on the tensile shear strength and wood failure percentage. Hence, they failed achieving the standards requirements of 6 MPa (compare Figure 13). The density of the used beech wood, which lay within the standards range, did not explain high tensile shear strength or their partly high variation. Relevant for all adhesive systems might have been the powder form of gallic acid and starch that could have enhanced the wetting of the adhesive systems leading to part starvation of the glue line. Contrary to this, linoleic acid seemed to dissolve into the vessels and partly exit on the other side of the 5 mm thick lamellas.

Based on the findings reported in the present study it could be clearly shown that the used model substances that represent common wood extractives can influence wood bonding and impact structural adhesive systems in a negative matter. Polyurethane adhesives showed a robust behavior against some substances and were mostly influenced by acids. One explanation of the high resistance could be the high solid content of the polyurethane system, as well as the excess use of isocyanate. The excessive amount of isocyanate could therefore compensate the reaction of extractives with isocyanate, still ensuring satisfying cross-linking reaction and density. It seems contradictory that the PRF and MUF adhesives, which obtain excellent bond performance, are sensitive to the used substances. On the other hand, the MUF and PRF systems obtain a high water content which could further support solving and distribution of the model substances in the adhesive systems (especially starch and gallic acid). MUF cures optimally under slight acid conditions but melamine as a good nucleophile can react and cure with the electrophilic formaldehyde under varying pH-conditions. This could be an explanation for its lower influence by these substances compared to PRF. Konnerth el al. [13] conclude that adhesive chemistry and molecular size of the PRF allow a cell wall penetration leading to a modification of the cell wall properties. In consequence of this modification, a reduction in swelling and shrinking behavior and therefore a better strength in humid conditions can be expected, as mentioned by Konnerth et al. [14]. Contrary to this are the low tensile strength~~s~~ values observed in wet conditions (treatment A4). A reason for this could be the use of a high model substance-adhesive~~s~~ ratio that exceeds the natural occurrence of wood extractives by multiple times. On the other hand, this ratio was necessary to derive tendencies and to compare the influence on the used adhesive systems. Own preliminary studies with 3% extractive-adhesive ratio (w/w) were not able to detect a particular influence due to high standard deviations, especially of the ATR-FTIR and the tensile shear test on beech wood. One limitation of this study can be seen in the separate investigation of the individual model substances. The simultaneous application of multiple model substances could further lead to interaction between the substances and bias their effects.

When comparing the results of this study with findings in hardwood bonding, some adhesion deficits of certain hardwood and softwood species have been documented. For example, black locust showed a lower delamination resistance in experiments conducted by Konnerth et al. [14] and it was stated by Magel el al. that this species most abundantly contains storage carbohydrates, flavanols and hydroxycinnamic acid derivate [15]. In general, polyurethane adhesives revealed the largest problems with bonding alternative wood species in comparison with established systems like MUF and PRF [14]. Bonding of white oak was demonstrated by Kuo et al. to be difficult with phenolic resins [16]. Similarities can be drawn for gallic acid and its negative influence on PRF bonds with beech wood. Problems with ash wood have been noticed by Knorz et al. [17] with PRF or PUR. The latter one requires an adhesion promotor (primer) prior to bonding to achieve satisfactory results. It is understood that this primer enhances the wettability of the adhesive on the adherend wood and enables more cross-links leading to a better bond performance. Acid extractives and fatty acids were expected to negatively influence the bonding of wood. Results of Ammann et al. show that species that are easy to bond like spruce contain more fatty acid and acetic acid than European beech and ash wood [18]. Contrary, our study revealed a negative influence of linoleic acid and acetic acids, especially on PRF. Most likely the effect of extractives in spruce wood is overlaid by its otherwise perfect properties such as homogenous cell structure and low swelling and shrinking coefficients.

To understand the influence of the used model substances, their functional groups must be considered. The aldehyde pentanal has only one functional group~~s~~ but can react with formaldehyde temporarily. However, its influence can be considered minor. The used terpenes, limonene and 3-carene, do not carry functional groups and their odor was still noticed when cutting the beech lap joints after full polymerization (three weeks). Next to their smaller influence on rheological and mechanical properties, they are expected to act as a local hinderer of the cross-linking up to a smaller degree. Starch and gallic acid could have reacted with their large amount of hydroxyl groups. This could explain the negative effect of starch on MUF as determined in other works of Kohlmayr et al. [19]. However, the effect of gallic acid was only detected for PRF. These hydrolyzed tannins can easily be dissolved in water and therefore also in MUF and PRF. Reducing sugars and polysaccharides with reducing ends under alkaline conditions can be transformed to acidic components, especially saccharinic acids. These acid~~s~~ components can neutralize the base catalysts in the phenolic resin and prevent proper setting and curing of the resin according to Wang [2]. This could be the explanation for the low tensile shear strength for PRF with starch and the acids.

When comparing statements of other works with the results of the present work, some interesting findings can be made. It was assumed by Popper, that carbohydrates do not influence wood bonding [20] – in opposition of our findings. Furthermore, it was shown, that most extractives do not extend gelation time, but accelerate it - contrary to earlier statements by Narayanamurti et al. [21].

While prior experiments of Bockel et al. [4] addressed the influence of model substances on the bulk material of 2C PUR, this study rather focused on their influence on the interface area. For 2C PUR it can be concluded that the influence of these substances is higher on the bulk adhesive than on the interface. This can be explained with a smaller exposition of substances towards the adhesive as well as partial deposition of liquid extractives into the wood vessels. The latter approach proved to show better differentiation and simulate a more realistic approach. When comparing the influence of artificial extractives on the adhesive by their origin in hard- or softwood, it can be concluded that there is no particular evidence for a special influence of one of these origins, except for gallic acid and phenol formaldehyde resin.

4. Conclusions

Different and novel approaches to determine the influence of artificial wood extractives on structural adhesives for hardwood bonding were carried out. These methods investigated the effect of model substances on fresh and cured adhesive systems as well on fully polymerized bonds on the adherend. Key findings were that some recent statements about extractives and their possible effect on wood bonding could be disproved. While ATR-FTIR showed limitations in determining the influence of these substances on the adhesive systems, the modified rheometer setup and the beech wood lap-joints led to good differentiation between the used model substances. It was found that polyurethane adhesives are negatively influenced by compounds that represent acid extractives. Further, melamine urea formaldehyde was degraded by starch and gallic acid. Phenol resorcinol formaldehyde showed a negative impact of starch and acid substances. However, the influence of artificial extractives could not just be assigned to their origin in hard- or softwood. Extractives that commonly occur in both types had a greater influence than the specific ones, except for gallic acid. Combining the results of different methods, it can be concluded that wood extractives play a crucial role in the bonding process. Their role can be even more important when extractives occur surface-wide and in high contents or when large changes in moisture content stress the interface area additionally, leading to higher adhesion deficits. Hence, their impact is more significant when the bond line is exposed to multiple negative aspects. Since surficial adherend treatments, e.g. extractions, are costly and imprecise, this problem should be addressed by the modification of the adhesive system. Therefore, wood species with similar extractive constitution should be grouped and adhesive systems modified to these.

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3.4. Paper IV

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Characterization of wood-adhesive bonds in wet conditions by means of nanoindentation and tensile shear strength

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Abstract

The performance of adhesive-hardwood bonds can often be sensitive to humidity and temperature variation. Therefore, it is frequently challenging to achieve standard requirements for structural applications. To gain a better understanding of the wood-adhesive bond, the properties of the individual constituents as well as the local interface of European beech (*Fagus sylvatica* L.) wood cell walls in contact with structural adhesives were analyzed by means of nanoindentation. These results are compared to classical lap-shear strength. As adhesives two different one-component polyurethane adhesives (1C PUR) and a phenol resorcinol formaldehyde adhesive (PRF) were used. In one case, the beech wood was additionally pre-treated with an adhesion-promoting agent (primer) prior to bonding with 1C PUR. Beech wood joints were analyzed subsequent to several treatments, namely standard climate, after wet storage and in re-dried conditions. In addition, the influence of the primer on the hydroxyl accessibility of beech wood was investigated with dynamic vapor sorption (DVS).

The lap-shear strength revealed good performance in dry and re-dried conditions for all adhesives on beech. Both polyurethane adhesives obtained deficits when tested in wet conditions. The use of a primer significantly improved the PUR performance in wet condition. DVS experiment demonstrated a decrease in hydroxyl group accessibility when using a high primer concentration. As novelty, nanoindentation was used for the first time to characterize the local wood-adhesive-interface properties in wet conditions. Nanoindentation showed that all tested 1C PUR perform quite similar in room climate, while PRF achieves considerable higher values for reduced E-modulus and hardness. Wet storage led to a considerable reduction in mechanical properties for all adhesives, while the highest relative change was observed for PRF. After re-drying, the adhesives re-gained a large part of their original mechanical properties in room climate. No distinct effect of the primer on the local micromechanical properties could be detected with nanoindentation in terms of specific work of indentation.

Key words: adhesives for wood, nanoindentation, hardwood, interfaces, lap-shear, polyurethane

1. Introduction

The on-going trend towards mixed forests in Europe and a growing stock of hardwood challenges wood industry and science for an increasing material usage of hardwood. Until now, most of the hardwood is used for thermal energy production. Adhesive bonding can be one way to enable the use of hardwood for structural applications, thus using hardwood in a more profitable, competitive and sustainable way. However, some hardwood species still show difficulties in meeting requirements for structural standard testing methods, such as delamination resistance according to EN 302-2 (Konnerth et al. 2016). While higher strength of hardwood balances positive in wood engineered products, the response to humidity reduces the competitiveness and potential of some hardwood species (e.g., beech wood).

One-component polyurethane adhesives (1C PUR) are being successfully used for structural applications using spruce as substrate. However, PUR is associated with comparably poor performance on some alternative wood species and some hardwoods, especially when tested for humid or very dry environments. In order to overcome these issues, adhesion deficits were addressed with the combination of different adhesion-promoting agents (primer) as reported in various studies (Ohnesorge et al. 2010; Amen-Chen and Gabriel 2015; Kläusler et al. 2014). Richter (1999) described the general characteristics of primers by a polar part that enables strong intermolecular interactions, a hydrophobic spacer grid and a part that enhances the wetting with the adhesive. The application of primers can enhance the mechanical performance of 1C PUR bonds on hardwood in order to allow for complying with standard requirements (Kläusler et al. 2014; Clerc et al. 2018). It was recently shown that a primer is capable of penetrating wood cells to a certain extent (Casdorff et al. 2018). However, the function of the primers at the local interface is not fully understood yet and demands further research. Similar to other references (e.g., Frihart 2012), in this context, the term "interphase" refers to the region within an adhesive bond where the adhesive penetrates the pores of the wood substrate. Within this interphase multiple local "interfaces" are present. The latter is defined as the direct (local) boundary between the wood cell wall and the adhesive.

Different approaches have been conducted to evaluate the performance of adhesives on wood (Amman et al. 2013; Konnerth et al. 2006; Kläusler et al. 2014). Testing of single and pure adhesive films might not be able to display the real conditions in a bond line, since the surrounding wood affects the curing, mechanical relaxation and morphology as found by Ren and Frazier (2012). Therefore, investigations on wood-polymer-interactions are preferably conducted in a real joint.

