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Hydrophilic Extraction Effects on Bonding of Silver Birch (*Betula Pendula* ROTH) Wood

Max Engelhardt

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1. Prof. Dr. Klaus Richter
2. Prof. Dr. Stephen Schrettl

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Abstract

The sustainment of forests and commercial silviculture remains a global challenge as the clearing of tropical forests continues, and the overall health of northern hemisphere woodlands is increasingly at risk. In the last 40 years, the damage rate of tree canopies in central Europe has doubled, and disturbances, such as extended droughts, heatwaves, fires, and storms, have left the forests – mainly spruce cultivations – susceptible to infestations, *e.g.,* by bark beetles. As a result, the share of damaged trees in the total German roundwood harvest escalated to 75% in 2020, a year in which the German woodlands incurred a canopy loss of approximately 5000 km². At the same time, global decarbonization efforts require the construction and housing industries to benefit from the ecological advantages of using wood instead of concrete and steel. Hence, the improvement of the forests' resilience and, thereby, the preservation of its functions and productivity is critical. These efforts involve shifting from coniferous plantations towards mixed deciduous forests.

Pioneer species like birches specialize in fast land conversion and reforestation, with low requirements on soil conditions. Moreover, birch wood holds high potential for structural applications due to its good mechanical properties. Hence, birch is gaining importance in climate-smart forestry, currently covering below 10% of European forest area. However, its use in engineered wood products (EWPs) is negligible, but it is mainly used as firewood. Past and current wood constructions rely almost exclusively on a few species of softwood. Following the ongoing silviculture transformations, a greater number and share of hardwoods will enter the market. For use in timber construction, the knowledge to ensure reliable and durable adhesion is crucial for the production of EWPs, among other parameters, but the knowledge of bonding wood for structural applications is limited for birch.

This thesis investigates the scientific principles of bonding of silver birch (*Betula pendula* ROTH) with regard to its soluble hydrophilic compounds. It focuses on *(i)* the extractives' interactions with reactive adhesives, *(ii)* the adherend (birch wood) properties to determine how they are modified by extraction, and *(iii)* the bond line properties to examine the extractives' influence on its formation and mechanical performance. Therefore, it was investigated how the adhesives, currently most common for the production of EWPs, *i.e.*, the hydrophobic solvent-free polyurethane (PUR) adhesive and the water-borne melamine-urea-formaldehyde (MUF) adhesive, interact with the hydrophilic extractives in silver birch wood. Comparative investigations on

adhesion-related surface and bulk properties should determine the potential effects of water extraction. Finally, the correlations of the mechanical performance and bond line morphology with hydrophilic extraction were analyzed and discussed.

Isolation and characterization of the water-soluble extractives in Finnish silver birch wood were conducted using multiple chromatography and mass spectrometry (MS) techniques. Chemical compound classes were identified, and the extraction kinetics were analyzed based on MS data using diffusion models. The curing kinetics and the mechanical characteristics of the adhesives post-curing were investigated as a function of extractives concentration. Small-angle oscillatory shear (SAOS) experiments with birch wood slabs as a lower plate were performed in a nested frequency and time sweep mode to evaluate time-dependent gelation and curing into a glassy state. Adhesive-extractive mixtures were cured as thin films and mechanically characterized by uniaxial tensile stress-strain measurements.

Water sorption behavior, free and restricted swelling, nanostructural characteristics, wetting and surface energy, and Young's modulus were analyzed in a broad screening of adhesion-related wood properties. By comparative analyses of measurements in pristine condition and extracted condition, as well as control measurements of specimens subjected to vapor treatment, the study was designed to differentiate secondary effects due to the extraction procedure from primary extraction effect, *i.e.*, resulting from extractives removal. Water sorption behavior was studied based on dynamic vapor sorption (DVS) measurements. Free swelling was measured after saturation by cyclic short-term immersion, and swelling pressure was performed by monitoring the compressive force exerted during a stepwise relative humidity increase. The nanostructural characteristics were analyzed based on X-ray diffraction patterns applying peak deconvolution models for cellulosic material. Wetting and surface energy were studied using contact angle measurements and inverse gas chromatography (IGC). Mechanical characterizations of the bulk wood before and after treatments were based on Young's modulus evaluations of prismatic specimens under quasi-static compression using a digital image correlation (DIC) technique for strain detection.

The role of extractives on the mechanical bond line performance, *i.e.*, shear strength, bond line stiffness, and elastic limits (yielding behavior), were studied using both MUF and PUR adhesive. For this purpose, the spatial distribution of the bond line deformation under tensile shear loading was recorded using 3D-DIC. With UV-microscopy and fluorescent dyes in the bond lines, high-resolution binary

wood/adhesive masks were generated, allowing for the visualization of the bond line morphology. Image processing procedures were deployed to evaluate local bond line thickness and local amounts and depths of adhesive penetration. These characterizations were performed on specimens of varying extraction degrees to investigate correlations with extractive concentration.

The isolated extractives comprised many organic compounds such as phenolic glycosides, (poly)phenols, saccharides, mono- or disubstituted glycerols, carboxylic (fatty) acids, and phospholipids. These compounds can potentially react with both MUF (*e.g.*, condensation reactions with hydroxyl groups, electrophilic aromatic substitution by formaldehyde) and PUR (urethane linkages of hydroxyl groups with isocyanate) adhesives. While these reactions might occur to some degree, chemical analysis with Fourier transform infrared spectroscopy (FTIR) of cured adhesive-extractive mixtures revealed no significant reaction pathways and mainly indicated some dilution effects from extractives addition.

MUF adhesive's curing process decelerated upon adding extractives, which was also seen comparing pure MUF on extracted (gel time of 5 h) and pristine wood (gel time below 4 h). Regression analysis showed a +1.0 h extension of gel time and +0.8 h extension of vitrification time per percent of added extractives. Identical experiments with PUR adhesive showed opposing effects – an acceleration of the curing reaction – when dispersing birch extracts into the adhesive. However, no differences were observed when comparing the curing kinetics of pure PUR on extracted and non-extracted wood. This can be a result of the reduced mobility (high initial viscosity) in PUR but, more importantly, of the low solubility of hydrophilic compounds in PUR prepolymers. Cured adhesive films of PUR and MUF showed significant negative correlations between Youngs's modulus, viscoelastic limit (yield point), tensile strength, and the added concentration of extractives. It is assumed that the presence of extractives in low concentrations of up to 1% (w/w) resulted in impurities disturbing the polymer network formation.

The extraction caused a reduced swelling pressure upon moisture uptake, possibly due to additional free volumes created in the xylem polymer matrix. The reaction in terms of vapor sorption behavior was surprising, as initially, an increased adsorption was observed. However, after several ad- and desorption cycles this trend changed, and in total, a lowered moisture uptake was determined, which was in line with the expectations regarding the removing of a highly hygroscopic extractives fraction. Moreover, following the water treatments, Young's modulus of the bulk wood

was reduced in all principal directions under compression loading. As was evident from control experiments with wood subjected to non-extracting water treatment (vapor phase saturation), the observed effects were – to a substantial percentage – originating from the introduction of water instead of the extractives removal. This was supported by the diffraction patterns from XRD analysis, which indicated a lower degree of crystallinity and some reduction in the characteristic crystallite length of the xylem carbohydrates after water treatments, both after extraction and vapor treatment. Due to the plasticization effects of water, the glassy biopolymers have an increased mobility, resulting in a reconfiguration under slightly more amorphous conditions. Depending on the subsequent redrying conditions after extraction, a quenching of the altered structural state might occur.

Overall, the adhesion-related birch wood properties were only slightly impaired by both hydrophilic extractives and the extraction treatment without raising concerns regarding glueability. Surface energy and wettability were not significantly affected. However, it remains unclear to which degree the observed changes in bulk wood properties following water treatments are permanent or temporary.

In the case of the hydrophobic PUR adhesive, the mechanical analysis clearly showed that the performance of the bond line was largely unaffected by the presence of extractives in birch wood. Morphology analysis of MUF bond lines showed thicker bond lines and reduced adhesive penetration when extractives were removed from the bonded boards - which is in line with the rheological studies previously performed. This, however, did not result in a negative impact on the mechanical properties. On the contrary, higher strength and an increase in bond line shear modulus following extraction were observed, possibly resulting from fewer defects in the cured adhesive network. When extrapolating the results to an extraction degree of 100%, the strength improvement was 17% and the yield stress improvement 29%.

From an applied perspective, the investigations support the fitness of use for further utilization of silver birch in bonded products for load-bearing applications without requiring procedural attendance to its water-soluble extractives.

Zusammenfassung

Die nachhaltige Nutzung von Wäldern und kommerziellen Forstflächen bleibt eine globale Herausforderung, da die Abholzung der Tropenwälder voranschreitet und der allgemeine Gesundheitszustand der Waldflächen auf der Nordhalbkugel zunehmend gefährdet ist. In den vergangenen 40 Jahren hat sich der Anteil an stark geschädigten Baumkronen – ein Indikator für den Gesundheitszustand – in Mitteleuropa verdoppelt, und Beeinträchtigungen durch lang anhaltende Dürren, Hitzewellen, Brände und Stürme haben die Wälder – hauptsächlich Fichtenreinbestände – anfälliger für Befalle, z.B. durch den Borkenkäfer, gemacht. Infolgedessen stieg im Jahr 2020 der Anteil an Kalamitäten an der gesamten deutschen Holzernte auf 75%, ein Jahr in dem auf 5000 km² der deutschen Waldfläche gemessen an der Baumkrone verloren gegangen waren. Gleichzeitig erfordern globale Bemühungen um eine Dekarbonisierung der gesellschaftlichen Aktivitäten, dass die Bauindustrien im Wohn- und Ingenieursbau-bereich sich die ökologischen Vorteile von Holz gegenüber Beton und Stahl zunutze macht. Demzufolge ist die Verbesserung der Widerstandsfähigkeit der Wälder und damit die Erhaltung ihrer Ökosystemleistungen und Produktivität von entscheidender Bedeutung. Dazu wird der Umbau der Waldstrukturen von Nadelholzmonokulturen zu resilienteren Laubmischwäldern als notwendig angesehen.

Pionierarten wie Birken sind auf eine schnelle Besiedelung von Freiflächen und damit Schaffung von Primärwäldern spezialisiert. Ihnen kommt daher bei der Wiederaufforstung geschädigter Waldflächen und bei der Waldanpassung an den Klimawandel eine besondere Rolle zu. Dabei stellen sie nur geringe Ansprüche an die Bodenbeschaffenheit. Darüber hinaus besitzt Birkenholz aufgrund seiner mechanischen Eigenschaften ein hohes Potenzial für strukturelle Anwendungen. Daher gewinnen Birken, die derzeit weniger als 10 % der europäischen Waldfläche beanspruchen, in der klimaschonenden Forstwirtschaft zunehmend an Bedeutung. Derzeit findet einheimisches Birkenholz jedoch noch kaum Verwendung in tragenden Holzwerkstoffen und wird stattdessen hauptsächlich als Brennholz benutzt. Der Holzbau basiert bisher hauptsächlich auf einigen wenigen Nadelholzarten. Um auch Birkenholz zukünftig zuverlässig für konstruktive Anwendungen nutzen zu können, ist das Wissen um die Holzeigenschaften und hier insbesondere um die Sicherstellung einer dauerhaft tragfähigen Verklebung eine wichtige Voraussetzung.

Diese Arbeit untersucht daher mit materialwissenschaftlichen Methoden die Verklebung des Birkenholzes am Beispiel der Weiß- bzw. Hängebirke (*Betula pendula*

ROTH) mit besonderem Bezug auf die hydrophilen Extraktstoffe. Die Schwerpunkte liegen dabei auf *(i)* den Wechselwirkungen der Extraktstoffe mit reaktiven Klebstoffen, *(ii)* den Holzeigenschaften der Fügeteile, um festzustellen, wie sie durch eine Extraktion verändert werden, und *(iii)* der Klebefuge, um den Einfluss der Extraktstoffe auf deren Morphologie und Belastbarkeit zu quantifizieren. Es wurde untersucht, wie zwei wichtige Klebstoffgruppen für die Herstellung von EWPs (Engineered wood products, konstruktive Holzwerkstoffe), nämlich hydrophober lösemittelfreier Polyurethanklebstoff (PUR) und wasserbasierter Melamin-Harnstoff-Formaldehyd Klebstoff (MUF), mit den hydrophilen Extraktstoffen des Birkenholzes interagieren. Vergleichende Untersuchungen verklebungsrelevanter Eigenschaften sollten potentielle Auswirkungen der Extraktion identifizieren. Außerdem waren die Zusammenhänge zwischen mechanischen Eigenschaften und der Morphologie der Klebefuge und der vorhandenen Extraktstoffe zu analysieren.

Die Isolierung und Charakterisierung der wasserlöslichen Extraktstoffe in finnischem Birkenholz erfolgte unter Verwendung mehrerer chromatographischer und massenspektroskopischer (MS) Methoden. Anhand einer chemischen Klassifizierung wurde die Extraktstoffzusammensetzung beschrieben. Die Kinetik der Extraktionsprozesse wurde basierend auf den MS-Daten unter Verwendung von Diffusionsmodellen analysiert. Die Aushärtungskinetik der Klebstoffe und deren mechanischen Eigenschaften nach dem Aushärten wurden in Abhängigkeit von der Extraktstoffkonzentration untersucht: Kleinwinkel-Oszillationsscherversuche (SAOS) mit Birkenholz als untere Platte wurden in Form verschachtelter Frequenz- und Zeitsweeps durchgeführt, um die Erreichungsdauer des Gelpunkts und des Glasübergangs zu detektieren. Klebstoff-Extraktstoff-Gemische wurden in Form von dünnschichtigen Klebstofffilmen ausgehärtet und durch einachsige Zugversuche mechanisch charakterisiert.

Am Holz selbst wurden das Sorptionsverhalten, freie Quellung und Quelldruck, nanostrukturelle Eigenschaften, Benetzungsverhalten und Oberflächenenergie sowie die mechanische Steifigkeit in einem umfassenden Screening von verklebungs-relevanten Holzeigenschaften analysiert. Vergleichende Analysen von Messungen im unbehandelten und im extrahierten Zustand sowie Kontrollmessungen an Proben, die einer Wasserdampfbehandlung unterzogen wurden, sollten sekundäre Effekte als Folge des Extraktionsverfahrens von primären Extraktionseffekten, d.h. infolge der Entfernung von Extraktstoffen, unterscheidbar machen. Das Sorptionsverhalten wurde basierend auf dynamischen Sorptionsmessungen mit Wasserdampf (DVS) untersucht. Die freie Quellung wurde nach Sättigung durch zyklisches Kurzzeiteintauchen gemessen, und

das Quelldruckverhalten wurde durch die Erfassung der durch einachsige Beschränkung ausgeübten Druckkraft während eines schrittweisen Anstiegs der relativen Luftfeuchtigkeit durchgeführt. Die Struktureigenschaften wurden basierend auf Röntgenbeugungsmustern analysiert, indem Faltungsmodelle für Zellulose angewendet wurden. Das Benetzungsverhalten und die Oberflächenenergien wurden durch Kontaktwinkelmessungen und inverse Gaschromatographie (IGC) untersucht. Die anisotropen Elastizitätsmoduln im quasi-stationären Druckversuch wurden unter Verwendung eines dreidimensionalen Grauwertkorrelationsverfahrens (3D-DIC) zur optischen Dehnungserfassung an prismatischen Proben ermittelt.

Die Rolle der Extraktstoffe auf die mechanische Leistungsfähigkeit und Beschaffenheit der Klebefuge, d.h. Scherfestigkeit, Schubmodul der Klebefuge und Elastizitätsgrenzen (Fließverhalten), wurde unter Verwendung von MUF- als auch PUR-Klebstoff untersucht. Zu diesem Zweck wurde die oberflächliche Klebefugendeformation des unter Scherung belasteten Bereichs mittels 3D-DIC aufgezeichnet. Mittels UV-Mikroskopie an den mit Fluoreszenzfarbstoff markierten Klebefugen wurden hochauflösende binäre Holz-/Klebstoff-Masken erzeugt, um die Klebefugenmorphologie zu visualisierten und statistisch abgesichert auszuwerten. Bildverarbeitungsverfahren wurden eingesetzt, um damit die lokale Klebefugendicke und die lokalen Ausmaße und Eindringtiefen der Klebstoffpenetration zu erfassen. Diese Charakterisierungen wurden an Proben unterschiedlichen Extraktionsgrads durchgeführt, um Korrelationen mit der Extraktstoffkonzentration zu untersuchen.

Die isolierten Extraktstoffe bestanden aus einer Vielzahl organischer Verbindungen wie phenolischen Glykosiden, (Poly)phenolen, Sacchariden, mono- oder disubstituierten Glyceriden, Carbon(fett)säuren und Phospholipiden. Diese Verbindungen können potenziell mit sowohl MUF (z.B. Kondensationsreaktionen mit Hydroxylgruppen, elektrophile Substitution von Aromaten durch Formaldehyd) als auch PUR (Urethan-Bindungen von Hydroxylgruppen mit Isocyanat) Klebstoffen reagieren. Obwohl diese Reaktionen in gewissem Maße aufgetreten sein könnten, ergab die chemische Analyse von ausgehärteten Klebstoff-Extrakt-Mischungen mittels Fourier-Transform-Infrarot-Spektrometrie (FTIR) keine signifikanten Umwandlungen und deutete hauptsächlich auf reine Vermischungseffekte nach Zugabe von Extraktstoffen.

Der Aushärtungsprozess des MUF-Klebstoffs verlangsamte sich durch Zugabe der Extraktstoffe, was sich auch beim Vergleich von reinem MUF auf extrahiertem (Gelbildung nach 5 h) im Vergleich zu unbehandeltem Holz (Gelbildung nach unter 4 h) zeigte. Die Regressionsanalyse zeigte eine Verlängerung der Gelzeit um +1,0 h und der

Zeit zur Erreichen des Glaszustands um +0,8 h je Gewichtsprozent zugegebenen Extraktstoffs. Identische Experimente mit PUR-Klebstoff zeigten einen entgegengesetzten Effekt – eine Beschleunigung der Aushärtungsreaktion – durch die Beimengung von Extraktstoff zum Klebstoffpräpolymer. Die Aushärtungsrate von reinem PUR auf unbehandeltem im Vergleich zu extrahiertem Holz zeigte jedoch keine Unterschiede. Dies kann auf eine geringe Mobilität (hohe Anfangsviskosität) im PUR zurückzuführen sein, vor allem jedoch auf die geringe Löslichkeit hydrophiler Verbindungen in den PUR-Präpolymeren. Ausgehärtete Klebstofffilme aus PUR und MUF zeigten signifikant negative Korrelationen zwischen Elastizitätsmodul, viskoelastischem Limit (Fließgrenze), Zugfestigkeit und der zugefügten Konzentration an Extraktstoffen. Das lässt darauf schließen, dass das Vorhandensein von Extraktstoffen bereits in niedrigen Gewichtsanteilen die Netzwerkbildung des Polymers beeinträchtigen können.

Die Extraktion verursachte einen niedrigeren Quellungsdruck bei Feuchteaufnahme, möglicherweise aufgrund zusätzlich entstandener freier Volumina in der Polymermatrix des Xylems. Die Auswirkungen der Extraktion in Bezug auf das Wassersorptionsverhalten war überraschend, da zunächst eine erhöhte Adsorption festgestellt wurde. Nach mehreren Sorptionszyklen jedoch wurde eine insgesamt verringerte Feuchtigkeitsaufnahme festgestellt, was den Erwartungen entsprach, die mit der Entfernung einer hochhygroskopischen Extraktstofffraktion postuliert waren. Darüber hinaus war nach den Wasserbehandlungen der Elastizitätsmodul des Holzes in allen Hauptrichtungen unter Druckbelastung reduziert. Wie aus Kontrollversuchen mit Proben hervorging, die einer nicht extrahierenden Wasserbehandlung (Dampfphasensättigung) unterzogen wurden, waren die beobachteten Effekte zu einem erheblichen Prozentsatz auf die starke Wasseraufnahme und nicht auf die Entfernung der Extrakte zurückzuführen. Dies wird auch durch die Analyse der Röntgenbeugungsmuster belegt, die einen geringeren Kristallinitätsgrad und eine gewisse Reduktion der charakteristischen Länge kristalliner Bereiche in den Kohlenhydraten des Holzgewebes, sowohl nach Extraktion als auch nach Dampfbehandlung, zeigten. Aufgrund der plastifizierenden Wirkung von Wasser weisen die Biopolymere eine erhöhte Mobilität auf, wobei diese in einen geringfügig amorpheren Zustand überführt werden. Durch anschließende Trocknung könnte dieser Zustand teilweise verstetigt werden.

Insgesamt waren die verklebungsrelevanten Eigenschaften des Birkenholzes sowohl durch hydrophile Extraktstoffe selbst als auch durch die Extraktionsbehandlung nur geringfügig beeinträchtigt, so dass keine Einschränkungen hinsichtlich der

Verklebungsfähigkeit wahrscheinlich sind. Oberflächenenergie und Benetzbarkeit wurden nicht signifikant beeinflusst. Es blieb jedoch unklar, wie dauerhaft die beobachteten Änderungen der Holzeigenschaften nach der Extraktion sind.

Im Fall von hydrophobem PUR-Klebstoff zeigte die mechanische Analyse deutlich, dass die Leistung der Klebefuge weitgehend unbeeinflusst von der Präsenz von Extraktstoffen in Birkenholz war. Der MUF-Klebstoff wies dickere Klebefugen bei gleichzeitig reduzierter Klebstoffpenetration auf, wenn Extraktstoffe aus den verklebten Platten entfernt wurden, was im Einklang mit den zuvor durchgeführten rheologischen Studien stand. Dies führte jedoch nicht zu negativen Auswirkungen auf die mechanischen Eigenschaften des Verbunds. Im Gegenteil, nach der Extraktion wurden eine höhere Festigkeit und eine Erhöhung des Scherelastizitätsmoduls der Klebefuge beobachtet, was möglicherweise auf weniger Defekte im ausgehärteten Klebstoffnetzwerk zurückzuführen ist. Bei der Extrapolation der Ergebnisse auf einen Extraktionsgrad von 100% betrug die Festigkeitsverbesserung 17%, die Erhöhung der Fließgrenze betrug 29%.