Next to standardized tests, nanoindentation (NI) has shown to be a reliable technique that allows for investigating essential parameters relevant for adhesive bonding. The usage of nanoindentation to determine the properties of wood cell walls was introduced by Wimmer et al. (1997). Various studies on wood cell walls, adhesives and their interactions at the interphase followed and contributed to a better understanding of the joint performance (Amman et al. 2016; Zhang et al. 2015; Jakes et al. 2008; Konnerth et al. 2006; Rindler et al. 2018; Obersriebnig et al. 2013). NI has also been used in high humidity environment as shown by

Jakes et al. (2015), but not yet applied to water-stored glue lines of hardwood in combination with a primer.

However, indentation values reported for studies on wood cell walls have to be interpreted carefully due to the three-dimensional stress state in combination with the anisotropic nature of wood, as well as the importance of proper sample preparation (Konnerth et al. 2009). NI is capable of analyzing the properties of the individual components present in the interphase region of wooden bonds (e.g., Zhang et al. 2015; Konnerth et al. 2006) as well as the performance of the local interface at the micro-scale level (Obersriebnig et al. 2013). Studies in this field mainly addressed the interphase region of wood-adhesive-bonds in dry conditions or the influence of moisture on polymer films (Konnerth et al. 2010). Mechanical properties of adhesives are typically available in dry conditions as summarized by Stöckel et al (2013). Literature using different climatic conditions is less frequently accessed (Rindler et al. 2018; Stöckel et al. 2013). Wood properties and their dependence on moisture are well described at the macroscopic level (Niemz and Sonderegger 2017).

Little information is available on micromechanical properties including the influence of moisture and the performance of the interface at the local level, possibly due to a lack in available methodology. One possible approach to test interface performance was proposed by Obersriebnig et al. (2013). Knowledge of moisture-dependent mechanical properties of single constituents present in hardwood bonds could therefore help to better understand the behavior of the joint and possible influence of a primer. Next to the wood-adhesive-interactions, the influence of primer on the surface hydroxyl accessibility is of high interest. The available hydroxyl groups are assumed to play a crucial role in the physiochemical interactions in the wood bonding process (Frihart, 2012). Dynamic vapor sorption analysis has shown to be useful for the determination of accessible hydroxyl groups of wood with deuterium (Sepall and Mason 1961; Thybring et al. 2017) and could be useful to describe the effect of primer application.

In the present study, the aim was a better understanding of the mechanisms contributing to moisture resistance of beech wood adhesive joints. Therefore, the following was investigated:

- Tensile shear strength and wood failure of beech wood bonds using different 1C PUR adhesives, partly in combination with a primer, and a PRF adhesive in dry, wet and re-dried conditions
- Influence of adhesion-promoting agent (primer) and lack of extractives (hot water and hexane) on hydroxyl groups accessibility of beech wood by Dynamic vapor sorption (DVS) analysis
- Mechanical properties of individual regions (adhesive, wood cells) of beech wood bonds by nanoindentation in dry, wet and re-dried conditions
- Performance of the local interface between cell wall and adhesive in dry, wet and re-dried conditions

2. Experimental

2.1. Wood

European beech wood (*Fagus sylvatica* L.) with an average density of 700 ± 34 kg/m^3 from one lot without any type of irregularities such as knots, heartwood or discoloration was selected and cut to lamellas of 10 mm thickness. The lamellas were stored in standard climate (20°C/65% relative humidity) until a moisture content of approximately 12% was reached. After conditioning, the material was planed with fresh knives down to 5 mm, cut to size and bonded according to EN 302-1 for single lap-joints within 30 minutes. Wood intended for nanoindentation and Dynamic vapor sorption (DVS) experiments was used from one single board and from the same annual ring.

2.2. Adhesives and wetting promoting agent

Two commercial one-component polyurethane (1C PUR) adhesives were tested in this study and compared with a commercial phenol resorcinol formaldehyde (PRF) adhesive. The 1C PUR adhesives mainly differ by their reactivity (open time). 1C PUR B is recommended to use with a wetting promoting agent (primer) and the other system can be used without primer when bonding alternative wood species, for example beech or larch. The primer was used with 1C PUR B to create variant 1C PUR C. The use of primer is further described in the literature (Amen-Chen and Gabriel 2015; Richter 1999).

PRF has proofed to reliably bond wood for structural and outdoor applications (Dunky and Niemz 2002). The selection of adhesives and some of their processing parameters are listed in Table 1.

Table 10 Selected properties of adhesives and their processing parameters

Adhesive	1C PUR (A)	1C PUR (B)	PRF
Viscosity @ 25°C (mPas)	20’000-30’000	24’000	400-1500
Open time (min)	< 60	70	120
Application (g/m^2) one side	160	160	450
Closed assembly time (min)	0	0	30
Pressure (MPa)	0.8	0.8	0.8
Press time (h)	10	10	10

2.3. Longitudinal tensile shear strength and wood failure on beech wood

The climatized and freshly planed lamellas were cleaned by compressed air prior to bonding. For the variants using a primer, the liquid primer was diluted in deionized water to a 10%-solution for variant (C). To ensure homogenous primer distribution, the lamellas were transported with a conveyor belt and a constant feed speed through a self-made spray application device. The defined amount of 20g/m^2 was afterwards controlled by a scale without giving the solution time for evaporation. The used spread rate and concentration have recently been determined to be ideal for hardwood bonding (Clerc et al 2018). After adhesive application the bonded lamellas were subsequently stacked into an apparatus to ensure precise pressure distribution and pressed in a hydraulic press (Lindenberg, Altendorf, Switzerland) for 10 hours at 0.8 MPa at ambient temperature for all adhesive systems. After pressing, the bonded lamellas were stored in standard climate for three weeks to ensure complete curing and sample conditioning. Subsequent to specimen treatment described in Table 2, lap joint specimens were tested in tensile shear mode according to EN 302-1 using a universal testing machine (Zwick 30 KN, Ulm, Germany). Specimens were tested in load-controlled mode at 2 kN/min. For each variant and treatment, 15 specimens were tested and compared with solid beech wood references using the same specimen geometry, but without an adhesive bond line. Wood failure percentage (WFP) was determined visually in 10%-steps.

Table 2 Treatment of tensile shear strength samples according to EN 302-1

Treatment	Definition
A1	Testing in standard climate 20°C/65% relative humidity
A2	4 days immersed in cold water (20 ± 5°C), testing of specimen in wet condition
A5	Boiling in hot water for 6 h, then 2 h cold water storage (20 ± 5°C), condition in standard climate until original mass is reached, testing in dry conditions

2.4. Dynamic vapor sorption analysis

For the gravimetric determination of hydroxyl group accessibility, the dynamic vapor sorption equipment (DVS-ET1, Surface Measurement Systems, London, UK) was used. The samples were prepared from one beech wood panel within the same annual ring. Approximately 10 g of early wood was separated with a razor blade and further cut into very thin sections. Any chemical modification to the wood cell wall is usually more pronounced in early wood than late wood. Therefore, early wood was chosen for this experiment.

Samples were dipped into solutions with distilled water and primer in the following concentrations 0.1%, 1% and 10% (based on weight). To determine the influence of wood extractives on the hydroxyl group accessibility, further samples were extracted (Automatic Solvent Extraction 200, Dionex, Reinach, Switzerland) with hot-water (at 100°C, 1 h) and hexane (at 60°, 1 h). For each variant, three replicates were tested. Specimens were dried at 0% RH and 60°C for 6 h while purging with dry nitrogen gas to remove the wood's bound water. A 1 h stabilization time at 25°C (deuteration condition) followed. Afterwards, samples were conditioned with D_2O (Liquid D_2O 99.9 atom% D, Sigma Aldrich, Buchs, Switzerland) for 10 h at 95% RH. Specimen weight was determined before and after conditioning and hydroxyl group accessibility was calculated from the corresponding difference. The number of accessible OH groups was quantified according to Väisänen et al. (2018) as follows:

Equation 1. $$A = \frac{m_f - m_i}{m_i * (M_D - M_H)} \ (mol\ g^{-1})$$

- A is the accessible OH group content in dry mass of the sample (mol g^{-1})
- m_i is the dry mass of the sample before exposing it to D_2O vapor (g)
- m_f is the dry mass of the sample after the D_2O exposure (g)
- M_D is the molar mass of deuterium (2.014 g mol^{-1})
- M_H is the molar mass of hydrogen (1.008 g mol^{-1})

2.5. Nanoindentation

Samples for the nanoindentation experiments were obtained from one beech wood lamella of 10 mm thickness. It was stored in standard climate (20°C, 65% RH) and small parts of around 25 x 25 mm were cut out with a chisel. Each time, two counterparts were used to create an adhesively bonded assembly. Prior to bonding, a fresh surface at its radial anatomical plane was created with the help of a rotary microtome (Leica RM2155, Wetzlar, Germany) in order to keep cell wall damage at a minimum level. The primer was applied to variant 1C PUR C with a spray bottle and its application weight was controlled with a scale before bonding with 1C PUR. Afterwards, the adhesive was applied with a spatula. For PRF, a closed assembly time of 30 min was used. Small screw clamps were used to pressurize both counterparts for 12 h and stored without clamps in standard climate for three weeks to allow for sufficient post-curing and conditioning of the sample. Samples for nanoindentation were cut out with a razor blade with a size of 5 mm length, 2 mm thickness and 2 mm width. The samples were then bonded by a two-component epoxy resin (UHU Plus Sofortfest, Bolton, Switzerland) to a metal disc with 12 mm in diameter to fit into the ultra-microtome sample holder. Further microtoming with diamond blades (Ultratrim and Histo, Diatome, Nidau, Switzerland) using an ultra-microtome (Ultracut-R, Leica, Vienna, Austria) ensured flat surface. To control surface quality and for pre-selecting proper indentation points, incident light microscopy (Axioplan 2, Zeiss, Jena, Germany) was used. To allow for testing multiple specimens simultaneously, samples were bonded to flat metal plates. Three samples at a time were surrounded by a polymer ring to enable storing the samples in water during the later indentation experiments. The prepared samples were clamped magnetically onto the indenter stage. All nanoindentation experiments were performed with a Hysitron TriboIndenter (Hysitron Inc., Minneapolis, USA) equipped with an extremely sharp cone-shaped tip with a total opening angle of 60°. The scanning probe microscopy mode of the indenter was used to control the precise positioning (Figure 1) of the indents. As recommended by Obersriebnig et al. (2013), indents were performed in a displacement-controlled mode with a maximum indentation depth of 850 nm. Load was applied in a three-segment load ramp with a load increase for 3 s, peak load holding for 20 s and 3 s of unloading.

Measurements were taken to analyze the individual components present in an interphase of a bond, namely the bulk adhesive, the wood cell wall (S2) and at the direct interface between the adhesive and the wood cell wall lumen (S3), as well as between the adhesive and the wood cell wall (S2) (Figure 1).

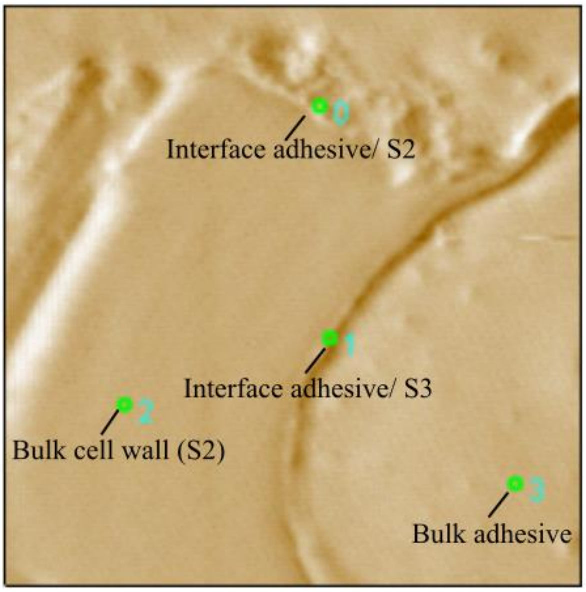

Figure 1 Scanning probe microscopy image (10 x 10 µm²) of a beech wood cell wall surrounded by adhesive and intended indentation positions at interface adhesive/wood cell wall S2, interface adhesive/wood cell wall S3, bulk wood cell wall and bulk adhesive.

For each climate condition and adhesive variant, eight wood cells were tested with eight indents. For bulk material properties, the obtained results were reduced E-modulus (E_r) and hardness (H), evaluated according to the method by Oliver and Phaar (1992). The specific work of indentation (W_d) spent during each indent at the interface between adhesive and wood cell wall was determined by integrating the total area under the load-displacement curve as proposed by Obersriebnig et al. (2012).

Statistical analysis of the results of nanoindentation and lap-joints on beech wood was conducted with a single factor variance analysis (ANOVA, 5% confidence interval) with a post hoc least significant difference to allow comparison between the mean values of each adhesive variant.

3. Results and discussion

3.1. Tensile shear strength and wood failure on beech wood

The results of tensile shear strength and wood failure percentage (WFP) are shown in Figure 2. After conditioning in standard climate, all adhesive systems were able to meet the standard requirement of 10 MPa according to EN 302-1. PRF even surpasses solid wood in tensile shear strength and had the highest wood failure percentage (90%) of all tested adhesives. While the PRF joints performed significantly higher than the 1C PUR adhesives joints, no significant difference was observed within the 1C PUR variants. All 1C PUR adhesive bonds were characterized by a similar wood failure percentage in standard climate conditions of around 30-40%.

The storage in water and subsequently testing in wet state (A2) showed a considerable reduction in tensile shear strength and wood failure percentage for lap-joints, including the solid wood reference, in comparison to the performance in dry climate (A1). However, the PRF maintained its high WFP. Characteristic for all 1C PUR variants was the absence of the wood failure for all cases. While the 1C PUR C with primer application demonstrated a similar tensile shear strength to PRF, the other PUR adhesive assemblies performed below 50% of the solid wood value reference. 1C PUR B was significantly lower in tensile shear strength than 1C PUR A. Despite no significant difference in strength, the type of failure between 1C PUR C and PRF differed considerably. The application of a primer led to a significant increase in tensile shear strength compared to the same adhesive applied without any adhesion promoter. Considering the standard requirements for A2 conditions, 1C PUR A and B were not able to reach the 6 MPa threshold value.

For treatment A5, specimens were re-conditioned to their original mass in standard climate, after boiling in water and cold-water storage. All adhesives joints were able to reach similar or even better values compared to their standard climate reference, which was in accordance with another study (Kläusler et al. 2014). Yet, significant differences appeared between all variants. The variant with applied primer (1C PUR C) obtained a significantly higher tensile shear strength than the variant 1C PUR B without primer and nearly the same as the variant 1C PUR A without primer, but this time with higher WFP than for the PRF.

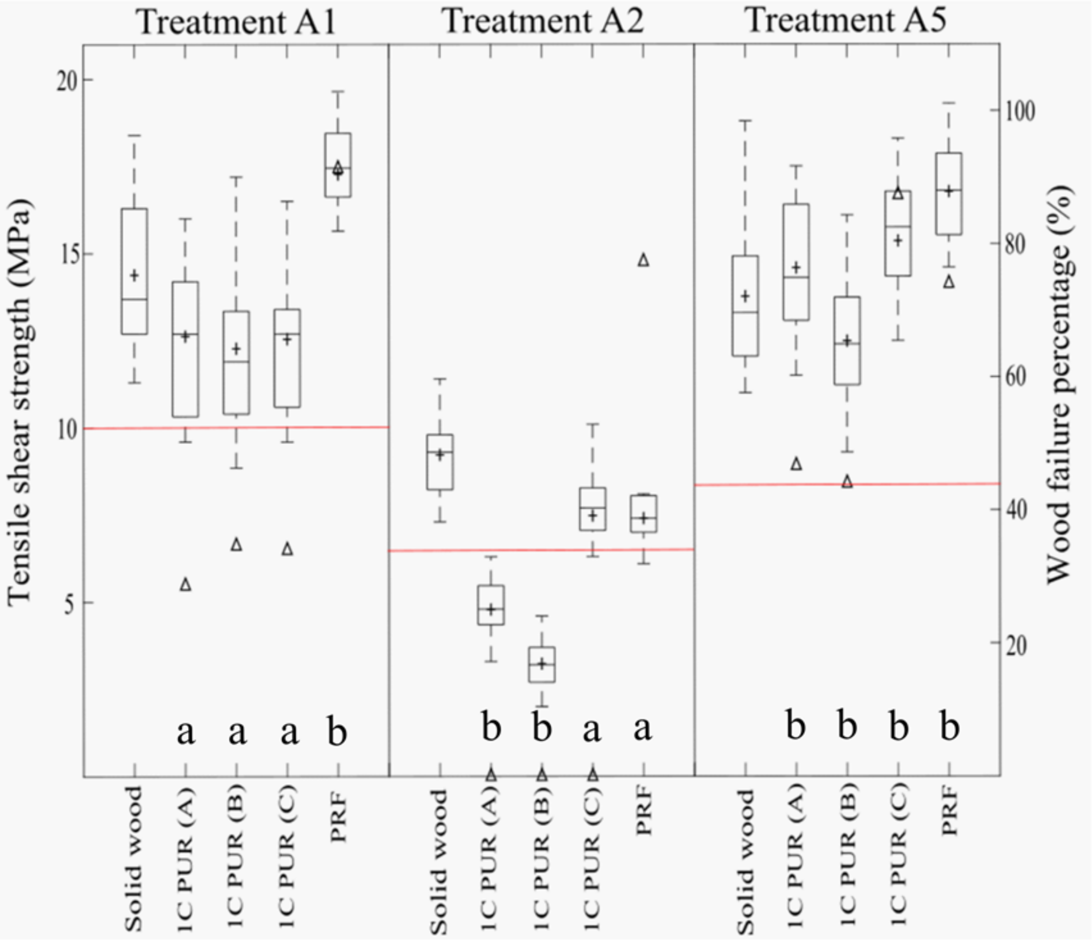

Figure 2 Boxplots of tensile shear strength (mean value marked as cross) and wood failure (triangle) after treatment A1, A2 and A5 for the adhesives 1C PUR (A, B and C) and PRF (n=15). Boxplots indicate median, interquartile range and minimum and maximum are shown as whiskers. Horizontal line mark standards requirement following EN 302-1. Statistically homogenous groups are indicated with letter a, significantly different variants with letter b. (ANOVA, significance level 5%).

As a main result from the macroscopic test it can be concluded that the investigated two commercial 1C PUR systems meet standard requirements when tested in dry ambient, while they lack in performance when tested in wet conditions. The well-established PRF adhesive joints were able to meet all standard requirements. The application of the primer (1C PUR C) sufficiently improved the bonding performance for surpassing the standard requirements in wet conditions (A2). However, the primer application did not increase the wood failure percentage for treatment A2.

3.2. Gravimetrically determined hydroxyl group accessibility to D_2O vapor

The results of the DVS experiments are depicted in Figure 3. The reference obtained an average value of around 7.5 mmol/g accessible hydroxyl groups for early wood of beech.

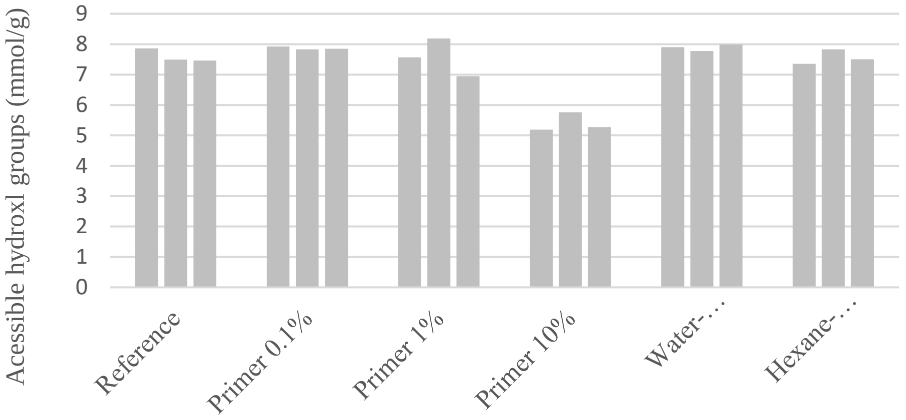

Figure 3 Single values of hydroxyl accessibility at 95% relative humidity determined gravimetrically by DVS for European beech early wood, with different primer concentrations, and wood powder previously treated by two different types of extraction.

No difference was observed between the reference and the samples immersed in 0.1% primer solution. The samples treated with 1% primer concentration obtained higher scattering and two out of three values with a lower amount of accessible hydroxyl groups, but no statistically significant trend could be determined. The variant exposed to 10% primer concentration showed a substantial decrease in hydroxyl group accessibility down to approximately two thirds of the reference accessible hydroxyl groups.

It is proposed that the primer may deposit on the wood polymer hydroxyl groups and could therefore block the access to deuteration in high concentrations of 10%. However, this concentration exceeds industrial primer application. Own studies with samples that have been sprayed with industrial application devices using a common spread rate and concentration showed a similar trend for samples but a considerable smaller influence on the hydroxyl accessibility (results not shown).

The extraction treatments applied to the beech wood did not show a difference in hydroxyl group accessibility. The hot water extraction aimed to mainly dissolve polar components such as tannins, organic salts and carbohydrates. Extraction with hexane focused on the dissolving of mainly non-polar extractives such as fats, waxes and phenols (Sixta 2006). Hypothesis of the study was that some extractives can reduce the hydroxyl group accessibility by creating a surficial chemical weak boundary layer of water-soluble extractives and when the extractives are dissolved the amount of accessible hydroxyl groups would be expected to increase. While the hot-water extraction showed consistently high hydroxyl group accessibility, a slightly higher scattering was observed for hexane-extracted wood, while no significant difference to the reference could be detected.

3.3. Nanoindentation

As optical focusing, proper positioning and subsequent tip approach with the nanoindentation device was not possible with the samples being covered in water. Therefore, after full sample immersion in water for 48 h, the water level was lowered below the sample surface 120 minutes prior to the first measurement for the condition “wet storage”. The ongoing shrinking of the swollen sample required permanent focus adjustment for each measurement. The results of the nanoindentation (NI) experiments on bulk materials (adhesive, wood cell walls) are summarized in Figure 4. In general, the PRF adhesive revealed an approximate three times higher reduced (red.) E-modulus and an approximate four times higher hardness than the polyurethane adhesives in dry conditions, which is in accordance to with other studies (Amman et al. 2013; Stoeckel et al. 2013) performed on similar substrates. Comparing all 1C PUR variants in room climate, no significant difference in mechanical properties was found. During storage in water, the red. E-modulus and hardness of all adhesive systems dropped considerably. Noticeable is the high relative change of PRF in comparison to all 1C PUR variants in terms of red. E-modulus and hardness. The polyurethane adhesives were reduced in red. E-modulus to around 70% and PRF to 10% of its initial values at room climate. The hardness of polyurethane adhesives was reduced to 30-40% and that of PRF to 30% of its original value.