Aus anwendungsorientierter Perspektive stützen die Untersuchungen die Eignung für die weitere Verwendung von Holz der Weiß-/Hängebirke in verklebten Holzbauprodukten für tragende Anwendungen, ohne dass eine prozedurale Beachtung ihrer wasserlöslichen Extraktstoffe erforderlich ist.

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List of Abbreviations

ATR.....attenuated total reflection
CLT.....cross-laminated timber
DIC ..... digital image correlation
DMA ..... dynamic mechanical analysis
DMDHEU ..... dimethyloldihydroxyethyleneurea
DVS ..... dynamic vapor sorption
DVT..... dynamic vapor transport
EMC ..... equilibrium moisture content
EPA.....U.S. Environmental Protection Agency
ESI ..... electrospray-ionization
EWP..... engineered wood product
FAO .....Food and Agriculture Organization of the United Nations
FSP..... fiber saturation point
FTIR.....Fourier-transform infrared spectroscopy
GC ..... gas chromatograph
GC-MS .....gas chromatography-mass spectrometry
GLT.....glued laminated timber
HILIC .....hydrophilic interaction liquid chromatography
IDA.....information-dependent acquisition mode
IGC ..... inverse gas chromatography
LC.....liquid chromatography
LSL.....laminated strand lumber
LVL ..... laminated veneer lumber, laminated veneer lumber
MALDI..... matrix-assisted laser desorption/ionization
MDI.....methylene diphenyl diisocyanate
MeCN ..... methyl cyanide (acetonitrile)
MS.....mass spectrometry
MS2..... mass spectra of ion fragments in tandem mass spectrometry
MSD ..... mass-selective detector
MUF.....melamine-urea-formaldehyde
NIH ..... National Institutes of Health
NIST .....National Institute of Standards and Technology
OSB.....oriented strand board
PET..... poly(ethylene terephthalate
PF..... phenol-formaldehyde
pMDI.....polymeric MDI (polyphenylpolymethylene polyisocyanate)

PRF ..... phenol-resorcinol-formaldehyde
PSL ..... parallel strand lumber
PUR ..... polyurethane prepolymer
PVAc ..... polyvinyl acetate
RH ..... relative humidity
RP ..... reverse phase
SAOS ..... small-amplitude oscillatory shear
ssNMR ..... solid-state nuclear magnetic resonance spectroscopy
SSO ..... sorption site occupancy
TIC ..... total ionization chromatogram
TMA ..... thermo-mechanical analysis
TOF ..... time-of-flight (measuring principle)
TSS ..... tensile shear strength
UHPLC ..... ultra-high performance liquid chromatograph
UHPLC-ESI-TOF-MS .... UHPLC coupled with electrospray ionization time-of-flight-MS
UN DESA ..... United Nations Department of Economic and Social Affairs
UN ECE ..... United Nations Economic Commission for Europe
v/v ..... volume per volume (volume fraction)
w/w ..... weight per weight (weight fraction)
WVC ..... wood veneer composite
xcms ..... extensible computational mass spectrometry
XRD ..... X-ray diffraction

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(**abbreviated captions**)

1. Introduction

1.1. Background and Motivation

The preservation and sustainable exploitation of our planet's natural resources, such as woodlands, is one of the critical responsibilities for global human action. Since the beginning of agriculture, a third of global forests have been lost to grazing, cropland, and urbanization (Ritchie 2021). While UN assessments show that global deforestation rates are slowing down, an average of about five million hectares of tropical forests are still lost to deforestation every year (FAO 2020). The total temperate forest area has slightly increased in recent decades. The overall health of the northern hemisphere silviculture forests, however, is becoming increasingly endangered (**Figure 1**).

Figure 1. Damaged spruce monoculture in the low-mountain region Bavarian Forest in Bavaria, DE, in 2018, depicting a high ratio of dead trees (Illustration. Photo by Felix Mittermeier, permitted use under the Pixabay Content License)

With field data and the availability of high-resolution Landsat data (Woodcock *et al.* 2008), more and more detailed and quantitative analyses arise, revealing the changes and disturbances of Earth's forests in direct reaction to climate change (Kennedy *et al.* 2010; Sexton *et al.* 2013; Hansen *et al.* 2013; Olofsson *et al.* 2014; Forzieri *et al*. 2023). While de- and reforestation in central Europe mostly leveled each other out with a slightly increasing growing stock (Korhonen and Stahl 2020), the canopy mortality has doubled since 1984 (Senf *et al*. 2018). In the past years, unprecedented forest disturbances occurred following extended droughts and heat periods (Senf and Seidl 2020, 2021). The weakened vegetation further resulted in a high susceptibility for fatal beetle infestation, which is correlated with the fraction of spruce trees (Stadelmann *et*

al. 2014). The following bark beetle pest outbreaks resulted in an unusually high loss in forest canopy cover in Germany, with over 500,000 ha (Thonfeld *et al*. 2022), leaving an already stressed ecosystem even more vulnerable. Consequently, the share of damaged trees in Germany's total roundwood harvest rose sharply from a previous average of 15% for the years 2010 to 2017 to record levels of 75% in 2020 (Federal Statistical Office Germany 2022).

The frequency and severity of droughts likely will increase in the decades to come (Vicente-Serrano *et al*. 2020; Ault 2020; McDowell *et al*. 2022). Moreover, environmental impacts from wildfires (Lindner *et al*. 2010; Dupuy *et al*. 2020; Grünig *et al*. 2023), windthrow from storms (Usbeck *et al.* 2010; Schelhaas *et al.* 2010; Schuck and Schelhaas 2013), and parasitic insect infestations (Seidl *et al*. 2017; Brockerhoff and Liebhold 2017; Forzieri *et al*. 2021) pose further challenges to sustain the forests, generating yields and raw materials from the commercial woodlands for the associated forest products industries.

At the same time, the global demand for timber is rising and is expected to grow (Lock *et al*. 2021; FAO 2022; Peng *et al*. 2023). With an estimated global population of over 10 billion by the end of the current century (UN DESA Population Division 2022), an equivalent increase in housing demand will ensue. Using wood in building construction offers significant ecological advantages to construction types that rely on masonry, concrete, and steel (Churkina *et al.* 2020; Bionova Ltd. 2021; Žemaitis *et al.* 2021; Azari and Singery 2022; Hansen *et al.* 2022) due to reduced environmental impacts, in particular lower greenhouse gas emissions (Skullestad *et al*. 2016; Peñaloza *et al*. 2016; Lu *et al*. 2017; Winchester and Reilly 2020).

The international decarbonization efforts (European Union 2021) rely on actions to preserve and improve the resilience and serviceability of forests (Stubenrauch *et al.* 2022). Due to European forests facing both increasing vulnerability and threat exposure, a more sustainable forest management (climate-smart forestry) strategy is required (Zak 1997; Von Teuffel *et al.* 2005; Keenan 2015). This involves substantial restructuring of commercial woodlands with a shift from coniferous monocultural plantations to mixed deciduous forests (Brang *et al*. 2014; Frischbier *et al*. 2019; Schwaab *et al*. 2020; Bauhus *et al*. 2021). Moreover, these measures are required to mitigate biodiversity loss (Storch *et al*. 2018; Lee *et al*. 2023).

Besides the incorporation of hardwood trees in the course of preemptive transformations of silviculture plantations, pioneer species are especially expedient for projects of land conversion (Zasada *et al*. 2014) and in the case of reforestation efforts

after natural or artificial disturbances (El Kateb *et al*. 2004; Vodde *et al*. 2010; Kulagin *et al*. 2018). Birch – especially silver birch (*Betula pendula* ROTH; in German Hängebirke, Sandbirke, Gemeine Birke, Weissbirke; syn. *Betula alba* L., *Betula verrucosa* EHRH.) – can vegetate open areas quickly (Fischer *et al.* 2002; Leuschner and Ellenberg 2017) and has moderate soil requirements (Schilling 1984). Therefore, silver birch is expected to become increasingly relevant in climate-smart forestry. It was estimated that silver and downy birch (*B. pubescent*) trees represent around 7% of the area in European (EU34) forests (Hemery 2008), a small fraction compared to the predominant wood species used in the timber industry. However, models of future forest developments (Oehmichen *et al*. 2018) expect an up to 50% increase in the German growing stock of so-called less common deciduous trees of shorter life expectancy (*e.g.*, birch, alder, or poplar) by 2052 compared to 2012 levels.

Identifying optimal strategies to act, which honor the environmental responsibilities for future generations while also being able to meet the current needs of the growing population, is highly complex. This is also true for the resource and ecosystem forest (Blattert *et al*. 2023), where trade-offs between benefits from non-use, *e.g.*, carbon storage in the growing stock, storage in wood products, and substitution potentials (*e.g.*, reduced fossil energy consumption or replaced high-emission materials) need to be balanced (**Figure 2**).

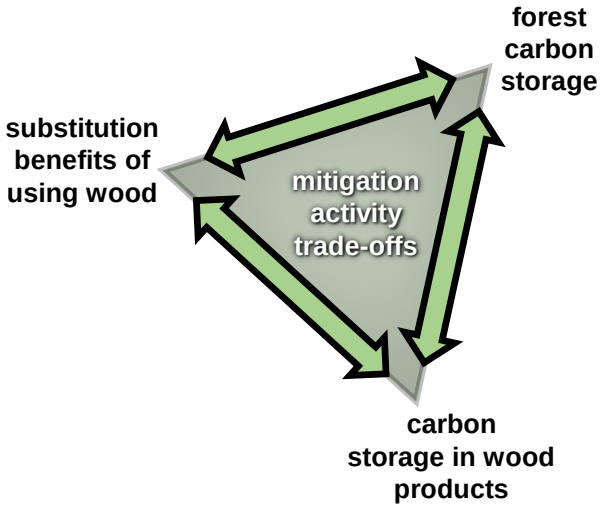

Figure 2. Trade-offs between possible climate mitigation activities in forestry: benefits of increasing live biomass stock in the forests, increasing the biomass storage in harvested wood and wood products, and increasing the substitution of higher-emission products or fossil-based fuels by using harvested biomass/wood.[1]

[1] graph based on Lemprière *et al.* (2013)

Utilizing these benefits is not a zero-sum game; some actions are generating more mitigation benefits than others.

Producing high-grade wood, *i.e.*, in large dimensions, will yield a high average forest carbon storage due to the necessary long rotation length, especially compared to plantations for biomass/energy production. By harvesting this wood to produce structural timber, long-term carbon storage in products of long service life is achieved. Moreover, since its level of disintegration is low, salvaged timber from deconstructed buildings has remarkable recycling potential (Horie 2002; Arbelaez *et al*. 2019), thus significantly extending the carbon storage duration. Moreover, structural timber usually substitutes alternative building products with a higher environmental impact. Finally, these substitution benefits can be maximized by utilizing biomass for biofuel, green chemistry applications in biorefineries, or energy generation.

Many types of load-bearing wooden constructions are not viable with simple lumber only but require the added flexibility of engineered wood products (EWPs), such as glued laminated timber (GLT), cross-laminated timber (CLT), or laminated veneer lumber (LVL). These EWPs allow the production of beams and panels with arbitrary cross-sections and lengths from smaller, defect-free lamellas, which results in more reliable structural performance due to homogenization effects (Niemz *et al.* 2023). Moreover, an optimized combination of lamellas with higher and lower quality/grades is possible (Obernosterer *et al.* 2023). Thus, EWP production enables a higher yield from available lumber, minimizing waste or inferior goods and, therefore, more efficient use of the harvested wood. Although some EWPs based on wooden dowel or nail connections to join the single lamellas exist, the most important EWP market is based on adhesively joined timber (mass timber, GLT, CLT), and veneers (LVL).

Apart from efforts to increase the efficiency of material consumption in timber products and establishing new ways to reuse materials – circular economy – (UNECE and FAO 2022, 2023), expanding the range of wood species used for structural timber is a key solution to allow for higher sustainable availability of EWPs and, subsequently, an increased share of timber constructions in the future building stock (Krackler and Niemz 2011). Therefore, the overarching goal motivating this research is to facilitate the use of a broader tree spectrum for high-value applications, which allows for better efficiency in deploying renewable but increasingly scarce wood resources.

1.2. Objectives

Like other temperate hardwoods, the wood from birch trees is still inefficiently used directly as firewood to an unsatisfactory high degree (Krackler *et al*. 2010; Roitto *et al*. 2015). The market share of hardwood in structural timber is currently low and, especially for EWPs such as CLT or GLT beams, virtually negligible (Ohnesorge *et al*. 2009; Ross and Shmulsky 2021). Nevertheless, the hardwood from silver birch is promising for use in load-bearing constructions because of its good mechanical characteristics (Jeitler and Augustin 2016; Schlotzhauer *et al*. 2017; Huber *et al*. 2023).

A lack of comprehensive understanding of the material properties, bonding behavior, experience, and trust in reliable processing for bonded hardwood timber products (Ohnesorge *et al*. 2009) inhibits its broader usage in EWPs. Therefore, this thesis aims to alleviate further the remaining uncertainty regarding the technological potential of silver birch wood for glulam or CLT in structural application, which has only been produced by a single company with its proprietary knowledge to date. Incentives are needed to motivate the utilization of new wood species in high-value-added products. By investigating potential technological issues for EWP production with promising candidate species, mitigation strategies or contributions to the proof-of-concept can be derived. Thus, the trust of market participants in these potential innovations can be increased. Bonding, the most indispensable joining technology for EWP production, can be impaired by the anatomical, physical, and chemical properties of the individual wood species. Hence, the usability of birch wood in EWPs can be facilitated by clarifying the typal peculiarities related to its glueability.

This thesis revolves around one of those peculiarities of silver birch wood, precisely the composition of its non-structural low molecular mass compounds – its extractives. The objectives of this thesis are divided into three higher-level goals, which are briefly detailed below, with separate study objects: the adhesive, the wooden substrate, and the final bond line.

Understanding the Extractives' Interactions with Reactive Adhesives

Wood adhesives for structural bonds are reactive adhesives, which cure from the liquid state by establishing covalent bonds in the polymer matrix, thus creating a solid polymer network. The presence of extractives during the curing process of reactive adhesives can impact the dynamics of curing, the final chemical structure, and the final mechanical properties of the polymer network.

Hence, these impacts need to be determined to assess these interactions and evaluate their relevance for bonding applications and mitigation methods. To assess

whether and how these extractives have to be considered in the bonding process, the curing dynamics need to be quantified in a rheological setup, which mimics real bonding conditions. The cured adhesives' final properties need to be characterized as a function of the presence of extractives, *i.e.*, concentration, by identifying and applying suitable sample preparation and measurement techniques for relevant mechanical and physicochemical properties.

Determining the Effects of Extraction on Wood Properties

Next to the adhesive properties, the bond quality and performance of the joint are highly influenced by the substrate, *i.e.*, the adherend. Apart from external characteristics, such as grain or growth ring orientations or surfacing methods, numerous intrinsic characteristics of wood – structural and physicochemical properties – can affect its glueability with a specific adhesive and bonding process. Some of these can be suspected to be altered by either the removal of the extractives with subsequent changes in chemical composition or by the extraction procedure itself. Therefore, suitable methods for characterization need to be identified or developed.

These include the analysis of the wood's wettability, which is governed by its free surface energy. As many adhesives are either water-based or contain compounds showing water reactivity, the wood's complex set of characteristics regarding the water-relations of wood – anisotropic sorption and diffusion with varying enthalpy – should be considered. Due to the changing humidity in the service environment of EWPs, the swelling and shrinkage behavior needs to be included in the consideration as well, as deformations and associated mechanical stresses on the bond line occur. Moreover, these investigations should allow the association of changes in bonding behavior with substrate modifications due to extraction. Distinguishing between direct effects due to the removal of hydrophilic extractives and inadvertent effects from the extraction procedure is an important target, which requires control experiments using vapor treatments.

Evaluating the Influence of Extraction on the Resulting Bond Properties

Critical mechanical properties of bond lines include their strength, often quantified by in-plane shear loading of the bond line. Additionally to the ultimate stress, the bond's stiffness and yielding behavior can provide information to estimate safe design parameters for EWP bonds. These are supposed to be examined in relation to the extractive content of the bonded wood. The potential effects of extractives on the adhesive curing dynamics will impact the bond line formation. Therefore, the bond line morphology, including the developed interphase established during curing by adhesive

penetration into the wood pores, must be captured with an appropriate imaging and computer vision evaluation method to analyze correlations between bond line morphology and its mechanical characteristics.

1.3. Scope

The study of adhesion is a highly intricate field, drawing on knowledge from various disciplines, including Physics and Materials Science, Polymer and Surface Chemistry, Rheology, (fracture) Mechanics, as well as Industrial Engineering and Manufacturing. This vast extent of the research fields in wood adhesion requires a multitude of limitations in this work's scope definition (**Figure 3**). Generally, this thesis examines the bonding of silver birch wood with a focus on its extractives. The scope of this work is further limited to the sapwood of silver birch without red or brown discolorations. Silver birch does not show heartwood formation (Piispanen and Saranpää 2001), and facultative/false heartwood (discoloration) has been shown to have little to no effect on adhesion performance in the case of beech wood (Pöhler *et al*. 2006).

Adhesion is never just a matter of the adherend (wood) or the adhesive itself but always a result of both as an interdependent system (Abbott 2015). Consequently, the bonding behavior and adhesion-related properties vary significantly between wood species (Konnerth *et al*. 2016).

This work focuses on the adhesion of wood from silver birch (*Betula pendula* ROTH) in the context of hydro- and amphiphilic extractives and aqueous extraction with two types of wood adhesives, *i.e.*, melamine-urea-formaldehyde (MUF) resin and one-component polyurethane (PUR) prepolymer adhesive. In common European hardwoods, water-insoluble extractives – also called wood resins – are mostly minor amounts of fats, steryl esters, and sterols stored in the parenchyma cells (Holmbom 1999). Having no oleoresin-producing resin canals, the resin concentration in hardwoods is low and, therefore, the source of difficulty in achieving good structural bonding. Water-insoluble extractive compounds are localized and mostly inert resinous substances.

Water-soluble extractives, however, are metabolites from energy storage and biosynthesis and comprise a diverse group of various glycosides, saccharides, amphiphilic lipids, phenolics, and others. Due to the presence of functional groups, *e.g.*, hydroxyl or carboxylic moieties, they can establish interactions with both wood biopolymers or adhesives in terms of physical interactions (*e.g.,* hydrogen bonds) and even chemical covalent bonds or have acidic/basic effects when dissolved. Moreover,

hydrophilic extractives are also focused on due to the fact that water was assumed to represent the only solvent, which offers a technically feasible option to perform extraction treatments on wood as a pre-bonding modification method.

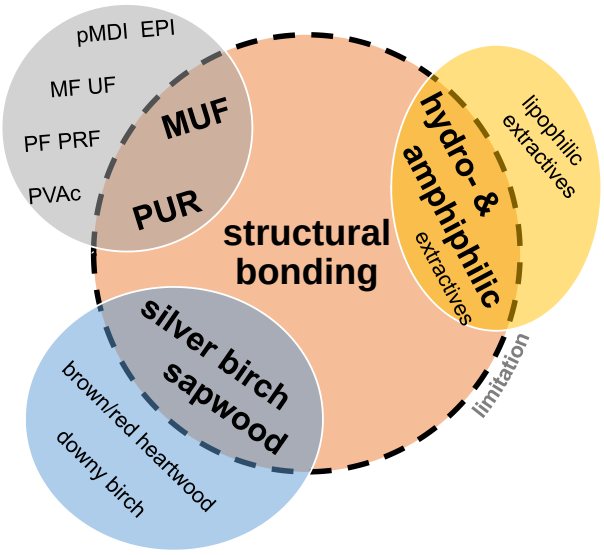

Figure 3. Graphical representation of the thesis scope and limitations.

Moreover, the structural bonding application in the scope of this thesis is limited to investigations of parallel-to-grain lamella bonding, omitting finger-jointing, or end-grain (butt) joining applications. Also, as typical in lamella bonding, it investigates room temperature bonding only, not including high-temperature curing as often used in veneer composite production or by means of high-frequency presses.

The scope of this work was structured by these primary research questions:

- Of what comprise the hydrophilic extractives of silver birch wood?
- Which interactions of adhesives and hydrophilic extractives are occurring, and how are the curing behavior and adhesive properties affected?
- How does the removal of extractives or the extraction procedure affect the bulk and surface wood properties?
- How are the formation and mechanical properties of the bond line affected by the extractives and the extraction of birch wood, respectively?

2. Fundamentals

2.1. Engineered Wood Products

Today, conceived as an alternative to conventional building styles – especially for larger civil engineering projects – constructions of engineered wood products (EWPs) have an extensive history. The oldest EWPs likely were wooden trusses similar to nail-laminated timber, developed in the 16th century by de l'Orme (Schickhofer 2006). The first construction using what can be considered glued laminated timber was the 1860-built assembly hall of the *King Edward College* in Southampton, UK. The introduction to the general market was achieved by the German manufacturer Otto Hetzer, who, in the early 1900s, first patented the production of laminated timber beams (Rug and Rug 1996) bonded with animal protein glue. His innovation was quickly adopted and licensed to other countries (Rinke 2015).

In general, all EWPs are characterized by controlled disintegration, selection and grading, and rearrangement of the disintegrated wooden parts (*e.g.,* lamella), which allows homogenization of the anisotropic properties, the reduction or distribution of defects, as well as mitigating internal stresses and associated crack formations. Moreover, the benefits of GLT and other EWPs were addressing the increasing scarcity and costliness of large-sized timber by allowing the flexibilization of beam cross-sections by simultaneous utilization of smaller-dimensioned wood.

Types of Engineered Wood Products

Wood veneer composites (WVCs) are plywood and Laminated Veneer Lumber (LVL). Plywood is a versatile EWP made of multiple layers of thin veneer sheets called plies. These plies are glued together under high pressure and high temperatures, with each layer's grain oriented perpendicular to adjacent layers. This cross-graining technique enhances the plywood's stability and resistance to cracking, shrinking, and warping. LVL consists of multiple thin layers of wood veneers, the majority oriented and glued with the same grain direction (**Figure 4A**).

Cross-laminated Timber (CLT) is a relatively recent EWP characterized by its unique layered construction (**Figure 4B**). It consists of at least three layers of timber boards stacked crosswise to each other and bonded together with structural adhesives. This cross-laminated structure provides remarkable strength and stiffness, making CLT suitable for floors, walls, and roofs in large-scale, multi-story wooden buildings.

Glue Laminated Timber (GLT) – or glulam – is an EWP composed of several lamellas of dimensional timber stacked upon each other with parallel grain direction and bonded together under pressure and without heat (**Figure 4C**). Unlike LVL, which uses thin wood veneers, glulam utilizes thicker sawn timber lamellas, which are lengthwise finger-jointed, allowing it to be formed into larger and longer columns, beams, and even curved shapes. This flexibility makes GLT a popular choice for architectural and structural applications where aesthetic appeal and strength are paramount.

Figure 4. Examples of EWPs for structural applications: (**A**) Wood Veneer Composite (WVC) beam. (**B**) Cross-laminated Timber (CLT). (**C**) Glue Laminated Timber (GLT) – two beams of similar strength, the left one of beech hardwood and the right one of spruce softwood, visualizing the difference in beam cross-sections[2].

By increasing the degree of disintegration, EWPs can also be produced from strands or, for non-structural applications, from particles and fibers. Oriented Strand Board (OSB) is constructed from compressed layers of wood strands mixed with adhesives. In the outer layers, the strands are aligned, while the inner layers have a cross-oriented pattern, contributing to its high mechanical properties and moisture resistance. Due to its strength and versatility, OSB can be a cost-effective alternative to WVC in sheathing, roofing, and flooring applications. Similar materials are Parallel Strand Lumber (PSL) and Laminated Strand Lumber (LSL), known as Parallam® and Timberstrand® (Lam and Prion 2003).

In contrast to the structural engineered wood products above, fiber- and particleboards are cheaper engineered wood but have a lower load-bearing capacity. Thus, they are used for non-structural applications, limited to in-plane loads for bracing (shear stiffening). They are made from wood fibers or chips bonded with a synthetic resin or binder under heat and pressure. This results in a more homogenous material free of knots and grain patterns, making them ideal for detailed and precise work, such as manufacturing furniture, cabinetry, and molding. Its smooth surface is well-suited for painting and veneering.

[2] photographic material by Ralf Rosin (HFM, TUM)

Hardwood Use in Engineered Wood Products

Historically, hardwoods were extensively utilized for building structures (Van Acker 2021). In the past decades, the production of hardwood-based LVL, like beech or birch plywood, has significantly decreased in Europe due to high costs and inefficient manufacturing processes. With the rising costs and shortages of softwood timber, a growing interest in using hardwood for EWPs in both scientific research and industry can be observed (Berthold *et al*. 2017).

At present, hardwoods occupy a minor fraction of both the North American and European EWP markets. However, efforts are underway to explore their use further (Teischinger *et al*. 2023). A recent survey of North American CLT manufacturers revealed that the main worry was securing a consistent supply of hardwood timber of adequate quality and volume. Utilizing non-dimensional grade hardwood timber necessitates extra processing and material removal, notably decreasing efficiency and elevating costs. They agree that to implement hardwood in CLT, the hardwood sawmills' ability to produce dimensional-grade hardwood timber is required (Adhikari *et al*. 2020).

The suitability of beech timber for EWPs has been subject to research for some time (Frese and Riedler 2010). LVL beams from European beech wood have been produced since 2014 by Pollmeier, known as BauBuche®, and have obtained approval for building applications in Germany. With this, significant material savings are possible due to slender cross-sections compared to softwood timber or GLT, especially for applications like supports and trusses, with loading parallel to the fibers (Hassan and Eisele 2015). Based on experimental work by Frese and Blaß (2005, 2006, 2007) and others, beech GLT was also approved for structural use in Germany. However, many design values for strength were comparable to or even lower than those of softwood glued laminated timber, failing to utilize beech's capabilities fully (Ehrhart 2019). This motivated further experimental work on beech wood strength properties and its strength grading by compression, tension (Stapel *et al*. 2017; Westermayr *et al*. 2018), and shear testing (van de Kuilen *et al*. 2017). Further, the wood from ash was investigated for EWP usage with promising results and solutions, overcoming adhesion issues due to high extractive concentrations in ash (Knorz 2015; Ammann *et al*. 2016; Clerc *et al*. 2018).

Regarding WVCs, birch is a common source of veneers for plywood, especially from North European production (Finnish Forest Industries Federation 2007). Due to its early and ongoing interest (*e.g*., historical use for airplane production), the mechanics of birch plywood are relatively well-studied (Hearmon 1943; Gerrand 1987; Grič *et al*. 2017). This includes its temperature dependence (Caetano *et al*. 2018) and moisture

effects (Siim *et al*. 2012) and issues such as lathe check effects (Rohumaa *et al*. 2013), layer build-up and thickness (Norris *et al*. 1961), or ply compression (Bekhta *et al*. 2009). GLT products from birch wood were successfully pioneered and are produced by Hasslacher Nordica Timber using a MUF adhesive system after demonstrating its mechanical potential and obtaining technical approval (Jeitler and Augustin 2016; Obernosterer *et al*. 2023). To date, they remain the only company offering birch GLT on the market.

2.2. The Species of Birches (*Betula* spp.)

Birch trees are found in most parts of the Northern Hemisphere (Ashburner and McAllister 2013), with some 50 recognized species of the *Betula* genus (Fontaine 1970). In northern America, for example, yellow birch (*Betula alleghaniensis* BRITTON), sweet birch (*Betula lenta* L.), and paper or white birch (*Betula papyrifera* MARSH.) are the predominant species for wood and veneer production (Wiemann 2010). The most essential birch types for European wood production, however, are silver birch (*Betula pendula* ROTH; syn. *Betula alba* L., *Betula verrucosa* EHRH.) and downy birch (*Betula pubescens* EHRH.). The attainable timber quality from silver birch is superior within the European species (Hynynen *et al*. 2010) with better straightness of stem growth (Heräjärvi 2001). Moreover, the height and diameter of silver birch are larger, and the yield is higher than that of downy birch (Reuhkala 2004).

Habitat and Climate Adaption of Birch in Europe

Europe is one of the main native habitats of birch trees, which were among the first species to proliferate there during the primary succession in the Preboreal stage of the Holocene after the last glacial period (Leuschner and Ellenberg 2017).

Figure 5A shows an autoecology graph of European forest field data considering the climatic factors temperature and precipitation with highlighted domains for silver and downy birch, as well as Norway spruce, for comparison. This evaluation shows a broad overlap of birch with the climatic conditions native to spruce.

In **Figure 5B**, the local frequency of silver and downy birch and estimated local survivability for birch species (*Betula* spp.) are displayed as overlays of the EU area map. This visualization indicates that central Europe has vast regions well-suitable for the growth of birch. In contrast, the current frequency of silver and downy birch occurrence is low, covering only 2.3% and 4.7% by area, respectively (Hemery 2008), resulting in making up 6.6% of the European forests' growing stock (Brändli 2020) due

to the historic dominance of softwood plantation in silviculture. While currently not native to some southeast European countries, some survivability is also expected there.

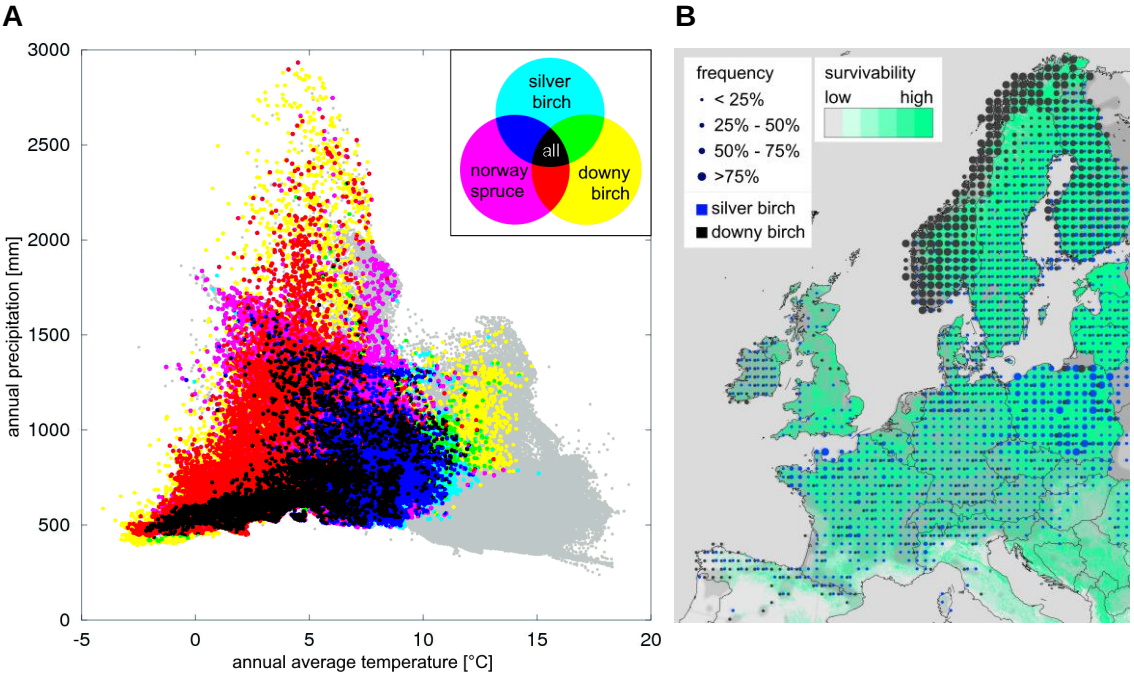

Figure 5. (**A**) Autoecology graph for tree species in the EU with highlighted domains for Norway spruce (*Picea abies*), silver birch (*Betula pendula*), and downy birch (*Betula pubescens*) with the parameters annual precipitation *vs*. annual average temperature. (**B**) Map overlaying for EU regions: (i) the relative frequency of silver birch trees (blue dots) and downy birch trees (black dots), (ii) the habitat suitability indicated by a survivability index (transparent to green overlay) for the *Betula* genus, (iii) and historic distribution areas (gray)[3]

Birch trees are native to most parts of Europe, except for the warmer summer-dry Mediterranean regions in the south (climate classification by Kottek *et al*. 2006). For Germany and many other parts of central and eastern Europe, the adaption of silver birch is well within the limits of its climate tolerance. Some authors (Buras and Menzel 2019) have estimated that, depending on the climate scenario used for modeling, some parts of Europe are expected to become too summer-dry for silver birch but would gain additional habitats in Scandinavia and north-east Europe. Depending on future emission pathways and climate scenario assumptions, long-term survivability is also expected when considering future expectations of climate shifts (Rubel and Kottek 2010).

Thus, silver birch's climate adaption militates for active integration in European current forest management concepts. Moreover, economic projections estimated profitability similar to spruce silviculture (Meyer *et al*. 2011).

[3] The data shown in Figure 5 are adaptions based on the *European Atlas of Forest Tree Species* (Beck *et al.* 2016; Caudullo *et al.* 2016); re-use permitted as *per* decision 2011/833/EU of the European Commission (2011). For further information regarding the data used in Figure 5, see de Rigo *et al.* (2016).

Characteristics of Birch Wood

Birch wood has long been recognized for its high technical utility value due to its anatomical features (Sachsse 1988), as well as strength properties (Sachsse 1989; Heräjärvi 2004). A recent review (Huber *et al*. 2023) recommends birch as a potential alternative for spruce in silviculture not only from a silvicultural but also from a technological point of view, as demonstrated by its average bending modulus (17-18 GPa) and bending strength values (135-158 MPa), which is higher when compared to most common European wood species (**Figure 6A**). Both density-specific strength (**Figure 6B**) and stiffness (**Figure 6C**) are also favorable to many other hardwood trees.

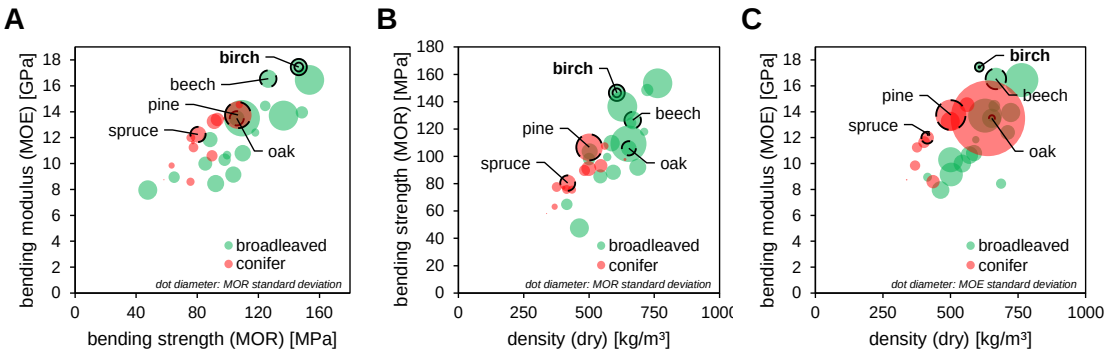

Figure 6. Comparison of bending properties of small defect-free wood for various deciduous broad-leaved (green) and coniferous (red) species: (**A**) bending modulus (modulus of elasticity MOE) as a function of bending strength (modulus of rupture MOR). (**B**) MOR as a function of dry bulk density. (**C**) MOE as a function of dry bulk density. Data points for birch wood are labeled and highlighted with double black edging. Values for Norway spruce, Scots pine, European oak, and European beech are labeled and highlighted with dashed black edging.[4]

Regarding its structure (**Figure 7A**), straight-grained silver birch secondary xylem cells comprise about 63% fibers, 24% vessels, and 14% parenchyma cells (Novitskaya *et al*. 2018). These elements build up a wood structure with an average density of 650 kg/m³ (Grosser and Teetz 1998) with relatively uniform growth ring formation and only minor density variations due to the diffuse-porous vessel arrangement (**Figure 7B**). It has a comparatively low number of small vessels (30–50 vessels/mm²) with an average diameter of around 90 μm (Grosser 1977). The fiber cells in birch wood are larger (**Figure 7C**) than most commercial hardwoods, with lengths up to 1.7 mm (Wagenführ and Wagenführ 2022). Additionally, the wood exhibits a uniform anatomical structure throughout the log cross-section, thus relatively small variations in properties and a

[4] The data shown in Figure 6 is based on multiple literature sources, as collected by Huber *et al.* (2023)

favorable fiber morphology, making it highly valuable in terms of technological utility (Sachsse 1988).

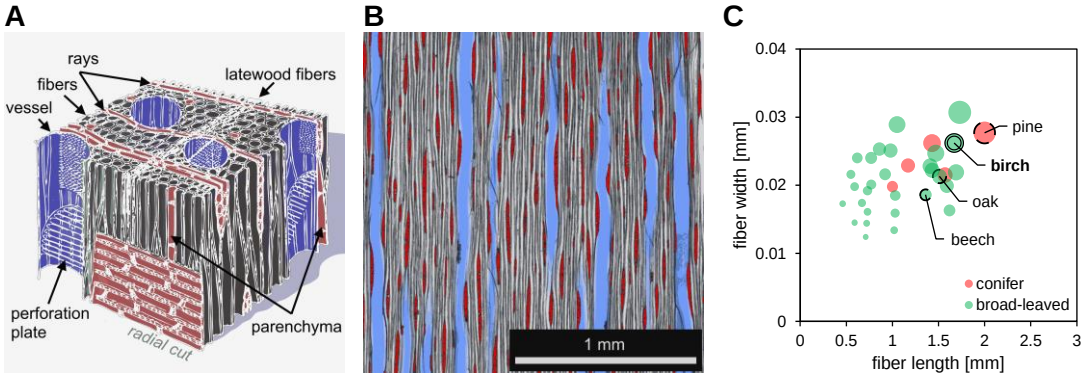

Figure 7. Ultrastructural characteristics of birch wood. (**A**) Microscopic schematic of birch xylem indicating characteristic cell types and anatomical features. (**B**) Microscopic image of a thin tangential cross-section. Colors indicate vessels in blue, parenchyma/rays in red, and fibers in gray. (**C**) Comparative microscopic data of average fiber width and length of various broad-leaved (green) and conifer (red) wood species. The dot area is proportional to the approximate fiber size[5].

In the case of fungal attack or injury, birch trees respond with widespread facultative heartwood formation – compartmentalization of damage. It is, however, due to its small-sized pits (Chattaway 1949), not able to form tyloses for vessel occlusion but builds layers of amorphous gum between the bars of its scalariform perforation plates (Dujesiefken *et al*. 1989). This should improve the reliability of bonding due to less obstructed adhesive penetration. On the other hand, native birch wood has, therefore, a low-rated resistance against fungal decay with a durability class 5 according to EN 350 (2016). This, however, does not inhibit usage in buildings to Eurocode (DIN EN 1995-1-1 2010) service classes 1 and 2. Birch wood can be subjected to thermal (Andersons *et al.* 2009; Lekounougou and Kocaefe 2012; Irbe 2017) or chemical (Fojutowski *et al.* 2013) wood modification methods or protection treatment via preservative impregnation (Birman *et al.* 2020) or combinations thereof (Ahmed *et al.* 2013), to increase its durability. Note that chemical (Mononen *et al.* 2005) and microstructural (Sehlstedt-Persson *et al.* 2006; Biziks *et al.* 2013) effects on mechanical (Wang *et al.* 2022, 2024; Al-musawi *et al.* 2023; Grinins *et al.* 2024) and other wood properties (Popescu *et al.* 2014; Vobolis and Albrektas 2014) due to such treatments need to be considered.

Apart from the main compounds or biopolymers of wood tissue – cellulose, hemicelluloses, and lignin – wood contains accessory components, which are a highly

[5] Figure 7A is redrawn and colorized artwork based on Matyssek *et al.* (2010), originally Mägdefrau (1951). The data shown in Figure 7C is derived from tabulated data from Conard and Thomas (1919)

diversified fraction of its composition when comparing tree species. These lower-molecular fractions without covalent bonding to the tissue matrix are removable with compatible solvents and are mostly referred to as extractives. They serve the tree's metabolism and energy storage and evolved to protect against environmental threads, *e.g.,* oxidative stress from injuries, pathogens, fungal attacks, or severe cold. The types and amounts of extractives vary highly between wood species, with coefficients of variance around 60–80% (Gérard *et al*. 2019).

Birch wood has a light pale color and no odor, suggesting low amounts of aromatic or low molar mass constituents. The total content of extractives in birch wood is moderate, ranging from 1% to 4% (Paasonen 1965; Björklund Jansson and Nilvebrant 2009). *Betula pendula* is known to contain no resin acids but a number of fatty acids, mainly linoleic, palmitic, and lignoceric acids (Björklund Jansson and Nilvebrant 2009). It further contains some lipophilic triglycerides (Piispanen and Saranpää 2004), phytosterols (Selleby 1960), and fatty acid esters of betulaprenols (Bergman *et al*. 1965). Moreover, carbohydrates (Lindberg *et al*. 1958), lignans (Roitto *et al*. 2015), flavonoids, and phenolic glycosides (Sutela *et al*. 2014) were previously identified in birch wood. Indirect indications of extractive substances in birch wood include observed damages to polyester varnish and, at times, biological effects, *e.g.*, dermatitis and blue stains due to metal corrosion (Wagenführ and Wagenführ 2022). However, data found in literature is mostly derived from lipophilic extraction analyses, *e.g.*, petroleum (Bergman *et al*. 1965; Fengel and Wegener 1984), thereby mainly obtaining non-polar extractives or other polar solvents, *e.g.*, methanol (Hiltunen *et al*. 2006; Sutela *et al*. 2014; Roitto *et al*. 2015) and acetone (Piispanen and Saranpää 2004; Sutela *et al*. 2009). Little is known about the composition of the water-soluble fraction, which can contain the amphiphilic and hydrophilic fractions of extractives or even micelles carrying hydrophobic extractives.

2.3. Adhesion and Adhesives

Adhesive forces can originate from a series of physical and chemical mechanisms (Baldan 2012). These are described by several theories of adhesion, the relative practical importance of which in adhesion applications was vehemently discussed in the past (McBain and Hopkins 1925; Browne and Brouse 1929; Marian and Stumbo 1962; Bikerman 1968; Collett 1972; Packham 1992; Packham and Johnston 1994). Almost always, an adhesive bond results from multiple of these mechanisms, and quantifying their relevance in joining wood is still under research.

2.3.1. Adhesion Mechanisms

The hypothesis of two rough surfaces interlocking when brought into contact and, therefore, increasing adhesion is based on a macroscopic idea, which was wrongfully applied to molecular-level contact phenomena (Kendall 2004). **Mechanical interlocking**, however, occurs when an adhesive flows into the porous structure of wood, filling the voids and locking itself into place upon curing and becoming a solid network, thus forming an interphase containing both wood tissue and adhesive. This mechanism relies heavily on the physical properties of the wood, such as its porosity, pore diameter, and surface roughness. The effectiveness of mechanical interlocking is influenced by the adhesive's viscosity and wettability, which determine its ability to penetrate the wood's surface. Upon hardening, the adhesive forms a physical bond by forming closure, anchoring itself to the wood, and ensuring a mechanical grip within its microstructure. The additional factor of an increased contact area between wood and adhesive domains, i.e., interface, to promote adhesion (Persson 2002) of rough surfaces is negligible (Ciavarella 2017).

The electrostatic theory is based on the fact that when electrons are transferred between surfaces, this double-layer of opposing charges generates an electrostatic attraction force (Derjaguin *et al*. 1969). This electron exchange mechanism occurs where adherend and adhesive have differing electron affinities. However, the extent to which such heteropolar bonds contribute to bond adhesion in wood is debated and likely negligible (Habenicht 2009).

The adsorption or wetting theory is based on the thermodynamics of the adhesive's interaction with the wood surface. It postulates that adhesion is achieved when the liquid adhesive spreads and wets the surface, establishing close interfacial contact at the microscopic and molecular levels. The degree of wetting is determined by the wood's surface energy and the liquid adhesive's surface tension. Good wetting is facilitated by intermolecular forces such as acid-base interaction (dative bonds) or secondary bonds or supramolecular interactions, *e.g*., van der Waals forces, London dispersion forces, dipole-dipole interactions, and hydrogen bonds. The thermodynamic compatibility between the adhesive and the wood surface is crucial for achieving strong adhesion through this mechanism (Mittal 1977).