No significant influence on bulk adhesive properties was observed when a primer was used. In general, the investigations on the bond line and the results for the bulk adhesive were comparable with earlier studies on moisture influence tested on cured adhesive polymer films (Konnerth et al. 2010). While the differences in dry and wet conditions for red. E-modulus and hardness were quite similar, the 1C PUR C had significantly lower values for red. E-modulus and hardness in re-dried conditions for the bulk adhesive as well as the cell wall. After testing in wet conditions, the samples were dried for two days in room climate. All bulk adhesives were able to re-gain a considerable part of their original mechanical properties in room climate. Indentations in the wood cell showed that the red. E-modulus at room climate was somewhat higher for the wood cells next to PRF compared to wood cell walls in contact with the group of 1C PUR. However, this effect is superimposed by a high degree of scattering resulting from the natural variability of the wood substrate. Higher mechanical values for cell walls in contact with in-situ polymerizing adhesives (Frihart 2012), such as the PRF used, can generally be expected by the penetration of low-molecular weight substances from the liquid PRF into the wood cell before curing. As a consequence, stiffening of the wood cell walls is frequently observed (e.g., Gindl et. al 2004; Konnerth et al 2006). However, this effect was not visible for the hardness of wood cells near PRF measured in other studies (Obersriebnig et al. 2013).

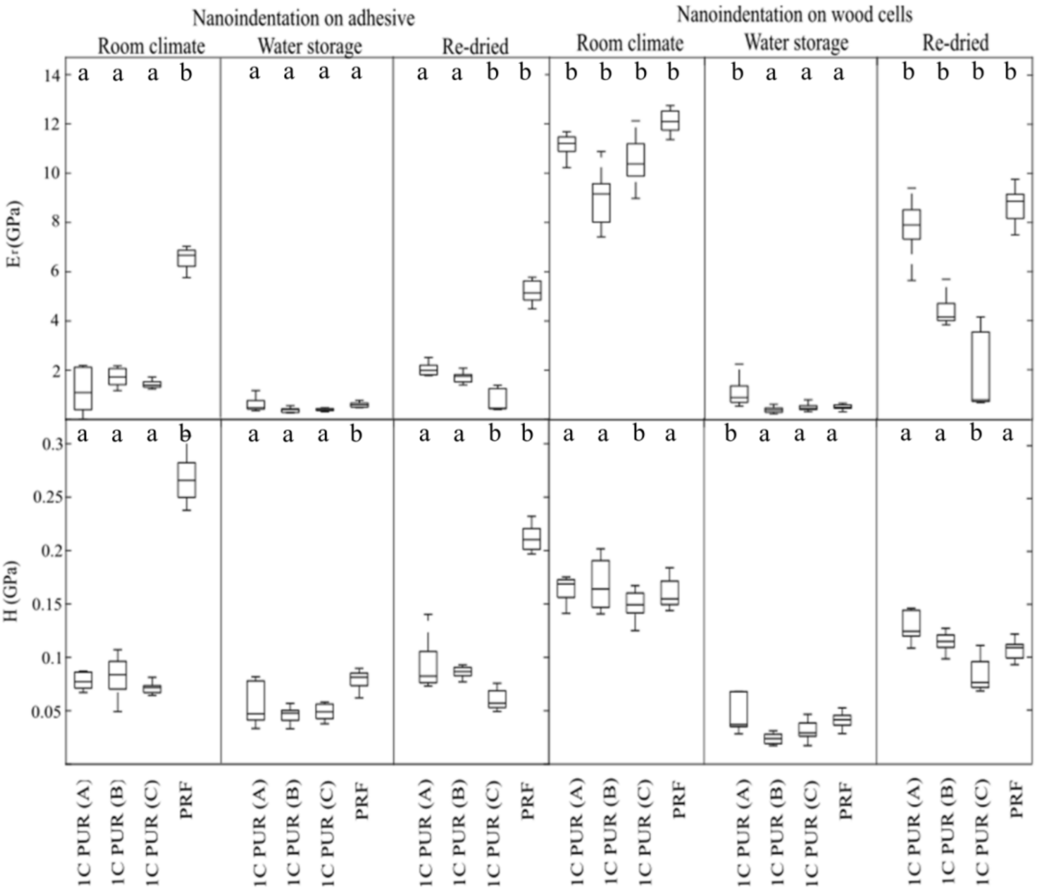

Figure 4 Results from nanoindentation on bulk adhesive and bulk secondary S2 wood cell walls from the interphase region for red. E-modulus (E_r) and hardness in room climate, during water storage and in re-dried conditions for specimens bonded with the adhesives 1C PUR (A, B, C) and PRF (n=12). Boxplots indicate median, interquartile range and minimum and maximum are shown as whiskers. Statistically homogenous groups are indicated with letter a, significantly different variants with letter b. (ANOVA, significance level 5%).

Between the 1C PUR variants, wood cells of 1C PUR A and 1C PUR C did not show any significant difference, while 1C PUR B was significantly lower. Due to the incapability of penetrating the cell walls, this difference may have its origin rather in the variability of the wood structure than by the influence of the adhesive. After water storage, variant 1C PUR A showed significantly higher red. E-modulus and hardness compared to the remaining variants, which did not show significant differences, including the PRF variant. After drying for two days, the red. E-modulus differed significantly for all variants. However, for hardness, only 1C PUR C showed a significantly lower hardness. As moisture is a main bias for mechanical properties of polymers, differences in drying rate of the individual adhesives and assemblies may be assumed. It remains unclear whether the mechanical properties are able to re-gain their original values for the case of longer storage times. Macroscopic properties observed using the lap-joints described above might be an indicator that properties lost during wet storage may be recuperated.

The results of the specific work of indentation at the direct interface between adhesive and wood, separated into the different contact regions between adhesive and the wood cell wall S2 and S3, are depicted in Figure 5.

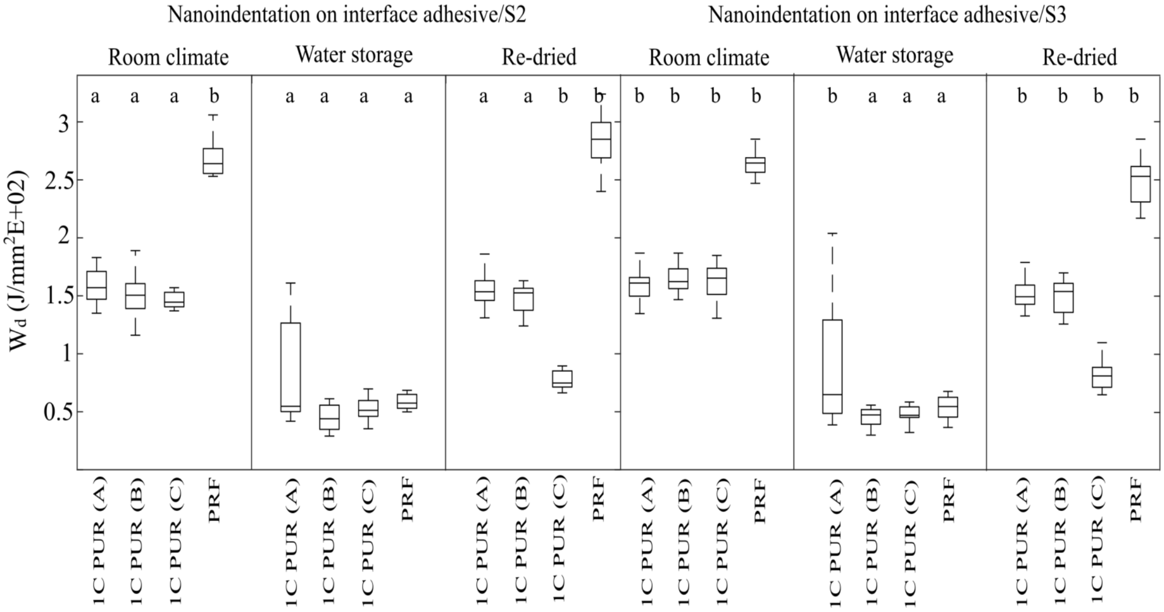

Figure 5 Specific work of indentation (W_d) for indentation at the interfaces between adhesive/secondary wood cell wall S2 and adhesive/lumen S3 in room climate, during water storage and in re-dried conditions for different 1C PUR (A - C) and PRF adhesives (n=12). Boxplots indicate median, interquartile range and minimum and maximum are shown as whiskers. Statistically homogenous groups are indicated with letter a, significantly different variants with letter b. (ANOVA, significance level 5%).

The specific work of indentation presented in Figure 5 consists mainly of the work consumed for deforming the wood cell wall and the adhesive. Only a comparably small amount of around 10-20% can be attributed to real adhesion as expected by Obersriebnig et al. (2012). However, a visible crack was observed by the authors which exceeded the size of the indentation tip towards a partly separating of both surfaces.

Due to methodological restrictions, differences in adhesion can only be observed when mechanical properties of the individual constituents are comparable. As a consequence, only differences in specific work of indentation between different contact regions (S2 vs. S3) of one adhesive assembly and condition state may be interpreted as adhesion differences. In contrast, the considerable differences between the specific work of indentation of different adhesives, as visible for PRF and the 1C PUR versions, may not be interpreted as differences in adhesion, but have their origin mainly from differences in mechanical properties of the constituent phases (cell wall, adhesive) in their corresponding state.

Considering these restrictions for interpreting the specific work of indentation, PRF was found to adhere similar to S2 and S3 cell wall areas in dry state, as well as after water storage. Only after re-drying, the adhesion towards S3 cell wall areas may be considered to be lower. For 1C PUR A, specific work of indentation at the interfaces between adhesive and both cell wall areas S2 and S3 was found to be similar in all three conditions. Since the similar 1C PUR adhesive was used to produce variant B and the primered variant C, a careful comparison can be drawn. 1C PUR B and the primered variant of the same adhesive 1C PUR C showed higher specific work of indentation at the adhesive/S3 interface in room climate, while no difference could be found for the other climatic conditions.

Before performing the present work, higher adhesion between PUR adhesive and cell wall areas was hypothesized when using a primer, especially in wet state as a high amount of adhesion failure (lack of wood failure) is frequently observed for PUR-wood bonds (Figure 2, A2 condition). Comparing the specific work of indentation at the interface of 1C PUR B and the primered variant of the same adhesive 1C PUR C, in wet state an insignificant specific work of indentation is visible for 1C PUR C. In re-dry state, specific work of indentation of 1C PUR C is significantly below the value of 1C PUR B. As considerable differences in bulk mechanical properties of the two PUR assemblies are evident for the same conditions, deriving information about adhesion differences is not possible.

4. Overall discussion

Lap-shear joints of beech wood demonstrated once again (Konnerth et al. 2016; Clerc et al. 2018) that the used PRF adhesive is capable of meeting standard requirements for all conditions. However, a formaldehyde free and color less alternative for safely bonding hardwood is frequently desired.

The used 1C PUR systems showed good performance in dry and re-dried conditions, but a primer was needed to surpass standards requirements in wet conditions on beech wood. Despite improving strength, the application of the primer did not lead to an improvement in wood failure percentage. Contrary, another study (Lüdtke et al. 2015) showed that WFP can be increased by using a primer. This difference may be explained by possible differences in the primer application, or by the small processing window of the primer (Clerc et al. 2018).

The investigated hydroxyl group accessibility of European beech wood was in accordance with findings by Tarmian et al. (2017). They further showed only minor differences between the hydroxyl group accessibility of European beech, spruce and pine wood. In contrast, Teleman et al. (2002) found a lower amount of accessible hydroxyl groups for hardwoods, for example beech wood, due to the beech's lower amount of hydroxyl groups of its hemicelluloses. However, this possible disadvantage of beech wood may only be a subordinated factor to explain the more challenging bonding of hardwood in comparison to softwood. Far more important for hardwood bonding could be their higher density as well as higher swelling and shrinking coefficients (Niemz and Sonderegger 2017). These properties result in higher stresses in the bond region as a result of changing moisture conditions.