Diffusion theory pertains to the molecular entanglement of the adhesive and the wood polymers at their interface (Voyutskii 1963). This mechanism is particularly relevant for thermosetting adhesives (Marcinko *et al*. 2001). The theory suggests that adhesive or adherend molecules diffuse across the interface. This interdiffusion results

in a gradation of concentration and, therefore, mechanical properties across the interface, leading to improved stress distribution of the bonded assembly (Wool 1995). The effectiveness of this mechanism is dependent on the molecular weight, polymeric structure of the adhesive, and the compatibility with the wood's molecular composition.

The chemical bonding theory explains adhesion in terms of covalent bonds formed between the adhesive and reactive sites on the surface. This mechanism provides a strong type of bond, as it involves the sharing of electrons between the adhesive and the wood, resulting in a permanent chemical linkage. The presence of reactive groups, such as hydroxyl groups (-OH) in wood biopolymers, facilitates the formation of covalent bonds. Chemical bonding requires specific conditions for the reaction, including appropriate curing times, temperatures, and the presence of catalysts or hardeners. Its existence in wood bonds has been speculated for some time (Gardner 2006). Despite the plausibility of covalent bonds forming with certain adhesives, there is an absence of empirical evidence supporting their enhancing contribution to the strength of adhesive bonds (Frihart and Hunt 2021).

The theory of weak boundary layers addresses the presence of weak or non-reactive layers at the adhesive-wood interface, which can significantly affect adhesion strength. These layers may arise from contaminants, low molar mass compounds, or incompatibility between the adhesive and the wood surface (Bikerman 1968). The presence of weak boundary layers reduces the effective stress transfer across the interface, leading to premature failure. Enhancing adhesion involves either removing these layers through surface preparation or modifying the interface chemically to improve compatibility with the adhesive (Stehr and Johansson 2000).

2.3.2. Adhesive Types

Until the 1930s, the standard adhesive for structural wood bonding was casein-based from the dairy industry. The development then accelerated with the invention of synthetic resins to better fulfill a multitude of requirements for adhesives in the wood industry. These were the joint strength, moisture and chemical resistance, shelf life, specific yield, setting speed, and wear on tools (Truax 1929).

The first synthetic adhesives were based on phenol-formaldehyde (PF) formulations (Frihart 2015), which are still being used in plywood applications. The potential of polyurethanes and polyureas (PUR) as adhesives was first recognized in the 1940s with the increasing availability of isocyanates (Bell 1993). Each type of adhesive brings its own set of characteristics and advantages that can affect the overall cost-efficiency and quality of bonding. Polyvinyl acetate (PVAc) is inexpensive, thus

considered one of the most cost-effective wood adhesives, but lacks requirements for structural applications, *e.g.*, strength, creep, water resistance, and durability against radiation or chemicals (saponification) because of its thermoplastic nature and, moreover, it does not form chemical networks. Phenolic resins dominate plywood production (Finnish Forest Industries Federation 2007). Based on survey data from Ohnesorge *et al.* (2009), the most common adhesive types for industrial GLT and CLT production are MF/MUF (50%), PUR (34%), and PF/PRF (9%).

Amino resins of melamine-urea-formaldehyde (MUF) are water-borne resins that contain hydroxymethylated monomers of melamine and urea of various substitution degrees (Barrett 1993) in the resin component (**Figure 8**). MUF adhesives are two-component systems with a water-based formic acid solution as a hardener to activate the polycondensation of the hydroxymethyl and amine groups, forming methylene or ether bridges, thus creating a cross-linked rigid thermoset (Ülker 2016).

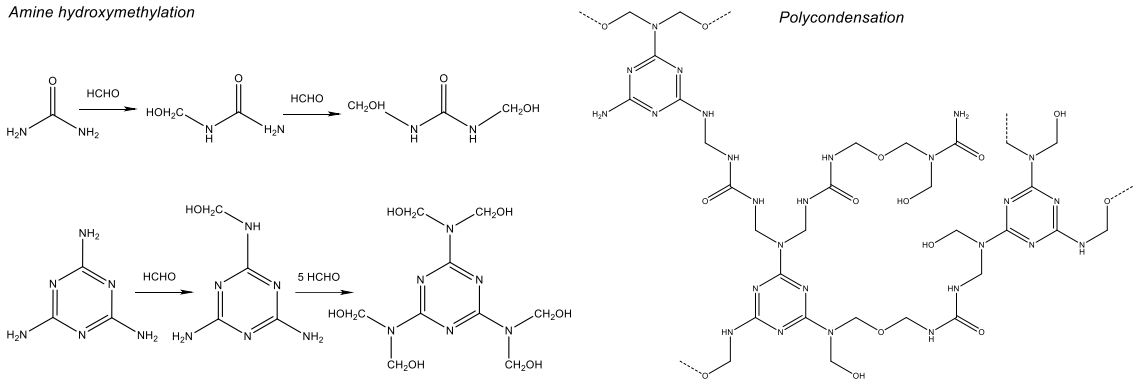

Figure 8. MUF polyaddition reactions of melamine and urea (left) with formaldehyde (hydroxymethylation) and exemplary cross-linked structure after polycondensation curing (right).

As a thermoset with short segmental molecular lengths, MUF adhesive possesses high mechanical strength. It also maintains good properties in humid or wet conditions, as the cross-linked network is highly water-resistant. However, it has some hygroscopicity and displays respective plasticization effects regarding its stiffness and strength up-on moisture uptake (Kläusler *et al*. 2013; Winkler *et al*. 2022). Amino (and phenoplastic) resins are characteristic in their considerable stiffness and brittle failure when breaking (Clauß *et al*. 2011b).

One-component polyurethane prepolymers (PUR) contain a mixture of diisocyanate-containing monomers (mostly MDI) or oligomers (pMDI) and isocyanate prepolymers when chain-extended. These react with moisture, forming amines under the release of carbon dioxide. Such amines readily react with the excess of isocyanates,

allowing for the polyaddition reaction and forming a urea linkage (**Figure 9**). The reactivity can be tuned widely from hours to minutes by catalyst addition.

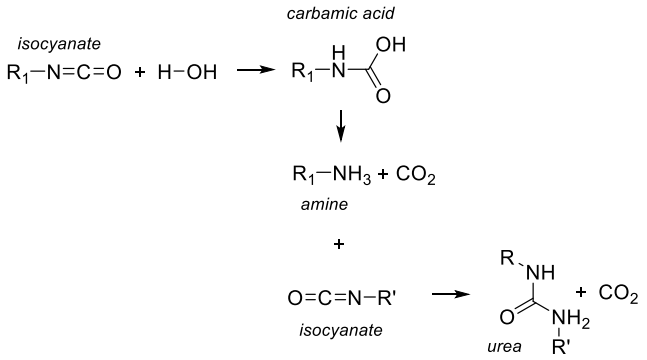

Figure 9. Moisture curing process of one-component PUR adhesives

While PUR can be produced in a wide range of Young's modulus E (Clauß *et al*. 2011a), common PUR wood adhesives are usually elastic polymers of $E < 1$ GPa upon curing (Konnerth *et al*. 2007). Depending on the prepolymer formulation, PUR adhesives can retain a high degree of flexibility upon curing, which allows the bond lines to accommodate high deformations without compromising bond integrity and the low shear modulus mitigates stress peaks in bonded joints (Goland and Reissner 1944; Delale *et al*. 1981). The cured PUR adhesive does not emit formaldehyde and is resistant to weathering, aging, and a broad spectrum of chemicals, ensuring long-term performance (Pizzi 2005). Due to the hydrophobic nature of the cured adhesive, lower effects of moisture uptake on mechanical properties are observed (Kläusler *et al*. 2013; Winkler *et al*. 2022). However, depending on the proportion of unreacted isocyanate groups, degree of polymerization, and reaction rate, the sensitivity of PUR bond lines to temperature-dependent creep can be problematic (Richter *et al.* 2006). Two-component polyurethane adhesives with a second component based on polyols are primarily used in special applications, *e.g.*, for fixing metal thread rods in wooden joints (Bockel *et al*. 2020).

Phenolic resins – phenol-formaldehyde (PF) or phenol-resorcinol-formaldehyde (PRF) adhesives are characterized by their superior resistance to moisture and significant bonding strength upon solidification. Their durability against chemical aging and temperature stability significantly exceeds wood's (Frihart and Hunt 2021). PF is thus highly suitable for use in exterior wood-based panel applications. Nonetheless, these adhesives exhibit certain limitations, such as pronounced dark color, the hard and brittle nature of the adhesive layer post-curing, and their high cost (Zhao *et al*. 2011).

2.3.3. Adhesive Joining of Hardwood

In many cases, hardwood species are more difficult to bond, and impaired bond performances can be obtained compared to softwoods (Pitzner *et al*. 2001). This is partly due to the diverse anatomical structure of hardwoods, regarding their proportions and distributions of cell types and their cell wall microstructure. Moreover, the chemical composition of the cell wall constituents and their extractives fraction can affect the wetting, spreading, and penetration of wood adhesives (River *et al*. 1991).

A high average density and the density variations in some hardwoods can complicate adhesion. Bonding high-density woods presents numerous challenges due to their resultant structural characteristics. The increased thickness of the cell walls and reduced diameter of the lumens hinder the penetration of adhesives into the wood's void spaces, thereby impeding the formation of sufficient mechanical interlocking. Furthermore, the enhanced strength and stiffness of high-density wood can necessitate higher bonding pressures to achieve sufficient compression, ensuring continuous contact between the wood surfaces and the adhesive (Frihart and Hunt 2021).

Because of the woods' hygroscopic nature, fluctuations in moisture levels can exert considerable mechanical stress on the adhesive bond when shrinking or swelling. This can further amplify the issue of surface warping before or during the curing process. Hardwoods exhibit a greater tendency to expand and contract compared to softwoods of similar density and can exert higher swelling pressures in a restricted environment, such as adjacent to bond lines (Schroeder 1972; Van Acker 2021).

2.3.4. Extractives–Adhesive Interactions

Accessory wood compounds are able to impact the performance of adhesive bonds (Chen 1970; Bockel *et al*. 2018, 2019; Alamsyah *et al*. 2021). However, this is not a necessary consequence and is highly specific to combining wood type and adhesive products. For example, impaired wettability or adhesive curing rates can occur without affecting the bond strength (Nussbaum and Sterley 2002; Roffael 2016). On the other hand, impaired bonding due to extractives can occur, while the wettability of the substrate remains unaffected by extraction (Dougal 1979).

High concentration levels of extractives on the surface can prevent the adhesive from establishing interactions with the adherend, acting as a barrier (Bikerman 1968). Such chemical weak boundary layers from surface contaminations (Stehr and Johansson 2000) can also affect the wetting process and, thereby, the ability of the adhesive to spread and penetrate effectively or the removal of solvents, *e.g.*, water.

When extractives are soluble in the liquid adhesive media, they can dilute and disrupt the adhesive's chemical structure (River *et al*. 1991).

Extractives may encompass compounds that can chemically bond to the adhesive's polymer matrix while it cures (Roffael *et al*. 2000; Künninger *et al*. 2006). For example, aliphatic alcohols or phenolic compounds can partake in urethane formation reactions with PUR isocyanates. Saccharides and other polyols can also react with isocyanates to form urethane linkages, leading to cross-linking due to their multifunctional nature.

Formaldehyde-based adhesives, such as MUF, can show reactions with or crosslink polysaccharides (Sridach *et al*. 2013) due to the fact that saccharides offer multiple reaction sites (OH-groups), a mechanism that is being utilized in DMDHEU modification treatments (Emmerich *et al*. 2019).

Alternatively, extractives might not bind directly but, nonetheless, can either slow down or speed up the curing process (Roffael 2016; Bockel *et al*. 2019), thereby affecting gelation, pressing time, and hardening. How quickly the adhesive sets and reaches its final strength impacts production speed. The gel time, the period until the adhesive begins to solidify, affects the workability and positioning time of the adherend parts. The pressing time – the duration the bond line needs to be pressurized to form a strong bond – directly impacts production throughput and equipment usage. Inhibition of curing reactions from wood extractives was observed in phenolic resins (Imamura and Takahashi 1970; Akaike *et al*. 1974) and amino resins (Mizumachi 1973; Mizumachi and Morita 1975), often associated with their sensitivity to pH changes. Therefore, non-soluble acidic groups bound to the wood have also been shown to affect the gel time of UF resins (Subramanian and Somasekharan 1983). The acidic/basic properties of extractives vary greatly between wood species (Wanschura *et al*. 2014).

Regardless of whether they chemically integrate into the polymer or remain separate, extractives can influence the polymer network's cross-linking density and its segmental molecular weight (Zegel'man *et al.* 1985; Schellenberg 2005; Du *et al.* 2024). Primarily lower-molecular weight extractives might also act as plasticizers. Consequently, this can alter the mechanical characteristics of the adhesive, impacting its stiffness (Young's modulus), elastic limits (yield), and strength (Long *et al*. 2018; Huang *et al*. 2022).

2.3.5. Extraction Effects on Wood Properties

Prior research into the complex effects of wood extractives on wood properties showed impacts on its moisture interaction, swelling behavior, and structural properties. These properties are, in turn, related to the glueability and bonding behavior of wood.

Moisture Interaction

Adhesive curing behavior often depends on moisture interactions with the adherend. With one-component PUR adhesives, the available water diffuses into the adhesive, enabling the curing reaction (Arnold *et al*. 1957). Both insufficient and excessive water amounts can impact the curing rate and the final quality of the bond (Shkapenko *et al*. 1960; Kägi *et al*. 2006; Bomba *et al*. 2014). On the other hand, water-based adhesives lose considerable amounts of water during curing through capillary action, the sorptive capacity, and diffusive water transport of the wood.

An effect of extractives on sorption behavior has been determined in various wood species: In most cases of tropical woods, a lowered equilibrium moisture content (EMC) was observed due to the presence of extractives (Choong and Achmadi 1991), but in cases of highly hygroscopic extractives, also elevated EMC was found (Hernández 2007). It has been postulated early on that bulking effects reduce the multilayer sorption and the fiber saturation point (Wangaard and Granados 1967). This was confirmed by Popper *et al.* (2006), who argued, using the isotherm deconvolution model by Hailwood and Horrobin (1946), that not the monolayer fraction but only the multilayer fraction of the adsorbed water was negatively correlated to (ethanol-toluene) extractives content of various tropical woods. However, Zhou *et al.* (2016) provided an opposing result in the case of poplar wood, showing that an extraction procedure with an ethanol-benzene mixture increased the monolayer sorption while the multilayer adsorption behavior remained unchanged. Nzokou and Kamdem (2004) performed sorption experiments on pristine and extracted oak, cherry, and pine wood with ethanol and water and also observed increased moisture uptake post-extraction. Therefore, one can assume that the differences in extractives' chemistry and the fact of which extraction procedure was used lead to sorptive alterations in wood by affecting different mechanisms: Predominantly, hydrophobic extractives are not binding to sorption sites, but by aggregation, they can block free volumes and, therefore, have a bulking effect.

The hydrophilic extractives are expected to establish hydrogen bonding with hydroxyl groups of wood, competing with water for sorption sites (*e.g.*, phenols, alcohols, and carboxylic acids), but depending on the number of functional groups, they

still offer additional sorption sites themselves, *e.g.*, polyols, simple sugars, or glycosides (Maréchal 2007; Peña *et al*. 2018).

Thus, the sorption effects of extraction depend on the extractives' nature in any specific wood. The extent and manner of the changes in sorption behavior are not well-studied for birch wood extractives. Moreover, the dynamics of moisture movement are of interest, as some studies indicate possible effects of extractives on moisture diffusivity (Chen 1994). Based on the temperature-dependence of the sorption isotherms, thermodynamic evaluations of the Clausius-Clapeyron type are possible (Hill 1949) to determine the isosteric heat, *i.e.*, the enthalpy of vapor sorption.

Swelling Behavior

For bonding purposes, the dimensional stability of wood is fundamental to ensure fitness for use in environments subject to fluctuating humidity. Removing extractives has been shown to affect not only the water sorption behavior but also the thereby occurring dimensional changes, *e.g.*, in studies on black locust wood (Adamopoulos and Voulgaridis 2012). More importantly than the free swelling behavior, the exerted stresses due to restricted swelling or shrinking are critical to the bond line performance (Hofferber *et al.* 2006; Frihart 2007). The swelling behavior of birch wood due to moisture uptake has been studied before (Kumar 1957; Noack *et al.* 1973; Giebeler 1983). However, the effect of extractives on swelling behavior is still unknown.

Microstructural Properties

While swelling in wood predominantly originates from water molecule uptake in the amorphous regions in the cell wall, the moisture also affects the ordered nanostructure of wood (microfibrils), which has been shown in increasing lattice dimensions and shape of crystalline cellulose via X-ray diffraction (XRD) analysis (Zabler *et al.* 2010; Müllner 2017). The imbibition by the solvent and the subsequent swelling and mobilization of the biopolymers during extraction treatment could result in residual structural reconfigurations after reconditioning, as suggested by drying and rewetting experiments with pine wood (Hill 2010). Moreover, interfacial regions to crystalline domains of the microfibrils might become increasingly disordered by the drying process (Leppänen *et al.* 2011), which can be detected with XRD.

Surface Properties

Solid surface energy has been shown to affect its bonding behavior (Fowkes 1987; Gent and Hamed 1990; Nussbaum and Sterley 2002), especially the bond's mechanical durability when exposed to shrinking and swelling stresses (Comyn 1992). In the case of wood substrates, the relevance of interfacial tension is reduced compared to flat-

surfaced bulk solids, as the adhesion is supported by mechanical interlocking (Vick and Kuster 1992; Allen 1993; Gardner *et al.* 2014). The compatibility of adhesive (liquid) and adherend (solid), however, can influence the process of bond line formation (adhesive penetration) and, therefore, the extent of such interlocking (Collett 1972). Extractives deposited on the outer cell wall layer (S3, lumen side) have been shown to affect the surface energy and, therefore, the wettability of wood surfaces (Nzokou and Kamdem 2004; Wolfrum *et al*. 2018; Jankowska *et al*. 2018).

Multiple methods based on contact angle measurements between test liquids and sample surfaces have been developed to determine materials' surface energy (Fowkes 1962; Owens and Wendt 1969; van Oss *et al.* 1990; Wu *et al.* 1995). For rough surfaces of open-porous, hygroscopic materials like wood, however, these approaches are subject to numerous sources of errors (Wenzel 1936; Cassie and Baxter 1944; Scheikl and Dunky 1998).

Alternatively, surface energy determination of wood by inverse gas chromatography (IGC) was demonstrated as a feasible method by Kamdem *et al.* (1993), who characterized extracted white birch (*Betula papyrifera* MARSH.) wood flour. With IGC, an increase in dispersive surface energy was observed after the extraction of resins from spruce wood (Wålinder and Gardner 2000) and even more so from pine wood (Tshabalala 1997; Liu *et al.* 1998), together with increasing acidic and basic interactions on extracted surfaces.

Mechanical Properties

A significant positive correlation between extractive content and transversal strength and Young's modulus was found for larch wood (Grabner *et al.* 2005). Accordingly, hot-water extraction treatments resulted in a reduction of both parameters. Identical tendencies in bending strength were observed for black pine (Lato *et al.* 2013). In contrast, Arganbright (1971) observed an increase in Young's modulus after removing extractives in redwood. Hypotheses on the correlations between extractives and mechanical properties like Young's modulus can be of chemical and physical origin. On the one hand, extractives dispersed in the polymer matrix can act as plasticizers (small molecules) or, on the other hand, even contribute to non-covalent crosslinking of the matrix *via* multiple hydrogen bonds (crosslinkers). The physical effects of extractives can originate from bulking action, *i.e.*, filling structural voids and reinforcing the material when deformed, particularly when compressed (Grabner *et al.* 2005). Similar investigations on the correlation of extraction treatment and mechanical properties are unavailable for birch wood.

3. Publications

This publication-based thesis is based on three first-authored full-length research papers in international, English language, peer-reviewed journals, published in 2023–2024, enumerated **Papers I**, **II,** and **III** and specified below.

Paper I (Engelhardt *et al*. 2023)

Engelhardt M., Böger T., Gigl M., Meng C.,
Soprunyuk V., Schranz W., Richter K., Sánchez-Ferrer A.

Interactions of hydrophilic birch wood (*Betula pendula* ROTH) extractives with adhesives for load-bearing timber structures

International Journal of Adhesion and Adhesives, **2023**, *125C*, 103447
DOI: 10.1016/j.ijadhadh.2023.103447

Paper II (Engelhardt *et al*. 2024b)

Engelhardt M., Gilg H.A., Richter K., Sánchez-Ferrer A.

Adhesion-related properties of silver birch (*Betula pendula* ROTH) wood as affected by hydrophilic extraction

Wood Science and Technology, **2024**, *58 (1),* 379–402
DOI: 10.1007/s00226-023-01526-x

Paper III (Engelhardt *et al*. 2024a)

Engelhardt M., Böger T., Gigl M., Meng C., Richter K., Sánchez-Ferrer A.

Mechanical and morphological bond line properties of silver birch wood pretreated by aqueous extraction

Journal of Wood Chemistry and Technology, **2024**, *44 (2)*, 114–132
DOI: 10.1080/02773813.2024.2314453

Following the updated *Regulations for Dissertations at the TUM School of Life Sciences*, the publications are not printed in full in the results section. All versions of record are made available to the public in print and online by the publishers.

3.1. Materials and Methods

3.1.1. Materials and Preparations

Defect-free boards from multiple logs (straight grain, flat-sawn, knot- and pith-free, sapwood with no discoloration) of 350 mm × 150 mm × 5.5 mm (L×W×T) were produced from silver birch (*Betula pendula* ROTH) from Lieska region (FI) and used in in the studies of **Papers I** and **III**. Such boards from both Lieska and Eberswalde (DE) regions were used to produce small-scale specimens in equal amounts for the investigations of **Paper II**. Wood material and wood samples were stored in a constant standard air climate of 20 °C and 65% relative humidity (RH) for further use.

Two adhesive products were used throughout the investigations in this thesis: Water-borne *in situ* polymerizing melamine-urea-formaldehyde (MUF) adhesive BASF Kauramin® 683/688 (standard resin-to-hardener ratio 100:25 (w/w)) and pre-polymerized water-free one-component polyurethane (PUR) adhesive Henkel Loctite PURBOND® HB S309 were used in this study[6]. As a UV-fluorescent dye, Rhodamine B (CAS No 64381-99-3) was added to the MUF (0.02% (w/w) in the studies for **Paper III**, while a UV dye was already included in the PUR product.

For investigations on extracted wood in **Paper I**, 16 boards, as specified above, underwent two subsequent cycles à 48 h of hydrophilic extraction in a 1:10 (v/v) solvent-to-solute ratio of deionized water (20 °C). Moreover, a solution of hydrophilic extractives was produced by dispersing 25 g/L (equivalent dry mass) wood particles (0.1 mm < mesh size < 0.3 mm) by constant stirring for 7 d at 20 °C before removing the solid fraction with a glass filter (< 16 µm). The particles for extraction were produced with low thermal stress from equal amounts of dry ice and 1 cm^3 cubes of wood using a cross hammer mill (screen mesh 0.75 mm). The extractives were isolated *via* rotary evaporation (40 mbar at 35 °C) and subsequent lyophilization.

Small-scale specimens (as described in 3.1.5 below) were prepared *(i)* in pristine condition, *(ii)* after an extraction treatment, and *(iii)* after vapor control treatment, for the glueability-related adherend characterizations of **Paper II.** The extraction treatment was conducted at 20±0.5 °C by submerging specimens in deionized water (volume ratio of 1:100 (v/v)) for 7 d. The solvent was exchanged every 24 h. The vapor treatment consisted of storing specimens in a 95% ≤ RH ≤ 100% environment for 7 d (sealed container with a water basin and air pump bubbler at 20±0.5 °C).

[6] Technical data sheets of MUF and PUR adhesives see Türmerleim GmbH (2008) and Henkel & Cie. AG (2015), respectively.

For the studies in **Paper III**, eight boards each were subjected to a hydrophilic extraction treatment in water (reverse-osmosis treated, constant 20 °C, solvent-to-solute ratio 10:1 (v/v), constantly stirred, daily solvent exchange) for durations of 4, 8, and 16 days. After extraction treatment, reconditioning was performed following an equilibration phase (stacked upon another for 72 h, weighted with 20 kg). Additional boards not subjected to extraction treatments were soaked by surface wetting and reconditioned to eliminate bias potential from any secondary water imbibition effects. During the extraction treatment, solvent samples of 300 mL were taken before exchange after 1, 2, 3, 4, 6, 8, 12, and 16 d.

All Papers: To eliminate differences due to sorption hysteresis (Willems 2014), the wood sample material (pristine and pretreated) reconditioning was done at 20 °C in a 2-step sequence at an initially lower RH (40 – 50%) and subsequently at 65% RH, reaching the final moisture conditions in an adsorption process.

3.1.2. Chemical Analysis (Paper I, III)

The content of inorganics in the extract sample of **Paper I** was estimated *via* its ash content by mass loss after full combustion in a muffle furnace at 550 °C.

Infrared spectrometry (Paper I)

Cured adhesive films with varying extractive concentrations were analyzed with a Thermo Fisher Scientific Nicolet iS50 FTIR equipped with a PIKE GladiATR monolithic diamond for ATR (attenuated total reflection) measurement in the wavenumber interval 4000 cm^{-1} to 650 cm^{-1} in 0.5 cm^{-1} resolution, averaged over 16 scans per position and ten positions per sample.

Gas chromatography-mass spectrometry (Paper I)

For untargeted gas chromatography-mass spectrometry (GC-MS) analysis in **Paper I** sample preparation, 1 mg of dry extract was solved in 0.2 mL dimethylformamide. Heneicosanoic acid was added as an internal standard. N,O-Bis(trimethylsilyl)-trifluoroacetamide and chlorotrimethylsilane were added (50 µL; CAS No: 25561-30-2) for subsequent sample silylation reaction at 80 °C over 1 h. Then, 1 µL per sample was injected into an Agilent 7890A GC with SGE™ BPX5 column (30 m, 250 µm) with a 1:30 split ratio (GC oven temperature 100 °C to 320 °C at constant gradient 10 K/min, interface temperature 250 °C; injector temperature 320 °C). Ionization and mass spectrometry were conducted with an Agilent A 5975C VL MSD. Using MSD ChemStation and NIST Mass Spectral Search Program V2.2, the mass spectra of the peaks (area > 0.2% of the maximum peak) in the total ionization chromatograms (TIC) were matched to database spectra (NIST/EPA/NIH Mass Spectral Library NIST 14) with

a probability-based algorithm (McLafferty *et al.* 1974). After reviewing the database matches for plausibility, the compound concentrations were calculated in a semi-quantitative approach with the internal standard.

Liquid chromatography (Paper I)

Free and hydrolyzable saccharide concentrations in the extract were analyzed by liquid chromatography using a sugar analyzer Onken ZA 3000 using external standard solutions (arabinose, cellobiose, galactose, glucose, mannose rhamnose, xylose). Therefore, extract samples were subjected to two alternative hydrolysis procedures following *(i)* Fengel and Wegener (1979) method (1 mL of 2 mol/L trifluoroacetic acid per mg of extract reacted at 102 °C for 1 h) and *(ii)* Fengel and Przyklenk (1986) method (0.375 g of trifluoroacetic acid per mg extract reacted at 102° C for 20 min, before adding 0.625 mL of water per mg extract and continue reaction for 1 h).

Liquid chromatography-mass spectrometry (Paper I and III)

Ultra-high performance liquid chromatography coupled with electrospray ionization time-of-flight mass spectrometry UHPLC-ESI-TOF-MS analysis of extractives of extractives produced in **Paper I** was performed on a Shimadzu Corp Nexera UHPLC with Kinetex XB-C18 reversed-phase column (2.1×100 mm, 1.7 µm particle size, 100 Å pore size) and Sciex TripleTOF6600 time-of-flight mass spectrometer in negative ionization mode. Solutions of 1 mg/mL extractives in acetonitrile water were separated by gradient elution (eluent A: 0.1% formic acid in water; eluent B: MeCN with 0.1% formic acid). De-noised MS data (centroid peaks), captured in information-dependent acquisition mode (IDA), was generated in mzXML format with msconvert (Kessner *et al.* 2008) and processed in the xcms pipeline (bioconductor R package: peak identification by matchedFilter algorithm, peaks grouping: peak-density-method by Smith *et al.* (2006)). Ion mass and MS2 fragmentation patterns were matched to database records of MSDIAL (Tsugawa *et al.* 2015). Using Sirius & FingerID (Dührkop *et al.* 2021), molecular structures were estimated to assist in the identification of chemical compounds and in compound classification.

Extract samples of **Paper III** were filtrated (P4 glass filter < 16 µm mesh) solvent samples were concentrated in a rotovap at 50 mbar and 35 °C and dried *via* lyophilization. Extract solutions at 1 mg/mL (solvent 10% (v/v) methanol in water) were prepared for UHPLC-ESI-TOF-MS analysis as described above, but with both the reverse phase (RP) column and a BEH Amide, 2.1 × 100, 1.7 µm hydrophilic interaction liquid chromatography (HILIC) column (eluent A: ammonium acetate (5 mM) in water; eluent B: ammonium acetate (5 mM) in acetonitrile water (95:5, v/v)). These analyses

were performed on all extractive samples, both in positive and negative ionization modes. The detected compounds passing a plausibility review were assigned a chemical class for further evaluation. Sample data of cumulative extractive content $C_W(t)$ and cumulative compound abundance data of each sample measurement $C_{MS}(t)$ were obtained and, assuming a diffusion process for extraction, a Weibull-type exponential function of extraction duration $C(t) = C_\infty \cdot (1 - e^{-(t/\tau)^\beta})$ was applied to both C_W and C_{MS} data, where C_∞ is the equilibrium estimate at complete extraction, and τ and β are kinetic parameters, which, with the gamma function Γ, yield the equivalent lifetime $\langle\tau\rangle = \tau/\beta \cdot \Gamma(1/\beta)$. The cumulative, m/z-weighted C_{MS} data of compounds within each compound class were similarly fitted according to this model.

3.1.3. Rheology of Isothermal Curing (Paper I)

The adhesive curing as a function of extractives addition was studied in time-sweep experiments in plate-plate configuration with a 25 mm upper disk plate and plates of extracted wood on its radial cut and 500-grit sanded surface. Additionally, comparative experiments with pristine wood plates and pure adhesives were conducted. Adhesive–extractive mixtures of known concentrations were produced by weighing the components using a Sartorius analytical balance 1712 MP8 (0.01 mg resolution) and manual dispersion for 60 s. The experiment sequence started 2:30 min after dispersion.

Small-amplitude oscillatory shear experiments (SAOS; constant strain amplitude γ = 0.1%) as repeating frequency sweeps (1 Hz, $\sqrt{10}$ Hz, 10 Hz, averaging time 30 s) over 18 h total were conducted on an Anton Paar MCR 301 rheometer. The initial gap size was based on manufacturer recommendations of the amount to be applied (MUF: 280 µm; PUR: 140 µm). For PUR, all exposed wood surfaces were covered with aluminum tape to restrict drying while measuring at 20 °C/< 2%-RH (gas flow 50 L_N/h, initial purging at 300 L_N/h for 10 min) to minimize curing at the exposed gap surface. PUR samples were measured in constant gap mode to counteract carbon dioxide foaming. MUF samples were measured in 20 °C/65%-RH environment and constant axial force mode (F < 100 mN) to allow gap reduction due to water loss.

Duration of the polymer network to achieve percolation –the gel time (t_{gel}) – was determined based on Chambon and Winter (1987) as to the time when the loss factor $tan\,\delta$ is constant with shear rate (frequency). The vitrification time as the duration to reach the glassy state (t_{glass}) was determined as the time at maximum loss modulus G'', and the viscosity criterion η^* > 100 Pa·s (Özparpucu *et al.* 2020) was used to obtain the time of curing onset t_η. To indicate changes in stoichiometric conditions of the curing

reaction (Suman and Joshi 2020), the relaxation exponent at gel time was calculated to $n_c = 2/\pi \cdot \tan^{-1} G''/G'$ following Winter (2002).

3.1.4. Mechanical Analysis of Cured Adhesives (Paper I)

Films of adhesive–extractive mixture (extractive concentrations (w/w): 0.05%, 0.1%, 0.2%, 0.5%, and 1.0% in MUF; 0.05%, 0.1%, and 0.2% in PUR) were cast at 0.5 m/min on PET substrate using a doctor blade (blade gap: MUF 0.2 mm, PUR: 0.1 mm). Removal from the substrate was 48 h after film casting. Strips of film with 6 mm width were cut using a pneumatic die cutter and fully cured for 100 d at 20 °C and 65% RH. Strip thicknesses were determined as the average of 5 positions on self-leveling support using a Heidenhain MT 101 M gauge (accuracy ±1 µm) with a disk probe (14 mm diameter) at 0.7 N compression.

After fixing the strips between padded parallel clamps of a universal test machine at 60 mm free length, the data of stress-strain experiments in tension at 1%/min constant elongation rate was recorded for the strips using an HBM S2 100 N load cell and an HBM WA50 displacement gauge. The maximum stress (tensile strength), Young's modulus in the strain interval 0.05% – 0.25% following DIN EN ISO 527–1 (2019), and the yield point calculated by the offset method (0.2% plastic deformation threshold) as described in Ross *et al.* (2022) were reported.

Using thermo-mechanical analysis (TMA) with a Mettler-Toledo TMA 40 (spherical 6 mm diameter probe tip, 150 mN contact force), the temperature-dependent softening of the adhesive films (stacks of 10 to increase signal) was evaluated with the Mettler STARe SW 14.00 software by calculating glass transition temperatures *via* midpoint criterion.

Additionally, rectangular cuboid 30 × 3 × 1 mm³ (L×W×T) specimens of cured PUR and MUF adhesive were studied by dynamic mechanical analysis (DMA) experiments in tension using a PerkinElmer Diamond DMA (temperature sweep; heating rate 2 K/min, -115 °C to 115 °C at 0.1, 1, 10, and 70 Hz in N_2 atmosphere) and PerkinElmer DMA 8000 (frequency sweep; 20 °C at 0.1 to 60 Hz, at 0, 65 and 90% constant RH).

3.1.5. Characterizations of Glueability-Related Wood Properties (Paper II)

Moisture Sorption Analysis

Disks with ~0.3 mm thickness and an 11 mm diameter, cut from earlywood with tangential surfaces, were analyzed in dynamic vapor sorption (DVS) experiments. The disks were characterized in pristine condition and after treatment (extraction or vapor)

as follows: Sequences of adsorption and desorption at constant 23 °C, 30 °C, 40 °C, and 50 °C in steps of ~10% RH from 0 – 90% RH were run using a Surface Measurement Systems DVS Elevated Temperature device (flow rate of 200 mL/min, step criterion for mass stability $1 \cdot 10^{-5}$/min) with a 0.1 µg ultra-balance recording the sample mass every 60 s. For specimens characterized in extracted condition, the sequence at 23 °C was repeated. Additionally, an adsorption sequence at 23 °C was measured on a 12 mg sample of birch wood hydrophilic extractives powder.

Mass progression data during each step was fitted to the stretched exponential function $m(t) = m_0 + (m_\infty - m_0) \cdot (P \cdot (1 - e^{-(k_1 t)^{\beta_1}}) + (1 - P) \cdot (1 - e^{-(k_2 t)^{\beta_2}}))$, with the initial step mass m_0, the estimated mass at equilibrium m_∞, the kinetic constants k_1, k_2, β_1, and β_2, and a weighting factor $0 < P < 1$. Each step's equilibrium moisture content $EMC = (m_\infty / m_{dry}) - 1$ was estimated. Solving $m\left(1/{k_{eq}}^{-1}\right) = m_\infty + (m_\infty - m_0) \cdot (1 - e^{-1})$ numerically, the equivalent kinetic constant k_{eq} was approximated.

Assuming unidirectional diffusion, the apparent diffusivity $D_{app}(RH) = (\pi \cdot V^2)/(4 \cdot A^2) \cdot k_{eq}(RH)$ was calculated (Neogi 1996), where V is the specimen volume and A the specimen's total exposed area. The activation energy of water diffusion E_a was determined for adsorption steps based on the diffusivities Arrhenius-like temperature dependence $D_{app}(T) = D_0 \cdot e^{-E_a/(R \cdot T)}$, with the pre-exponential factor D_0, the molar gas constant R, and the measurement temperature T in K. The EMC results were fitted to the modified GAB isotherm model by Viollaz & Rovedo (1999). Using Willems' (2014, 2015) sorption site occupancy (SSO) model and following the fitting procedure in Sánchez-Ferrer *et al.* (2023), the monolayer water sorption capacity M^0_{SSO} and with that the concentration of available sorption sites $c_{SS} = M^0_{SSO}/mw_{H_2O}$ was approximated (with mw_{H_2O} being the molar mass of water).

To analyze the binding energy of water to the pristine or extracted wooden substrate, the net isosteric heat $q_{st}(EMC) = -R \cdot \partial \ln a_w / \partial T^{-1}$ in adsorption based on the Clausius–Clapeyron equation (Hill 1949; Iglesias and Chirife 1976) was calculated, where R is the universal gas constant, a_w is water activity, and T the (absolute) temperature, using linear regression of the modified GAB functions for adsorption isotherms at the temperatures 23 °C, 30 °C, and 40 °C. The total enthalpy of adsorption per wood mass Q_{st} was obtained by integrating q_{st} over EMC.

Swelling and Swelling Pressure Determination

Three groups of cubic specimens (number of specimens n = 24 per treatment group) of 1 × 1 × 1 mm³ from silver birch sapwood, cut along the wood's principal directions,

were exposed to water extraction treatment, vapor treatment (control), or no treatment (pristine) in 3 equal-sized batches and subsequently dried at 20 °C / 0% RH. Linear swelling coefficients for tangential and radial direction were determined by comparing sample dimensions in dry conditions *vs.* fiber saturation point (FSP) reached by storing them in sealed containers at 95% – 100% RH and repeated wetting with liquid water until obtaining stable dimensions. The uniaxial swelling pressure from restricted swelling in both radial and tangential direction was studied by fixation (initial contact force ~1–2 N) between parallel polished metal surfaces with the upper plate connected to a 500 N load cell and increasing RH by approx. 10% every 24 h, until ~90%.

Microstructural Analysis by X-ray Diffraction

Batches (n = 6 specimens per batch) of wood slices (24 × 24 × 1 mm^3) with radial surfaces *(i)* in pristine condition, *(ii)* following water extraction, and *(iii)* following vapor treatment (control) underwent a conditioning sequence from 50% to 65% RH after treatment. Structural properties were characterized utilizing X-ray diffraction (XRD) of amorphous crystalline domains of lignocellulosic material. Scattering patterns of a collimated $\lambda_{Cu\,K\alpha}$-X-ray-source ($\lambda_{Cu\,K\alpha}$ = 1.55·10^{-10} m, 15 mm irradiated length on specimen with automatic divergence slit; primary soller slit 2.5°) in the scattering angle 2θ range of 2° – 40° (0.01° resolution), *i.e.,* the scattering wave vector q range of 1.4 nm^{-1} – 27.9 nm^{-1}, were recorded using a Lynxeye XE-T detector (behind anti-air-scatter screen; secondary soller slit 2.5°) in a Bruker AXS D8 Advance Eco diffractometer. The 200 ms detector exposure was increased to 1000 ms in the 30° > 2θ < 40° interval.

Pseudo-Voigt functions were fitted to the diffraction patterns using *Fityk* (v.1.3.2, GNU General Public License 2.0), obtaining the diffraction peak positions q_{110}, $q_{1\bar{1}0}$, q_{020}, q_{004} and amorphous peaks after linear background elimination (denominated by their respective scattering wave vectors $q_i = 4\pi \cdot \sin\theta_i/\lambda_{Cu,K\alpha}$). Applying the monoclinic lattice model of Zabler *et al.* (2010), the unit cell spacings a, b, c, and inclination angle γ were calculated. Based on the peak full width half maxima ω_{020} and ω_{004}, the characteristic width ξ_{020} and length ξ_{004} of the cellulose microfibrils was approximated, respectively, using the relation $\xi = 2\pi/\omega$ (Arcari *et al.* 2019).

Adhesive contact angle measurements

Fresh knife-cut radial surfaces of pristine and extracted birch wood blocks (n = 20 each) were prepared. Drops of 15 µL MUF or PUR adhesive were applied using a motorized syringe with an 18 gauge needle to perform sessile drop contact angle measurements with the Krüss Easy Drop camera setup. Drop shape analysis was conducted with Krüss

DSA4 software. Using Shi and Gardener's (2001) dynamic wetting model $\theta(t) = \theta_i \cdot \theta_e \cdot \left(\theta_i + (\theta_e - \theta_i) \cdot e^{K(\theta_e/(\theta_e-\theta_i))t}\right)^{-1}$, were θ_i and θ_e are the initial and final contact angles, respectively, and the combined adhesive spreading and penetration kinetic factor K, were estimated.

Inverse gas chromatography

Samples of 1 – 2 g wood particles (mesh size > 0.3 mm), both in pristine condition and after hydrophilic extraction, were analyzed *via* inverse gas chromatography (IGC) conducted by Adscientis (Wittelsheim, FR) in infinite dilution method (Henry's law region) on a series of probe gases using an Adscientis neuronIC measuring the retention volume V_G in a 4 mm column at 25 °C.

The dispersive surface energy γ_s^d was approximated applying the regression method by Dorris & Gray (1980) using linear alkane probes C6 – C9. Specific interactions (I_{SP}) were determined with a series of polar probe gases to compare acidic and basic surface interactions. The model applicability for γ_s^d was assessed based on the surface solubility and nano-roughness parameters as described by Brendlé & Papirer (1997) using V_G of n-octane and cyclooctane.

Anisotropic Young's modulus in Uniaxial Compression

Prismatic specimens (n = 30) of birch wood 45 × 15 × 15 mm³ (L×W×T), cut along the three principal wood directions, were prepared to investigate Young's modulus E in compression experiments by measurement in pristine condition and repeated measurement post-treatment (vapor (control) or water extraction). A GOM Aramis 12 MP variable base 3D digital image correlation system was used for strain monitoring in a 15 × 10 mm² area, as described in Ożyhar *et al.* (2013). The compression experiment was conducted with a 20 kN force transducer (class 1 ISO 7500-1) on a ZwickRoell type 1455 universal testing machine. Non-destructive measurement in the linear visco-elastic domain, the specimens oriented in the longitudinal, radial, and tangential direction were loaded at a constant loading rate of 2.0 kN/min, 0.5 kN/min, and 0.3 kN/min until reaching a maximum stress of 2 kN, 0.5 kN, and 0.3 kN, respectively. Linear regression in the interval from > 50% of the maximum stress was performed to calculate E.

3.1.6. Mechanical Bond Line Analysis (Paper I, III)

For a simple comparative study in **Paper I**, lap shear samples, as described in DIN EN 302–1 (2013), were prepared with MUF and PUR adhesive (bonded without spacers or grooves; average bond line thickness 70–80 µm and 30–40 µm for MUF and PUR, respectively) using pristine and extracted boards of silver birch. Before gluing, the

surfaces were sanded (200-grit) and cleaned with pressurized air. Batches of n = 18 of the specimens from each wood-adhesive combination were subjected to A1, A2, A4, and A5 treatments of EN 302-1 (A1: equilibrate at standard climate (20 °C/65% RH), measurement in standard climate (20 °C/65% RH); A2: A1 + 4 days soaking in cold water at 20 °C, measurement in wet state; A4: A1 + 6 h soaking in boiling water, 2 h soaking in cold water (20 °C), measurement in wet state; A5: A1 + 6 h soaking in boiling water, 2 h soaking in cold water (20 °C), measurement after reconditioning in standard climate). Tensile shear strength (TSS) was determined by a Type 307 load cell (5 kN) on a Test 112 (Test GmbH) universal testing machine with wedge clamps. The wood failure percentage was determined visually following DIN EN 302-1.