The removal of polar and nonpolar extractives did not show any considerable influence on the hydroxyl group accessibility of beech wood. Its low extractive content of around 2% based on the dry wood mass (Jiang et al. 2014) could be the reason for not revealing a possible influence. Hence, this approach could have more impact on wood species with considerably higher extractive contents such as larch or pine.

The primer is expected to enhance wetting of 1C PUR on hardwood as well as to increase the adhesion. With the methods used, an improvement of the adhesion at the interface due to primer application could not be found. As the mechanical properties of the bulk wood cell wall remained at a lower level after the two days of re-drying, a possible influence of the primer on the water absorption and/or release rate in the interphase area could be assumed. Studies by Väisänen et al. (2018) demonstrated that there is a connection between the equilibrium moisture content and the accessibility of hydroxyl groups, while another study revealed only poor correlation (Rautkari et al. 2013). In this regard, the deep penetration of primer in wood cell walls as shown by Casdorff et al. (2018) might be favorable. However, this finding could not be validated in the present study, as the amount of primer necessary to decrease the hydroxyl accessibility noticeably exceeds industrial application rates by far. Therefore, a reduction in hydroxyl group accessibility under optimal industrial primer application cannot be proven.

As a novelty, the nanoindentation experiments revealed that water-stored wood-adhesive composites can also be tested in wet conditions. However, analyzing the specific work of indentation did not show any influence of the applied primer on the adhesion in different climate conditions. The proportionally higher reduction in red. E-modulus and hardness of PRF can be attributed to a softening of the polymers as a result of water uptake. Wimmer et al. (2013) revealed that PRF adhesive can take up to 18% moisture, while 1C PUR only gained 3.5%, which was explained by the process of polycondensation and the production of methylol phenol derivates. The involved hydroxyl groups may take up two water molecules (Bentz and Neville 1949). Furthermore, the hydromechanical performance of PRF was considered to be similar to wood (Musznyski et al. 2002). In combination with cell wall impregnation and the reduction in local swelling and shrinking in the interphase, PRF is capable of creating a moisture-resistant composite with high mechanical strength even in wet conditions.

Kläusler et al. (2013) showed that the tensile strength of 1C PUR polymer films was reduced by 19% to 30% when ambient moisture was increased from standard climate to a relative humidity of 95%. In addition, its E-modulus was reduced in these conditions between 31-56%. In comparison, PRF did not show a decline in tensile strength with increasing moisture content, but the E-modulus was significantly reduced to 50%. For polyurethane, it can be expected that water uptake is also leading to structural changes such as free volume variations, relaxation effects and changes in visco-elastic behavior (Smith et al. 2004).

5. Conclusion

The novel and challenging approach to characterize wood-adhesive interfaces of bonds in wet conditions by nanoindentation extends possible applications for nanoindentation and was expected to provide new insights into the mechanisms how a primer is affecting PUR bonds. In contrast to the authors` assumptions, no measurable effect of the primer on the local adhesion between adhesive and cell wall by specific work of indentation could be observed.

While macroscopic mechanical performance of PRF adhesive bonds are on a high level, the storage in water showed a dramatic reduction in mechanical properties of the PRF adhesive itself. This effect was much less pronounced for the polyurethane adhesives. No direct influence of the primer on the local micro-mechanical properties of the bonding line could be found in dry and wet conditions. Only after re-drying, the mechanical properties of the wood cell walls pre-treated with the primer remained longer on a lower level, while other adhesives re-gained their original values already. It was further shown that the primer application can reduce the hydroxyl accessibility of beech wood, when applying high spread rates. The mechanism of the primer responsible for improving 1C PUR adhesive bonds is still not fully understood and requires further research.

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4. Discussion and main findings

4.1. Modification of 2C PUR

Prior to this study, the adhesive manufacturer Collano AG developed an experimental 2C PUR system for structural hardwood bonding. The system was modified analog to the present study and the experimental variant was characterized in Paper I. The 2C PUR has been adapted by calcium carbonate as filler with the aim of increasing the modulus to a range analogue to the ones typical for amino- and phenol based adhesive.

The polyol component of the 2C PUR was a polyester-polyether-polyol (molecular weight ~3000g/mol) with 60% calcium carbonate as the standard setting. The hardener was Desmodur VK 10 from Covestro AG (Leverkusen, Germany), a mixture of diphenylmethane-4,4'-diisocyanate (MDI) with isomers and higher functional homologues (PMDI) with NCO of 31.5%.

The behavior of the liquid adhesive was characterized by surface tension, polarity and its contact angle on beech wood. The 2C PUR with 60% filler content showed an average surface tension of 32.7 mJ/m^2 with a polar part of 9.8 mJ/m^2 and a disperse part of 22.8 mJ/m^2. The contact angle of 2C PUR on freshly planed beech wood on the radial plane was 73.8°. The adherend beech wood obtained after planing on its radial plane a contact angle with distilled water of 56.1° which slightly decreased after 24 h which is in accordance with other findings [96]. The surface free energy after planning was determined following the model of Owens, Wendt, Rabel and Kaelbe (OWRK) [97] to be 50.2 mJ/m^2. The polar part of the beech surface directly after planning obtained 8.7 mJ/m^2 and the disperse part 41.6 mJ/m^2.

The tested industrial 1C PUR showed a contact angle of 69° with a polar part of 8.8 mJ/m^2 and a disperse part of 27.6 mJ/m^2. Therefore, the tested 1C PUR and 2C PUR are considered as comparable in their wetting properties. In contrast to the polyurethane adhesives, PRF showed a very high contact angle on beech of 108° with a comparingly low surface tension of 20.8 mJ/m^2. The in comparison with polyurethane higher contact angle may be explained by the phenyl rings presented in PRF [21]. However, a study of Stehr et al. [98] showed that the contact angle decreases after a short while.

From these results it can be concluded that the tested 2C PUR is compatible with the adherend beech wood and has similar wetting properties as industrial 1C PUR. A surface tension of the 2C PUR lower than the free surface energy of the adherend ensures wetting. In addition, a contact angle below 90° results in good wetting performance according to Habenicht [42].

Microscopical analysis of the bond line (results not shown) further proofed that the high filler content (60% wt) led to the formation of an even bond line of 0.2-0.3 mm thickness and a penetration into cell lumina of approximate 1-2 mm on each side. The absence of filler in the polyol component (0%) led to a high adhesive penetration and adhesive was found up to 5 mm away from the center of bond line. Deep penetration of 1C PUR adhesives without filler content was also shown by Hass et al. [99]. While for phenolic resins the depth of penetration had a positive effect on the fracture toughness on pine wood [100], reduced penetration into cell lumina favors higher tensile shear strength on beech wood with polyurethane [13]. It can be expected that for adhesives which are known to penetrate the wood cell wall [62] and therefore modify the interphase of the compound, a deeper penetration of adhesive is favorable to the performance. In contrast, pre-polymerized adhesives such as polyurethane are not capable of penetrating the wood cell wall [62]. Therefore, a wide adhesive penetration into cell lumina seems more disadvantageous and a lower penetration depth prevents a possible bond line starvation.

The curing behavior of 2C PUR was further analyzed chemically by attenuated total reflectance fourier-transform-infrared-spectroscopy (ATR-FTIR) and physically by rheology in Paper II & III. However, these experiments mainly aimed to analyze the influence of wood and did not investigate differences between polyurethane formulations. Yet, some findings can be added to the modification of 2C PUR.

The ATR-FTIR experiments showed, that around 90% of the isocyanate conversion in 2C PUR was completed after the first 24 h and full curing was achieved after 3 days. Clauß et al. [13] found that a full conversion of isocyanate in 1C PUR was realized after 6 days. Reason for this difference could be the moisture-depending curing of 1C PUR and a possible lack of ambient humidity in contrast to 2C PUR which cures by its own components.

Rheological behavior was analyzed by rheometer in a plate-to-plate experiment in terms of gel point and storage modulus. The gel point describes the point where the gelation of the polymer starts. The storage modulus in a dynamic measurement is similar to an elastic modulus of a static testing [101]. The adhesive was applied on a thin beech wood veneers on the stamp with a bond line thickness of 0.5 mm. The gel point of 2C PUR in Paper I was obtained after 230 min at room temperature. Another study [102] showed a gel point for 1C PUR of approximate 180 min. Though different experimental setup are limited in comparison, it can be expected that the curing speed is in a similar magnitude. The storage modulus of 2C PUR measured after 12 h showed to be 19.9 MPa. The predominant elastic behavior at the start of the bonding process is a desired feature to prevent glue line starvation and was also observed by Stapf et al. [102].

Accelerated measurements in Paper II at 40°C revealed a gel point for 2C PUR of 55 min and for PRF of 18 min. The fast curing MUF adhesive was measured at 20°C and showed a gel point after 30 min. For PRF, gel points between 42 and 62 min at room temperature were observed in another study [103]. After two hours, the storage modulus for 2C PUR obtained 0.5 MPa, the one for MUF 0.9 MPa and 2.85 MPa for PRF. However, no data was obtained for 1C PUR as discussed before in context with the ATR-FTIR experiments. Stapf et al. [102] showed for MUF a storage modulus after 12 h of 3.5 MPa.

It can be expected that analog to Paper I, the storage modulus of these adhesive is higher when final storage modulus is obtained.

The mechanical properties of the cured adhesive were determined on thin polymer films by tensile strength (TS) and E-Modulus (MOE) at room temperature following ISO 527-1 [44]. The 2C PUR variant without filler content revealed a TS of 47 MPa and an MOE of 2.3 GPa. Adding 15% wt filler to the polyol led to a TS of 33 MPa and an MOE of 1.7 GPa. Increasing the filler content to 30% wt reduced the TS to 28 MPa and raised the MOE to 2.5 GPa. Adding 60% filler (wt) to the polyol component led to a reduction in TS to 28 MPa but an increase in MOE to 4.4 GPa. Decrease in tensile strength of the variant with 60% filler content may be explained by the inert behavior of calcium carbonate towards polyurethane, resulting in phase separation and reduction of crystallinity, as observed by Donate-Robles and Martin-Martinez

[104]. In comparison, a study of Kläusler et al. [43] showed tensile strengths for industrial 1C PUR of 24 - 27 MPa with an MOE of 1.0-1.1 GPa and were in accordance with research summarized by Stöckel et al. [105].

Hence, the formulation of the 2C PUR with 60% wt filler content revealed a comparingly higher MOE than other industrial 1C PUR and even higher than PRF with 3.4 GPa [43]. In comparison, MUF showed a TS of 29.5 MPa and an MOE of 3.1 GPa as determined by Clauß et al. [13].

The adhesives performance on beech wood was tested in lap-joints following EN 302-1 [35]. The selected process parameters in this study were topic to prior investigations of the adhesive manufacturer Collano AG (results not shown). Wood surfaces were always freshly planed by using sharp knives before adhesive application. There is consensus about long pressing times (>8 h) and a considerable high applied pressure (≥0.8 MPa) for hardwoods in comparison with softwoods, in order to ensure a high degree of curing the development of efficient wood-adhesive-bonds. These parameters were further in accordance with other experiments [59] [12] [26] and mainly aim to firmly place together hardwood of higher density and strength in comparison with softwood. Another reason for long pressing time can be seen in the use of adhesive systems with lower curing reactivity, which are known to increase the bonding performance of hardwood [106]. This should allow for proper penetration in the adherend, while high curing speeds can lead towards insufficient penetration. In addition, the findings of ATR-FTIR and Rheometer support the extension of pressing time.