To obtain correlation patterns of extractives concentration in wood and the mechanical performance of the wooden bonds, in **Paper III**, tensile shear strength (TSS) specimens, based on the DIN EN 302-1 (2013) standard, with silver birch boards, pretreated with various extraction durations and sanded (220-grit) to 5.0 mm thickness, were produced with MUF and PUR adhesive (bonded according to manufacturer specifications in the datasheets). Tensile shear experiments (n = 36 per pretreatment-adhesive combination, 288 in total) were performed in 20 °C / 65% RH equilibrium conditions at 1 mm/min using a ZwickRoell materials testing machine type 1455 with the specimens fixed in ZwickRoell type 8306 wedge screw grips and metal guide attachments to minimize peeling forces due to specimen bending. The side surface deformation of the specimen's 10 × 10 mm² overlap area was recorded at a spatial resolution of < 80 µm using a GOM Aramis adjustable base 12MP 3D digital image correlation (DIC) system, set up to a field of view of 20 × 15 mm² (two monochrome cameras type Baumer VCXU-123M.K06 with fixed focal length lenses Schneider Titanar B 75 in vertical alignment at incident angle 25°). The bond line stiffness $G_a = d\tau/d\bar{\gamma}_{bl}$ was calculated by optimizing the upper interval end for linear regression in the linear visco-elastic domain to attain the highest goodness-of-fit ($\max(R^2)$ with τ being the tensile shear stress and $\bar{\gamma}_{bl}$ being the mean engineering shear strain of the bond line observed *via* DIC. The offset method, as described in Ross *et al*. (2022) with a plastic deformation offset of $2 \cdot 10^{-3}$, was applied for yield point determination based on the G_a regression results to determine yield strength τ_e (elastic shear stress limit). Profile data of shear deformation, both along and perpendicular to the adhesive bond line, were generated and compared at reference conditions of equal $\bar{\gamma}_{bl}$. The strain distribution was analyzed by fitting the shear profile data perpendicular to the bond lines in the linear visco-elastic domain ($\tau < \tau_e$) to a pseudo-Voigt peak function $\gamma(y,t) = \bar{\gamma}_{bl}(t) \cdot ((1-s) \cdot e^{-ln(2)\cdot(2y/W)^2} + s/(1+(2y/W)^2))$, with time t and distance from bond line y and where

W is the full width at half maximum of the peak and s a shape parameter. Failure mode analysis was conducted by capturing top-view images of the fracture surfaces of all tensile shear specimens with a 5MP CCD color camera with 365 nm UV illumination at 20 µm resolution. An image processing script was developed using ImageJ (v.1.53q) macro language, which generates binary masks of both surfaces by detecting the fluorescent adhesive using color thresholding and determining the wood failure percentage (WF), the adhesion failure percentage (AF) and the cohesive failure (CF) in the adhesive layer by applying Boolean operations to both surfaces' binary masks.

3.1.7. Morphological Bond Line Analysis (Paper III)

By repeated sanding until 800-grit, both transversal surfaces of the broken tensile shear specimens of **Paper III**, sawn off at the notches, were prepared for optical analysis. The bond lines at the transversal surfaces were illuminated with 365 nm Nichia NCSU 276AT UV diodes, and the fluorescent excitation was captured along the bond line with a modified Carl Zeiss Stemi II reflective microscope *via* a Sony IMX477R (12 MP) digital CCD sensor at 0.8 µm²/px. With automated processing of the captured imaging (stitching algorithm by Preibisch *et al.* (2009) and subsequent color thresholding using ImageJ (v.1.53q)), binary masks – adhesive areas in black; no adhesive in white – were generated for processing.

After applying a thinning algorithm (Lee *et al.* 1994; Polder *et al.* 2010) based on Floyd (1962), the path along the medial axis of the bond line mask was identified by the algorithm of Arganda-Carreras *et al.* (2010) *via* the AnalyzeSkeleton function of ImageJ. By using a local thickness algorithm (Dougherty and Kunzelmann 2007) on the binary mask and reading the results along the identified path, a pixel-wise profile of bond line thickness across the specimen width. This data was aggregated and reported as the mean local thickness th per specimen. Moreover, of all masked areas of adhesive located not in the continuous bond line but of isolated adhesive penetrated into the interphase, the center position and size (area in µm²) was recorded. With this, an adhesive penetration factor $APF = 1/L \cdot \sum(d_{p,i} \cdot A_{p,i})$ was calculated for each specimen, where $A_{p,i}$ is the area of adhesive-filled areas in the interphase, indexed with i, $d_{p,i}$ is the penetration depth as the minimum distance to the bond line, and L is the total observed bond length.

3.2. Publication Summaries

The summaries below provide a brief overview of the publications focusing on the methodologies and experimental results. The final paragraphs of each summary highlight the candidate's contributions to the publication.

Paper I – Interactions of birch wood extractives with adhesives

This study focused on how extractives of silver birch wood interact with standard adhesives used in engineered wood products (EWPs) – melamine-urea-formaldehyde (MUF) and one-component polyurethane (PUR). The objectives were to identify the extractives and how they affect the curing kinetics, as well as to determine if extractives introduce any physicochemical changes to the adhesives. Moreover, it was of interest to identify how extractives impact the mechanical properties of the cured adhesives as well as in the bond line when bonding wood.

After a gravimetric analysis of the extractives, compounds there were further characterized via gas chromatography/mass spectrometry (GC-MS), ultra-high performance liquid chromatography coupled with electrospray ionization and a time-of-flight mass spectrometer (UHPLC-ESI-TOF-MS), as well as a liquid chromatography (LC) sugar analyzer. These allowed the prediction of possible interactions of such extractives with the adhesives. Small-amplitude-oscillatory shear (SAOS) experiments were developed to mimic the moisture conditions of adhesives in the bond line between the birch wood adherends and monitor the curing process. A rheometer in a plate-plate configuration was used for combined time and frequency sweeps. Adhesive-extractive mixtures in varying concentrations were applied to quantify the impact of extractives on the curing behavior of the adhesive, and comparative experiments were conducted with the adhesives on both pristine and extracted wood surfaces. Additionally, cured films of pure adhesive and adhesive mixtures with varying concentrations of extractives were prepared. These films were subjected to chemical analysis using Fourier-transform infrared spectroscopy (FTIR) with an attenuated total reflection (ATR) technique. Tensile tests on film strips were conducted to evaluate the adhesive's strength, stiffness, and deformability as affected by extractives. Additionally, a set of tensile shear strength experiments using both pristine and extracted birch wood with MUF and PUR adhesives was conducted, following specimen treatments A1, A2, A4, and A5, as specified in DIN EN 302-1.

Chemical analysis showed extractives contain mainly phenolic glycosides, saccharides, and some carboxylic acids, which can chemically interact with the reactive functional groups of both studied adhesives. Rheological experiments indicated that the

presence of extractive decelerated the curing process of MUF and slightly accelerated PUR curing, as seen in the evaluations of vitrification- and gel time. The gel time of MUF on extracted birch wood was reduced to under 4 h compared to 5 h on a pristine wood surface, which corresponded to the gel time obtained by 1.3% (w/w) extractives addition. The vitrification time – the duration required to achieve a glassy state – was less affected when extractives were added to MUF. Vitrification time could be lowered when extractive was added to PUR, but no significant differences in curing kinetics for pure PUR on extracted *vs.* pristine wood were found due to the extractives' limited solubility in this hydrophobic adhesive. Infrared spectroscopy experiments on cured adhesive films showed minor differences in the absorbance spectra for both MUF and PUR adhesives with varying extractive concentrations, only showing dilution effects. The results indicated that the extractives did not chemically react in a significant manner, mainly acting as impurities. This finding suggests that the presence of extractives physically affects the bulk properties of the adhesive bond – like plasticizers – rather than chemically altering the adhesive composition, or it disturbs the crosslinking process, introducing defects in the final polymer network. The uniaxial tensile stress-strain experiments of cured adhesive films showed significant losses in stiffness, the elastic stress threshold, and tensile strength of both MUF and PUR adhesive as a function of added birch extractives concentration. Comparative analyses of tensile shear strength of MUF-bonded specimens with pristine *vs.* extracted wood showed an enhancement upon extraction from 7% (A1 treatment) to 19% (A2 treatment). The adhesive strength of PUR bond lines exhibited minimal influence from the extraction process with non-significant changes (+11%, A1 treatment), probably due to the low solubility of such compounds in the hydrophobic PUR matrix.

The **contributions of the candidate** to Paper I included performing the major conception and design tasks of the study. He was highly involved in the experimental work and the associated planning, execution, and data acquisition. Further, the candidate took the lead in the processing and analysis of data from rheological experiments, mechanical testing of adhesive films, and tensile shear strength measurements, interpreting the results and proposing the conclusions. He participated in the analysis of spectrometric data, *e.g.*, FTIR and UHPLC-ESI-TOF-MS, led by the second corresponding author. The candidate's contributions extended to the writing of the manuscript, including visualizations in Figures and Supplementary Material, discussing all results and interpretations with the supervisors and coauthors, as well as revisions and correspondence during peer review.

Paper II – Adhesion-related wood properties

A multitude of material properties and behavior characteristics of wood can be decisive for the bonding performance. It was unknown how the presence/removal of hydrophilic birch wood extractives might modify the adherend's properties. Therefore, this study investigated the influence of hydrophilic extractives on various adhesion-related properties of silver birch wood, *i.e.*, vapor sorption, swelling behavior, microstructure, wettability, and mechanical properties.

Silver birch wood specimens were prepared in pristine condition after water extraction treatment and after a control vapor treatment for a set of comparative characterizations. Thin disc specimens were used for isothermal dynamic vapor sorption (DVS) experiments, which were conducted from 0-90% relative humidity (RH) in a temperature range from 23 to 40 °C. Based on the DVS data, RH-dependent diffusivity, activation energy of diffusion, and sorption enthalpy were derived. A modified GAB model was applied to construct moisture sorption isotherms, and accessible hydroxyl-group concentrations were determined following procedures as described in Sánchez-Ferrer *et al.* (2023). Swelling pressure was measured by fixing cubic specimens between two opposed metal surfaces and recording the compressive stress as RH was increased in 10% steps from 0 to 90% RH. Swelling coefficients were determined from dimensions in the dry state and above the fiber saturation point (FSP). X-ray diffraction (XRD) measurements were performed on radial cut wood slices to observe changes in the cellulose nanostructure due to water extraction or vapor treatments. Contact angle measurements were conducted by applying adhesive drops directly to the wood surfaces. Inverse gas chromatography (IGC) was performed at 25 °C to investigate extraction effects on surface energy. Compression experiments were conducted to investigate the effects of water extraction and vapor treatment on the anisotropic Young's modulus of prismatic specimens.

A moderate increase in water adsorption – predominantly in the range of 70-90% RH – was observed following the extraction treatment, which could be an indication of some physical bulking action of extractives in nanoporous domains. However, this increase was of a temporary nature. Upon repetition of the adsorption-desorption cycle, a slight reduction in adsorption and a 2.2% decrease in estimated sorption sites were obtained. Overall, the changes in sorptive capacity due to hydrophilic extraction were small and within the typical intraspecific variance. Due to the extractives' mobility, their alignment and denticity when forming hydrogen bonds are superior to wood's structural biopolymers. This was expected to have caused the observed 15% decrease in the calculated sorption enthalpy after extraction.

While the extraction reduced the swelling pressure and Young's modulus (reduction of 10–12% in compression), control experiments with vapor treatment indicated that these effects were due to water uptake rather than the removal of extractives. XRD results supported this hypothesis, showing similar effects of crystallinity reduction by 5% for both vapor and extraction treatments and coinciding with a shorter cellulose crystallite length. Surface free energy and wettability were not significantly affected by either treatment, as indicated by contact angle measurements and inverse gas chromatography. It is concluded that water acting as a plasticizer during extraction facilitates the rearrangement of the glassy wood polymer domains and possibly affects the terminal regions of crystallites in cellulose nanofibril chains. Some of the observed effects, such as mechanical softening, reduction in swelling pressure, and structural alterations, can, however, be amplified by removing extractives by creating additional free volumes (absence of bulking action) and additional hydrogen bonds.

Although hydrophilic extraction procedures can influence certain adherend properties, in the case of silver birch, the effects are minimal. From a practical point of view, the impacts of extractives on the bulk and surface properties under investigation were considered minor in terms of their effect on the utility, namely glueability, of wood in bonded applications.

The **candidate's contributions** to Paper II included taking the leading role in designing the study, conducting experiments on moisture sorption, swelling behavior, and mechanical behavior, and carrying out the evaluations and analyses of the associated experimental data. The candidate's design and construction of new experimental setups included the determination of swelling pressure and an associated programmable humidity generator. The candidate was responsible for drafting the manuscript, discussing all results and interpretations with the supervisors, revising the manuscript, and correspondence and leading actions during the peer review process.

Paper III – Mechanical and morphological bond line properties

The effects of the presence, respectively the removal, of hydrophilic extractives in silver birch wood on the properties of the wood's adhesive bonds were investigated. The study examined how these extractives influence the mechanical performance and bond line morphology when bonding. Two common and different types of adhesives were used within the study: water-borne melamine-urea-formaldehyde (MUF) and hydrophobic solvent-free polyurethane (PUR) adhesive.

The adhesives were used to bond silver birch boards, which were pretreated by water extraction procedures of varying durations of up to 16 days. During each extraction period, multiple solvent water samples were collected. Cumulative extractive content curves were calculated from the extractive solid mass data. The extractive samples were analyzed via UHPLC-ESI-TOF-MS, and the release patterns were evaluated. Lap shear experiments with surface deformation measurements in the specimen's overlapping region were performed using digital image correlation (DIC). This method allowed for *in-situ* detection of apparent bond line stiffness, determination of the bond line's yielding behavior, and the analysis of strain distributions. The specimens were also used for microscopic analysis post-testing. Bond lines were visualized using a digital reflective microscope with a UV light source, creating binary masks of wood and adhesive areas by means of a fluorescent dye mixed into the adhesive. Automated image processing was developed and performed to measure bond line thickness and evaluate the extent and depth of adhesive in the interphase.

The kinetic parameters of extraction were determined for individual compounds and classes based on MS abundance data, showing a high variance within and between classes and no correlation to the molar mass of each compound, whose weighted averages ranged from 200 Da for fatty acids to 759 Da for saccharides. By considering the UHPLC/MS mode data for each compound class, which yielded the respective maximum total detection rate, semi-quantitative concentrations were calculated for the compound classes, *i.e.*, phenolic glycosides (38%), phospholipids (19%), saccharides (11%), glycerolipids (10%), fatty acids and conjugates (10%), and others (10%). Given the comparable kinetic parameters among the compound classes and, therefore, the similarity in extract compositions across different extraction durations, the discussion focused on the relationship with the weight-based cumulative extraction degree.

In the case of PUR-bonded shear specimens, extraction resulted in a slight increase in WF percentage and a thinner bond line, suggesting an enhanced adhesive flow. However, the shear measurements indicated that the mechanical properties of the

PUR bond line were unaffected by extraction. For specimens bonded with MUF adhesive, an increased degree of extraction has led to a reduced penetration of the adhesive into the subsurface wood zones, coinciding with thicker bond lines, possibly due to a faster curing reaction of the reactive resin compounds. This was interpreted as an *in situ* verification of the rheological data in Engelhardt *et al.* (2023), which demonstrated an increased reactivity upon reducing extractives concentration and are in good agreement with this study's morphology data. Extraction duration correlated with a moderately more resilient MUF bond line with a similar increase in both yield stress and shear strength. An extrapolation to 100% extraction degree estimated a 17% increase in shear strength, 29% for yield stress, and 28% for the apparent shear modulus of the bond line. This indicated that using extracted wood resulted in fewer defects in the polymer network of MUF, which did not happen to PUR bond lines due to the low miscibility of the extractives with PUR prepolymer. Additionally, the study observed that Young's modulus of the adhesive affects the stress distribution and deformation characteristics across and within the bond line and its adjacent interphases.

With this study, the mechanical implications and the effects on bond line formation due to the interaction of wood extractives with different adhesive types were identified and quantified. The study further contributes to the understanding of wood-adhesive interactions during bonding. The good fitness for use in load-bearing products and, simultaneously, the limited potential and thus need for aqueous extraction as a pretreatment method to further improve the bonding quality of birch wood in EWPs was shown.

The **contributions of the candidate** to Paper III included the primary responsibilities for the research design, the conduct and supervision of experimental procedures, the processing of collected data, and the analysis of evaluation results. Experimental procedures for extraction treatments, sample preparation, mechanical testing, and microscopic imaging were developed primarily by the candidate, with the support of the second author. The candidate performed data processing and evaluation of the tensile shear experiments with digital image correlation and developed computer vision procedures for bond line evaluation and fracture analysis. A review of UHPLC-ESI-TOF-MS data was performed under the supervision and support of the second corresponding author. The candidate drafted the manuscript, discussed the manuscript versions with the supervisors, and performed the finalization of the manuscript, including all visualizations. The candidate was responsible for revisions and correspondence during peer review.

3.3. Other Publications

During the graduation period, the candidate contributed to several research projects and co-authored publications as a research assistant in the *Wood Materials Science group* at the TUM Chair of Wood Science. Of those, selected peer-reviewed papers, which are in a broader sense related to the thesis topic, are briefly summarized below.

Sánchez-Ferrer A., Soprunyuk V., Engelhardt M., Stehle R., Gilg H. A., Schranz W., Richter K.

Polyurea Networks from Moisture-Cure, Reaction-Setting, Aliphatic Polyisocyanates with Tunable Mechanical and Thermal Properties

ACS Applied Polymer Materials, **2021***, 3 (8),* 4070–4078

DOI: 10.1021/acsapm.1c00578

Sánchez-Ferrer *et al.* (2021) dealt with the development of solvent-free reactive adhesives for wood bonding applications, which may offer significant advantages over existing solutions. The utilization of aliphatic isocyanates, offering more durable, stable, and less toxic properties than PMDI, to create polyurea networks with tunable mechanical and thermal properties through moisture-curing reactions, was investigated in this study. Microphase-segregated block copolymer networks with two glass-transition temperatures were achieved by combining soft polypropylene oxide segments with hard segments of tri-isocyanate molecules. Characterizations with calorimetric, spectroscopic, and scattering techniques, as well as mechanical testing, were conducted, which showed promising properties and fitness for use in a broad range of industrial applications.

Both viscoelastic and viscoelastic properties could be achieved, indicating the polymers to be a good candidate for adhesive and sealant formulations, respectively.

The **candidate's contributions** to this publication include the design and construction of the experimental setup for mechanical analysis of polymer films (tension mode) and conducting tensile experiments. Further, the candidate assisted with the writing by providing method descriptions and revising and commenting on the manuscript draft.

Sánchez-Ferrer A., Engelhardt M., Richter K.

Anisotropic Wood-Water Interactions Determined by Gravimetric Vapor Sorption Experiments

Cellulose, **2023***, 30 (6),* 3869–3885
DOI: 10.1007/s00226-023-01508-z

In Sánchez-Ferrer *et al.* (2023), gravimetric vapor sorption experiments were conducted on beech specimens to evaluate the sorption behavior and directional permeability and diffusivity along the wood's orthotropic directions. Applying Dynamic Vapor Sorption (DVS) techniques, the study assessed the diffusion rates by analyzing the kinetic sorption behavior by applying a double-stretched exponential model, yielding superior data fitting compared to common models, *e.g.*, Ritger-Peppas. This fitting allowed for the determination of diffusivity parameters as a function of relative humidity levels, which varied significantly based on the wood's orientation. Sorption isotherms were analyzed using a modified version of the Guggenheim-Anderson-de Boer (GAB) model and a sorption site occupancy model to calculate the sorption coefficients and enable the determination of sorption site (mostly -OH groups) concentration, respectively. Additionally, Dynamic Vapor Transport (DVT) experiments were developed and performed to obtain the wood's permeability, calculated based on the water-vapor flow rate in quasi-static conditions. The results showed the wood's variability in sorption behavior dependent upon the direction of the vapor flow and the humidity conditions.

The outcomes of these experiments confirm the efficacy of such a methodological framework for comprehensively quantifying the interactions between wood and water by reliably determining all relevant hygroscopic characteristics of anisotropic solid wood.

The **candidate's contributions** to this publication include participating in its conception and design, performing relevant parts of the data analysis, and designing and constructing the setup for DVT experiments. Additionally, he was involved in commenting on previous versions of the manuscript and reviewed and approved the final manuscript.

Böger, T., Engelhardt, M., Suh, F.T. , Richter K., Sánchez-Ferrer A.

Wood-water interactions of primers to enhance wood-polyurethane bonding performance

Wood Science and Technology, **2024**, *58 (1),* 135–160
DOI: 10.1007/s00226-023-01508-z

Böger *et al.* (2024) explored how pretreating the wood surface by applying a primer as an adhesion promoter can benefit meeting structural requirements, namely on the product's bond strength and delamination behavior, since the working mechanisms of primers on the wood are still subject to current research. Possibly, primers reduce the hygroscopic activity in treated wood, which mitigates stress development within the adhesive bond line due to swelling or shrinking. In this context, the effects of three primer systems – based on Polysorbate 20, polyethylene glycol, and hydroxymethylated resorcinol – when applied to beech, birch, larch, and Douglas fir, were investigated.

It was revealed that all primers partially permeate into the cell walls of the wood. The primed surfaces facilitated the adhesive flow into the wood's subsurface pore structure (lumen filling), coinciding with thinner bond lines. In sorption experiments, it was observed that the impacts on the wood's moisture absorption capacity and diffusivity within the wood were different depending on the primer system used. The permeability, however, remained unaffected. All tested primers increase the bond's tensile shear strength. However, the changes in water sorption due to priming are too small to fully explain their observed effectiveness. Instead, the primers' ability to penetrate cell walls and to support the adhesive's capacity to flow into lumina (adhesive penetration) was demonstrated and is likely to be more significant for performance enhancement.

The **candidate's contributions** to this publication included assistance in the study's conception and design, material preparation, data collection, data processing, and analysis. In particular, the candidate performed data processing and analysis of Dynamic Vapor Sorption experiments. Additionally, the candidate revised the initial versions of the manuscript and approved the final manuscript.

4. Synthesis

Based on the examinations of the physicochemical effects of birch wood extractives on the curing kinetics and final properties of adhesives (**Paper I**), comparative characterizations of adhesion-related wood (adherend) properties (**Paper II**), and the resultant mechanical and morphological characteristics of adhesive bonds (**Paper III**), the thesis objectives of understanding the extractives' interactions with reactive adhesives, determining the effects of extraction on wood properties and evaluating the influence of extraction on bond properties were achieved to a high degree, respectively.

4.1. Main Results

Of the obtained findings through the investigations in Papers I – III, the main ones regarding the three respective thesis objective areas are summarized below.

Extractives and their Interactions with Reactive Adhesives

- The chemical composition of water-soluble extractives in silver birch wood is a highly complex mixture, mainly consisting of phenolic glycosides, (poly)phenolics, saccharides, (fatty) carboxylic acids, and amphiphilic lipid types (*i.e.*, phospholipids, glycolipids, and glycerolipids).
- UHPLC-ESI-TOF-MS is a powerful technique for screening hydrophilic extractive compounds in wood. With the applied sampling sequence, the dynamic of extraction (release patterns) for individual compounds can be identified.
- The chemical reactivity of MUF or PUR adhesives with water-soluble birch extractives is low, as indicated by the spectroscopic FTIR analysis. Limited extractive concentrations and the reactivity of the adhesives themselves prevent the development of significant secondary reaction pathways with the extractives.
- The presence of hydrophilic birch extractives caused MUF adhesive to cure with reduced rates, reaching gelation and vitrification after prolonged durations. With added extractive concentration, the stiffness and tensile strength of cured MUF adhesive also reduced proportionally.
- The interactions of PUR adhesive and water-soluble birch extractives are negligible: Although the curing behavior and adhesive properties are modifiable by forced addition, equivalent changes were not evident in bonding applications due to the low solubility/miscibility of birch extractives in the hydrophobic prepolymer liquid medium.

Effects of Extractives Removal and Extraction Procedures on Wood Properties

- Extraction procedures have complex effects on the bulk properties – not only because of the compositional changes but even more so as consequences of the pronounced swelling and redrying processes involved. The thesis results indicated that these affect the xylem's (hemi)cellulose polymer configurations and, thus, the overall degree of crystallinity, swelling pressure, adsorption, and Young's modulus.
- As the biopolymers of wood are constantly subject to changes due to their hygric history, these effects of water treatments are likely temporary, and further studies into the dynamics of these alterations are opportune.
- The surface energy properties of birch wood and its wetting behavior did not significantly change following a hydrophilic extraction treatment.
- From an application perspective, the extractives only insignificantly impaired the adhesion-related properties. This supports the assessment of the good fitness of silver birch in bonded products for load-bearing applications without requiring procedural attendance to its hydrophilic extractives concentration.

Influence of Extraction on Bond Properties

- The bond line stiffness was successfully quantified using optical deformation analysis *via* DIC. A slight increase in the apparent shear modulus of MUF adhesive with a higher degree of extraction was detected. This aligns with the adhesive property changes observed in tensile testing and indicates the dilution of extractives from the cell walls into the MUF bond line.
- The mechanical tensile shear properties of the MUF bond line were slightly improvable *via* hydrophilic extraction of the birch wood before the bonding process.
- The bond line formation with MUF appeared affected by the retarding effects of extractives on curing kinetics: With higher amounts of extractives in the wood, slightly thinner bond lines and more adhesive lumen penetration were observed.
- These observed effects on bond line performance can be considered to originate primarily from the detrimental effects of extractives on the adhesive's final mechanical properties since the adhesion-related wood property alterations by extraction were relatively small.
- The properties of bond lines with PUR adhesive were not proven to be affected by extractives: Mechanical strength was independent of the presence of extractives. Also, the apparent shear modulus remained constant, suggesting that any curing interference due to extractive diffusion into PUR while curing was negligible.

4.2. Discussion

This chapter concludes the presentation of the thesis results with a discussion of the main findings, including reflections on the existing literature and the objectives of this thesis.

4.2.1. Extractives Composition

The water extractive content of silver birch is usually given in literature with 1 – 2% (w/w) (Roitto *et al*. 2015), and the total extractive content reported in the literature varies between 0.8% up to 5% (w/w) (Routa *et al*. 2017). In the birch samples analyzed within this thesis, contents of 1.2% (w/w) (**Paper III**) and 1.4% (w/w) (**Paper I**) were determined and, therefore, ranked at the lower end of the reported range.

Compound classes

Based on the UHPLC-MS abundance data of **Paper III**, phenolic glycosides were the largest group of extractives in the hydrophilic birch extract (**Figure 10A**). This compound class comprises a complex plurality of molecules combining glycone moieties – primarily simple sugars, di- or trisaccharides – with a large variety of (poly)hydroxy aromatic compounds via glycosidic bonds. Their molecule size (average dimensionless mass-to-charge ratio $m/z > 500$ Da) is relatively large, potentially causing most physical disturbance in the adhesive polymer networks. Most but not all aromatic compounds were identified in the form of glycoside esters. Also, lignans, lignin precursors, and diarylheptanoids were present in the hydrophilic extracts.

The reported 19% total abundance of the phospholipid class was higher than prior literature findings (Hillinger *et al*. 1996; Piispanen and Saranpaa 2002). The ionization probability of phospholipids might be elevated compared to other compound classes and are easily detected in mass spectrometry setups using ESI (Engel and Popkova 2019), as they are zwitterionic molecules or naturally negatively charged. When measured in mixtures, there was also evidence of ion suppression (Furey *et al*. 2013) by phospholipids of other compounds in MS. Moreover, they can self-assemble in micelle structures, increasing their dispersibility during extraction procedures and allowing even lipophilic fractions to incorporate into their inner structure (nanocarriers). An indication of self-assembly was the detection of identical ions at multiple retention times in the UHPLC-ESI-TOF-MS data.

The saccharides quantified *via* calibrated LC in the extract were predominantly glucose (**Figure 10B**), other hexoses (*e.g.*, galactose, mannose, rhamnose), and

pentoses (*e.g.*, xylose, arabinose), as well as di- and oligosaccharides (*e.g.*, sucrose, raffinose).

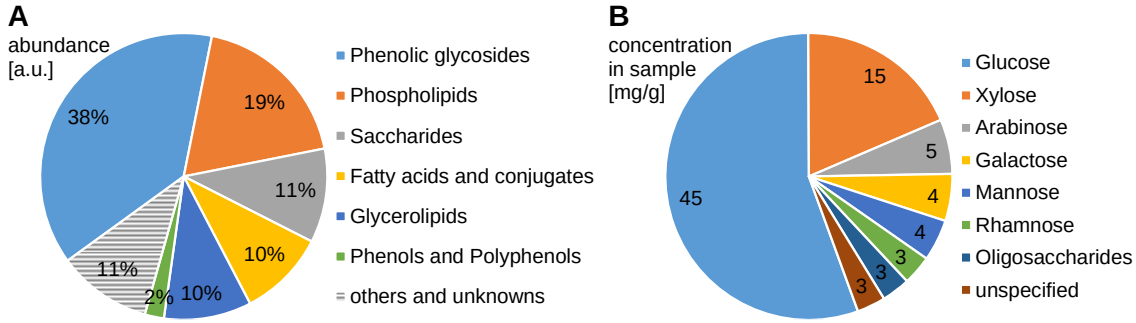

Figure 10. (**A**) Cumulative abundance (peak areas) of extractive compound classes as reported in **Paper III**, detected by UHPLC and ESI modes with the highest detection rates. (**B**) The concentration of free and hydrolyzed saccharides in birch wood cold-water extractive (LC sugar analyzer), as reported in **Paper I**.

Additionally, compounds of carboxylic fatty acid and glycerolipid class were found with about 10% of total abundance each.

The identified glycerolipids were mostly monoglycerides and diglycerides. Due to the free hydroxyl group(s) of the glycerol moiety, they maintain some solubility/dispersibility in water. As shown in previous works, they can even form lyotropic liquid crystals (Negrini *et al*. 2014; Fong *et al*. 2017) and are, therefore, considered non-ionic surfactants.

Extraction procedure and extraction conditions

Lachowicz *et al.* (2019) reported that extractive contents for birch wood doubled when using hot water instead of cold water. While extracting with hot water may have benefits in removing more potentially interacting compounds and extracting the birch extractives considerably faster, cold-water extraction was chosen in the studies here for the following reasons: *(1)* Hot-water extraction of wood has shown to also remove some hemicellulose fractions in the kDa range, which, however, is difficult to detect with the available chromatographic analytics, and attributable to the xylems biopolymer matrix; *(2)* all experiments were performed at room temperature to set the conditions close to actual procedures because of the production parameters of glulam or CLT - the bonding of the wood elements is commonly conducted at room temperature; *(3)* another issue is the preservation of the extractive composition, where hydrolysis with hot-water extraction is considerably more probable due to the acidic compounds of wood extractives (Wojtasz-Mucha *et al*. 2021); and *(4)* cold-water extraction avoided additional uncertainty regarding possible interactions from thermal effects in terms of improving the general understanding of the bonding effects.

It cannot be ruled out that the chemistry of extractives is somewhat different in the isolated and analyzed state compared to the initial pristine state in the wood polymer matrix since during the isolation process (dissolved liquid stage), interactions of the extractives with each other are potentially enabled. This, however, is a general issue of wet chemistry methods when working with heterogeneous mixtures of plant extractives.

4.2.2. Adhesive Interactions

The identified extractive composition gives rise to several interaction hypotheses of possible chemical reaction types between extractive compounds and the reactive MUF and PUR adhesives.

- As glycosides, saccharides, and (poly)phenols all constitute alcohols, they partake in condensation reactions with the hydroxymethylated compounds of MUF (Sridach *et al*. 2013; Wang *et al*. 2016; Emmerich *et al*. 2019).
- Free formaldehyde can react under acidic conditions *via* electrophilic substitution with aromatic structures (Forney and Jurewicz 1971), *e.g.*, with lignans, phenolic glycosides, or (poly)phenols.
- The pH level in the water fraction governs the amino resin curing rate (Bentley 1999). The MUF formulation used in the presented studies contains formic acid in the hardener component, which, with a pK_a of 3.7, is the strongest unsubstituted monocarboxylic acid. Formic acid ester formations with extractives can neutralize pH levels and reduce curing reactivity.
- The extractive's acidic components are generally weak acids, which, therefore, barely protonate in the already acidic environment of curing MUF adhesive and can have buffer effects. Acidic compounds are, however, expected to increase the reactivity of PUR (Ni *et al*. 2000) if dissolved effectively.
- With PUR, the isocyanate reaction with hydroxyl groups could form urethane linkages with alcoholic extractives, producing either cross-links, dangling or extended chains, which might result in defects in the adhesive network similar to those caused by adding an excess amount of cross-linking agent (Arora *et al*. 2020).

In **Paper I**, chemical reactions with the extractives with adhesive have been investigated on fully cured mixtures *via* FTIR. In the cases of both adhesives, the spectral analysis of mixtures with realistic concentrations revealed only minor changes. Some characteristic peaks decreased in reasonable correlation with extractive concentration and were attributed to physical dilution effects due to the mixing (**Figure 11A** and **11E**). No

additional or elevated absorption peaks were identified that would constitute significant covalent integration of these extractives into the polymer matrix. However, the absence of novel absorbance peaks is no exclusion criterion for potential reactions, as the resulting vibrational modes might be too similar. Here, advanced mass spectrometry methods for solids, *e.g.*, MALDI-TOF, might reveal more sensitive insights. Studies on other hardwood species obtained similar results for amino- (Özparpucu *et al*. 2020), phenolic- (Özparpucu *et al*. 2022b), or isocyanate-based (Özparpucu *et al*. 2022a) adhesives, where no significant modifications of the adhesives' chemical composition based on FTIR or solid-state nuclear magnetic resonance spectroscopy (ssNMR) were observed.

Although reaction pathways exist, the reactivity of both adhesive types studied is likely too high (Ionescu 2016) to allow significant chemical integration of extractive compounds into the polymer networks before achieving gelation, thus high immobilization during curing. Reactions were further limited due to the low concentration and mobility (rising viscosity of adhesives) and, in the case of PUR, the limited solubility. Since the extractives naturally are deposited within the xylem cell walls, the fact that the solvent-free PUR adhesive does not enter the cell walls, while the water-fraction of MUF can dissolve and mobilize extractives from the cell wall, is essential for the understanding of non-chemical interaction differences between MUF and PUR adhesives.

Rheological measurements and tensile experiments in **Paper I** revealed that hydrophilic extractives from silver birch significantly influence adhesives' curing kinetics and mechanical properties, respectively. The nature of the adhesive interaction with wood extractives can vary significantly depending on the adhesive's chemical composition. Extractives decelerated the curing process of MUF adhesives. The average time to reach gelation on extracted wood $\bar{t}_{gel}$ was 3.8 ± 0.7 h, the time increased to 5.0 ± 0.3 h when using pristine birch specimens or when adding about 1.3% (w/w) of dry extractives to the MUF adhesive. This coincides reasonably well with the wood's extractive content of 1.4% (w/w). Extractive addition had a less pronounced but opposite effect on curing PUR adhesives. The prolonging effect on MUF curing and, in the case of PUR adhesive, the slight accelerating effects (**Figure 11B** and **11F**), as seen in the vitrification- and gelation time, are in good agreement with the results of Özparpucu *et al.* (2020, 2022a) observed with the hydrophilic hardwood extractives in chestnut and oak. However, the accelerating effect on the isocyanate-based emulsion polymer adhesive observed by Özparpucu *et al.* (2022a) was more pronounced, likely due to its water component, which provides solubility and mobility for these extractives.

Apart from curing kinetics, the presence of impurities in the form of extractives had an apparent effect on the final mechanical properties of MUF and PUR after curing. The tensile experiments on film samples in **Paper I** to evaluate Young's modulus E (**Figure 11C** and **11G**) and tensile strength σ (**Figure 11D** and **11H**), showed significant decreases with only small concentrations of extractives in both adhesives studied by introducing defects into the adhesive polymer network. Similar effects were obtained when testing bond lines of water-borne MUF adhesive with pristine birch yielding lower strength and stiffness, while PUR bond lines show no changes in shear strength or shear modulus, as also seen in **Paper III** since the extractives apparently diffuse into MUF but not into PUR adhesive during curing. This coincides well with literature findings, suggesting that water-borne resins diffuse into the cell walls, where the extractives can be dissolved, while polyurethane prepolymers do not diffuse into cell walls (Gindl *et al.* 2004; Konnerth *et al.* 2008; Jakes *et al.* 2015; Casdorff *et al.* 2018).

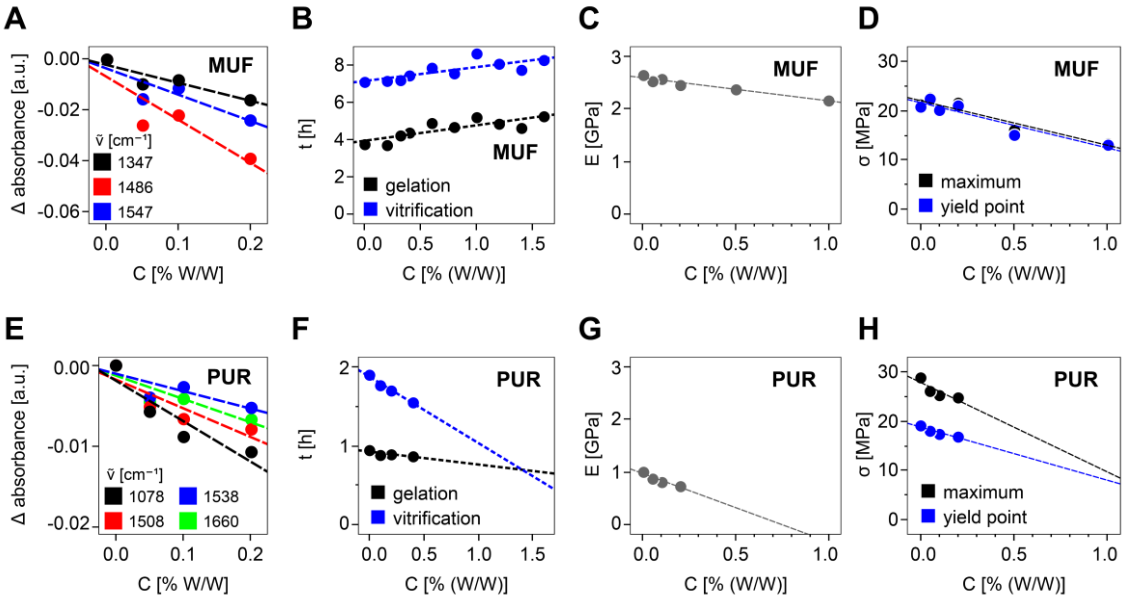

Figure 11. Summary of chemical analysis, curing behavior and tensile testing results of cured adhesive films, showing average results for sample groups of varying concentrations C of water-soluble silver birch extractives added to MUF (top) and PUR (bottom) adhesive before curing, as reported in **Paper I**. (**A** and **E**) FTIR evaluation of correlating peaks in cured adhesives; (**B** and **F**) rheometry results with duration to reach gel state/percolation (black) and vitrification/glass formation (time at maximum G'', blue); (**C** and **G**) Young's modulus E of adhesive films in tension; (**D** and **H**) tensile strength (black dots) and elastic yield limit (blue dots) of adhesive films. Average results for all sample groups are shown, dashed lines indicate linear regression trends.

As far as the limited similarity of prior studies regarding sample preparation, testing methods, and adhesive formulations allow, the results agreed with the literature data. Since the experimental design of determining mechanical adhesive characteristics as a

function of extractive concentration was novel, only data on pure adhesive specimens is available in the literature, *e.g.*, by Kläusler *et al.* (2013).

4.2.3. Wood Adherend Properties

The studies in **Paper II** focused on how removing hydrophilic extractives from silver birch wood affects its adhesion-related properties as an adherend for reactive adhesives. It was demonstrated that extracting these components alters the wood's moisture interaction behavior. The extraction procedure further decreased both dimensional stability and the swelling pressure in the unidirectional restriction of silver birch wood. It also led to a slightly lower Young's modulus value, which was analyzed in compression mode. Structural analysis based on the birch wood's X-ray diffraction pattern before and after treatments with water suggested nanostructural changes, which can explain these bulk property alterations.

As the specific surface of porous materials is correlated with adsorption capacity in the hygroscopic range, it can be a cause for elevated adsorption after extraction since the inner surface area is increased by extraction due to the newly created free volumes. These volumina are not necessarily stable as inter-molecular forces can lead to structural rearrangement. After initially measuring an increased physisorption, a reduction of moisture sorption was observed after repeating sorption cycles. Evaluation *via* the SSO model indicated a 2.2% decrease in sorption site concentration (**Figure 12A**) after multiple sorption cycles. As the hydrophilic extractives are also highly hygroscopic, they increased the sorption site concentration even when establishing hydrogen bonds to the biopolymer matrix themselves due to their high number of OH groups.

The apparent moisture diffusivity measured at room temperature (**Figure 12B**) slightly increased after both extraction and vapor treatment in the RH interval below 60%. Based on the temperature-dependence of adsorption, isosteric heat evaluations showed a significant loss of sorption enthalpy in dry conditions $q_{st,0}$ after extraction (**Figure 12C**). Presumably, this occurred since the more mobile extractives can align better and thereby establish stronger hydrogen bonds compared to large biopolymers of the xylem with higher glass transition temperatures.

The availability of diffused water in the adhesive affects PUR curing kinetics, while the water mass flow from the adhesive into the wood affects the required time for MUF bonding. The estimated net effect of extraction on curing of PUR since the increased diffusivity and lowered sorption enthalpy can suggest a faster propagation of vapor toward the bond line. However, the slightly reduced moisture concentration has

an opposing effect. The drying rate of MUF during curing is likely similar for the cases of extracted and pristine wood, considering there were no differences in diffusivity at increased RH levels observed.

In the radial direction, an average 10% and 25% relative increase of free swelling upon soaking was observed after vapor treatment and extraction treatment, respectively (**Figure 12D**). In the tangential direction, the results were less conclusive, giving similar values for treatment types. This can be a result of the mechanical coupling of earlywood and latewood regions in this direction. At the same time, the pressure in unidirectionally restricted swelling experiments (**Figure 12D**) was lowered after extraction treatment. However, control experiments with vapor treatment resulted in similarly lower swelling pressures, which suggests that this was due to alterations of polymer configurations, such as a lowered crystallinity from the water imbibition, not the extractives removal itself.

The XRD patterns indicate a somewhat more amorphous, *i.e.*, disordered state after extraction or vapor control experiment, was reached with a 5% lower degree of crystallinity χ, relative to pristine conditions, and a shorter characteristic crystallite length ξ_{004} (**Figure 12E**). While the observed drop in ξ_{004} and χ was significant, absolute values should be considered with care, *e.g.*, since the applied model for crystallite characterization (Zabler *et al*. 2010) assumes pure cellulose. The relevant interpretation relies on the similar impact of both treatment methods, which allows the conclusion that nanostructural changes were primarily originating from the solvent and not the solvate.

In comparative compression tests, reductions in average Young's modulus $\Delta\bar{E}/\overline{E_0}$ of 11% in the longitudinal direction, 12% in the radial direction, and 10% in the tangential direction were observed (**Figure 12F**). Thus, the stiffness reduction was quite similar in all anatomical directions. This backs the expectation that the structural changes presumed due to the XRD results are mainly found in the amorphous domains. At the same time, cellulose fibers are highly resistant to the applied treatments when using only water as a solvent at room temperature.