The modification of the polyol component in 2C PUR by 0, 15, 30 and 60% revealed different performance in lap-joints on beech wood. While the variant with 0% and 60% filler surpassed the requirements of 10 MPa following EN 302-1, the variants with 15% and 30% did not met the requirements. In wet condition (A4), no variant was able to surpass the standards requirements of 6 MPa. The selected standard variant with 60% filler content was further tested in water-stored (A2) and re-dried (A5) conditions. The TSS after treatment A2 obtained 3.2 MPa with no presence of WFP. In re-dried conditions, the 2C PUR with 60% wt filler content surpassed the requirements in re-dried conditions with a TSS of 11.5 MPa and a WFP of 10%.

While using the same adhesive formulation and similar wood from the same lot, the present study differs in their low TSS on beech wood in wet conditions from prior findings of Harling et al. [10], who were able to reduce the delamination on beech wood from 100 to 30% by adding 60% wt of calcium carbonate as a filler to the polyol component. An explanation of this discrepancy has not been found yet. Still, improvements were observed for TSS in dry conditions as mentioned earlier.

Studies of Clauß et al. [13] revealed a higher bond performance of 1C PUR in dry condition by adding high filler contents. However, the filler had no substantial effect on the TSS when the bond was exposed to high moisture contents. Further, Kläusler [107] showed that a high WFP can be obtained by adhesives with high MOE such as MUF and PRF, as well as with adhesives of low MOE such as 1C PUR in combination with chemical reactive primer. Therefore, he concluded that hardness, MOE and cohesive strength are not the most crucial factor for obtaining high bond strength, e.g. high WFP.

According to Frihart [62], wood adhesives can be categorized into in-situ polymerized and pre-polymerized adhesives. In-situ polymerized adhesives such as PRF have a higher MOE in comparison with PUR and are able to penetrate the wood cell wall [62] and therefore modify the interphase. This modification can result in a higher WFP and improve performance in wet conditions. Pre-polymerized adhesives such as PUR (1C PUR & 2C PUR) are not expected to penetrate the wood cell wall due to their higher molecular weight. Therefore, they are not able to modify the wood cell wall but their lower degree of cross-linking leads to higher flexibility and the ability to distribute stress concentrations within the bond line. The key factor in durable wood bonds is the distribution of swelling strain across the wood interphase to lower interfacial stresses according to Frihart [62].

It was not possible in this study to improve the performance in wet conditions of 2C PUR by increasing the MOE and aiming to achieve higher WFP. It remains worth discussing if the higher MOE with absence of WFP in wet conditions therefore could have resulted in increased local stresses (stress concentrations) at the interface.

The results indicate that the improvement of MOE by high filler content in dry conditions is primarily attributed to good wetting performance on beech wood and subsequently an improved bond line development. However, the hypothesis (No. 1) that 2C PUR modified by filler with a higher MOE can surpass standard requirements following EN 302-1 in dry and wet conditions, can only be verified for the dry conditions, but not for the more critical performance in wet conditions.

4.2. Influence of wood extractives

The influence of wood extractives on the chemical and physical curing behavior of structural adhesives as well as on the performance of wooden bonded joints was analyzed in Paper II and Paper III. The analyzed adhesives were 1C PUR, 2C PUR, MUF and PRF.

The ATR-FTIR experiments investigated the influence of wood extractives on the chemical curing behavior of adhesives. The extractives were blended into the liquid adhesives in a ratio of 10% to the adhesives weight and measured multiple times within 24 h.

The isocyanate conversion, which represents the progress of the polyaddition of polyurethane, was mainly accelerated in 2C PUR by linoleic acid and acetic acid. For 1C PUR, the speed of isocyanate conversion was primarily increased by linoleic acid and starch. However, the isocyanate conversion of 1C PUR was slower than 2C PUR, probably due to a lack in ambient moisture content. MUF was influenced in its progress of curing by acidic extractives (linoleic acid, acetic acid and gallic acid). Curing of PRF was not measurable affected in its curing speed by extractives.

The methodological approach by ATR-FTIR revealed a detectable influence on polyurethane adhesives especially by acidic extractives (acetic acid, linoleic acid) and partly starch. Analyzing the curing behavior of adhesive systems such as MUF and PRF has been successfully carried out [41] [108]. However, the approach also showed limitations in interpretation for MUF and PRF adhesives. The influence of extractives in low concentrations in MUF by ATR-FTIR was also reported to be limited by Özparpucu et al. [93]. For MUF, a specific way to analyze the polycondensation is the triazine ring at ca. ~812 cm^1. Due to the overlapping with water, clear indication was aggravated. The difficulty for PRF can be seen in the fact that many related isomers are found very closely [109]. Further functional groups of the extractives, such as methyl and methylene may have further influenced the spectra. Hence, ATR-FTIR can be considered to be more precise in determining the influence of wood extractives in polyurethane adhesives in comparison with PRF and MUF.

The influence of wood extractives on the physical curing behavior was determined by rheometer in plate-to-plate mode in terms of gel point and storage modulus. The adhesives 2C PUR, MUF and PRF were tested. For 1C PUR, no useable data was obtained probably due to the release of CO_2 within the curing process and an expansion of the polymer during testing which is in accordance with another study [110]. Stapf et al. [102] enabled the measurement of 1C PUR by rheometer through mounting two solid wood parts to the plate-to-plate setup of the rheometer. However, in the present study only thin wood veneers were chosen to maintain the influence of this modification on the setup at a minimum.

While the extractives were blended into the adhesive (2C PUR) in Paper II, the extractives were applied on beech veneer bonded on the aluminum plates of the device in Paper III. The first approach revealed for 2C PUR a reduction of the reference gel point by acetic acid (-75%) and linoleic acid (- 73%). The gelation was further accelerated by gallic acid (- 30%) and starch (- 18%). For the remaining extractives, an extension of gelation was observed with heptanal (+36%), 3-carene (+41%), pentanal (+76%) and limonene (+111%) in comparison with the reference. The second approach with applied extractives on beech veneers showed a reduction of the reference gel point of 2C PUR by acetic acid (- 61%) and linoleic acid (- 15%). The other extractives (starch, pentanal) did not influence the gelation or slightly increased the corresponding time. Hence the acceleration of the 2C PUR's gel point by the extractive acetic acid and linoleic acid was less pronounced when the extractives were applied on the interface. MUF was influenced by all extractives, but starch led to the highest reduction in gel time (- 68%). The remaining extractives decreased the gel point of the reference between 34 and 46%. PRF showed the proportionally highest influence by extractives of all tested adhesives. Highest acceleration of the gel point was measured for acetic acids with (- 83%) of the reference. Remaining extractives reduced the gelation for PRF (- 61 - 78%) except for 3 - carene.

The storage modulus was measured after 2 h. At this point, the curing of the polymers was very advanced, but not completed. Due to the high E-Modulus of 2C PUR, this time was evaluated to ensure reliable values within the sensitive rheometer. The reference storage modulus of 2C PUR (0.5 MPa) was influenced by all extractives but the highest reduction was obtained for acetic acid (- 77%). MUF showed a reduction of storage modulus for some extractives, but mainly by acetic acid (- 54%) and pentanal (- 46%) in comparison to the reference of 0.9 MPa. PRF obtained the highest reduction of its reference value of 2.85 MPa by acetic acid (- 99%) and linoleic acid (- 94%), while starch increased the storage modulus (+ 217%).

The influence of wood extractives on the wood-adhesive-joint performance was tested by lap-shear joints in dry and wet conditions following EN 302-1. The tensile shear strength (TSS) and the wood failure percentage (WFP) were analyzed in this study. Similar to the rheology setup, the extractives were blended into the adhesive (2C PUR) in Paper II and applied on the surface prior to bonding in Paper III. When extractives were blended into 2C PUR and the composite tested in standard climate (A1), all extractives except for pentanal and linoleic acid revealed a lower TSS and WFP than the reference (TSS: 11.7 MPa, WFP: 60%). After boiling and cold water storage (A4), no significant change in TSS and WFP by extractives was noticed. However, TSS was observed to be quite low when applying gallic acid (TSS: 2.1 MPa) or acetic acid (TSS: 1.7 MPa). Reason for this could be seen in the low performance of the reference (TSS: 3.4 MPa, WFP: 0%).
When extractives were applied on the surface prior to bonding with 2C PUR and tested in dry conditions (A1), no significant influence of wood extractives on TSS was determined. But noticeable was the increase of WFP for starch of 90% in comparison with the reference (30%). However, in wet conditions (A4), starch led to a decrease of the performance (TSS: 1.6 MPa, WFP: 0%). In addition, gallic acid, linoleic acid and acetic acid reduced TSS and WFP largely. Similar to 2C PUR, wood extractives did not show a significant influence the performance of 1C PUR after treatment A1. When tested in wet conditions, 1C PUR was reduced in TSS by starch and the acids linoleic acetic acid and linoleic acid.
The tested MUF did not show any influence by extractives after A1, but after A4, starch led to a significant reduction (TSS: 3.9 MPa, WFP: 60%). In addition, limonene decreased the performance (TSS: 5.3 MPa, WFP 0%)., as well as gallic acid (TSS: 4.5 MPa, WFP 10%). For PRF in dry conditions, only gallic acid led to a reduction of performance (TSS: 8.7 MPa, WFP 0%) in comparison with the reference (TSS: 12.8 MPa, WFP 100%). In wet conditions (A4),

the extractives pentanal, starch, acetic acid and linoleic acid reduced TSS and WFP. The highest decrease was observed with gallic acid (TSS: 1.7 MPa, WFP 0%).

The findings in this study show in some cases a comparability between the applied methods, while other findings are limited to a method.

For 1C PUR, linoleic acid and acetic acid accelerated the isocyanate conversion as determined by ATR-FTIR. While dry testing lap-joints did not show a negative influence of wood extractives on TSS, the wet testing revealed very low TSS when linoleic acid and acetic acid were applied. A reduction of TSS was also visible for starch. Even though no data was obtained by the rheometer, it can be expected that the performance is similar to 2C PUR.

The 2C PUR was accelerated in curing speed by acetic acid and linoleic acid and further highly reduced in gel point and a reduced storage modulus by these extractives. These findings were not clearly visible in lap-joints tested in dry conditions, except for a slight decrease for both acids in WFP. In wet conditions, acetic acid clearly reduced the TSS.

Polyurethane adhesives in this study were primarily influenced by acetic acid, as an acidic extractive with a very low molecular weight. The low molecular weight may have favored the reactivity with the isocyanate groups of the extractives. This carboxyl acid most probably reacted with isocyanate producing amine groups [65]. Their formation leads to a release of CO_2 bubbles which can weaken the polymer locally and was observed during the experiments. In case of 1C PUR, this can additionally increase the formation of bubbles in the polymer next to its general curing process. Furthermore, an acceleration of the isocyanate conversion is expected to take place by acid extractives. Interesting in this context was the performance of linoleic acid, which influenced the curing behavior of PUR adhesives as shown by ATR-FTIR and rheometer but did not lead to a negative bonding performance in lap-joints. An explanation can be seen in the long-chained character and its much higher molecular weight in comparison with acetic acid. The high solid content of polyurethane adhesives as well as their excess formulation of isocyanate may favor a certain robustness against the influence of wood extractives. On the other hand, the influence of wood extractives may be more crucial, when the adhesive systems are suffering from adhesion deficits on hardwood in wet conditions.

The curing of MUF was mainly accelerated by the acid’s linoleic acid, acetic acid and gallic acid as shown by ATR-FTIR. The gel point of MUF was influenced by all extractives, but the extractives acetic acid and pentanal mainly reduced the storage modulus. The extractives that influence the adhesive systems in terms of curing are mainly acid extractives, which is in accordance with a study of Özparpucu et al. [93]. Contrary, these extractives did not show a negative influence on bonding performance of lap-joints in TSS or WFP. Yet, MUF as a good nucleophile can react with the electrophilic formaldehyde under varying pH-conditions and is therefore expected to be more robust against extractives, which is accordance with the results of the lap-joints, except for the extractive starch. The TSS was reduced by starch in wet conditions largely. Even though starch can be used as a binder in adhesives to stabilize viscosity or control adhesive penetration into the adherend, its availability in granules often reduces its reactivity [111]. In the present case it can be expected that the applied starch acted as a barrier and reduced the adhesives reaction with the adherend. From these results it can be summarized that the tested MUF adhesive is considerable robust in bond performance against wood extractives with the exception starch.

A precise determination of the influence of wood extractives on PRF was not possible by ATR-FTIR. The gelation of PRF was influenced by all extractives, but mainly acetic acid accelerated it. The storage modulus was further highly reduced by acetic acid and linoleic acid and starch increased it significant. This is in accordance with findings Jost et al. [112] who showed that the addition of ray flour significantly postponed the curing process of phenol-formaldehyde.
PRF cures optimally under alkaline conditions. Therefore, the influence of acid extractives seems to have led to an incomplete curing and defective bonding performance in case of gallic acid. Alamsyah et al. [113] explained the influence of acid extractives on phenol formaldehyde adhesive at the example of tropical wood species by the formation of large quantities of dimethylene ether linkages due to the lower pH-value. The acceleration of curing for PF adhesives by tannins was also observed by Kulvik [114].
The TSS and WFP in dry condition was reduced by gallic acid highly. In addition, the acids linoleic acid and acetic acid reduced the WFP. These results are underlined by studies on the problematic bonding of white oak (*Quercus alba* L.) and red oak (*Quercus rubra* L.) wood with phenolic resins [19]. These wood species are characterized by their content of gallic acid and other acid extractives [115] [116]. Contrary, Konnerth et al. [26] showed that sessile oak (*Quercus petraea* Liebl.) was able to surpass standard requirements in delamination following EN 302-1.
In general, it can be concluded that PRF showed the highest influence of wood extractives between the tested adhesive systems. It seems remarkable that the analyzed MUF and PRF generally obtain excellent bond performance on various wood species in dry and wet conditions but are sensitive to the tested wood extractives. Though both adhesives are water-based and therefore facilitate the blending with extractives, especially with gallic acid and starch. In case of PRF, its sensitive dependence on the pH-value seems to be the primarily reason for comparingly high influence of wood extractives. Still the adhesives high performance on various wood species including hardwood, can be explained by the adhesive's modification of the interphase, which further enables the performance in wet conditions. Even though wood extractives can influence curing time of PRF largely, in overall context its properties are expected to overlay a possible influence of wood extractives.

Some of the findings in this thesis stand in contrast to other research: Popper [20] stated that carbohydrates do not influence wood bonding in opposition to our findings. However, this statement was not confirmed by a study. Another study showed the use of wheat flour as a natural filler in phenol formaldehyde adhesives [117]. Moubarik et al. [118] used cornstarch and tannins as a natural binder and phenol source to bond plywood with modified phenol formaldehyde adhesive resulting in higher mechanical properties and especially water resistance. Carbohydrates in general, and the starch used in this study, contain large number of hydroxyl groups and therefore their negative influence seems probable. In addition, it can be considered a major difference if an adhesive systems is modified by natural fillers or if these occur at the interface of the adherend and possibly hinder the bonding process. The negative influence of the carbohydrate arabinogalactan in high concentrations on 1C PUR bonds has also been shown by Künniger et al. [91]
The influence of extractives on the reduction of gel time and a premature gelation was stated by Kuo and Hse [19] as well as Nussbaum and Sterley [88] which is accordance with the

present study. However, these findings might not account for other adhesives systems. Narayanamurti et al. [90] stated that extractives do extend the gelation time at the example of casein adhesives.

The experimental approach in this study also shows some limitations. The selected extractives do not cover the full range of wood extractives and are of synthetic origin. In addition, the amount of applied extractives exceeded natural occurrence by far. Still, these experiments were chosen to demonstrate possible effects, which were not detectable in earlier experiments at very low concentrations between 1 and 3% (results not shown). A recent study of Özparpucu et al. [93] analyzed the influence of very low extractive contents in MUF by combined ATR-FTIR and rheology. However, only for very acid extractives a negative influence was measured. Difficulties were observed in their study with correlating spectral changes with chemical reactions when the amount of added extractives was between 0.06-2%.

The present study can be seen as a relevant complement to the state of the art in the field of wood extractives and structural wood bonding. Until present, no comprehensive analysis of relevant wood extractives on various modern adhesive systems has been carried out in combination with the used methods. The influence of wood extractives on the adhesive's performance, when TSS and WFP were reduced, indicate the formation of a chemical weak boundary layer which was first described by Stehr and Johansson [64]. This study can further specify this theory to mainly acidic extractives and partly starch for representative structural adhesives.

The hypothesis (No. 2) that wood extractives influence structural adhesive systems can be verified with the present results. In order to access the findings of the study, extractive content in relevant wood species have to be considered. Amman et al. [22] showed that Norway spruce (*Picea abies* L.) contains more fatty acid and acetic acid than European beech (*Fagus sylvatica* L.) and European ash (*Fraxinus excelsior* L.). Another study of Jung and Roffael [119] showed in opposition that beech has higher contents of acetic acid than spruce but a lower amount of formic acid. Different extraction methods and approaches complicate a direct comparison, but it can be assumed that in general acid extractives and partly starch mainly influence structural wood bonding. Hence, the assumption that wood extractives which typically originate in hardwoods cause the adhesion deficits, especially on polyurethane adhesives, can't be confirmed. In contrast, the results of this study show that extractives which commonly occur in soft and hardwood have a higher influence on the adhesive systems and their performance on the adherend, than the extractives specific to hard or softwood. In addition, it can be expected that the extractives may function as local hinderer of the cross-linking density. Therefore, it can be expected that a higher cross-linking density favors the influence of wood extractives, e.g. PRF. It can be further assumed that the influence of extractives play a subordinate role in the context of bonding. It seems therefore, that in the context of hardwood bonding their mechanical and physical wood properties, such as density, strength, as well as swelling and shrinking behavior dominate the performance, e.g. delamination behavior. Furthermore, the adhesives performance can overcome deficits caused by extractives when having a general high performance, even on hardwood.

4.3. Influence of primer

In Paper IV, the influence of a water-soluble polyol-based primer on the mechanical performance of lap-joints following EN 302-1 bonded with 1C PUR adhesive in terms of TSS and WFP was analyzed. In addition, the effect of different primer concentrations as well as the removal of extractives on the hydroxyl group accessibility of beech wood was investigated by dynamic vapor sorption analysis (DVS). Further, bond lines of 1C PUR with and without applied primer were analyzed in dry, water-stored and re-dried conditions by nanoindentation. The latter experiment investigated the influence of primer on the mechanical performance of the interface as well as the bulk material in terms of red. E-Modulus, hardness and specific work of indentation.

To determine the influence of primer on the performance of lap-joints, a variant was produced with 1C PUR and priorly applied primer. The same adhesive was tested without primer and further compared with another 1C PUR adhesive and a PRF adhesive. The primer was applied on beech wood in a concentration of 10% and a surface spread of 20g/m^2 shortly before adhesive application and bonding. These parameters were found as the most efficient primer application for hardwood according to Clerc et al. [12]. Their study showed that an increase in primer concentration to for example 20% reduces the improvement which can be obtained by a concentration of 10%. In our study, all 1C PUR variants (with primer and without) revealed similar TSS and WFP between the variants as well as between the treatments in dry (A1) conditions. In wet conditions (A4), the 1C PUR adhesives without primer revealed TSS of 3.2 - 4.8 MPa and therefore were not able to surpass the standard requirements of 6 MPa. In comparison, the application of primer lead to a TSS of 7.5 MPa in wet conditions which is accordance with the literature [12] [26]. However, the WFP of the variant with primer did not increase – contrary to a study of Lüdtke et al. [59], where the primer application always led to a high increase in WFP on beech wood. In re-dried conditions (A5), all variants surpassed the standard requirements of 10 MPa and re-gained their TSS and WFP in comparison with A1 and partly even increased their performance. The variant of 1C PUR with primer had a comparable TSS in A1 and A5, but the WFP was increased from 30% towards 50%.

Another experiment was analyzing the influence of different primer concentrations on the hydroxyl group accessibility on beech wood by DVS. The non-treated references obtained an average hydroxyl group accessibility of 7.5 mmol/g which was in accordance with findings of Tarmian et al. [120]. In comparison with the reference, no influence of primer was shown in concentrations of 0.1% and 1%. Though, using high concentration of primer (10%) the hydroxyl group accessibility was reduced to 5.40 mmol/g. In addition, an increase in mass weight and equilibrium moisture content was observed for the application of 10% primer. The higher obtained moisture content reached may indicate that the primer possess a high amount of hydroxyl groups. Therefore, it is proposed that the primer in high concentrations could deposit on the wood polymer hydroxyl groups and therefore block the access to deuteration. However, the applied concentration and weight probably exceeded the applied amount of efficient primer applications shown by Clerc et al. [12] by far. Own studies with samples treated under industrial primer application did not show any influence on the hydroxyl group accessibility. However, a chemical modification of the wood surface by a non-reactive primer systems seems rather unlikely, especially the conversion of partly acetylated hydroxyl groups. It can be concluded that the primer application in concentrations applied in the industry does not influence the hydroxyl group accessibility of beech wood considerably.

The removal of wood extractives in beech wood aimed to evaluate the effect of wood extractives on the hydroxyl group accessibility of the adherend. A study of Popper et al. [85] states that the equilibrium moisture content at fiber saturation is reduced with increasing extractive content. However, the extractive content did not show an influence on the monocular bonded water. The change in sorption behavior is addressed by the blocking of the woods porous structure. Contrary, another study of Borgin and Corbett [120] determined that hydrophobic extractives can form a layer on the wood surface and hydrophilic extractives may even act as hydrophilic-hydrophobic bridging agents. Therefore, a blocking of hydroxyl groups by a layer of extractives might take place.

In addition, Hardwood often shows a high degree of acetylation in comparison with softwood [46] and can therefore be disadvantageous in bonding. The extraction methods were chosen carefully to preferably not dissolve all structural wood components. While the hot-water extraction aimed to mainly dissolve polar components such as tannins, organic acids and carbohydrates, the extraction with hexane focused on dissolving non-polar extractives such as fat, waxes and phenols [55]. Polar extractives such as starch can favor the hydroxyl group accessibility by their multiple hydroxy groups. In contrast, fats or waxes are expected to decrease the hydroxyl group accessibility by forming a chemical weak boundary layer.

The removal of extractives in beech wood by hot water or hexane did not show a differences to the average hydroxyl group accessibility of the reference. Reason for this can be seen in the low extractives content of beech wood of around 2% [122]. However, this approach may have more impact when analyzing wood species with a considerably higher extractive content such as larch or pine. It can be concluded that wood extractives are not expected to considerably influence the hydroxyl group accessibility in beech wood.