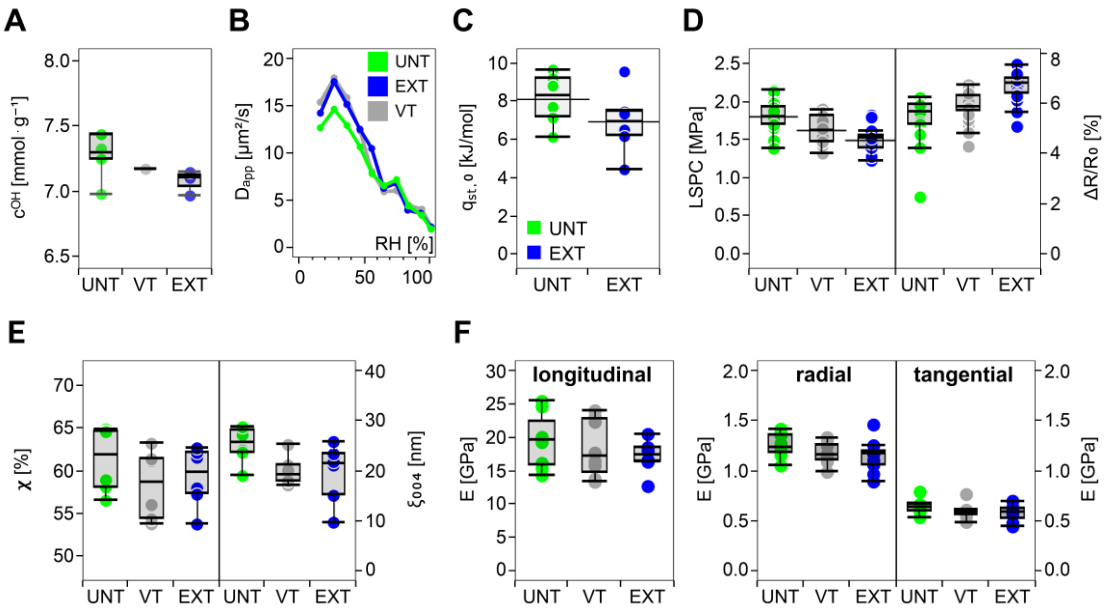

Figure 12. Comparison summary of adhesion-related properties of birch wood in pristine/untreated (UNT), after vapor treatment (VT) and extraction treatment (EXT) of results as reported in **Paper II**: (**A**) adsorption capacity in hydroxyl-group concentration c^{OH}; (**B**) apparent water vapor diffusivity D_{app} as a function of relative humidity RH; (**C**) adsorption enthalpy $q_{st,0}$; (**D**) swelling pressure coefficient $LSPC$ as the pressure increase (linear gradient) per 100% RH increase (left) and free swelling as the dimensional change in the radial direction from dry to soaked state $\Delta R/R_0$ (right); (**E**) XRD evaluation results of degree of crystallinity χ (left) and correlation length ξ_{004} (cellulose crystallite length, right), (**F**) Young's modulus E in compression mode in longitudinal (left), radial (middle), and tangential loading direction (right).

The nanostructural changes related to the XRD results are likely connected to swelling and mechanical properties and the actual observed changes coincide with the theoretical implications of partial amorphization, *i.e.*, the initially observed higher vapor sorption, increased swelling (Tammelin *et al*. 2015; Guo *et al*. 2017; Ottesen and Syverud 2021), lower swelling pressures (Arzola-Villegas *et al*. 2019) and the loss in mechanical stiffness (Eichhorn and Young 2001; Batista *et al*. 2016). Apart from the cellulose fraction, which is difficult to amorphize (Ioelovich 2021), these changes seen in XRD data can also stem from amorphization in the hemicellulose domains contributing to the X-ray diffraction, as hemicelluloses have been proven to assemble in semi-crystalline structures to cellulose fibrils (Berglund *et al.* 2020), *e.g.,* as shown for xylans and mannans in softwoods (Terrett *et al.* 2019) and galactoglucomannan in seed mucilage (Yu *et al.* 2018).

Contact angle measurements did not show significant changes in surface energy properties attributable to the extraction process. Also, inverse gas chromatography data evaluations showed mainly identical results for untreated and extracted wood. With a dispersive surface energy γ_s^d of 39 mJ/m² and a sum of specific interactions $\sum I_{SP}$ if 83 kJ/mol in the pristine state and γ_s^d of 38 mJ/m² and $\sum I_{SP}$ of 84 kJ/mol on extracted

wood, both disperse and polar interactions remain fairly constant. Therefore, the observed surface wetting characteristics in silver birch were barely influenced by the presence of its hydrophilic extractives. Extractive diffusion might reduce the surface energy of liquid adhesives, which would facilitate wetting and, therefore, adhesive penetration. However, in contact angle measurements of pure adhesive drops on pristine *vs*. extracted wood surfaces, negligible effects on wetting were observed.

The result highlighted the importance of separating the desired treatment effect types – in this case, the removal of extractives – from secondary effects on the remaining bulk wood. The water introduced during extraction is a strong solvent and, thus, acts as a plasticizer, facilitating reconfiguration of the wood's glassy polymer backbone of wood and potentially affecting the crystalline domains of cellulose. The control experiments indicate those secondary effects to be the predominant factor for the observed mechanical softening, reduced swelling pressure, and nano-structural changes. The removal of extractives, however, could amplify these effects due to free volume increases, the elimination of bulking action, and the reduced sorptive capacity.

4.2.4. Bonding Performance

For improved comparability between results in **Papers I** and **III**, the estimated hydrophilic extractives concentration C of the tensile shear samples in **Paper III** was calculated based on the extraction degrees ED and estimated total extractives content $C_{W,\infty}$, as $C = (1 - ED) \cdot C_{W,\infty}$. An overview of the observed correlations of the average mechanical bond line characteristics and C is given in **Figure 13** for MUF-bonded (blue) and PUR-bonded (red) tensile shear specimens.

The shear strength τ_m (**Figure 13A**) of MUF-bonded specimens (measured after A1 conditioning of DIN EN 302-1 in **Paper III**) decreased with higher extractives concentration C from 13 MPa at 0.25% (w/w) to 11 MPa at 1.2% (w/w). Similar trends of lowered τ_m bonding following a 4 d extraction procedure were obtained in **Paper I**, with -10% after A1 treatment after extraction, -18% after A2 (soaking), -10% after A4 (soaking and redrying), and -17% after A5 (boiling and redrying) treatment. Thus, the highest differences occurred in wet conditions (A2) as they might be amplified by increased hygroscopicity of the adhesive layer containing some diffused hydrophilic extractives. When redrying the soaked specimens (A4), reduction levels similar to A1-conditioned specimens were reached.

While a comparison of strength values τ_m suggests that the bond line performance of PUR adhesive was superior when considering the yield stress τ_e. (**Figure 13B**) of both adhesives reveals that the linear viscoelastic behavior of MUF bond

lines allowed an equivalent (in pristine condition) τ_e of 9 MPa or even higher yield stress after extraction compared to PUR. From this perspective, the structural performance of both adhesives is very similar. The shear strain at the elastic limit γ_e (**Figure 13C**), *i.e.*, the shear deformation at the yield point was independent of C, with 0.01 for MUF bond lines and about double with 0.02 for PUR, which reflects the differences in deformability already observed in tensile testing of adhesive films.

Analysis results of failure modes as the shear specimens' overlap area percentages of wood failure WF, adhesive failure AF, and cohesive failure of the adhesive CF are shown in **Figure 13D**. Birch wood with higher extractive concentration correlated with a slightly increased WF percentage in the case of MUF. Since this coincides with lower strength values, the presence of extractives might shift the failure location into the interphase, where extractive diffusion is most prevalent.

The apparent shear modulus G_a (**Figure 13E**) of MUF bond lines decreased with extractives concentration C. The decrease of bond line stiffness in pristine condition was 21% when compared to the extrapolated linear regression result at 0% (w/w) extractives concentration. This indicates extractives in the adherend result in an MUF polymer network with more defects and, therefore, cause a softening.

With higher extractive concentration, the density of absorbed deformation energy until reaching plastic deformation is reduced similarly as G_a and τ_e , since linear-viscoelastic deformability remained constant but under a lower stress response. The volumetric deformation energy in linear viscoelastic range – or resilience U_r is shown in **Figure 13F**. This is in good agreement with the narrowed shear strain distribution perpendicular to the MUF adhesive layer, as indicated by the lowered full-width at half maximum W, a parameter obtained from pseudo-Voigt peak function regressions (**Figure 13G**), was observed. This was a result of the softening of the bond line (reduced G_a), whereby concentrating the deformation increasingly in the adhesive layer.

The shear strength τ_m, the yield stress τ_e, and the corresponding shear strain γ_e of PUR-bonded specimens showed average levels not significantly correlated to extractives concentration C of $\overline{\tau_m}$ = 14 MPa, $\overline{\tau_e}$ = 9 MPa, and $\overline{\gamma_e}$ = 0.02. Due to this indifference of strength, yielding behavior, and material stiffness to variations in C, also the resilience U_r and strain distribution width W were not affected by extractive concentration.

A slight negative correlation of WF percentage with extractives concentration was observed on PUR-bonded shear specimens. This can be a result of the higher thickness of the bond lines at increasing C, which leads to reduced stress in the

wood/interphase under shear loading. The bulk properties of PUR adhesive in bond lines were not affected by extractives concentration in the adherend, as no significant changes in G_a of 0.5 MPa were detectable.

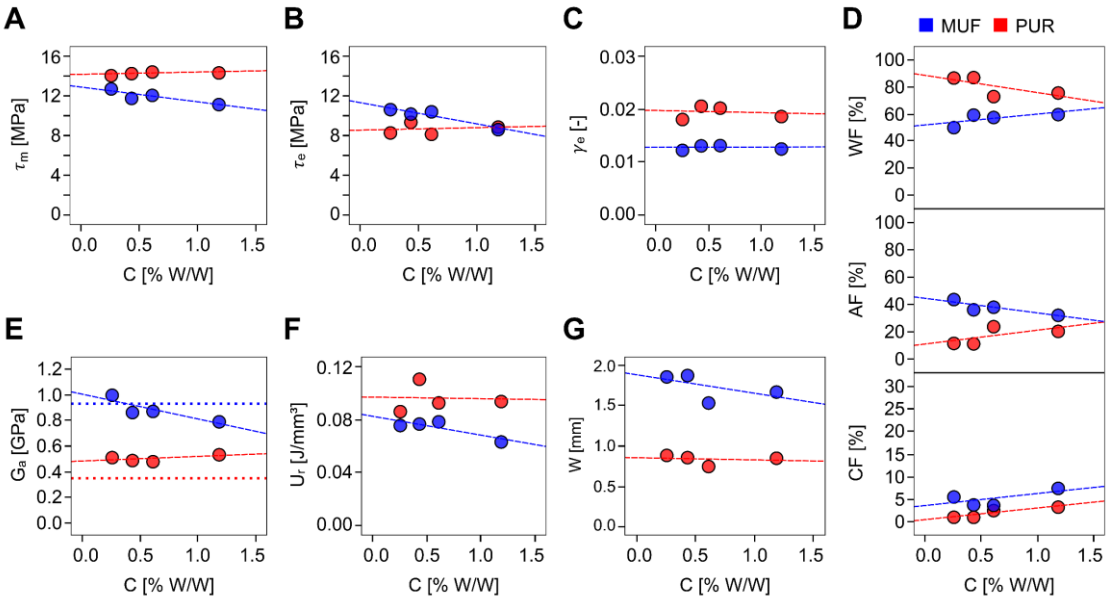

Figure 13. Summary of mechanical bond line characteristics of tensile shear specimens as reported in **Paper III** (A1 treatment). Mean values of specimen groups bonded with MUF (blue dots) and PUR (red dots) adhesive as a function of water-soluble extractives content C in the wood prior to bonding: (**A**) tensile shear strength τ_m; (**B**) elastic limit/yield (shear) stress τ_e and (**C**) corresponding shear strain γ_e; (**D**) failure modes as described in area percentages of wood failure WF, adhesion failure AF, and cohesive failure in the adhesive CF; (**E**) apparent bond line stiffness/shear modulus G_a; (**F**) volumetric deformation energy in linear viscoelastic range/resilience U_r; (**G**) full width at half maximum W of shear strain distribution in the linear-viscoelastic regime *via* pseudo-Voigt peak model regression. Average results for individual sample groups are shown; dashed lines indicate linear regression.

Interestingly, the area percentage of cohesion failure in the adhesive CF was (weakly) correlated for both adhesives with C, which might suggest some weakening at higher concentrations.

The ultimate stress (tensile shear strength) τ_m and the yield stress (elastic limit) τ_e of MUF bond lines were highly correlated (**Figure 14A**) but not in the case of PUR (**Figure 14B**). The fact that, for lower-strength specimens, the yielding (plastic deformation) is also initiated at a lower shear stress level was interpreted as a strong indication that the impact on bond performance is mainly due to the bulk property changes of the amino resin – as also seen in **Paper I** in tensile tests on films – as opposed to surface phenomena, *i.e.,* impaired wetting/reduced adhesion at interfaces.

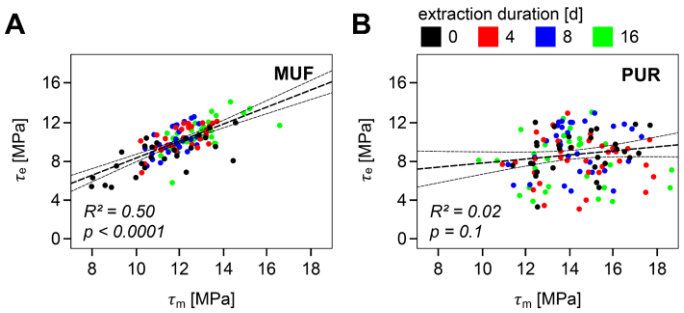

Figure 14. Yield stress (elastic stress limit, as determined *via* proof method) from tensile shear experiments of specimens bonded with MUF (**A**) and PUR (**B**) in **Paper III** as a function of their ultimate stress (tensile shear strength).

While some prior shear strength investigations, *e.g.*, by Boruszewski *et al.* (2011), reported a shear strength (EN 205) of birch with both MUF and PUR adhesives significantly below the required 10 MPa levels, other prior art reports acceptable bond line performance (Jeitler and Augustin 2016; Morin-Bernard *et al*. 2020).

As extractives are one of many factors that might affect bond line performance, their effects can be masked when comparing wood species: In a survey of tropical hardwoods by Iždinský *et al.* (2020), no correlation between a species' hydrophilic extractive concentration in a range of 1–4% and its tensile shear strength with PVAc was observed.

4.2.5. Bond Line Formation

The average bond line thickness th of tensile shear specimens is shown in **Figure 15A**, and the adhesive penetration factor APF – the area-weighted depth of filled adhesive lumina per length of analyzed bond line cross-section –, as reported in **Paper III**, is depicted in **Figure 15B**.

The significant positive correlation of APF with C in the case of MUF specimens, coinciding with thinner bond lines, suggests a more pronounced MUF adhesive flow from the bond line into the interphase upon higher extractives concentration, which is in line with the prolonged curing behavior observed in the rheological investigation (as summarized in section 4.2.2) in **Paper I**, as the rate of curing can constitute the major limiting factor in adhesive penetration (Mendoza et al. 2012). Although some assumptions were postulated, no direct evidence of an effect of adhesive penetration levels on mechanical bond strength has been provided in the literature (Suchsland 1958; Kamke et al. 2014). Likewise, in this work, the increase in adhesive penetration did not correlate with higher mechanical strength.

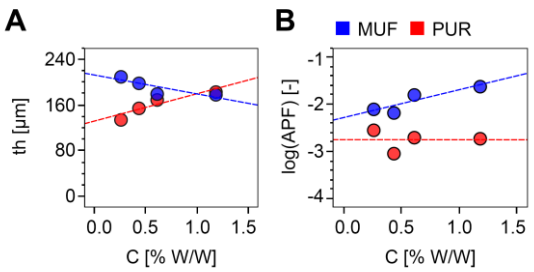

Figure 15. Bond line morphology evaluation results of tensile shear specimens in **Paper III**. (**A**) Average bond line thickness and (**B**) adhesive penetration factor.

The average PUR adhesive bond line thickness increased with C (indicative of a reduced flow due to accelerated curing, as polyols, *e.g.,* lignans (West and Banks 1986), or carboxylic acids, could react with NCO groups in PUR (Ionescu 2016)) while the observed adhesive penetration, as measured in APF, was very low and appeared non-correlated to extractives concentration. An explanation for this imbalance could be a reduced squeeze-out of adhesive from the boards during pressing time that, however, was not quantified at the time.

4.2.6. Practical Implications

The studies on birch extractives and adhesive interactions offer new insights for EWP development. Taking the wood extractive content of wood species into consideration in adhesive selection and formulation, as well as process parameters in wood bonding, is beneficial when aiming to maintain exhaustive control of the adhesion process and to enhance bond quality and product durability. In particular, accounting for the impact of extractives on adhesive curing kinetics can guide the optimization of manufacturing processes and ensure that EWPs meet the desired mechanical properties. The chemical nature of the adhesive plays a crucial role in its interaction with wood extractives. Thus, adhesive formulation and wood pretreatment need to be carefully considered in EWP manufacturing.

Especially the rheological analyses showed that with more extractives present, a prolonged processing time for EWP bonding with MUF could be the result. This, however, can be offset by modifying the hardener formulation, *e.g.*, the concentration of acidic catalysts. Using faster curing mixtures might suppress effects from extractive diffusion on MUF bulk properties. Mechanical testing indicated that some improvement in MUF bond line strength is achievable with water extraction treatment. However, the gain of bond strength was not distinctive enough to consider hydrophilic extraction a viable option in EWP production, especially when regarding the adequate bonding performance of the pristine wood used in this thesis. Instead, tuning the adhesive

penetration behavior by adjusting adhesive formulations to keep the desired reactivity or bonding pressure is expected to be a sufficient strategy. The findings advocate for a tailored approach to adhesive selection and formulation, as well as wood preparation, to create new innovative EWPs from hardwoods such as silver birch.

When bonding birch with PUR adhesive, the implications from hydrophilic extractives were negligible, as the extractive content did not significantly affect any mechanical bond line characteristics. Specifically, there were no notable alterations in bond strength, yield properties, or bond line stiffness. Therefore, the findings suggest that the presence of hydrophilic extractives in birch wood, utilized as a raw material for EWPs, does not impact the performance when PUR adhesive is employed for bonding. Nonetheless, the observed increase in reactivity due to extractives may become more problematic for PUR bonding: In the case of slower-curing PUR formulations with lower catalyst concentrations, as used in the here presented studies, the observed reaction kinetics increase might become more relevant.

A general conclusion from all the presented studies is that hydrophilic extractives in silver birch do not constitute a substantial difficulty for structural bonds. While bonding with PUR adhesive was basically unaffected, some interference with MUF was observed, which is of tolerable or manageable practical impact. Moreover, comparative studies consistently reveal only minor changes in moisture sorption, dimensional stability, surface energy, and mechanical properties. This is a confirmation and extension of the assumption that birch is generally suitable for an increased use in future EWPs, when climate-smart forestry is able to produce the required birch wood qualities and volumes.

The good usability of birch wood, which has been confirmed in this fundamental research, leads to the need for further initiatives and progressive change along the supply chain from silviculture to the sawmill industry and processing industries. It is opportune to regularly examine whether sustainable political support and targeted public funding in the area of hardwood markets, expansion of hardwood timber production capacities, and application-oriented research are necessary and sensible. There is currently great untapped potential through silvicultural treatment and management of birch trees in European forests.

4.3. Limitations and Potential for Future Research

The most apparent limitations in the experimental studies and points for future research activities arise directly from the limitations of the thesis scope regarding the investigated wood, the solubility of extractives, the selected adhesives, temperature conditions, and modes of mechanical loading.

Extractions were performed with water and at room temperature. Thus, possible effects of highly hydrophobic extractive fractions, which were not removed by the aqueous extraction treatment, remained unknown. Freire *et al*. (2006) found 0.27% of fatty acids (mostly C16 and C18 acids) and only 0.12% of other lipophilic compounds. The present research was also restricted to room temperature curing, and both high-frequency and hot press curing were omitted. The complex interactions of gradients of temperature, moisture content, and time certainly need to be addressed in targeted research.

With the presented extraction procedure in Paper III, the kinetic parameters of extraction are specific to the chosen board dimensions. To obtain more general information on the extractive's diffusivity in the xylem, one-dimensional diffusion experiments in all principal growth directions of wood are required.

The investigations suggest that using extracted birch wood is beneficial for bonding with MUF in multiple regards. However, further studies on alternative mitigation methods should be conducted before considering the hydrophilic extraction of solid wood with water as a feasible means to modify the bond line performance properties.

Specifically, the results of this investigation can provide insights to optimize wood adhesive formulations and procedures for use with birch wood: The thesis focused on single, exemplary adhesive formulations of both the MUF and PUR types. However, formulations of prepolymers/precondensates, as well as catalysts/hardeners and additives, can vary in bonding applications. Adjustments in the hardener concentration of MUF and catalyst concentrations in PUR may well be able to offset any measured effects of the bond line curing behavior and the resulting morphology of the bond line and interphase. Adhesive formulation adjustments may also countervail the softening effects of extractives on the cured adhesive. Research in adapting formulations to decrease the sensitivity to extractive diffusion or to offset their effects in terms of curing behavior or mechanical properties would constitute an interesting field, more so in combination with problematic wood species regarding extractive concentration. Moreover, the extent to which the observed strength-reduction of MUF bond lines is attributable to altered curing behavior and resulting adhesive penetration

or to the softening effects of extractives on the cured adhesive is subject to further investigation. Filler components in adhesives can phase-separate due to size exclusion effects during penetration into the wood structure. This results in high local variations in Young's modulus, as shown *via* the nanoindentation technique by Winkler *et al.* (2023). Spatial deformation analysis of bond lines *via* DIC could, therefore, be utilized in filler optimization research.

Investigations on primer treatments prior to gluing have shown the potential of chemical surface priming to mitigate impacts from extractives and to improve the bond line performance (Böger *et al*. 2022). Thus, this research could be extended to birch wood in future studies. Using suitable primers can improve the PUR bond performance with birch (Böger *et al*. 2024) and might be effective for water-borne adhesives as well.

The results from rheological experiments of isothermal curing could be translated to pressing time requirements derived from bonding experiments determining the kinetics of adhesion for specific adhesives, *e.g.*, by using an automated bonding evaluation system (ABES method, ASTM D7998-15). Generally, systematic investigations on the conditions of bonding and the applied bonding parameters allow optimized bonding performance with specific hardwood species (Knorz 2015). Such applied studies have yet to be conducted and published in the case of birch wood.

The mechanical bond line performed in this thesis was characterized only in shear loading experiments. The effectiveness of the multiple adhesion mechanisms involved in a bond can differ for perpendicular loading modes like peeling. These occur predominantly on bonds on transverse-cut surfaces, *e.g.*, butt joints of lamellas, finger jointing, and scarf joints. Peeling stress is also a critical loading type that occurs in delamination tests or causes delamination in exposed components.

Finally, the development of structural grading rules of birch timber for structural timber and EWP production and extensions of building codes to expand hardwood usage is still underway and should be facilitated in upcoming applied research activities.

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