A novel approach to determine the influence of primer at the interface of wood composites in dry, water-stored, and re-dried conditions was performed by nanoindentation. Beech wood joints prepared with two different 1C PUR adhesives and PRF were prepared. In addition, one variant was created by applying primer prior to the bonding with 1C PUR. Sections of their bond lines were subsequently analyzed in dry, water-stored (24 h) and re-dried (48 h) conditions. In dry conditions, PRF obtained an approximate three times higher red. E-Modulus and an approximate four times higher hardness than the tested 1C PUR adhesives, which is in accordance with the literature performed on similar substrates [22] [123].

No significant difference was found in dry conditions between the 1C PUR variants, including the variant with applied primer. During water storage, the mechanical properties of all adhesives dropped considerably as for the lap-joint tests. The red. E-Modulus of 1C PUR adhesives was reduced to around 70% and PRF noticeably to 10% of the initial values in dry climate. The hardness of 1C PUR was reduced to 30-40% and of PRF to 30% of the dry reference value. The different reduction in of red. E-Modulus and hardness of 1C PUR and PRF was also observed by Konnerth et al. [33]. The authors further showed that 1C PUR polymer films have a comparingly low water uptake of 6.4%, while PRF obtained a water content of 25.3% after three days water storage. The high reduction in mechanical strength of

PRF can be seen as similar to the hydromechanical properties of the adherend wood and therefor favors constant mechanical performance in alternating climatic conditions, as stated by Muszynski et al. [124]. An explanation for the higher water uptake and the reduction in mechanical properties of PRF can be seen in its high content of hydroxyl groups as well as alkali content, which leads to higher water absorption and equilibrium moisture content [57]. Further Wimmer et al. [125] explained the higher water uptake by the polycondensation process and the production of methylol phenol derivates. The hydroxyl groups involved in this process may take up two water molecules as discussed by Bentz and Neville [126]. After re-drying the adhesives were able to re-gain their initial values of the dry conditions, which was also observed in another study [36]. The specific work of indentation, a parameter assumed to reflect the magnitude of adhesion, was further analyzed by nanoindentation in the present setup. This setup analyzed the adhesion between adhesive and the adherend at the S2- and S3-layer.Similar to the investigations at the bulk material (red. E-modulus and hardness), the specific work of indentation revealed considerably higher values of PRF in comparison with the 1C PUR variants. Between the 1C PUR variants, no detectable influence was measured in dry and water-stored conditions. Hence the hypothesis that primer can measurably increase the specific work of indentation between both materials in water-stored conditions, could not be verified. After re-drying, the samples regained the specific work of indentation similar to initial values in dry conditions, except for the variant of 1C PUR with applied primer. The primer may have affected the drying behavior, similar to the findings of the DVS experiments, where mass weight and equilibrium moisture content were increased with higher primer application. However, this assumptions could not be further verified within this study.

When revising the literature, various studies have been dealing with chemical-reactive primer such as hydroxy methyl resorcinol (HMR) [72] [28] [127] or dimethyl formaldehyde (DMF) [73]. Their application is mainly possible at laboratory scale level due to their toxic character [73]. The HMR primer is strongly being absorbed by the wood surface and enriches the adherend by functional hydroxy methyl groups, which support the adhesion with 1C PUR according to Vick et al. [126].

Water-soluble polyol-based primer are not expected to modify the interphase of the adherend chemically. These are based on surfactants and reduce surface tensions of the adhesive to improve the wetting of the adherend [57]. Only few studies have been carried out analyzing these primer. Kanis [128] showed, that primer applied in 10% concentration and 20 g/m^2 surface weight did not influence the contact angle of 1C PUR on beech wood. Primer concentrations of 20% with the same surface spread reduced the contact angle. In contrast, the results on ash wood indicated a reduction of the contact angle of 1C PUR in concentration of 10% and 20 g/m^2. Probably the ring-porous character of ash wood influenced the wetting performance in combination with primer. Therefore, it can be concluded that primer enhances the wetting of 1C PUR on hardwood. Clerc et al. [12] showed that the window of optimal primer application is quite narrow as mentioned before. In addition, Lüdtke et al. [59] demonstrated that the primer function is also sensitive to the certain mechanical surface preparations. While peripheral planing and primer application reduced the delamination on ash wood considerable, face milling and primer application reduced the delamination noticeable less. Hence the fibrillation of the surface by face milling as well as the ring-porous surface of

ash seemed to influence the primer's effectiveness. In addition, the homogenous surface of beech and surface were expected to favor the function of the primer. Konnerth et al. [26] showed further that the use of water soluble polyol-based primer can improve the bonding of various wood species, which few exceptions.
Casdorff et al. [75] analyzed the influence of water-based priming systems on bonds with 1C PUR adhesives. They showed by atomic force microscopy that the primer penetrates the wood cell up to a certain extent, based on differences observed in adhesion. Hence, they concluded that the primer application leads to a near surface impregnation of the adherend and/or enhance the adhesion at the interface with 1C PUR. In context with primer application on hardwood, studies under the supervision of Prof. Niemz have been carried out, that used near infrared spectroscopy (NIR) to monitor the industrial bonding process of glue laminated timber with 1C PUR and primer [127] [128]. In these studies, NIR was used to analyze the hardwoods chemical surface composition, surficial moisture content, surface roughness as well as the influence of primer. Next to an evaluation of the surface properties, this approach can help to control the primer application and improve manufacturing of glued laminated timber in the industry. These findings will be published in near future.
Concluding from the results in this study and the research in literature, only a physical function of the primer can be expected. The primer was shown to reduce the contact angle of 1C PUR on hardwood and thus improve its wetting performance. The application is very critical as shown by Clerc et al. [12], which indicates that the amount of applied surfactants probably underlies restrictions of the model of critical micelle concentrations. It is defined as the concentration of surfactants where micelles form and where all surfactants are added to the micelles. They lower the surface energy and remove the hydrophobic parts of the surfactant from contact with water [130]. This concentration can be determined by analyzing the surface tension of surfaces applied by different solution concentrations [131]. However, on wood this approach is to be expected to perform rather difficult as shown by Kanis [126].

The hypothesis (No. 3) that primer can influence the adhesion between adhesive and adherend was not verified within this study by nanoindentation. The primer application led to an increase in TSS in wet conditions, however no increase in WFP or specific work of indentation was measured. Therefore, NI was only able to detect a minor influence of primer on the adhesion on re-dried samples. The primer was applied in very low contentions and surface spread. Hence, the presence of primer at the tested indents was not verified in particular. In addition, the primer seems to have influenced the re-drying behavior of the sample. Whether this behavior indicates a modification of the interphase by the primer, cannot be answered within this study.
The present study contributes to the state of the art with the following findings: The influence of primer in industrial applications does not influence the hydroxyl group accessibility. In addition, it was shown that the primer application does not influence the specific work of indentation between 1C PUR and wood cells in water-stored conditions. However, a novel approach to analyze bond lines in water-stored conditions by nanoindentation was proven to be successful. Further investigations are required to fully understand the function of the primer at the interface of wood.

5. Conclusions

The findings of this thesis are summarized and compared with the initially created hypothesis as follows:

The hypothesis that 2C PUR modified by fillers towards a higher E-Modulus can enable passing requirements following EN 302-1 in dry and wet conditions was not verified. While the adhesive modification resulted in a higher E-Modulus of the adhesive and led to an improvement in dry conditions for tensile shear strength and wood failure percentage, this modification was not able to increase the performance in wet conditions. This finding is contrary to prior findings of the project. Therefore, it can be inferred that the E-Modulus is not the most critical factor in 2C PUR formulation and further adjustments are required to overcome adhesion deficits at the interface of the adherend hardwood.

The assumption that wood extractives influence the curing behavior and bonding performance of structural adhesives to different degrees was verified in this study. While various extractives influenced the curing speed of the adhesive, the influence on bond performance was mainly limited to acidic extractives, partly starch and gallic acid. Hence, it can be concluded that wood extractives, which origin in softwood as well as in hardwood, such as organic acids and starch, have a higher negative impact on the curing and performance of bonded joints, compared to extractives characteristic for soft- or hardwoods. Gallic acid, which is typically found in oak, represents an exception. Polyurethane adhesives (1C PUR and 2C PUR) are mainly negatively influenced by acetic acid. MUF showed to be robust against extractives, except for starch. In comparison of the tested adhesive, PRF was influenced the most by extractives. Acidic extractives and starch showed to influence the adhesive systems largely. In general, the influence of extractives is considered to play a decisive role for specific cases in wood bonding. These results can further be an assistance for manufacturer of bonded hardwood products to select the right adhesive system for the application (wood species and given extractive composition). In addition, the planing of the adherends surface shortly before bonding reduces the possible impact of water-soluble extractives (e.g. starch) or volatile extractives (aldehydes) which can migrate to the surface during kiln drying. Since surficial extractions are imprecise and costly, a modification of the adhesive system towards the surface chemistry of the adherend seems to be more appropriate.

The hypothesis that the application of primer can increase the adhesion between wood cell wall and adhesive in wet conditions was not verified within this study by nanoindentation. Though primer application improved the performance of 1C PUR joints on beech wood to surpass standard requirements but analyzing these bonds in wet conditions on a micro-scale by nanoindentation, did not show a difference between treated and non-treated samples in dry and wet conditions. However, various studies indicate the improvement in adhesion and most probably this finding is limited by the applied method. Still an influence of primer on the re-drying behavior of beech wood was observed. Therefore, the primer may have affected the re-drying behavior.

The findings underline the importance of precise process control in primer application in order not to eliminate the primers effectiveness. Further these parameters need to be adapted to the anatomical and chemical properties of each wood species as well as their surface preparation to ensure its effectiveness.

6. Outlook

The research presented in this thesis contributes to a further understanding of wood-adhesive-interactions in terms of wood extractives and primer, as well as the development of polyurethane adhesives. Some general statements can be added to the findings of this thesis:

Polyurethane adhesives have been increasingly used for wood bonding in the last 30 years. However, the bonding of hardwood still requires significant improvement, especially in humid conditions. As shown in the present studies, modification of the adhesive system to increase the bonding performance on the interface are needed. For adhesive manufacturer, the development of a polyurethane adhesive, which does not require any surficial pretreatment can be a profitable product and increase the existing market share for polyurethane adhesives in general.

Yet wood extractives play a subordinate role in common adhesion deficits, the adapting of the adhesive towards the occurrence and higher concentrations of extractives can be another approach to optimize the use on specific wood species. Therefore, wood species may be grouped together for similar properties and adhesive systems can be modified specifically for them.

Hardwood as an ecological and renewable material has a high potential to be used for structural wood constructions. Its substantial and profitable use can further support the implementation of mixed forest and prepare the environment for expected climate changes. In addition, the decline in harvest of former typical wood supplier for construction such as Norway spruce or Scots pine require a rethinking of existing products and production processes. The more complex and costly processing of hardwood implies modern technologies and process controls in order to be competitive. When hardwood-based products for construction and interior use become affordable for customer with lower budgets, their market share could grow largely. There is no evidence for this market trend yet, but the recent years with low precipitations and high bark beetle infestations in softwood forestations indicate a rapid transformation in the next years.

Research about adhesive development and wood-adhesive interactions is not exhausted yet and the increasing hardwood harvest in the next decades requires considerable efforts in this field to efficiently and sustainably use this raw material.

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Publications and other scientific contributions

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Eidesstattliche Versicherung

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Stefan Bockel, Pforzheim, den 30.04.2020